

**FIRST PRINCIPLE STUDY OF $\text{Na}_x[\text{Ti}_y\text{Zn}_z\text{Mn}_w]\text{O}_2$ AS A CATHODE MATERIAL
FOR SODIUM-ION BATTERIES**

BY

TSHIFHIWA STEVEN RANWAHA

(11612891)

**SUBMITTED IN FULFILMENT FOR THE REQUIREMENTS OF THE DOCTOR OF
PHILOSOPHY (PhD) DEGREE IN PHYSICS**

AT THE

FACULTY OF SCIENCE, ENGINEERING AND AGRICULTURE

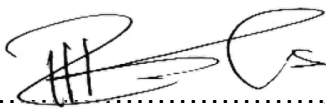
UNIVERSITY OF VENDA

SUPERVISORS: PROF N. E MALUTA (UNIVEN)

PROF R. R MAPHANGA (CSIR)

DECLARATION

I, Ranwaha Tshifhiwa Steven declare that this thesis is submitted to the University of Venda titled “**First principle study of $\text{Na}_x[\text{Ti}_y\text{Zn}_z\text{Mn}_w]\text{O}_2$ as a cathode material for sodium-ion batteries**” for the Doctor of Philosophy (PhD) degree in physics and is my original work, and has not been submitted for a degree at any other university. The report does not contain other people’s writing unless specifically acknowledged and referenced accordingly.

Signed (student):  at Thohoyandou(UNIVEN)
On.....25.....day of April 2025

DEDICATION

To my beloved mother, whose love, sacrifices, and unwavering belief in my potential continue to guide me even in her absence. Losing you during the first year of my undergraduate journey was the most profound loss of my life, yet your strength and wisdom have remained my greatest source of inspiration.

This PhD thesis is a tribute to your dreams for me, your endless encouragement, and the values you instilled in me. Though you are not here to witness this milestone, I know you are watching over me with pride. I dedicate this work to your memory, with love and gratitude that words can never fully express.

Rest in peace, Mom. This is for you.

ACKNOWLEDGEMENTS

I am grateful to my supervisors, Professor N.E Maluta and Professor R.R Maphanga, for their assistance during the course of this research. Additionally, I would like to express my appreciation to the Department of Physics at the University of Venda for providing me with the opportunity to continue my PhD studies.

I am particularly grateful to the material modelling research group, which is led by Professor N E Maluta, and the CSIR design and optimization group, which is led by Professor RR Maphanga, for their support and assistance throughout this voyage. Finally, I would like to express my gratitude to the CSIR Next Generation Enterprises and Institutions for their financial assistance.

ABSTRACT

The fast-growing energy generation from renewable sources such as solar, wind, and waves is calling for reliable energy storage technologies with high energy density, high power, and low cost, because the energy harvested from these renewable energy sources is intermittent. Currently, the leading technology in energy storage is the lithium-ion battery (LIB). While lithium possesses numerous electrochemical advantages that make it a critical component in modern energy storage technologies, its continued viability is increasingly challenged by the rapid depletion of accessible lithium reserves and its uneven geographical distribution, which pose significant constraints on sustainable and equitable resource utilization. The development of electric vehicles and plug-in hybrid electric vehicles has raised everybody's expectations as well as requirements for the materials employed. That is why there is an urgency to find alternative technologies which would replace LIBs. In search of alternative technology, sodium-ion batteries are a promising solution for large-scale electrochemical energy storage, owing to their low cost, materials abundance, good reversibility, and decent energy density. For sodium-ion batteries to achieve comparable performance to current lithium-ion batteries, significant improvements are still required in cathode, anode, and electrolyte materials. In this study, first-principles method based on the density functional theory was used to investigate the structural, electronic, mechanical and thermodynamics properties of Na intercalated electrode material Na_xMnO_2 electrode materials doped with Titanium (Ti) and Zinc (Zn) using random substitution doping method. The investigation was based on the effect of Na atom de-intercalation on the $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercells. The effects of dopants Ti and Zn on the Na_xMnO_2 stretch the lattice

parameters, resulting in volume expansion, this is because the atomic radii of the dopants are not the same as those of the host Mn. The electronic properties of the two doped systems show that the band gap is reduced by the effect of the dopants. The calculated elastic constants for the $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ bulk structures, as well as the $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercells, indicate mechanical stability for this compound as they meet the monoclinic structure mechanical stability criterion. In further investigation, the voltage window for the Ti-doped system was found to be between 3.410 V and 4.132 V. We found the voltage window for the Zn-doped system to lie between 2.221 V and 4.337 V. The calculated formation energies are negative, indicating that the material is thermodynamically stable and potentially amenable to synthesis under standard conditions. This inherent stability, coupled with favorable electrochemical characteristics such as appropriate voltage profiles, sufficient capacity, and adequate ionic conductivity, positions the material as a promising candidate for cathode applications in sodium-ion batteries.

Furthermore, the cluster expansion formalism was used to investigate the $\text{Na}_x\text{MnTiO}_2$ and $\text{Na}_x\text{MnZnO}_2$ phase stabilities. The method determines stable multi-component crystal structures and ranks metastable structures by the enthalpy of formation while maintaining the predictive power and accuracy of first-principles density functional methods. The findings predict that all nickel-doped LMO structures on the ground state line are most likely stable. Relevant structures are NaMnO_2 , NaTiO_2 , $\text{NaTiMn}_2\text{O}_2$ and $\text{NaTi}_2\text{MnO}_2$ for $\text{Na}_x\text{MnTiO}_2$ CE-predicted structures and NaMnO_2 , NaZnO_2 , $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$ and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ for $\text{Na}_x\text{MnZnO}_2$ CE-predicted structures. They were selected based on how well they weighed the cross-validation score (CVs) of 1.7 meV for $\text{Na}_x\text{MnTiO}_2$ CE-predicted structures and 1.9 meV $\text{Na}_x\text{MnZnO}_2$ CE-predicted structures, which is a statistical way

of describing how good the cluster expansion is at predicting the energy of each stable structure. Although the structures have different symmetries and space groups, they were further investigated by calculating the structural, electronic, mechanical, and thermodynamical properties. The results show that all CE-predicted structures have a wide diffusion compared to the parent structure (NaMnO_2). The reduction of band gap was also observed which give evidence that the structures are becoming metals and have an improved conductivity. The results showed that all the predicted structures met the stability requirements for monoclinic structures and were stable in terms of thermodynamics. For Ti-doped systems, the ductility was only observed on $\text{NaTiMn}_2\text{O}_2$ CE-predicted structure NaMnO_2 doped with Zn found to be ductile which implies that these materials can bend without deformation, resulting in fewer cracks during battery operation. This study enhances the fundamental understanding of dopant-induced effects on NaMnO_2 -based cathode materials, providing a prospective option to improve Na^+ mobility, electrical conductivity, and structural stability. It presents a comprehensive analysis of the beneficial effects of Ti and Zn doping in the enhancement of sodium-ion battery performance. It provides the theoretical framework that underpins the development of advanced, cost-effective, economical, and thermally stable cathode materials which are crucial large-scale energy storage applications.

Table of Contents

DECLARATION.....	i
DEDICATION.....	ii
ACKNOWLEDGEMENTS.....	iii
ABSTRACT	iv
LIST OF ABBREVIATIONS.....	x
LIST OF FIGURES	xii
CHAPTER 1	17
1. Introduction	17
1.1. General Introduction	17
1.2. Sodium-Ion Battery.....	20
1.3. Working Principle of Sodium-Ion Battery	22
1.4. Electrode Materials for Sodium-Ion Batteries.....	23
1.5. Purpose of the study	25
1.5.1. Aim.....	25
1.5.2. Research Problem	25
1.5.3. Research Motivation.....	26
1.5.4. Significance of the Research	27
1.5.5. Objectives	28
REFERENCES.....	29
CHAPTER 2	32
2. Literature Review.....	32
2.1. Cathode Materials.....	32
2.1.1. Layered Metal Oxides Cathode Materials	32
2.1.2. Polyanion Compounds as Cathode Materials	36
2.2. Anode Materials	38
2.3. Electrode Material Optimization	40
REFERENCES.....	46
CHAPTER 3	50
3. Methodology	50
3.1. Density Functional Theory	50
3.2. Approximations	54
3.2.1. Local Density Approximations	54
3.2.2. Generalized Gradient Approximation.....	57
3.3. Planewave Pseudopotential Method	57
3.3.1. Planewave Basis.....	57
3.3.2. Pseudopotential Method	59

3.3.3. Norm-Conserving Pseudopotential	61
3.3.4. Ultrasoft Pseudopotentials	62
3.4. Brillouin Zone	62
3.5. k-Point Sampling	63
3.6. Universal Cluster Expansion	66
3.6.1. Effective Cluster Interaction	67
3.6.2. Inversion and Least Square Fitting	69
3.6.3. Selecting Cluster Interactions Using the Genetic Algorithm	70
3.6.4. Iterative Optimization of the Training Set	71
3.6.5. Cluster Expansion Flowchart	72
3.6.6. Structure Selection in Complex Systems	75
3.6.7. Miscible Constituents.....	78
3.6.8. Miscibility Gap	78
3.7. Theoretical Background of Calculated Properties	79
3.7.1. Electronic Properties.....	79
3.7.2. Equilibrium Voltage and Voltage Profile.....	81
3.7.3. Phase Stability and Na-ion Ordering	82
3.7.4. Phase Stability and Voltage Profile at Finite Temperatures	83
3.7.5. Elastic Properties	83
3.8. Thermodynamic Properties	86
3.9. Computer Codes.....	87
3.9.1. Vienna Ab initio Simulation Package	87
3.9.2. MedeA UNCLE.....	87
REFERENCES.....	89
CHAPTER 4	98
4. Random Substitution of Ti and Zn into NaMnO ₂	98
4.1 Introduction	98
4.2 Computational Method	99
4.3. Results and Discussion	100
4.3.1 Structural Properties	100
4.3.2 Electronic Properties.....	104
4.3.2.1 Density of States for NaMnO ₂ , Ti or Zn Doped NaMnO ₂ Bulk and NaMnO ₂ 2 x 1 x 1 Supercell	104
4.3.2.2 Energy Band Gap	107
4.3.2.3 Density of States for De-Intercalated Systems	110
4.3.3. Voltages/Redox Potential and Formation Energy.....	113

4.3.5. Thermodynamic Properties	127
4.4. SUMMARY	136
REFERENCES.....	138
CHAPTER 5	141
5. Predicted Ti Doped NaMnO ₂ Structures Using Cluster Expansion Approach....	141
5.1 Introduction	141
5.2 Computational Method	142
5.3 Structure Prediction	142
5.4 Structural Properties	145
5.5 Electronic Properties.....	147
5.6 Mechanical Properties.....	150
5.7 Thermodynamic Properties	154
5.8 Summary	159
REFERENCES.....	160
CHAPTER 6	162
6. Predicted Zn Doped NaMnO ₂ Structures Using Cluster Expansion Approach...	162
6.1 Introduction	162
6.2 Computational Method	162
6.3 Structure Prediction	162
6.4 Structural Properties	163
6.5 Electronic Properties.....	165
6.6 Mechanical Properties.....	168
6.7 Thermodynamic Properties	173
6.8 Summary	178
REFERENCES.....	179
CHAPTER 7	181
CONCLUSION	181

LIST OF ABBREVIATIONS

LIB	Lithium-Ion Battery
SIB	Sodium-Ion Battery
a.u.	Arbitrary Unit
TMO	Transition Metal Oxide
MD	Molecular Dynamics
Cvs	Cross Validation Score
HEV	Hybrid Electric Vehicle
Nm	Nanometer
Li ⁺	Lithium Ions
Na ⁺	Sodium Ion
Mn	Manganese
O	Oxygen
Ti	Titanium
Zn	Zinc
DFT	Density Functional Theory
LDA	Local Density Approximation
PBE	Perdew-Burke-Ernzerhof
PWP	Plane-Wave Pseudopotential
VASP	Vienna Ab-Initio Simulation Package
UNCLE	Universal Cluster-Expansion
GGA	Generalised Gradient Approximation
CE	Cluster Expansion
DOS	Density of States
PDOS	Partial Density Of States

B	Bulk Modulus
G	Shear Modulus
E	Young's Modulus
ν	Poisson's Ratio
A	Shear Anisotropy Factor
C_{ij}	Elastic Constants
θ_D	Debye Temperature
K	Boltzmann's Constant
BBGKY	Bogo Liubov–Born–Green–Kirkwood–Yvon

LIST OF FIGURES

Figure 1. 1: Illustration of the elemental abundance in the Earth's crust [13].	18
Figure 1. 2: Some of the electrode materials studied for application in sodium-ion batteries as reported in reference [15].	21
Figure 1. 3: Schematic illustration of the working mechanism of Na-ion batteries [16].	22
Figure 2. 1: Stability diagram of P2 $\text{Na}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_2$ as described by the formation energy with respect to the fully sodiated and desodiated compounds based on DFT calculations [23].	41
Figure 2. 2: Fraction of Na-ion site occupancy in P2 $\text{Na}_{1/2}\text{Co}_{1-y}\text{Mn}_y\text{O}_2$ from AIMD simulations [24].	42
Figure 3. 1: Comparison of a wave function in the Coulomb potential of the nucleus (blue) to the one in the pseudopotential (red). The real and pseudo wave functions and potentials match above a certain cut-off radius r_c .	60
Figure 3. 2: Schematic representation of a cluster expansion model [36].	67
Figure 3. 3: Cluster selection using the genetic algorithm [39].	71
Figure 3. 4: Flowchart of the improved validation of trial CEs using probe structures [41].	73
Figure 3. 5: Schematic representation of CEs constructed from the conventional procedure [41].	77
Figure 3. 6: A Binary ground state diagram illustrating a miscibility gap [50].	79
Figure 4. 1 Spin-polarized crystallographic relaxed structures of $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, and $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	100
Figure 4.2: 2Spin-polarized DOS near the Fermi level of bulk NaMnO_2 material.	105

Figure 4. 3: Spin-polarized PDOS of the (a) $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ bulk structure and (b) $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercell.....	106
Figure 4. 4: Spin-polarized PDOS of the (a) $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ bulk structure and (b) $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell.	106
Figure 4. 5: Spin-polarized PDOS of $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercell (a) $x = 0.75$, (b) $x = 0.5$, (c) $x = 0.25$, (d) $x = 0$	110
Figure 4. 6: Spin-polarized PDOS of $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell (a) $x = 0.75$, (b) $x = 0.5$, (c) $x = 0.25$, (d) $x = 0$	112
Figure 4. 7: Deintercalation potentials (V) for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$)	116
Figure 4. 8: Deintercalation potentials (V) for $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$).	116
Figure 4. 9: Temperature versus specific heat at constant volume (C_v) for $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).....	130
Figure 4. 10: Temperature versus specific heat at constant volume (C_v) for $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	131
Figure 4. 11: Entropy versus Temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	132
Figure 4. 12: Entropy versus Temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	133
Figure 4. 13: Free energy versus temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	134
Figure 4. 14: Free energy versus Temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	135
Figure 5. 1: An isotropic volume optimized binary ground state diagram of $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ with a cross-validation score of 1.7 meV.	144
Figure 5. 2: Spin-polarized DOS for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures..	149
Figure 5. 3: Specific heat vs. temperature for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures.	156
Figure 5. 4: Entropy vs. temperature for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures.	157

Figure 5. 5: Free energy vs. temperature of $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures.....	158
Figure 6. 1: An isotropic volume optimized binary ground state diagram of $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ with a cross-validation score of 1.9 meV	163
Figure 6. 2: Spin-polarized DOS for $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ CE predicted stable structures.	167
Figure 6. 3: Specific heat vs. temperature for CE-predicted $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ structure.	175
Figure 6. 4: Entropy vs. temperature for CE predicted $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ structure. ...	176
Figure 6. 5: Free energy vs. Temperature for CE-predicted $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ structure.	177

LIST OF TABLES

Table 1. 1: Comparison between lithium and sodium alkali metals.	20
Table 4. 1: Calculated structural parameters of NaMnO_2 compared with literature results.	101
Table 4. 2: Lattice parameters of the NaMnO_2 , $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercells during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).	102
Table 4. 3: Lattice parameters of NaMnO_2 , $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).	103
Table 4. 4: Calculated energy band gap of NaMnO_2 , $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercell during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).	108
Table 4. 5: Calculated energy band gap of NaMnO_2 , $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).	109
Table 4. 6: Cathode voltage/redox potential and formation energy for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$).	114
Table 4. 7: Cathode voltage/redox potential and formation energy for $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$).	115
Table 4. 8: Elastic constants (C_{ij}) for $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	118
Table 4. 9: Elastic constants (C_{ij}) for $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	119
Table 4. 10: Bulk, shear and Young's moduli, Poisson's and Pugh's ratio for $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	120
Table 4. 11: Bulk, shear and Young's moduli, Poisson's and Pugh's ratio for $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).	121
Table 4. 12: Anisotropy in shear elastic factor (A_i , with $i = 1, 2, 3$) and anisotropy in compressibility and shear moduli (A_B and A_G in %) for de-intercalated $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	123

Table 4. 13: Anisotropy in the shear elastic factor A_i (with $i = 1,2,3$) and the anisotropy in compressibility and shear moduli (A_B and A_G in %) for de-intercalated $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$.	125
Table 4. 14: Calculated volumetric density, sound velocities, and Debye temperature for $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$.	127
Table 4. 15: Calculated volumetric density, sound velocities, and Debye temperature for $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$.	129
Table 5. 1: Structural properties for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures...	145
Table 5. 2: Calculated energy band gap for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures.	148
Table 5. 3: Elastic constant (C_{ij}) for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE-predicted stable structures...	150
Table 5. 4: Bulk, shear, and Young's modulus, and Poisson's ratio for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE-predicted stable structures.	151
Table 5. 5: Anisotropy in the shear elastic factor (A_i with $i = 1,2,3$) and anisotropy in compressibility and shear moduli (A_B and A_G) for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE-predicted stable structures.	152
Table 5. 6: Calculated, volumetric density sound velocities and Debye temperature for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures.	154
Table 6. 1: Lattice parameters of $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ CE-predicted stable structures....	164
Table 6. 2: Energy gap of $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ CE predicted stable structures	166
Table 6. 3: Elastic constants (C_{ij}) for $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ CE-predicted stable structures	169
Table 6. 4: Bulk, shear and Young's moduli, Poisson's and Pugh's ratio for $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ CE-predicted stable structures.	170
Table 6. 5: Anisotropy in the shear elastic factor (A_i with $i = 1,2,3$) and anisotropy in compressibility and shear moduli (A_B and A_G) for $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ CE-predicted stable structures.	171
Table 6. 6: Calculated volumetric density longitudinal sound velocities and Debye temperature θ_D for $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ CE-predicted stable structures.	173

CHAPTER 1

1. Introduction

1.1. General Introduction

Owing to the pressing issues of climate change, depletion of fossil deposits, coupled with adverse pollution caused by the massive consumption of fossil fuels, there is an urgent demand to shift to green and sustainable energy sources such as solar, wind, and tidal power. However, complete utilization of these renewable energy sources requires affordable and highly efficient stationary energy storage systems due to the inherently fluctuating nature of electricity generated by the sources. Rechargeable batteries are found to be the best candidate to store energy generated from the different renewable energy technologies since they can be used many times [1].

Since the first commercialization of lithium-ion batteries (LIBs) in 1991, the use of LIB has rapidly penetrated daily life for their use in portable electronic devices [2-5]. Compared to other types of rechargeable battery systems, LIBs exhibit superb performance in terms of energy density [5-8]. Small and light battery packages have enabled the worldwide use of portable electronics (e.g., laptops, cellular phones, MP3 players, cameras, etc.) for the past decades. In recent years, driven by the increased desire for 'green' technologies, the use of LIBs has expanded from portable electronics to large scale applications such as in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [5]. However, there is a concern that the amount of the lithium (Li) resources that are buried in the Earth's crust would not be sufficient to satisfy the ever-growing demands of LIBs [9]. While there is ample evidence that this is no cause for immediate concern, a very large market share of electric vehicles can put a strain on Li production capability [10]. According to a Japanese report published in 2010, about

7.9 million tons of metallic Li will be required when 50% of the oil-driven cars in the world are replaced by electric vehicles [9,11]. Sodium, the second smallest and - lightest alkali metal element (just below lithium in the periodic table), is one of the most abundant elements in the ocean and Earth's crust, as shown in Figure 1.1. This means that Na supplies are almost infinite and most importantly are of low cost. More striking is the fact that sodium has similar chemical properties as lithium, since they are in the same group in the periodic table, the chemical potential difference of the alkali-ion (Li or Na) between two electrodes (anode and cathode) creates a voltage on the cell. During charging and discharging, the alkali ions shuttle back and forth between the two electrodes. This is the reason why rechargeable sodium-ion batteries (SIBs) have recently attracted a great deal of attention as a promising alternative to lithium-ion batteries for large-scale applications [12-14].

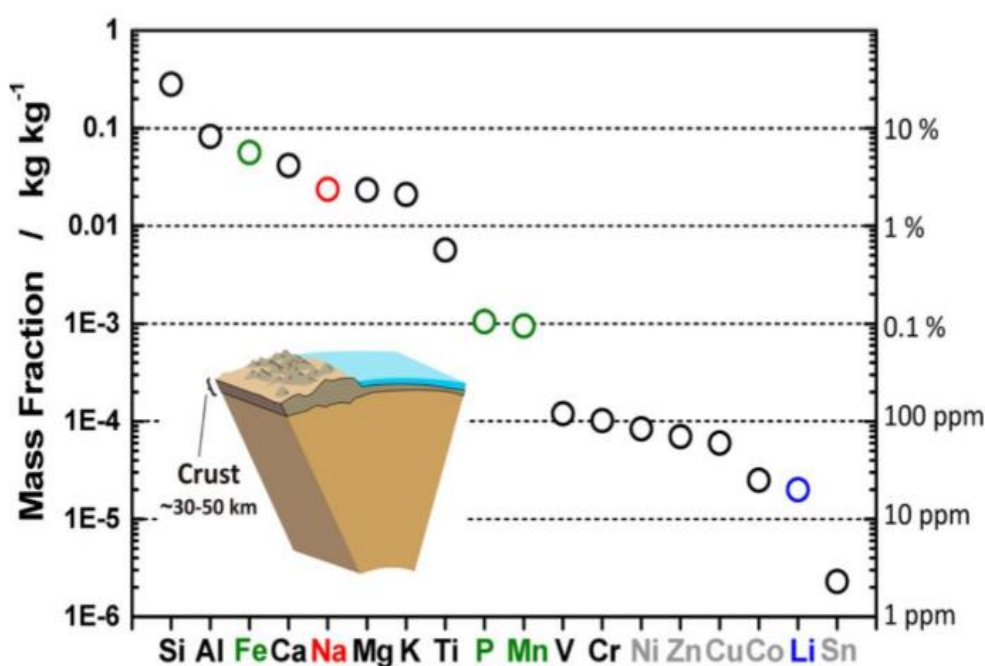


Figure 1. 1: Illustration of the elemental abundance in the Earth's crust [13].

However, even though sodium displays similar electrochemical nature to lithium, the larger ionic radius, mass and reduction potential of Na^+ than Li^+ is a crucial factor to the performance of SIB electrodes, see performance related properties listed in Table 1.1.

Table 1. 1: Comparison between lithium and sodium alkali metals.

Category	Lithium Ion	Sodium Ion
Relative atomic mass	6.94	22.99
Ionic radius (Å)	0.76	1.02
E (vs. Li/Li ⁺)	0	0.3 V
Abundance in the earth crust (mg/kg)	20	23.6×10 ³
Cost of carbonates (\$/ton)	5000	150
Capacity (mAh/g), metal	3829	1165
Coordination preference	Octahedral and tetrahedral	Octahedral and prismatic

1.2. Sodium-Ion Battery

Sodium-ion batteries are a type of rechargeable battery that uses sodium ions as charge carriers. Na-ion batteries are remarkably similar in design to Li-ion batteries. Consequently, many of the most studied electrode materials in Na-ion batteries were first utilised in their lithium counterparts. However, research has shown that what works for LIBs does not necessarily work for SIBs; many of the best electrode materials perform very well when paired with lithium, however, for example, graphite has proved disappointing when combined with sodium [15]. Favourable, the battery-grade salts of sodium are much cheaper and abundant, in contrast to those of lithium. This makes them a cost-effective alternative especially for applications where weight and energy density are of minor importance, such as in grid energy storage for solar and wind renewable energy sources. The search for commercially viable Na-ion

batteries demands finding and optimizing new electrode materials and electrolytes, to get more economic, safer, and long-life batteries. One of the ways to get more economic systems would be searching for an aqueous electrolyte battery that would not need ultra-dry fabrication conditions and would not use higher-cost organic electrolytes, such as sodium fluorinated salts. Another indirect saving could be the use of cheaper materials in the assembly of the battery, for example, the current collectors. Figure 1.2 depicts the most important cathodic and anodic materials for sodium-ion batteries, indicating their specific capacity and operating voltage. Many materials have been proposed in the literature as possible cathodes for Na-ion batteries, whereas only some carbon-based anodes have been pointed out for this storage technology [15].

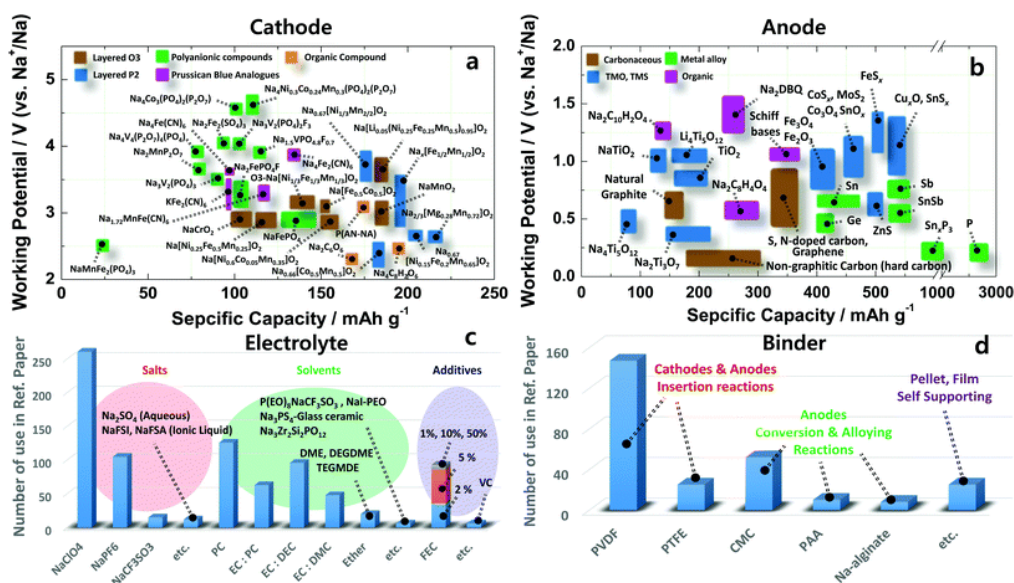


Figure 1. 2: Some of the electrode materials studied for application in sodium-ion batteries as reported in reference [15].

1.3. Working Principle of Sodium-Ion Battery

Figure 1.3 depicts the structural components of SIBs and charge storage mechanisms similar to those of LIBs, except that lithium ions are now replaced by sodium ions. A full sodium-ion battery is composed of four parts: anode (negative electrode), cathode (positive electrode), electrolyte, and separator. The typical working mechanism is that during the charging process, sodium ions are extracted from the cathode material (above 3.0 V vs Na^+/Na) and inserted into the anode material (below 1.0 V vs Na^+/Na). At the same time, the electrons move from cathode to anode through the external circuit and supply power to the device. During the discharge process, the reverse reactions take place. Thus, the electrons move from anode to cathode through the external circuit, while the sodium ions are inserted back into the cathode materials [16,17]. All the processes have remarkably high reversibility, so the sodium-ion battery is chargeable and can be cycled thousands of times.

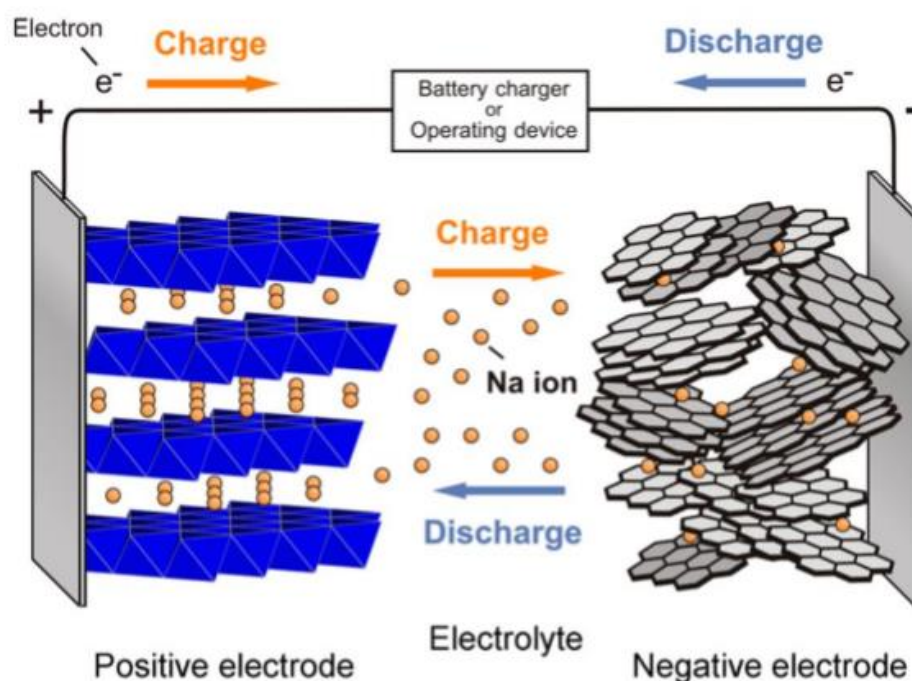
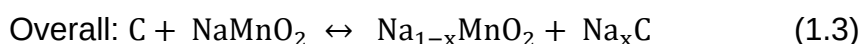
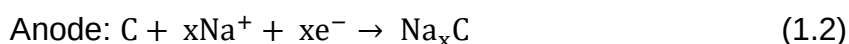
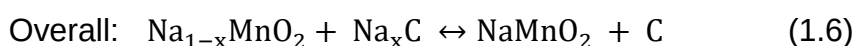
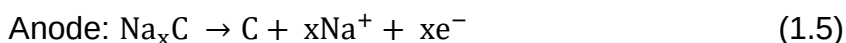
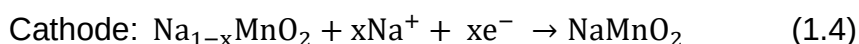


Figure 1. 3: Schematic illustration of the working mechanism of Na-ion batteries [16].

The charging and discharging process occurs through the intercalation/de-intercalation at the electrode, which is driven by the increase/reduction of the electrochemical potential of the alkali ion. During the charging process, the Na ions are de-intercalated from the cathode to the anode as presented in equations 1.1 to 1.3, which is a layered NaMnO₂ compound [18]:



During the discharging process, the reactions at both electrodes occur in the reverse direction. Na ions are de-intercalated from the anode and intercalated into the cathode material as shown in equations 1.4 to 1.6.



1.4. Electrode Materials for Sodium-Ion Batteries

Electrode materials for SIBs include inorganic compounds such as metal oxides, phosphates, fluorides, sulphides, phosphides, alloys, Prussian blue analogs, carbonaceous materials, and organic compounds [19]. Many inorganic compounds contain toxic metals, causing further concerns over resources and environmental contamination. Also, the inorganic compounds undergo the insertion-type sodium storage mechanism. During the intercalation and de-intercalation of sodium ions (with a radius of 1.02 Å), large volume changes and irreversible phase transitions may occur, leading to low reversible capacity and poor cycling performance [20].

Redox-active organic materials are gaining increasing research interest due to several intrinsic advantages [21]. Firstly, organic materials contain no heavy metals, an increasingly important consideration for the development of green energy storage devices. Secondly, the cost can be reduced because organic materials can be produced from renewable natural resources. Thirdly, various polymer structures with different surface functionalities can be designed at the molecular level. Fourthly, organic materials exploit an alkali ion storage involving reactions of chemical bonds, making them less sensitive to the large sodium ions [21,22]. Finally, organic materials are inherently flexible, making realizing commercial flexible energy storage devices possible. Despite these advantages, there are still challenges, such as their propensity to dissolve in the liquid electrolyte, resulting in inadequate cycle stability and constraining their practical applicability. Furthermore, organic materials frequently demonstrate low conductivity and may encounter challenges in attaining high energy densities relative to inorganic cathode materials [22,23].

Metal oxides, particularly transition metal oxides, are considered one of the most promising cathode materials for sodium-ion batteries (SIBs) due to their high energy density, good structural stability, relatively low cost, and abundant availability, making them a superior choice compared to other cathode materials for large-scale energy storage applications [24,25]. In this study, inorganic metal oxide NaMnO_2 are investigated using first principle density functional theory (DFT) and cluster expansion (CE) methods to determine the stability of doped NaMnO_2 and related physical properties. The study shares insights on developing novel electrode materials that can be used in SIBs.

1.5. Purpose of the study

1.5.1. Aim

This study aimed to design and develop electrode materials with desired properties related to energy storage performance using both the DFT and CE methods. The desired characteristics include a high specific capacity, outstanding sodium ion diffusion, structural, thermal, and chemical stability, affordability, environmental sustainability, and good electronic conductivity.

1.5.2. Research Problem

Although SIBs present a promising alternative to LIBs, they typically exhibit lower electrochemical activity. This is primarily due to two intrinsic shortcomings associated with Na. First, Na has a lower ionization potential than Li, resulting in lower operating voltages and, consequently, lower energy densities in comparison to LIBs. Second, Na ions are larger and heavier than Li ions, which leads to slow diffusion within a solid electrode during the cycling of SIBs. This also causes greater volume expansion of the electrode and contributes to the reduced energy densities relative to LIBs.

These intrinsic deficiencies necessitate the development of unique crystalline structures that feature an open framework or 3D structure with large insertion channels. Such designs are essential to facilitate the intercalation- intercalation process of the larger sodium ions. Despite significant advancements in the field, there remains a notable lack of cathode materials capable of integrating the essential characteristics needed for the practical implementation of SIB technology. These characteristics include high specific capacity, structural stability during operational cycling, fast Na⁺ diffusion kinetics, minimal volumetric expansion, environmental sustainability, cost-effectiveness, and compatibility with current electrolyte systems.

The absence of materials that meet all these requirements poses a significant barrier to the widespread adoption of SIBs, especially for large stationary energy storage applications where durability, safety, efficiency, and cost-effectiveness are critical. In response to these challenges, this study employs advanced computational modelling techniques, including Density Functional Theory (DFT) and Cluster Expansion (CE), to design, investigate, and optimize doped NaMnO₂. The focus is on identifying optimal dopants and their concentrations as well as understanding the impact of dopants on

essential characteristics such as Na^+ mobility, material stability, electronics structure, and the overall charge and discharge rates.

1.5.3. Research Motivation

Sodium-ion batteries (SIBs) are emerging as a highly attractive alternative to lithium-ion batteries (LIBs) for several compelling reasons. One of the most significant advantages is that sodium is not a limited resource; it is abundant both in the Earth's crust and in seawater, ensuring a more sustainable and readily available supply. Additionally, sodium-based battery components can potentially offer much faster charging times, provided that the appropriate crystal structure design is achieved. This faster charging capability could potentially enhance the efficiency and practicality of batteries in various applications. However, despite these advantages, sodium cannot be directly substituted for lithium in current battery materials. Sodium ions have a larger ionic radius, and slightly different chemical properties compared to lithium ions, which necessitates the development of entirely new materials specifically tailored for SIBs. This presents a significant challenge, as researchers must identify the optimal cathode materials from a vast array of possibilities. Traditionally, this process involves a trial-and-error approach, which is both costly and time-consuming.

To address these challenges, this study employs advanced computational modelling techniques to develop novel cathode materials for sodium-ion batteries. By using computational methods, researchers can simulate and predict the performance of various materials, thereby streamlining the discovery process and reducing the reliance on expensive and lengthy experimental trials. This approach accelerates the identification of suitable materials and provides deeper insights into the fundamental properties that make them effective.

This research aimed to pave the way for more efficient and sustainable energy storage solutions. This study's outcomes have significant implications for the future of energy storage, potentially leading to the widespread adoption of sodium-ion batteries in numerous applications, from portable electronics to large-scale renewable energy storage systems.

1.5.4. Significance of the Research

In today's world, the continuous use of mobile electronic devices such as mobile phones, cameras, and laptops has become an integral part of our daily lives. These devices rely heavily on batteries for power, making efficient and reliable battery technology crucial. As battery applications expand beyond personal electronics to include large-scale storage solutions such as in electric vehicles and stationary storage systems connected to renewable energy sources, the demand for robust and sustainable battery technology increases. For these large-scale applications, the focus shifts from high energy density to other critical factors such as cost-effectiveness, durability, and environmental impact.

It becomes paramount to develop electrode materials that are not only efficient but also composed of Earth-abundant elements. This approach can significantly reduce production costs and mitigate the environmental footprint associated with battery manufacturing. The transition to these sustainable materials is essential for the broader adoption of renewable energy storage solutions. Consequently, research in this area is of utmost importance. Hence, the importance of this study is to explore and develop new materials for renewable energy storage, addressing the challenges of scalability and sustainability. By focusing on materials that are abundant and cost-effective, more affordable and environmentally friendly battery technologies can come into being. Such advancements are crucial for supporting the growing infrastructure of

renewable energy systems and electric vehicles, ultimately contributing to a more sustainable future. Therefore, this research holds significant potential in transforming how we store and utilise energy on a large scale, paving the way for greener and more efficient energy materials and solutions.

1.5.5. Objectives

The objectives of this study were to:

- i. Determine the ground state properties of NaMnO_2 by optimizing the structure
- ii. Dope NaMnO_2 bulk system with Ti and Zn separately by varying the concentration of Mn with an equivalent concentration of the dopants (Ti and Zn), to give rise to $\text{Na}_x[\text{Ti}_y\text{Mn}_z]\text{O}_2$ and $\text{Na}_x[\text{Zn}_y\text{Mn}_z]\text{O}_2$, respectively.
- iii. Calculate the electronic properties, namely, band structure, the total density of states, the partial density of states, and conductivity of $\text{Na}_x[\text{Ti}_y\text{Mn}_z]\text{O}_2$ and $\text{Na}_x[\text{Zn}_y\text{Mn}_z]\text{O}_2$.
- iv. Determine the intercalation voltage and Na mobility within doped systems.
- v. Estimate the open-circuit voltage of $\text{Na}_x[\text{Ti}_y\text{Mn}_z]\text{O}_2$ and $\text{Na}_x[\text{Zn}_y\text{Mn}_z]\text{O}_2$ systems.
- vi. Predict new stable structures using cluster expansion approach, which uses DFT calculated structures and properties as input data for predicting new structures.
- vii. Calculate structures' structural, electronic, mechanical, and thermodynamic properties of the newly predicted stable structures.

REFERENCES

1. Zhu, X., Mochiku, T., Fujii, H., Tang, K., Hu, Y., Huang, Z., & Wang, L. (2018). A new sodium iron phosphate as a stable high-rate cathode material for sodium ion batteries. *Nano Research*, 11(12), 6197-6205.
2. Nishi, Y. (2001). Lithium-ion secondary batteries; past 10 years and the future. *Journal of Power Sources*, 100(1-2), 101-106.
3. Megahed, S., & Scrosati, B. (1994). Lithium-ion rechargeable batteries. *Journal of Power Sources*, 51(1-2), 79-104.
4. Ozawa, K. (1994). Lithium-ion rechargeable batteries with LiCoO_2 and carbon electrodes: the LiCoO_2/C system. *Solid State Ionics*, 69(3-4), 212-221.
5. Tarascon, J. M., & Armand, M. (2011). Issues and challenges facing rechargeable lithium batteries. In *Materials for sustainable energy: a collection of peer-reviewed research and review articles from Nature Publishing Group* (pp. 171-179).
6. Scrosati, B. (2000). Recent advances in lithium-ion battery materials. *Electrochimica Acta*, 45(15-16), 2461-2466.
7. Palacin, M. R. (2009). Recent advances in rechargeable battery materials: a chemist's perspective. *Chemical Society Reviews*, 38(9), 2565-2575.
8. Dunn, B., Kamath, H., & Tarascon, J. M. (2011). Electrical energy storage for the grid: a battery of choices. *Science*, 334(6058), 928-935.
9. Shibata, A., & Sato, K. (1999). Development of vanadium redox flow battery for electricity storage. *Power Engineering Journal*, 13(3), 130-135.
10. Aurbach, D., Gofer, Y., Lu, Z., Schechter, A., Chusid, O., Gizbar, H., & Levi, E. (2001). A short review on the comparison between Li battery systems and rechargeable magnesium battery technology. *Journal of Power Sources*, 97, 28-32.

11. Blurton, K. F., & Sammells, A. F. (1979). Metal/air batteries: their status and potential—a review. *Journal of Power Sources*, 4(4), 263-279.
12. Palacin, M. R. (2009). Recent advances in rechargeable battery materials: a chemist's perspective. *Chemical Society Reviews*, 38(9), 2565-2575.
13. Yabuuchi, N., Kubota, K., Dahbi, M., & Komaba, S. (2014). Research development on sodium-ion batteries. *Chemical Reviews*, 114(23), 11636-11682.
14. Kim, S. W., Seo, D. H., Ma, X., Ceder, G., & Kang, K. (2012). Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries. *Advanced Energy Materials*, 2(7), 710-721.
15. Dobján, T., & Kósa, J. Á. (2017). Ag/Zn Batteries in Hibrid Aircraft Systems. *GRADUS*, 4(2), 380-385.
16. Kang, H., Liu, Y., Cao, K., Zhao, Y., Jiao, L., Wang, Y., & Yuan, H. (2016). Correction: Update on anode materials for Na-ion batteries. *Journal of Materials Chemistry A*, 4(20), 7962-7962.
17. Pan, H., Hu, Y. S., & Chen, L. (2013). Room-temperature stationary sodium-ion batteries for large-scale electric energy storage. *Energy & Environmental Science*, 6(8), 2338-2360.
18. Xiang, X., Zhang, K., & Chen, J. (2015). Recent advances and prospects of cathode materials for sodium-ion batteries. *Advanced Materials*, 27(36), 5343-5364.
19. Hwang, J. Y., Myung, S. T., & Sun, Y. K. (2017). Sodium-ion batteries: present and future. *Chemical Society Reviews*, 46(12), 3529-3614.
20. Zhao, Q., Whittaker, A. K., & Zhao, X. S. (2018). Polymer electrode materials for sodium-ion batteries. *Materials*, 11(12), 2567.

21. Wei, X., Pan, W., Duan, W., Hollas, A., Yang, Z., Li, B., ... & Sprenkle, V. (2017). Materials and systems for organic redox flow batteries: status and challenges. *ACS Energy Letters*, 2(9), 2187-2204.
22. Lin, Y., Peng, Q., Chen, L., Zuo, Q., Long, Q., Lu, F., ... & Meng, Y. (2024). Organic Liquid Electrolytes in Sodium-Based Batteries: Actualities and Perspectives. *Energy Storage Materials*, 103211.
23. Rajagopalan, R., Tang, Y., Jia, C., Ji, X., & Wang, H. (2020). Understanding the sodium storage mechanisms of organic electrodes in sodium ion batteries: issues and solutions. *Energy & Environmental Science*, 13(6), 1568-1592.
24. Gao, H., Zeng, J., Sun, Z., Jiang, X., & Wang, X. (2024). Advances in layered transition metal oxide cathodes for sodium-ion batteries. *Materials Today Energy*, 101551.
25. Wang, Y., Ding, N., Zhang, R., Jin, G., Sun, D., Tang, Y., & Wang, H. (2024). Rational design of practical layered transition metal oxide cathode materials for sodium-ion batteries. *Frontiers of Chemical Science and Engineering*, 18(7), 80.
26. Sawicki, M., & Shaw, L. L. (2015). Advances and challenges of sodium ion batteries as post lithium ion batteries. *RSC Advances*, 5(65), 53129-53154.

CHAPTER 2

2. Literature Review

2.1. Cathode Materials

Cathode electrode materials have been the object of comprehensive studies, as they play a significant role in the operation of Na-ion batteries; the materials determine battery's energy capacity, voltage, cycle life, and safety [1]. They offer sources of Na^+ for the Na-ion "shuttle" between the cathode and anode. Good cathode materials must meet the following requirements: stable structure for repeated Na-ion intercalation/de-intercalation, high potential relative to Na/Na^+ reference electrode, high capacity to contain Na^+ , high electronic conductivity, high sodium chemical diffusion coefficient, low cost, and safety. A broad variety of compounds are being researched as potential candidates for cathodic materials in Na-ion batteries [1]. The subsections below summarize related previous work on layered metal oxides and polyanion compound cathode materials.

2.1.1. Layered Metal Oxides Cathode Materials

It is no wonder that sodium layered oxide compounds Na_xMO_2 (M=transition metal elements) have drawn significant attention as cathode materials for Na-ion batteries considering that their Li analogs have been comprehensively investigated for the past decades. The layered Na_xMO_2 materials can be categorized into two major groups, which are the P2 and O3 types. The first letter "P" or "O" refers to the nature of the site occupied by alkali-ion (prismatic or octahedral), and "2" or "3" refers to the number of transition metal layers in the repeat unit perpendicular to the layering [2]. The structural properties of Na_xMO_2 were first studied by Delmas *et al.* in the 1970's [3]. Earlier, Na_xCoO_2 proved to show reversible phase transformations by electrochemical charge and discharge demonstrating the feasibility of Na_xMO_2 as a cathode material [3]. However, limited efforts continued on Na-ion batteries research during the past two

decades due to the tremendous success of Li-ion batteries. Several studies on P2 or O3 type Na_xCrO_2 [4], Na_xMnO_2 [5] and Na_xFeO_2 [6] have been conducted in the early 1980's to 1990's, but the researchers were limited to the structural studies with up to 3.5 V versus sodium upon the first cycle mostly due to the instability of the electrolyte. Recent studies on O3- Na_xMO_2 compounds started to reveal the fact that these materials can be utilised as a cathode electrode with excellent electrochemical properties in Na-ion cells.

Di Lecce *et al.* investigated the degradation mechanism in a sodium cell of a layered $\text{Na}_{0.48}\text{Al}_{0.03}\text{Co}_{0.18}\text{-Ni}_{0.18}\text{Mn}_{0.47}\text{O}_2$ (NCAM) cathode with P3/P2 structure by revealing the changes in microstructure and composition upon cycling [7]. Their work aims to rationalise the gradual performance decay and the alteration of the electrochemical response in terms of polarization, voltage signature, and capacity loss. Spatial reconstructions of the electrode by X-ray computed tomography at the nanoscale supported by quantitative and qualitative analyses show fractures and deformations in the cycled layered metal-oxide particles and inorganic side compounds deposited on the material [7]. These irreversible morphological modifications reflect structural heterogeneities across the cathode particles due to forming various domains with different Na^+ intercalation degrees. Besides, X-ray photoelectron spectroscopy data suggest that the latter inorganic species in the cycled electrode are mainly composed of NaF, Na_2O , and Na_2CO_3 formed by parasitic electrolyte decomposition. The precipitation of these insulating compounds at the electrode/electrolyte interphase and the related structural stresses induced in the material leads to a decrease in cathode particle size and partial loss of electrochemical activity. The retention of the NCAM phase after cycling suggests that electrolyte upgrades may improve the performance of the cathode to achieve practical application for sustainable energy storage [7].

Zhao et al. [8] have explored intercalation of ions in electrode materials to improve the rate capability in lithium batteries and supercapacitors due to the enhanced diffusion of Li^+ or electrolyte cations. Here, they described a synergistic effect between crystal structure and intercalated ion by experimental characterization and ab initio calculations, based on more than 20 nanomaterials: five typical cathode materials together with their alkali metal ion intercalation compounds A-M-O ($\text{A} = \text{Li, Na, K, Rb}$; $\text{M} = \text{V, Mo, Co, Mn, Fe-P}$). Their focus was on nanowires is motivated by general enhancements afforded by nanoscale structures that better sustain lattice distortions associated with charge/discharge cycles [8]. They showed that the intercalation of alkali metal ions in V-O and Mo-O yields substantial improvement in the Li-ion charge/discharge cycling and rate, compared to A-Co-O , A-Mn-O , and A-Fe-P-O . Diffraction and modelling studies reveal that pre-intercalation with K and Rb ions yields a more stable interlayer expansion, which prevents the destructive collapse of layers and allows Li ions to diffuse more freely. Their study demonstrates that appropriate alkali metal ion intercalation in admissible structure can overcome the limitation of cyclability as well as rate capability of cathode materials, besides, the intercalation strategy provides an effective method to enlarge the diffusion channel at the technical level, and more generally, it suggests that the optimised design of stable intercalation compounds could lead to substantial improvements for applications in energy storage [8].

Pandit *et al.* developed manganese oxide ($\alpha\text{-MnO}_2$) nanorods for SIB applications. The crystal structure, crucial for high-performance energy storage, is examined systematically for the metal oxide cathode [9]. The intercalation of sodium into the $\alpha\text{-MnO}_2$ matrix was studied using the theoretical density functional theory (DFT) studies. The DFT studies predict Na ions' facile diffusion kinetics through the MnO_2 lattice with

an attractively low diffusion barrier (0.21 eV). When employed as a cathode material for SIBs, MnO_2 showed a moderate capacity ($109 \text{ mAh}\cdot\text{g}^{-1}$ at C/20 current rate) and superior life cyclability (58.6% after 800 cycles) in $\text{NaPF}_6/\text{EC}+\text{DMC}$ (5% FEC) electrolyte. It shows a much higher capacity of $181 \text{ mAh}\cdot\text{g}^{-1}$ (C/20 current rate) in NaClO_4/PC (5% FEC) electrolyte, though it suffers fast capacity fading (11.5% after 800 cycles). Our findings show that high crystallinity and hierarchical nanorod morphology of the MnO_2 are responsible for better cycling performance in conjunction with fast and sustained charge-discharge behaviours [9].

Sudarshan *et al.* reported the thermodynamic properties of the monoclinic NaMnO_2 and their analysis was based on density functional theory [6]. The cluster expansion method was used to find the minimum formation energy configurations at different concentrations of Na removal. The material showed a strong Na vacancy ordering during the extraction of Na from the host structure. The cluster expansion method predicted several ground state configurations as a function of Na composition. The thermodynamic intercalation potential of the electrode was calculated using Monte Carlo simulation. The stability of the cathode material at higher temperatures was also analysed, and the results showed that the material was highly stable at higher temperatures, suggesting its suitability for use as a cathode material for Na ion batteries [6].

Zhang *et al.* used first-principles calculations to investigate the electrochemical performance of the monoclinic NaMnO_2 for the sodium-ion batteries [10]. The study reported that NaMnO_2 possessed a voltage window of 3.54–2.52V and a theoretical reversible capacity of $136 \text{ mAh}\cdot\text{g}^{-1}$. The findings showed that the metallicity of the monoclinic NaMnO_2 gradually increases during Na extraction. Moreover, the

computed Na migration energy barrier in the monoclinic NaMnO_2 was 0.18 eV, ensuring ideal conductivity and reversible capacity. Although the Jahn-Teller distortion effects limited the enhancement of the reversible capacity of the monoclinic NaMnO_2 , it was still regarded as a good cathode material for the sodium-ion batteries [10].

Electrochemical characteristics of monoclinic $\alpha\text{-NaMnO}_2$ was further investigated as a positive electrode material for sodium-ion batteries by Ma *et al.* [11]. The study reported that about 0.85 Na could be de-intercalated from NaMnO_2 and 0.8 Na could be intercalated back during potentiostatic intermittent charge and discharge. Galvanostatic cycling between 2.0 V and 3.8 V gave 185 mAh/g discharge capacity for the first cycle at C/10 rate and 132 mAh/g remains after 20 cycles. Charge and discharge curves were significantly different indicating more hysteresis than is typical for lithium intercalation compounds [11].

2.1.2. Polyanion Compounds as Cathode Materials

In recent years, polyanion compounds have garnered significant attention as potential cathode materials for sodium-ion (Na-ion) batteries, due to their ability to accommodate Na-ions via their open channels. These materials are typically composed of tetrahedral polyanion units, $(\text{XO}_4)^{n-}$ where X = P or S, which are linked with transition metal polyhedra, MO_6 (M = transition metal), to form stable structures. The strong covalent bonding within the $(\text{XO}_4)^{n-}$ groups results in high thermal stability, making polyanion-based cathodes attractive for large-scale energy applications. Additionally, the operation voltage of these materials can be tailored based on the local environment of the polyanions, making them versatile for various electrochemical systems [12].

NASICON-type (sodium super-ionic conductor) compounds, known for their three-dimensional (3D) structures and large Na-ion diffusion channels, have been widely studied for both their structural stability and fast ionic conduction properties. These materials have been primarily researched as solid electrolytes, but they have also shown promise as insertion materials for Na-ion batteries. Their general formula, $A_xMM'(XO_4)_3$, consists of MO_6 and XO_4 polyhedra, which are corner shared to form a framework. Delmas *et al.* [3], (1987, 1988) demonstrated that NASICON-type $NaTi_2(PO_4)_3$ could reversibly intercalate sodium ions. However, subsequent studies focused on Li-ion systems due to the relatively inferior performance of Na-ion cells [9]. It was not until Yamaki *et al.* [14], synthesized $Na_3V_2(PO_4)_3$ that interest in Na-ion batteries began to grow. This compound exhibited two distinct voltage plateaus at 1.6 V and 3.4 V, which allowed it to function as both a cathode and an anode in symmetric cells. However, the cycling stability of such symmetric cells remained a challenge. Recent efforts have focused on improving the electrochemical performance of $Na_3V_2(PO_4)_3$ through carbon coating, leading to an enhanced cycling stability and rate capability [14].

Despite the success of $LiFePO_4$ in lithium-ion batteries, its sodium analogue, $NaFePO_4$, has not been extensively explored. The sodium version can be synthesized by removing Li-ions from $LiFePO_4$ and subsequently inserting Na-ions into $FePO_4$. Na-ion extraction leads to the appearance of two voltage plateaus due to two successive first-order transitions, resulting in the formation of an intermediate $Na_{0.7}FePO_4$ phase. Interestingly, only a single plateau is observed during discharge, suggesting different reaction mechanisms during charge and discharge cycles [15]. Other variations of this system, such as $NaFe_{0.5}Mn_{0.5}PO_4$, have been synthesized to investigate alternative

behaviours. While this compound exhibited a sloping voltage profile, the solid solution mechanism responsible for this behaviour remains unclear [12].

In the search for novel cathode materials, sodium vanadium fluorophosphates such as NaVPO_4F , $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, and $\text{Na}_{1.5}\text{VOPO}_4\text{F}_{0.5}$ have shown promise due to the high potential of the $\text{V}^{3+}/\text{V}^{4+}$ redox couple [16]. $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, first reported by Meins *et al.* [14], has demonstrated good cyclability, while $\text{Na}_{1.5}\text{VOPO}_4\text{F}_{0.5}$ has shown reversible capacity during galvanostatic cycling. Another interesting compound, $\text{Na}_2\text{FePO}_4\text{F}$, contains two-dimensional iron phosphate sheets that host two Na^+ -ions and exhibit reversible two-plateau behaviour in electrochemical profiles [14].

Pyrophosphates are another family of Na-ion battery materials, and their open frameworks enable efficient Na-ion diffusion. Recently, a Fe-based pyrophosphate, $\text{Na}_2\text{FeP}_2\text{O}_7$, was reported as a cathode material with a reversible capacity of 90 mAh g^{-1} , exhibiting excellent thermal stability up to 500°C [12]. Moreover, sodium transition metal fluorosulphates, NaMSO_4F , have been shown to exhibit high ionic conductivity and satisfactory performance in hybrid Li^+ -ion batteries. However, their reversibility in Na^+ -ion cells remains a challenge [17].

2.2. Anode Materials

The negative electrode of a sodium-ion battery intercalates sodium-ions during charge and de-intercalates Na^+ ions during discharge. There are three basic requirements for anode materials: (a) the potential of sodium insertion and extraction in the anode versus sodium must be as low as possible, (b) the amount of sodium that can be accommodated by the anode material should be as high as possible to achieve high specific capacity, and (c) the anode host must endure repeated sodium insertion and extraction without any structural damage to obtain long cycle life [18].

The search for appropriate anodes for Na-ion batteries is complex, and, although a vast variety of phases that can potentially be used as positive electrodes have been identified, very few materials have been reported to be useful as negative electrodes. Graphite, which is the most used anode material in Li-ion batteries, has a moderate Li storage capacity (350 mAhg^{-1}) at approximately 0.1 V vs. Li⁺/Li. Recent studies indicate that Na cannot be inserted into the graphite layer [19]. This phenomenon might be related to thermodynamic stability issues. To date, very few anode materials have been reported as viable. The use of metallic sodium is not advisable because of dendrite formation, as for metallic lithium. Thus, identifying an anode with a proper Na storage voltage, large reversible capacity, and high structural stability is urgently needed for the development of Na-ion batteries [20].

Luo *et al.* [21] reported the recent development on anode materials for NIBs the study focused mainly on the carbon-based and alloy-based anodes and highlighted progress made by various groups in this field. The review starts by firstly presenting what is known about the failure mechanism of graphite anode in NIBs, then go on to discuss studies on hard carbon anodes, alloy-type anodes, and organic anodes. Especially, the multiple functions of natural cellulose that is used as a low-cost carbon precursor for mass production and as a soft substrate for tin anodes were highlighted. The strategies of minimizing the surface area of carbon anodes for improving the first-cycle Coulombic efficiency are also outlined, where graphene oxide was employed as a dehydration agent and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was used to unzip wood fiber [21]. Furthermore, surface modification by atomic layer deposition technology was introduced, where it was discovered that a thin layer of Al₂O₃ can function to encapsulate Sn nanoparticles, leading to much-enhanced cycling performance.

The study also highlighted recent work about the phosphorene/graphene anode, which outperformed other anodes in terms of capacity. The aromatic organic anode was also studied as anode with extremely high initial sodiation capacity. Furthermore, electrochemical intercalation of Na^+ ions into reduced graphene oxide was applied for fabricating transparent conductors, demonstrating the great feasibility of Na ion intercalation for optical applications [21]. The electrolyte and separator materials are beyond the scope of this work and have not been discussed.

2.3. Electrode Material Optimization

Developing high-performance cathode materials is crucial for enhancing battery performance. The focus is on designing and synthesizing materials with higher capacity, improved sodium-ion diffusion kinetics, and structural stability. Doping with other elements can enhance the performance of many cathode materials. However, the interpretation of doping effects can be complicated due to the interrelations between doping and microstructural morphology [19]. Nonetheless, one of the strategies to advance the physical properties of cathode materials is to dope with the metals. According to the previous literature [20], this approach has been widely applied to the standard Li-based cathode materials. W. Sukkabet [22] deployed doping strategy to enhance the electrochemical properties in NaMnO_2 compound using density functional theory. In the study, Sukkabet used the substitution doping method, where Mn atom was substituted by several transition metals (namely, Cr, Fe and V) in monoclinic NaMnO_2 compound. The results showed that transition metal dopants were responsible for the electronic conductivity and volume expansion [22].

In another study, Zheng *et al.* [23] performed DFT calculations in GGA and GGA+U to study the effect of Co doping on NaMnO_2 by mixing Co–Mn on Na orderings in $\text{P2 Na}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_2$. From GGA energy calculations, six ground-state Na orderings were

identified in mixed-transition metals $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{Na}_x\text{Co}_{1/3}\text{Mn}_{2/3}\text{O}_2$, whereas the single-transition metal Na_xCoO_2 had eight ground-state orderings as shown in Figure 2.1 below:

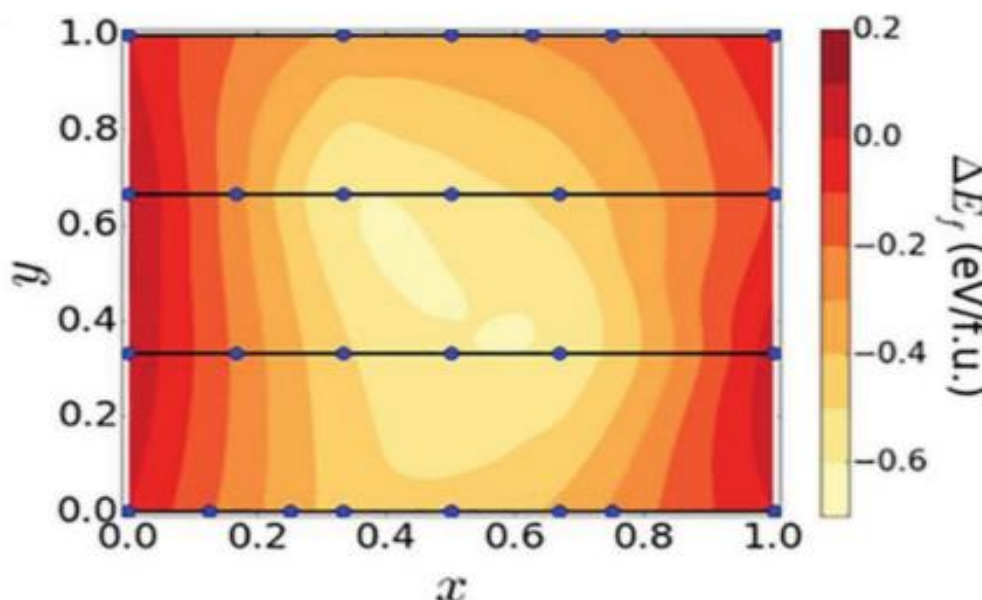


Figure 2. 1: Stability diagram of P2 $\text{Na}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_2$ as described by the formation energy with respect to the fully sodiated and de-sodiated compounds based on DFT calculations [23].

These computational results suggest that transition metals mixing suppresses the Na-vacancy ordering. As a result of fewer ground-state orderings, the calculated voltage profile of mixed- transition metals $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{1/3}\text{O}_2$ shows fewer voltage steps than the single- transition metals Na_xCoO_2 . In addition, the calculations by Velikokhatny *et al.* [24] revealed that the change of the Na-vacancy orderings in mixed-transition metals compounds was caused by the differences of Na₁ site energy facing different transition metals. The ab initio molecular dynamics (AIMD) simulations of $\text{Na}_{1/2}\text{Co}_{1-y}\text{Mn}_y\text{O}_2$ found a higher occupancy of Na₁Co-Co site sharing faces with two CoO_6 octahedra than that of Na₁Mn–Mn site at Mn concentration y from 1/6 to 1/2 shown by Figure 2.2.

Therefore, Mn substitution increases the site energy of the Na₁ site facing Mn. In addition to Na orderings and voltage profiles, transition metals mixing also impacts the Na⁺ diffusion.

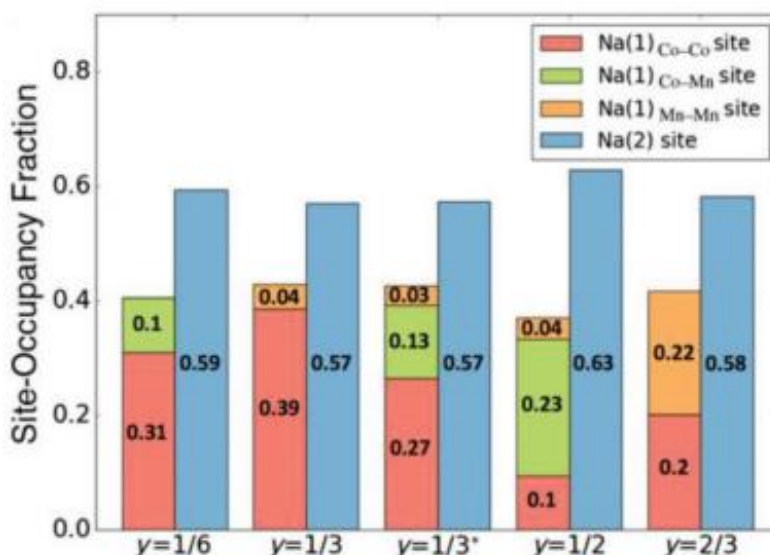


Figure 2. 2: Fraction of Na-ion site occupancy in P2 Na_{1/2}Co_{1-y}Mn_yO₂ from AIMD simulations [24].

The structural stability of NaB_xMn_{1-x}O₂, where x = 0.0 – 0.375 has been studied using density functional theory within the generalized gradient approximation (GGA). In addition, the structural stability of the oxides with 75% vacancy of Na ions for each concentration of B has been investigated. To validate the results of the ab initio study, a series of experimental investigations have been conducted for NaB_xMn_{1-x}O₂ and LiB_xMn_{1-x}O₂ synthesized via conventional solid-state and the chimie douce ion-exchange reactions [22]. Results of the simulation show that the monoclinic phase of these oxides is thermodynamically stable for all the B concentrations studied. Moreover, substitution of a larger amount of boron results in a higher energy difference between the monoclinic phase and its nearest concurrent orthorhombic phase. Also,

de-intercalation of Na ions from the parent oxide has shown that the monoclinic phase is stable and the energy difference between the monoclinic and spinel crystal structures increases with increasing amounts of boron. A rationale for this electrochemical response of boron substituted sodium manganese oxide was offered. Electrochemical cycling results of the experimentally synthesized materials were also discussed considering these theoretical predictions [22]. Billaud *et al.* [25] studied the electrochemical properties of P2- $\text{Na}_{0.67}\text{MnO}_2$ with various ratios x of Mg dopants ($0 \leq x \leq 0.2$). Their current-voltage measurements showed that Mg-doped $\text{Na}_{0.67}\text{MnO}_2$ had smoother voltage profiles than the undoped one. $\text{Na}_{0.67}\text{MnO}_2$ with optimal amount of Mg contents showed a high-capacity retention during cycling. This improvement was due to the presence of Mg in the lattice that increases the oxidation state of Mn to close to 4^+ [25]. Llave *et al.* [26] combined experiments and DFT-PBE+U calculations to investigate the effect of Li doping on the structural stability of P2- $\text{Na}_{0.6}\text{MnO}_2$. By XRD and current-voltage curves, the study found that $\text{Na}_{0.6}\text{Li}_{0.2}\text{Mn}_{0.8}\text{O}_2$ undergoes less phase transitions compared to $\text{Na}_{0.6}\text{MnO}_2$. The oxidation state of Mn^{4+} was found by XPS measurement for $\text{Na}_{0.6}\text{Li}_{0.2}\text{Mn}_{0.8}\text{O}_2$, showing the suppression of Jahn–Teller distortion [24]. Their DOS plots also confirmed the charge state of 4^+ for Mn cations. $\text{Na}_{0.6}\text{Li}_{0.2}\text{Mn}_{0.8}\text{O}_2$, thus shows a reasonable reversible capacity during charging/discharging [26].

Double dopants in NaMnO_2 have also been explored for SIBs. For example, Yang *et al.* [27] studied the effect of Li and Fe co-doping on the cycling stability of $\text{Na}_{0.66}\text{MnO}_2$. They found that $\text{Na}_{0.66}\text{MnO}_2$ with Li and Fe dopants, $\text{P2} \rightarrow \text{O2}$ phase transition for $\text{Na}_{0.66}\text{MnO}_2$ was eliminated. This was attributed to the presence of Li in the transition metal sites, which stabilized the P2 structure [27].

Zhou *et al.* investigated the co-doping of β -NaMnO₂ with Ti atoms, known for enhancing structural stability, and Cu atoms, which facilitate de-intercalation, using first-principles calculation and crystal orbital Hamilton population (COHP) analysis. β -NaMn_{0.8}Ti_{0.1}Cu_{0.1}O₂ exhibits a notable increase in reversible specific capacity and remarkable rate properties [28]. Operating at a current density of 0.2C (1C = 219 mA·g⁻¹) and within a voltage range of 1.8–4.0 V, the modified material delivers an initial discharge capacity of 132 mAh·g⁻¹. After charge/discharge testing at current densities of 0.2C, 0.5C, 1C, 3C, and 0.2C, the material still maintains a 110 mAh·g⁻¹ capacity. Their results show that doping with Ti atoms slows down the changes in the crystal structure, resulting in only minimal variation in the lattice constant c/a during the de-intercalation process. Mn and Cu engage in reversible redox reactions at voltages below 3.0 V and around 3.5 V, respectively. The extended plateau in the discharge curve below 3.0 V signifies that Mn significantly contributes to the overall battery capacity. Their study provides insights into modifying β -NaMnO₂ as a cathode material, offering experimental evidence and theoretical guidance for enhancing battery performance in Na-ion batteries [28].

Bass *et al.* [29], employed Molecular Dynamic Simulation based on the density functional theory to investigate the effect of molybdenum dopants on the performance of the mechanical, structural, and electronic properties, as well as thermodynamic stability of O3-type NaNi_{0.25}Fe_{0.25}Mn_{0.5}O₂ layered oxide cathode material for sodium-ion batteries. Their results show that molybdenum in NaNi_{0.25}Fe_{0.25}Mn_{0.5}O₂ material positively affected structural and mechanical stability, improved conductivity, and thermodynamic stability. The molybdenum-doped material at 10% (Na(Ni_{0.25}Fe_{0.25}Mn_{0.5})_{0.9}Mo_{0.1}O₂) delivered superior performance than that with 5% and 15% molybdenum (Na(Ni_{0.25}Fe_{0.25}Mn_{0.5})_{0.95}Mo_{0.5}O₂). Therefore, it can be concluded

that the $\text{Na}(\text{Ni}_{0.25}\text{Fe}_{0.25}\text{Mn}_{0.5})_{0.9}\text{Mo}_{0.1}\text{O}_2$ material is an effective strategy for layered transition metal oxide cathode material for commercialized rechargeable sodium-ion batteries [29].

The present study employed first-principles density functional theory to examine the influence of transition metal dopants Ti and Zn in NaMnO_2 . The investigation focused on calculating electronic, structural, mechanical, and thermodynamic properties and assessing the impact of Na de-intercalation on the two doped systems, explicitly analyzing the de-intercalation voltage of these systems. The Universal Cluster Expansion (UNCLE) program was utilized to set up, construct, and automatically converge a cluster expansion for Ti and Zn in NaMnO_2 , thereby producing distinct structures within the random combinations of Ti and NaMnO_2 and Zn and NaMnO_2 , respectively. The DFT-based calculations of electrical, structural, mechanical, and thermodynamic parameters were subsequently performed for the Cluster Expansion predicted stable structures.

REFERENCES

1. Dobján, T., & Kósa, J. Á. (2017). Ag/Zn Batteries in Hibrid Aircraft Systems. *GRADUS*, 4(2), 380-385.
2. Sawicki, M., & Shaw, L. L. (2015). Advances and challenges of sodium ion batteries as post lithium-ion batteries. *RSC Advances*, 5(65), 53129-53154.
3. Delmas, C., Braconnier, J. J., & Fouassier, C. (1987). Electrochemical intercalation of sodium in NASICON-type compounds. *Solid State Ionics*, 28-30, 419-423
4. Bai, Q., Yang, L., Chen, H., & Mo, Y. (2018). Computational studies of electrode materials in sodium-ion batteries. *Advanced Energy Materials*, 8(17), 1702998.
5. Kim, S. W., Seo, D. H., Ma, X., Ceder, G., & Kang, K. (2012). Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries. *Advanced Energy Materials*, 2(7), 710-721.
6. Sudarsanan, V., Augustine, A. M., & Ravindran, P. (2019, July). Ab-initio based thermodynamic study on α -NaMnO₂ for Na-ion battery applications. *In AIP Conference Proceedings* (Vol. 2115, No. 1, p. 030586). AIP Publishing LLC.
7. DiLecce , D., Marangon, V., Isaacs, M., Palgrave, R., Shearing, P. R., & Hassoun, J. (2021). Degradation of Layered Oxide Cathode in a Sodium Battery: A Detailed Investigation by X-Ray Tomography at the Nanoscale. *Small Methods*, 5(10), 2100596.
8. Zhao, Y., Han, C., Yang, J., Su, J., Xu, X., Li, S., ... & Zhang, Q. (2015). Stable alkali metal ion intercalation compounds as optimized metal oxide nanowire cathodes for lithium batteries. *Nano letters*, 15(3), 2180-2185.

9. Pandit, B., Rondiya, S. R., Dzade, N. Y., Shaikh, S. F., Kumar, N., Goda, E. S., ... & Salunkhe, R. R. (2021). High stability and long cycle life of rechargeable sodium-ion battery using manganese oxide cathode: a combined density functional theory (DFT) and experimental study. *ACS applied materials & interfaces*, 13(9), 11433-11441.
10. Zhang, R., Lu, Z., Yang, Y., & Shi, W. (2018). First-principles investigation of the monoclinic NaMnO_2 cathode material for rechargeable Na-ion batteries. *Current Applied Physics*, 18(11), 1431-1435.
11. Ma, X., Chen, H., & Ceder, G. (2011). Electrochemical properties of monoclinic NaMnO_2 . *Journal of The Electrochemical Society*, 158(12), A1307
12. Balaya, P., Li, H., Kienle, L., & Maier, J. (2003). Sodium-ion storage in nanostructured NASICON materials. *Electrochemical Society Interface*, 12(4), 44-48.
13. Delmas, C., Braconnier, J. J., & Fouassier, C. (1987). Electrochemical intercalation of sodium in NASICON-type compounds. *Solid State Ionics*, 28-30, 419-423
14. Yamaki, J. I., Takahashi, K., & Takeda, Y. (2002). Sodium intercalation in NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ for Na-ion batteries. *Electrochemistry Communications*, 4(6), 509-512.
15. Nazar, L. F., Ellis, B. L., & Makimura, Y. (2010). Sodium iron fluorophosphates for next-generation batteries. *Nature Materials*, 9(6), 404-409.
16. Ma, X., Chen, H., & Ceder, G. (2011). Electrochemical properties of monoclinic NaMnO_2 . *Journal of The Electrochemical Society*, 158(12), A1307.

17. Mukherjee, S., Bin Mujib, S., Soares, D., & Singh, G. (2019). Electrode Materials for High-Performance Sodium-Ion Batteries. *Materials*, 12(12), 1952.
18. J.W. Fergus, "Recent developments in cathode materials for lithium-ion batteries," *Journal of Power Sources*, vol. 195, pp. 939-954, 2010
19. Kim, H., Hong, J., Yoon, G., Kim, H., Park, K. Y., Park, M. S., ... & Kang, K. (2015). Sodium intercalation chemistry in graphite. *Energy & Environmental Science*, 8(10), 2963-2969.
20. Lee, B., Paek, E., Mitlin, D., & Lee, S. W. (2019). Sodium metal anodes: emerging solutions to dendrite growth. *Chemical reviews*, 119(8), 5416-5460.
21. Luo, W., Shen, F., Bommier, C., Zhu, H., Ji, X., & Hu, L. (2016). Na-ion battery anodes: materials and electrochemistry. *Accounts of chemical research*, 49(2), 231-240.
22. Sukkabot, W. (2020). First-principles calculations of the monoclinic transition-metal doped NaMnO₂ cathode material. *Philosophical Magazine*, 100(7), 917-926.
23. Zheng, H., Lee, J., Lee, W., & Ceder, G. (2017). Effect of Co–Mn mixing on Na orderings in P₂ Na_xCo_{1-y}Mn_yO₂. *Chemistry of Materials*, 29(2), 669-679.
24. Velikokhatnyi, O. I., Choi, D., & Kumta, P. N. (2006). Effect of boron on the stability of monoclinic NaMnO₂: Theoretical and experimental studies. *Materials Science and Engineering: B*, 128(1-3), 115-124.
25. Billaud, J., Armstrong, A. R., Gonzalo, E., & Bruce, P. G. (2014). Na_{0.67}Mn_{1-x}Mg_xO₂ (0 ≤ x ≤ 0.2): A layered cathode material for sodium-ion batteries. *Journal of Materials Chemistry A*, 2(7), 1494-1500.

26. Llave, E., Moyer, S. J., & Malik, R. (2016). Li-doping effect on structural stability and electrochemical performance of $P_2\text{-Na}_{0.6}\text{MnO}_2$. *Journal of Power Sources*, 316, 1-10.
27. Yang, X., Li, X., Zhang, H., & Xia, X. (2019). Li and Fe co-doping on cycling stability of $P_2\text{-Na}_{0.66}\text{MnO}_2$ for sodium-ion batteries. *Electrochimica Acta*, 298, 670-678. <https://doi.org/10.1016/j.electacta.2018.12.103>
28. Zhou, J., Li, X., Zhao, X., Wang, Y., Song, E., & Liu, J. (2024). Rate and Cycling Performance of Ti and Cu Doped $\beta\text{-NaMnO}_2$ as Cathode of Sodium-ion Battery. *无机材料学报*, 39(12).
29. Bass, S. B., Azambou, C. I., Anyanwu, J. O., Akalezi, C. O., Ayogu, I. I., & Oguzie, E. Improving Stability and Performance of O3-Type $\text{Na}_{0.25}\text{Fe}_{0.25}\text{Mn}_{0.5}\text{O}_2$ Layered Oxide Cathode Material by Molybdenum Additives—a First Principle DFT Study. *Available at SSRN 5078399*.

CHAPTER 3

3. Methodology

3.1. Density Functional Theory

Density functional theory (DFT) is a computational quantum mechanical method used in physics, chemistry, and materials science to examine the electronic structure (principally the ground state) of numerous systems, in particular atoms, molecules and the dense stages [1]. DFT calculations are based on solving Kohn–Sham equation, which is the Schrödinger equation of an invented system of non-interacting particles that produce an indistinguishable density from any given arrangement of connected particles [2, 3]. The Kohn–Sham equation is characterized by a nearby viable outside potential in which the non-cooperating particles move, commonly meant as $V_s(r)$ or $V_{eff}(r)$, called the Kohn–Sham potential. As the particles in the Kohn–Sham equation are non-collaborating fermions, the Kohn–Sham wavefunction is a solitary Slater determinant developed from an arrangement of orbitals that are the most minimal energy. The wave function equation is then given by [1]:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r)\right)\phi_i(r) = \varepsilon_i\phi_i(r) \quad (3.1)$$

This eigenvalue equation is the typical representation of the Kohn–Sham equations. where, ε_i is the orbital energy of the corresponding Kohn–Sham orbital, ϕ_i , and the density for an N-particle system is given by [4]:

$$\rho(r) = \sum_i^N |\phi_i(r)|^2 \quad (3.2)$$

In Kohn-Sham density functional theory, the aggregate energy of the system is described as a useful charge density given as:

$$E[\rho] = T_s[\rho] + \int dr V_{ext}(r)\rho(r) + E_H[\rho] + E_{xc}[\rho] \quad (3.3)$$

where T_s is the Kohn–Sham kinetic energy described as the Kohn–Sham orbitals and is given by:

$$T_s[\rho] = \sum_{i=1}^N \int dr \phi_i^*(r) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(r) \quad (3.4)$$

V_{ext} is the outside potential following up on the cooperating system (at least, for an atomic system, the electron-cores), E_H is the Hartree energy given as:

$$E_H = \frac{e^2}{2} \int dr \int dr' \frac{\rho(r)\rho(r')}{|r-r'|} \quad (3.5)$$

and E_{xc} is the exchange-correlation energy. The Kohn–Sham equations are found by varying the total energy expression with respect to a set of orbitals to yield the Kohn–Sham potential as [5]:

$$V_{eff}(r) = V_{ext}(r) + e^2 \int \frac{\rho(r')}{|r-r'|} dr' + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \quad (3.6)$$

where the last term is depicted by:

$$v_{xc}(r) \equiv \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \quad (3.7)$$

is the exchange-correlation potential. These terms and the corresponding energy expression are the only unknowns in the Kohn–Sham approach to density functional theory. An approximation that does not vary the orbitals is Harris functional theory.

The Kohn–Sham orbital energies ε_i generally have little physical meaning. The sum of the orbital energies is related to the total energy by:

$$E = \sum_i^N \varepsilon_i - V_H[\rho] + E_{xc}[\rho] - \int \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \rho(r) dr \quad (3.8)$$

Because the orbital energies are non-unique in the more general restricted open-shell case, this equation only holds true for specific choices of orbital energies. Since the orbital energies are non-one of a kind in the broader limited open-shell case, this condition remains constant for particular decisions of orbital energies [6, 7].

The modern DFT is founded on Hohenberg–Kohn theorems and the two theorems relate to any system consisting of electrons moving under the influence of an external potential.

Theorem 1. The external potential (and hence the total energy) is a unique functional of the electron density.

If two systems of electrons, one trapped in a potential $V_1(\vec{r})$ and the other in $V_2(\vec{r})$ have the same ground-state density $n(\vec{r})$, then $V_1(\vec{r}) - V_2(\vec{r})$ is necessarily a constant.

Corollary: The ground state density uniquely determines the potential and thus all properties of the system, including the many-body wave function. In particular, the $H - K$ functional, defined as $F[n] = T[n] + U[n]$, is a universal functional of the density (not depending explicitly on the external potential).

Theorem 2. The functional that delivers the ground state energy of the system, gives the lowest energy if and only if the input density is the true ground state density.

For any positive integer n and potential $V(\vec{r})$, a density functional $F[n]$ exists such that:

$$E_{(v,N)}[n] = F[N] + \int v(\vec{r})n(\vec{r})d^3r \quad (3.9)$$

The density functional obtains its minimal value at the ground-state density of N electrons in the potential $(\vec{r})$. The minimal value of $E_{(V, N)}[n]$ is then the ground state energy of this system [8].

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist that permit the calculation of certain physical quantities quite accurately [9].

To get the exchange-correlation potential, there are two major approximations to solve this problem: the local-density approximation (LDA) and the generalized gradient approximation. In LDA approximation it is assumed that the exchange-correlation energy per electron is equal to the one in a homogeneous electron gas. In GGA approximation, the detailed deviation of the exchange-correlation potential curve is taken into consideration and used as the criterion to determine the exchange-correlation energy [10,11]. However, in transition metal ions, the highly localized d electrons could cause the main error of calculation accuracy because of the lack of cancellation of electron self-interaction [11].

To avoid electron self-interaction errors that occur in standard LDA or GGA for strongly correlated electronic systems, DFT + U methods are often used for open-shell transition metal compounds, where U is an on-site Coulomb interaction parameter [12]. The U parameter is derived either by fitting experimental data (e.g. cell voltages, band gaps) or by self-consistent calculations. There is an increase in the use of hybrid functionals, which include a fraction of the Hartree–Fock exchange and can also correct for self-interaction present in the Hartree term. Although the amount of exact exchange required can also be system dependent introducing another empirical term [13].

Besides the electron-electron interaction, the electron-ion interactions are also difficult to deal with because of the huge number of core electrons of each ion. Since the core electrons are tightly bonded with the nuclei, many wave functions are needed for the Fourier transformation, which will raise the cost of computation. It is necessary to do the full electron calculation if dealing with the fine electronic structure of the materials. However, most of the time, the major physical properties of the materials are determined by the valence electrons [14]. Thus, the pseudopotential approximation is developed so that all the core-electrons are simplified as a core and the ion is divided into two parts - the “core” and the valence electrons. A local pseudopotential is set up that will be the same with the core electron potential beyond a critical distance, r_c , from the nuclei. On one hand, the consistency between pseudopotential and full-electron potential beyond r_c ensures the correction of the properties that determined only by the valence electrons. On the other hand, the complicated core-electrons are substituted by only one potential function therefore the computation cost is significantly reduced. Again, since the pseudopotential of each element is only determined by the atomic number of the element, it could also be determined in a self-consistent way.

3.2. Approximations

3.2.1. Local Density Approximations

Local density approximation is a class of approximations to the exchange-correlation (XC) energy functional in density functional theory. It depends exclusively upon the estimation of the electronic density at every point in space. Numerous methodologies can yield local approximations to the XC energy. Overwhelmingly effective approximations nearby can be also defined as those that have been established from the homogeneous electron gas (HEG). In such a manner, LDA is, for the most part, synonymous with functionality considering the HEG estimate, which is then connected to practical frameworks.

For a spin-unpolarized framework, a local density approximation for the trade connection energy is expressed as [15,16]:

$$E_{xc}^{LDA}[\rho] = \int \rho(r) \epsilon_{xc}(\rho) dr \quad (3.10)$$

where ρ is the electronic density, ϵ_{xc} is the exchange-correlation energy per molecule of a homogeneous electron gas of charge density. The exchange-correlation energy is decayed into exchange and correlation terms linearly and can be expressed as [17]:

$$E_{xc} = E_x + E_c \quad (3.11)$$

so that different expressions for E_x and E_c are looked for. The exchange term goes up against a straightforward systematic frame for the HEG. Just restricting expressions for the relationship thickness are known precisely, prompting various distinctive approximations for E_c .

Local density approximations are imperative in the development of more complex approximations to the exchange-correlation energy, for example, generalized gradient approximations or hybrid functionals, as an attractive property of any exchange-correlation functional, is that it duplicates the correct consequences of the HEG for non-differing densities. In that capacity, LDA's are frequently an express segment of such functionals [15].

The extension of density functionals to spin-polarized systems is straightforward for exchange, where the exact spin-scaling is known, but for correlation further approximations must be employed. A spin polarized system in DFT employs two spin-densities, $\rho\alpha$ and $\rho\beta$ with $\rho = \rho\alpha + \rho\beta$, and the form of the local-spin-density approximation (LSDA) is:

$$E_{xc}^{LSDA}[\rho\alpha, \rho\beta] = \int dr \rho(r) \epsilon_{xc}(\rho\alpha, \rho\beta). \quad (3.12)$$

for the exchange energy, the exact results are known in terms of the spin unpolarized functional:

$$E_x [\rho\alpha, \rho\beta] = \frac{1}{2} (E_x [2\rho\alpha] + E_x [2\rho\beta]) \quad (3.13)$$

The spin-dependence of the correlation energy density is approached by introducing the relative spin-polarization:

$$\zeta(r) = \frac{\rho\alpha(r) - \rho\beta(r)}{\rho\alpha(r) + \rho\beta(r)}. \quad (3.14)$$

$\zeta = 0$ corresponds to the paramagnetic spin-unpolarized situation with equal α and β spin densities whereas $\zeta = \pm 1$ corresponds to the ferromagnetic situation where one spin density vanishes. The spin correlation energy density for a given value of the total density and relative polarization, $\varepsilon_c(\rho, \zeta)$, is constructed to interpolate the extreme values. Several forms have been developed in conjunction with LDA correlation functional [18].

The LDA assumes that the density is the same everywhere. Because of this, the LDA tends to underestimate the exchange energy and over-estimate the correlation energy. The errors due to the exchange and correlation parts tend to compensate each other to a certain degree. To correct this tendency, it is common to expand in terms of the gradient of the density to account for the non-homogeneity of the true electron density. This allows for corrections based on the changes in density away from the coordinate. These expansions are referred to as GGA and are discussed in the next subsection [19].

3.2.2. Generalized Gradient Approximation

As the LDA approximates the energy of the genuine density by the energy of a local constant density, it falls flat in circumstances where the thickness experiences quick changes, for example, in atoms. A change to this can be made by considering the slope of the electron density, the alleged GGA. The LDA exchange-correlation is an inhomogeneous system in non-local density as for electrons it encompasses, and this is alluded to as inclination amendment or generalized gradient approximation (GGA). The GGA exchange-correlation energy is given as [15,16]:

$$E_x^{GGA}c(n) = \int dn(r)\epsilon_{xc}^{GGA}[n(r), \|\nabla n(r)\|] \quad (3.15)$$

where ϵ_{xc} is the exchange-correlation energy and $n(r)$ is the gradient term. The GGA has been broadly utilized and has turned out to be very fruitful in remedying a portion of the inadequacies of the LDA [17].

3.3. Planewave Pseudopotential Method

3.3.1. Planewave Basis

Plane-wave basis sets are used in quantum-chemical simulations. Typically, the choice of the plane wave basis set is based on a cutoff energy. The plane waves in the simulation cell fit below the energy criterion and are then included in the calculation [18]. These basis sets are popular in calculations involving three-dimensional periodic boundary conditions.

The main advantage of a plane-wave basis is that it is guaranteed to converge in a smooth, monotonic manner to the target wave function. In contrast, when localized basis sets are used, monotonic convergence to the basis set limit may be difficult due to problems with over-completeness. In a large basis set, functions on different atoms start to look alike, and many eigenvalues of the overlap matrix approach zero [19].

In addition, certain integrals and operations are much easier to program and carry out with plane-wave basis functions than with their localized counterparts. For example, the kinetic energy operator is diagonal in reciprocal space. Integrals over real-space operators can be efficiently carried out using fast Fourier transforms. The properties of the Fourier transform allow a vector representing the gradient of the total energy with respect to the plane-wave coefficients to be calculated with a computational effort that scales as $NPW \cdot \ln(NPW)$ where NPW is the number of plane-waves. When this property is combined with separable pseudo potentials of the Kleinman-Bylander type and pre-conditioned conjugate gradient solution techniques, the dynamic simulation of periodic problems containing hundreds of atoms becomes possible [18,19].

In practice, plane-wave basis sets are often used in combination with an 'effective core potential' or pseudopotential, so that the plane waves are only used to describe the valence charge density. This is because core electrons tend to be concentrated very close to the atomic nuclei, resulting in large wavefunction and density gradients near the nuclei which are not easily described by a plane-wave basis set unless a very high energy cut-off, and therefore small wavelength, is used. This combined method of a plane-wave basis set with a core pseudo potential is often abbreviated as a PSPW calculation [20].

Furthermore, as all functions in the basis are mutually orthogonal and are not associated with any atom, plane-wave basis sets do not exhibit basis-set superposition error. However, the plane-wave basis set is dependent on the size of the simulation cell, complicating cell size optimization [19].

Due to the assumption of periodic boundary conditions, plane-wave basis sets are less well suited to gas-phase calculations than localized basis sets. Large regions of

vacuum need to be added on all sides of the gas-phase molecule to avoid interactions with the molecule and its periodic copies. However, the plane waves use a similar accuracy to describe the vacuum region as the region where the molecule is, meaning that obtaining the truly noninteracting limit may be computationally costly [20].

3.3.2. Pseudopotential Method

A pseudopotential or effective potential is used as an approximation for the simplified description of complex systems. Applications include atomic physics and neutron scattering. The pseudopotential approximation was first introduced by Hans Hellmann in 1934 [21].

The pseudopotential is an attempt to replace the complicated effects of the motion of the core electrons of an atom and its nucleus with an effective potential, or pseudopotential, so that the Schrödinger equation contains a modified effective potential term instead of the Coulombic potential term for core electrons normally found in the Schrödinger equation.

The pseudopotential is an effective potential constructed to replace the atomic all-electron potential such that core states are eliminated and the valence electrons are described by pseudo-wavefunctions with significantly fewer nodes [22]. This allows the pseudo-wavefunctions to be described with far fewer Fourier modes, thus making plane-wave basis sets practical to use. In this approach usually only the chemically active valence electrons are dealt with explicitly, while the core electrons are being considered together with the nuclei as rigid non-polarizable ion cores. It is possible to self-consistently update the pseudopotential with the chemical environment that it is embedded in, having the effect of relaxing the frozen core approximation, although this is rarely done. In codes using local basis functions, like Gaussian, often effective core potentials are used that only freeze the core electrons.

First-principles pseudopotentials are derived from an atomic reference state, requiring that the pseudo- and all-electron valence eigenstates have the same energies and amplitude (and thus density) outside a chosen core cut-off radius.

Pseudopotentials with larger cut-off radii are said to be softer and more rapidly convergent, but at the same time, less transferable, which is less accurate in reproducing realistic features in different environments [23].

Early applications of pseudopotentials to atoms and solids based on attempts to fit atomic spectra achieved only limited success. Solid-state pseudopotentials achieved their present popularity largely because of Walter Harrison's successful fits with the nearly free electron Fermi surface of aluminum to the covalent energy gaps of silicon and germanium [24].

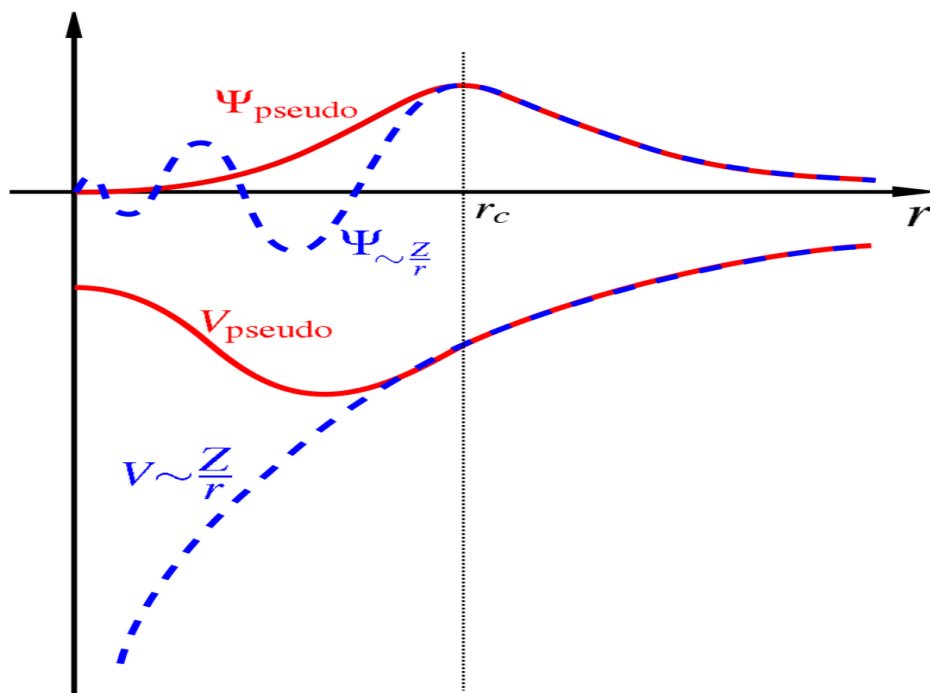


Figure 3. 1: Comparison of a wave function in the Coulomb potential of the nucleus (blue) to the one in the pseudopotential (red). The real and pseudo wave functions and potentials match above a certain cut-off radius r_c .

3.3.3. Norm-Conserving Pseudopotential

Norm-conserving and ultrasoft are the two most common forms of pseudopotential used in modern plane-wave electronic structure calculations. They allow a basis-set with a significantly lower cut-off (the frequency of the highest Fourier mode) to be used to describe the electron wave functions and so allow proper numerical convergence with reasonable computing resources. An alternative would be to augment the basis set around nuclei with atomic-like functions, as is done in linearized augmented planewave (LAPW). Norm-conserving pseudopotential was first proposed by Hamann, Schlüter, and Chiang (HSC) in 1979 [25]. The original HSC norm-conserving pseudopotential takes the following form:

$$\hat{V}_{ps}(r) = \sum_i \sum_m |Y_{im}\rangle V_{im}(r) \langle Y_{im}| \quad (3.16)$$

where $|Y_{im}\rangle$ projects a one-particle wave function, such as one Kohn-Sham orbital, to the angular momentum labeled by $\{l, m\}$. $V_{im}(r)$ is the pseudopotential that acts on the projected component. Different angular momentum states then feel different potentials; thus, the HSC norm-conserving pseudopotential is non-local, in contrast to local pseudopotential which acts on all one-particle wave-functions in the same way.

Norm-conserving pseudopotentials are constructed to enforce two conditions.

1. Inside the cut-off radius r_c the norm of each pseudo-wave function be identical to its corresponding all-electron wave function [20]:

$$\int_{r_c}^r dr^3 \phi_{R,i}(\vec{r}) \phi_{R,j}(\vec{r}) = \int_{r_c}^r dr^3 \tilde{\phi}_{R,i}(\vec{r}) \tilde{\phi}_{R,j}(\vec{r}) \quad (3.17)$$

where $\phi_{R,i}$ and $\tilde{\phi}_{R,i}$ are the all-electron and pseudo reference states for the pseudopotential on atom R .

2. All-electron and pseudo wave functions are identical outside cut-off radius r_c .

3.3.4. Ultrasoft Pseudopotentials

Ultrasoft pseudopotentials relax the norm-conserving constraint to reduce the necessary basis-set size further at the expense of introducing a generalized eigenvalue problem with a non-zero difference in norms we can now define [20] :

$$q_{R,ij} = \langle \phi_{R,i} | \phi_{R,j} \rangle - \langle \tilde{\phi}_{R,i} | \tilde{\phi}_{R,j} \rangle \quad (3.18)$$

And so, the normalized eigenstate of the pseudo-Hamiltonian now obeys the generalized equation:

$$\hat{H}|\Psi_i\rangle = \epsilon_i \hat{S}|\Psi_i\rangle \quad (3.19)$$

Where the operator $\hat{S}$ is defined as:

$$\hat{S} = 1 + \sum_{R,i,j} |PR, i\rangle q_{R,ij} \langle PR, j| \quad (3.20)$$

where PR, i are projectors that form a dual basis with the pseudo reference states inside the cut-off radius, and are zero outside:

$$\langle PR, i | \tilde{\phi}_{R,j} \rangle_{r < r_c} = \delta_{i,j} \quad (3.21)$$

A related technique is the projector-augmented wave (PAW) method [11].

3.4. Brillouin Zone

In mathematics and solid-state, the first Brillouin zone is a uniquely defined primitive cell in reciprocal space. In the same way, the Bravais lattice is divided up into Wigner–Seitz cells in the real lattice, the reciprocal lattice is broken up into Brillouin zones. The boundaries of this cell are given by planes related to points on the reciprocal lattice. The importance of the Brillouin zone stems from the Bloch wave description of waves

in a periodic medium, in which it is found that the solutions can be completely characterized by their behavior in a single Brillouin zone [18].

The first Brillouin zone is the locus of points in reciprocal space that are closer to the origin of the reciprocal lattice than they are to any other reciprocal lattice points (see the derivation of the Wigner-Seitz cell). Another definition is as the set of points in k -space that can be reached from the origin without crossing any Bragg plane. Equivalently, this is the Voronoi cell around the origin of the reciprocal lattice [19].

3.5. k -Point Sampling

For a periodic system, the k -points appearing in the wave function belong to the first Brillouin zone, by Bloch's theorem. In the case of samples with defects, which are aperiodic, the cell that contains the defects is periodically repeated, using periodic boundaries. The Bloch theorem can therefore be applied to this supercell, the dimension of the Brillouin zone being determined by the dimension of the supercell itself, i.e., the larger the supercell, the smaller the Brillouin zone should be [20].

To calculate the energy band, or the charge density for example, the sum over these k -points must be done. Therefore, choosing a sufficiently dense mesh of summation is crucial for the convergence of the results. Monkhorst and Pack [20,21] proposed a scheme where the k - points are distributed homogeneously in the Brillouin zone according to:

$$\mathbf{k} = x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3 \quad (3.22)$$

where $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are the reciprocal lattice vectors, and

$$x_l = \frac{1}{n_l} \quad l = 1, \dots, n_1 \quad (3.23)$$

where n_l are the folding parameters [14,15].

The k-points are specified in the Cartesian input format as follows:

$$\vec{k} = \frac{2\pi}{a} (x_1, x_2, x_3) \quad (3.24)$$

The unit cell of a face-centered cubic lattice is defined by the subsequent basis vectors:

$$A = \begin{pmatrix} 0 & \frac{a}{2} & \frac{a}{2} \\ \frac{a}{2} & 0 & \frac{a}{2} \\ \frac{a}{2} & \frac{a}{2} & 0 \end{pmatrix} \quad (15)$$

The reciprocal lattice is defined as the matrix:

$$2\pi B = \begin{pmatrix} -1 & -1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \quad (2.26)$$

Determining the appropriate number of k-points to utilize in PWP calculations is essential for achieving both rapid convergence and accurate total energy results. The maximum accuracy is attained through the k-points utilized by Hohenberg and Kohn, Kohn, and Sham [27]. This study employed the Monkhorst-Pack method to identify an optimal set of special k-points for application [28]

Usually, total energies of different structures are compared. Therefore, if the two structures have the same unit cell, the same set of k-points should be used. Since only the difference in the energies of the two structures is required, possible errors from a non-converged k-point sampling may cancel out. The computational effort could, therefore, be reduced by using a carefully chosen small k-point set.

An alternative method for choosing k-point mesh has been proposed by Chadi and Cohen [29], based on ‘shells’ analysis. This concept can be explained by considering the Bloch function for a specific band as [30]:

$$\varphi_k(r) = \frac{1}{\sqrt{N}} \sum_{R_j} \exp(iK \cdot R_j) \varphi(r - R_j) \quad (3.27)$$

The charge density for this specific state is therefore:

$$p_k(r) = \frac{1}{N} \sum_{R_i, R_j} \exp[iK \cdot (R_i - R_j)] \varphi^*(r - R_j) \varphi(r - R_i) \quad (3.28)$$

which can be rewritten as:

$$p_k(r) = \frac{1}{N} \sum_{R_i} |\varphi(r - R_i)|^2 + \frac{1}{N} \sum_{R_i} \sum_{R_j} \exp[iK \cdot R_j] \varphi^*(r + R_j + R_i) \varphi(r - R_i) \quad (3.29)$$

where the prime in the second sum is overall l , except the $R_i = 0$ term. Equation (3.29) should be compared to the total charge density, given by:

$$p(r) = \sum_k p_k(r) = \sum_{R_i} |\varphi(r - R_i)|^2 \quad (3.30)$$

One can see that the first term in equation (3.18) is the average charge density for the band considered. It could therefore be a reliable approximation to the total charge density, providing a good choice of k-points that are chosen that minimize the second term in equation (3.18) [21,22].

3.6. Universal Cluster Expansion

The cluster-expansion approach is a technique in quantum mechanics that systematically truncates the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy problem. The BBGKY hierarchy sometimes referred to as Bogoliubov hierarchy is a set of equations describing the dynamics of a system of many interacting particles that arise when quantum dynamics of interacting systems is solved. In statistical mechanics, the cluster expansion (also called the high temperature expansion or hopping expansion) is a power series expansion of the partition function of a statistical field theory around a model that is a union of non-interacting 0-dimensional field theories. Cluster expansions originated in the work of Bogoliubov, N [31] and Gaspard, P [32], unlike the usual perturbation expansion, it converges in some non-trivial regions when the interaction is small. The cluster expansion is a power series expansion of the partition function of a statistical field theory around a model that is a union of non-interacting of 0-dimensional field theories. Modern DFT methods can calculate material properties with reasonable to high precision (depending on the quality of the approximations to the exchange and correlation effects). Standard DFT applications are, however, restricted to unit cells of a few hundred of atoms [33]. If one wants to model an alloy with varying atomic concentrations and crystal structures a huge number of very large supercells would be needed if one would try to solve the problem using an abrupt force. Therefore, the process would be deemed fatal. A successful strategy to overcome this limitation is offered by the cluster expansion [34, 35] when combined with Monte Carlo simulations. From an optimized cluster expansion, a set of effective cluster interactions can be extracted and used in large-scale Monte Carlo simulations to explore order-disorder phenomena and phase segregation processes as a function of temperature [35].

3.6.1. Effective Cluster Interaction

On a basic lattice, various atoms, for example of type A and B, are distributed to define the structure, $\vec{\sigma}$ as a periodic configuration of A and B atoms. This configuration is described by the pseudo spin operator $\sigma_q = \pm 1$, which has the value +1 if atom A sits onsite q or -1 if that atom is on site B [36].

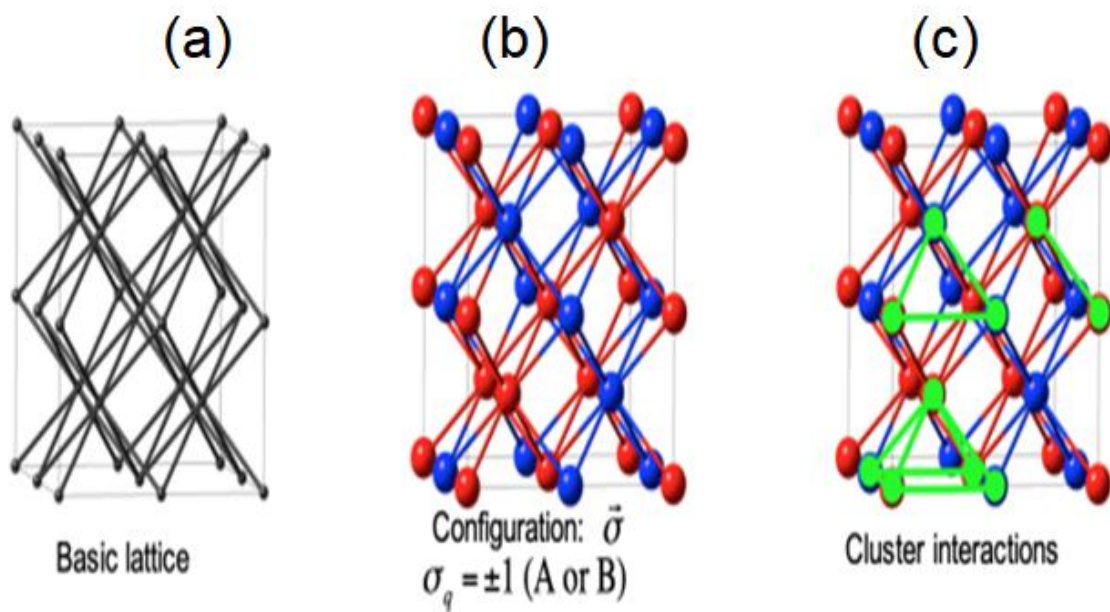


Figure 3. 2: Schematic representation of a cluster expansion model [36].

Figure 3.2(a) illustrates the basic lattice structure, which serves as the foundation for the model, Figure 3.2(b) shows a specific configuration, where lattice sites are occupied by atoms of type A (blue) or B (red), with the occupation represented by $\sigma_q = \pm 1$ for atoms A or B, respectively. Figure 3.2(c) depicts the interactions between clusters of atoms (highlighted in green) within the lattice, demonstrating the effective cluster interactions that contribute to the system's energy [36].

Energy $E(\vec{\sigma})$, associated with structure $\vec{\sigma}$ can be described by an expansion of cluster interaction and their respective interaction energies, J using the expression [37]:

$$E(\vec{\sigma}) = J_0 + J_1 \sum_i \vec{\sigma}_i + \sum_{i>1} J_{ij} \sigma_i \sigma_j + \sum_{i>1>k} J_{ijk} \sigma_i \sigma_j \sigma_k + \dots \quad (3.31)$$

In equation (3.31), the first term J_0 , describes a constant, configuration-independent contribution. The second term is concentration-dependent and is a sum over all N sites of structure $\vec{\sigma}$ with onsite energy J_i times the pseudo spin operator σ_i at each site i . Further terms describe the cluster interactions between multiple sites, for example, two-body interactions J_{ij} or three-body interaction J_{ijk} . They contain spin products $\sigma_i \sigma_j \dots$ overall $\vec{f}$ vertices of a cluster times its effective cluster interaction energy J_{ij} summed up over all the possible ways that the cluster can be placed on the lattice of structure $\vec{\sigma}$ [37,38] In other words, the energy $E(\vec{\sigma})$ of structure $\vec{\sigma}$ is broken down into clusters with their associated effective interaction energies. The core issue of cluster expansion is identifying a universal set of interactions, J best suited to describe a given model. To accomplish this, it is useful to reformulate the above equation into the more compact form given by:

$$E(\vec{\sigma}) = \sum_{C \in \vec{C}} J_C \Pi_C(\vec{\sigma}) \quad (3.32)$$

The cluster expansion equation sums up the product of cluster', C 's interaction energy, J_C with its correlation function:

$$\Pi_C(\vec{\sigma}) = N^{-1} \sum_{i=1}^N \sum_{k \in C} \prod_{v \in f} \sigma_v \quad (3.33)$$

The expression represents the summation of all potential configurations in which a cluster C , consisting of $\vec{f}$ vertices, can be positioned on the N sites of the structure. The correlation function involves the summation of the spin product $\sigma_1 \dots \sigma_f$ across all $\vec{f}$ vertices inside the cluster. In the current analysis, only clusters that exhibit distinct symmetry are considered. Additionally, clusters that are part of an expansion can be gathered using the vector $\vec{C} = \{C_1, \dots, C_1\}$ [38]

3.6.2. Inversion and Least Square Fitting

To find the solution for the cluster expansion, that is to identify appropriate effective cluster interactions, a training set of structures is needed. Such a training set contains m structures $\{\vec{\sigma}_1, \dots, \vec{\sigma}_m\}$ with the corresponding energies $\vec{E} = (E_1, \dots, E_m)^T$. Together with the cluster vector $\vec{C} = (C_1, \dots, C_n)^T$, containing all n inequivalent clusters, and the corresponding effective cluster interactions $\vec{J} = (J, \dots, J_n)^T$ the $m \times n$ correlation matrix:

$$\bar{\Pi} = \begin{pmatrix} \Pi_{C_1}(\vec{\sigma}_1) & \cdots & \Pi_{C_n}(\vec{\sigma}_1) \\ \vdots & \ddots & \vdots \\ \Pi_{C_1}(\vec{\sigma}_m) & \cdots & \Pi_{C_n}(\vec{\sigma}_m) \end{pmatrix} \quad (3.34)$$

defined using this correlation matrix, the cluster expansion problem can be formulated as:

$$\bar{E} = \bar{\Pi} \vec{J} \quad (3.35)$$

Inversion is a simple method for defining the values of the effective cluster interactions $\vec{J}$.

$$\vec{J} = \bar{\Pi}^{-1} \bar{E} \quad (3.36)$$

However, this approach has serious drawbacks. The number of clusters, n must equal the number of structures, m in the training set. Therefore, such an approach comes without redundancy. If the energy of a new structure is evaluated, a new cluster has to be added to the cluster expansion. This makes an efficient ground-state search or a Monte Carlo simulation unfeasible. Another issue is that the values of the energies of the training set structures usually have an uncertainty attached to them, they are noisy. A perfect fit with inversion will also fit the effective cluster interactions to that noise and not to actual physics. A better approach to identify the effective cluster

interactions is to use a least-square fit on a larger training set with m structures in the set and $m > n$:

$$(\vec{E} - \bar{\Pi}\vec{J})^T(\vec{E} - \bar{\Pi}\vec{J}) \rightarrow \min \quad (3.37)$$

3.6.3. Selecting Cluster Interactions Using the Genetic Algorithm

Cluster selection is performed using the genetic algorithm on a single training $\{\vec{\sigma}_1, \dots, \vec{\sigma}_m\}$ of structures with the corresponding energy values $\vec{E} = (E_1, \dots, E_m)^T$. The process is stochastic in nature meaning that an identical training set yields slightly different results if the genetic algorithm is repeated. However, if the cluster expansion has converged such fluctuations are negligible. As a fitness criterion the leave-one-out cross-validation score (CVS) is used. It is evaluated by removing each structure once from the training set and using the remaining $N - 1$ structures in a least-square fit to determine $\vec{J}$. The thus obtained effective cluster interaction energies $\vec{J}$ are used to predict the energy of the one structure removed from the training set which is then compared with its actual value. This is done for all N structures in the training set and evaluated as a standard deviation of the predicted energies from the actual energies [39, 40].

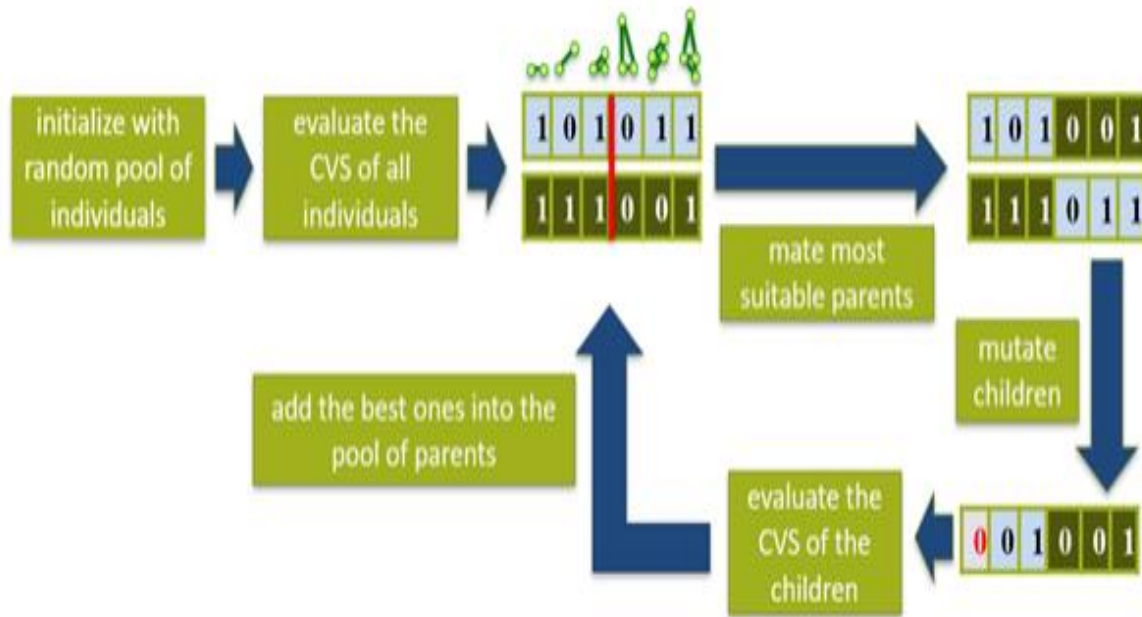


Figure 3. 3: Cluster selection using the genetic algorithm [39].

3.6.4. Iterative Optimization of the Training Set

The iterative procedure by which the structures for the training set are selected differs if the model has a miscibility gap or miscible constituents. To distinguish these two types of models, the heats of formation, $\Delta H_f(\vec{\sigma})$ are evaluated for all structures in the training set. It is defined by

$$\Delta H_f(\vec{\sigma}) = \frac{E_{DFT}(\vec{\sigma}) - \sum n_i(\vec{\sigma}) E_{DFT}^i}{\sum n_i(\vec{\sigma})} \quad (3.38)$$

wherein $E_{DFT}(\vec{\sigma})$ describes the DFT total energy of the structure $\vec{\sigma}$, $n_i(\vec{\sigma})$ is the number of atoms of atomic species i contained in $\vec{\sigma}$, and E_{DFT}^i denotes the DFT total energy of the pure phase of atomic species i . The sums go over all types of atoms contained in the structure $\vec{\sigma}$. Models with miscible constituents have structures with negative ΔH_f , (thermodynamically stable, ordered structures), while models with a positive ΔH_f , where none of the ordered structures is thermodynamically stable and phase separation occurs, have a miscibility gap [39]. Medea Universal Cluster Expansion

(UNCLE) (MedeA UNCLE) initializes the iterative procedure by adding a user-defined number of independent and identically distributed structures (given by the parameter Number of structures to initialize the first iteration in the configuration panel) to the training set. As a default behavior, after the first iteration, the type of model is automatically identified and the procedure switches to the suitable miscibility mode [40].

3.6.5. Cluster Expansion Flowchart

A flowchart of iterative procedure is shown in Figure 3.4. In principle, this procedure is different from the conventional procedure only in the way that the additional structures are selected. The probe structures are selected to decrease the variance of the CE energy [41]. The reduction in the cluster expansion (CE) error over a wide range of configurations is the prime objective of the use of probe structures. The structure that contributes the most to reducing is chosen first. Structures are then selected by order of merit. This procedure can, therefore, optimize the CE more efficiently than the conventional procedure, in which the ground and near-ground states are used for the validation [41,42]. Therefore, the ground-state search is omitted in the present procedure to show the validity of the present procedure. In a simple system, the ground-state search need not be omitted. The ground-state search can be combined with the present procedure. Confirming the ground-state behavior improves the reliability of the CE.

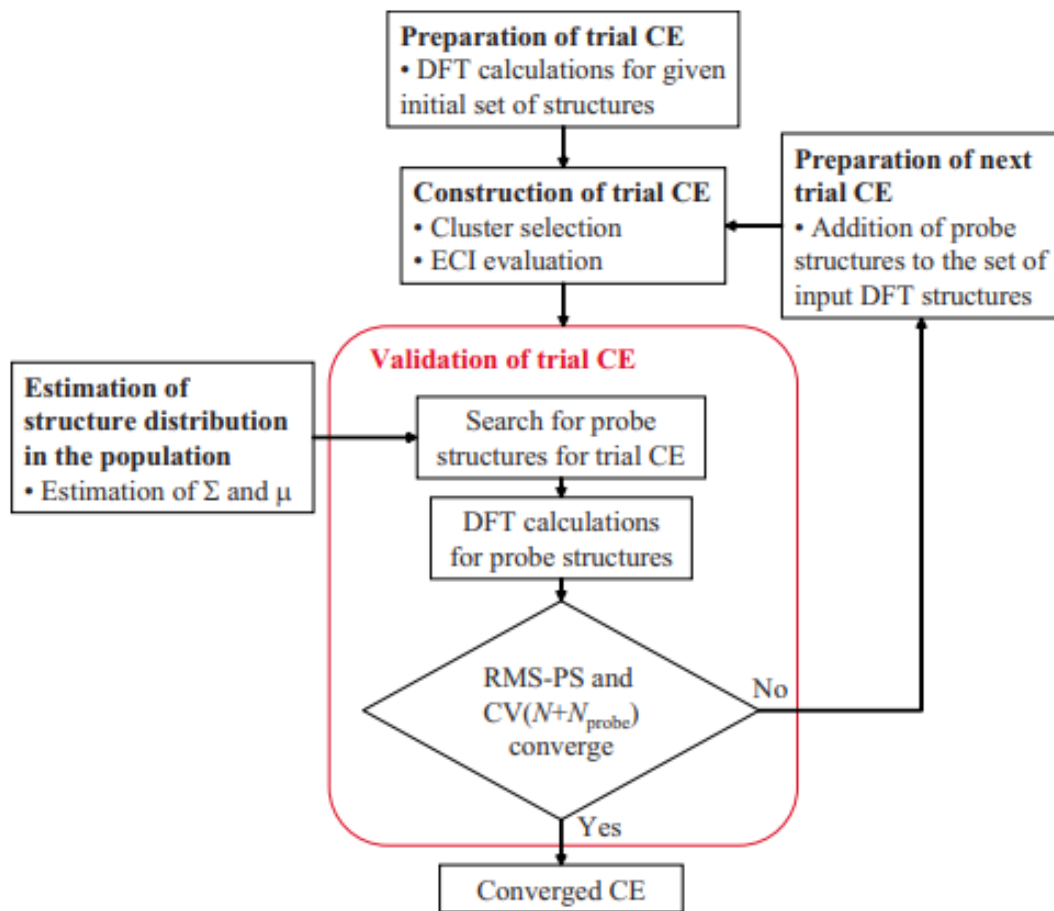


Figure 3. 4: Flowchart of the improved validation of trial CEs using probe structures [41].

In systems with a large unit cell the exhaustive ground-state search, in which the energies of all configurations are calculated, cannot be performed since the number of configurations increases exponentially with the system size [41, 43]. The procedure is divided into five stages:

- Stage 1: Preparation of the initial set of input structures and calculate their DFT energies.
- Stage 2: Construction of a trial CE by searching for an optimal set of clusters that minimizes the CV score. Here, we minimize the leave-one-out CV score by

using the genetic algorithm¹⁰ for the selection. The predictive power of the CE is improved by using the leave-many-out CV scheme. Even if the leave-many-out CV score is used as the prediction score, the predictive power for structures far from the inputs is generally lower than that for structures near the inputs, since the leave-many-out CV score is calculated using the sample inputs. Therefore, the quality of the trial CE, which minimizes the leave-many-out CV score, should be validated using out-of-sample structures.

- Stage 3: Searching for N_{probe} probe structures that reduce the coefficient A in equation 3.38 by the greatest amount.
- Stage 4: Then, the DFT energies of the probe structures are calculated.
- Stage 5: Validation of the trial CE using the probe structures. A candidate score used in the validation of the trial CE is simply the root-mean-square RMS difference between the DFT and CE energies of the probe structures RMS-PS. RMS-PS is expressed by:

$$(\text{RMS} - \text{PS})^2 = \frac{1}{N_{probe}} \sum_i^{N_{probe}} |E_{CE}(i) - E_{DFT}(i)|^2 \quad (3.39)$$

where N_{probe} denotes the number of probe structures. $E_{CE}(i)$ and $E_{DFT}(i)$ denote the CE and DFT energies of probe structure i , respectively. If RMS-PS is much larger than the CV score, the trial CE fails. However, it is expected to be difficult to rigorously validate the trial CE using RMS-PS because it is more biased than the CV score. A more suitable score for verifying the convergence of the CE is the CV score for $N + N_{probe}$ structures with clusters selected from N structures, i.e., $CV(N + N_{probe})$. If $CV(N + N_{probe})$ is larger than CV_N evaluated in stage 2, the trial CE is considered to

fail. The probe structures are then added to the input set and a new iterative step starting from stage 2 is performed using $N+N$ probe structures. The iterative steps are repeated until $CV(N + N_{\text{probe}})$ converges. In this study, we use both RMS-PS and $CV(N + N_{\text{probe}})$ to validate the trial CE [43,44].

3.6.6. Structure Selection in Complex Systems

Generally, it is more difficult to construct an accurate CE when crystal structures are more complex. Therefore, the use of probe structures is more important in complex systems. There are three reasons why it is difficult to construct an accurate CE in a complex system:

- There are many candidate clusters. Sampling important structures to increase the accuracy of the CE for all clusters is a difficult task. In simple systems, it is easy to sample independent structures over a wide range of the configuration space [43,45].
- Many clusters are required to express configurational thermodynamics. A CE with many clusters has a large uncertainty of the predicted energy easily. Therefore, the CE can only attain the required precision using a larger number of input structures. In simple systems, a smaller number of clusters are needed to describe the configurational thermodynamics [3,45].
- There are no proper guides for the selection of the number of input structures, N , and the number of clusters, m . In simple systems, because many CE calculations can be found in the literature, appropriate values for N and m can be learned. In the absence of such references, N and m should be determined by trial and error. For these reasons, our procedure involving the use of probe structures is much more useful in complex systems [46].

Since the set of optimal clusters and the set of necessary DFT structures are related, they can be selected simultaneously during an iterative procedure. Initially, a small

number of ordered structures are prepared as inputs. An optimal set of clusters that minimizes the cross-validation CV score is searched for from the pool of candidate clusters using general minimization algorithms [47]. Since the CV score is calculated using the sample inputs, the predictive power for structures far from the inputs is generally lower than that for structures near the inputs. Therefore, the quality of the trial CE should be validated using out-of-sample structures. In the conventional scheme, the predicted ground states and near ground states are used as additional structures for validation. The procedure is repeated until the predicted ground states and near-ground states converge. The CE error is reduced through the appropriate selection of clusters and the validation of the trial CE using out-of-sample structures. The conventional iterative procedure has been successfully used to search for the ground and near-ground-state structures. It has also been used to predict properties at finite temperatures. However, it must be noted that the CE error over the whole range of configurations is not necessarily fully reduced by the conventional procedure. In other words, the converged CE obtained by the conventional scheme is not necessarily the optimal CE, in which the CE error is fully reduced as shown in Figure 3.5 [48].

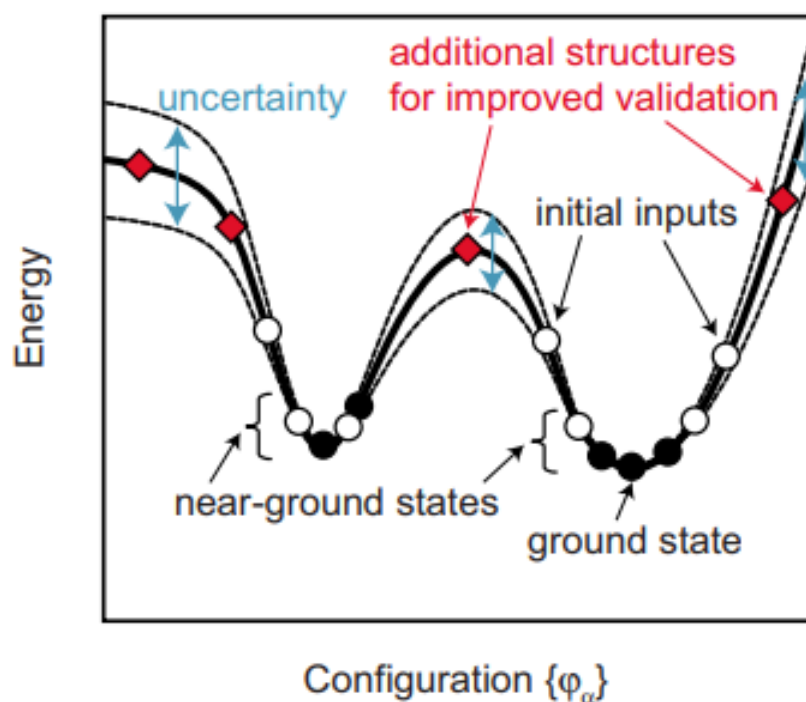


Figure 3. 5: Schematic representation of CEs constructed from the conventional procedure [41].

Initial input DFT structures are shown by the open circles. Input DFT structures obtained from ground-state searches using trial CEs are shown by the closed circles. Structures far from the input structures have a large uncertainty of predicted energy. To reduce the CE error over the whole range of configurations, additional structures, as shown by the closed diamonds, are required for improved validation of the CE.

Figure 3.5 schematically illustrates that a structure's energy near the input structures can be predicted with a small uncertainty. On the other hand, the energy of a structure far from the input structures cannot be predicted precisely owing to the larger uncertainty of the CE. When input structures with strong correlations are prepared, the predicted energy of a structure far from the input structures has a particularly large uncertainty. To calculate the configuration-dependent properties at finite temperatures, for example, the configurational free energy as a function of

temperature, the error of CE over the whole range of configurations, including all excited states, should be carefully examined [48,49].

3.6.7. Miscible Constituents

If a model has miscible constituents, the structures with energies close to the ground states, that is, those structures with the lowest ΔH_f at a given concentration, are the most important ones, and the cluster expansion should be most accurate for those. To accomplish this, those structures predicted by the cluster expansion to be more favourable (with a lower ΔH_f) and are not yet part of the training set are added to the training set. This is done iteratively until no new structures are predicted by cluster expansion to be more favourable than those created and included in the training set. At this point, the cluster expansion has converged, and the thermodynamically stable structures considered by the cluster expansion have been identified [50].

3.6.8. Miscibility Gap

When a model is a phase separating, no stable ordered structures exist apart from the two pure phases and all structures are equally important to the cluster expansion. Therefore, the selection process of structures to be added to the training set must improve the quality of the cluster expansion for all structures considered, irrespective of their formation energies, ΔH_f . The stochastic nature of the genetic algorithm is then used to determine how good (or bad) the energies of the structures predicted by the cluster expansion [50,51]. Then, the multiple cluster expansions are performed using an identical training set. The energy of all considered structures is then predicted by these multiple J 's, and a standard deviation of the predicted energies is evaluated. Structures with the highest standard deviation are those whose description by the cluster expansion is the worst [42]. Therefore, these are added iteratively to the training set.

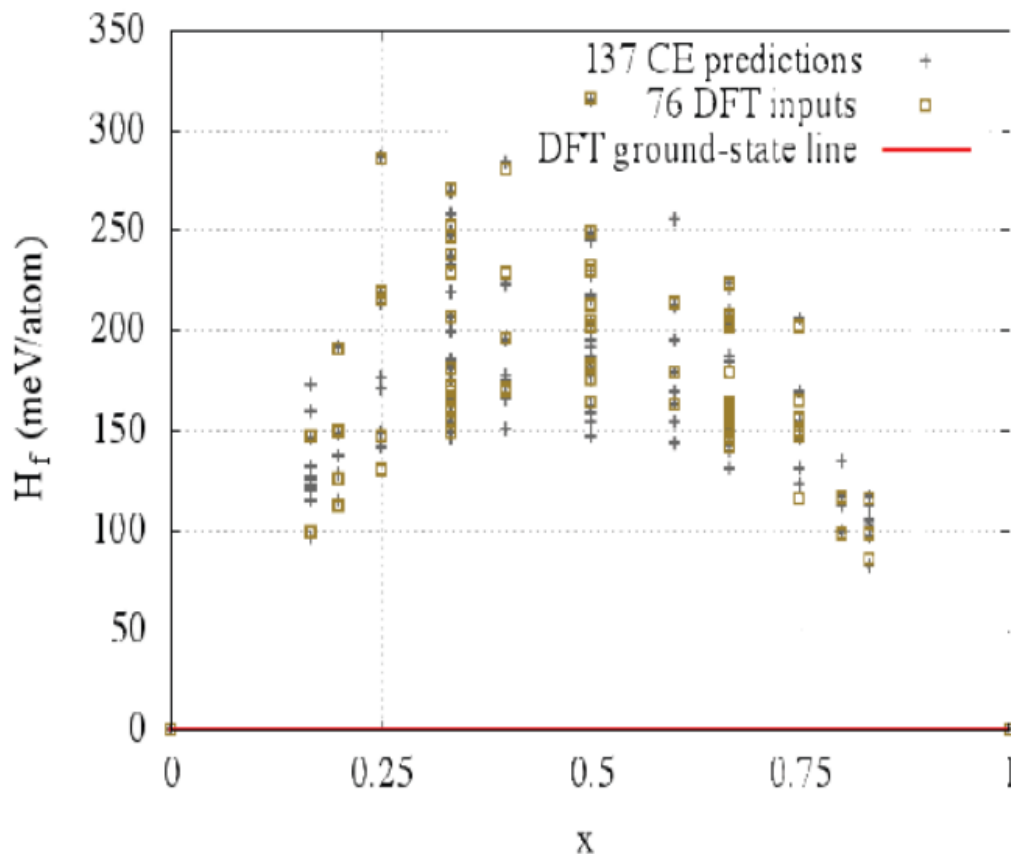


Figure 3. 6: A Binary ground state diagram illustrating a miscibility gap [50].

3.7. Theoretical Background of Calculated Properties

3.7.1. Electronic Properties

The quantity of states at each energy level that can be inhabited is called the density of states (DOS). A zero density of states at an energy level indicates that no states are available for occupation. This mathematical notion facilitates integration related to electron energy, serving as an alternative to integration across the Brillouin zone. Furthermore, the Density of States (DOS) is frequently employed for rapid visual assessment of the electronic structure [50,52]. Attributes such as the valence band width, the energy gap in insulators, and the quantity and intensity of principal characteristics are important in qualitatively analyzing experimental spectroscopic data. The nearest band above the bandgap is called the conduction band, whereas the nearest band below the bandgap is known as the valence band. The Fermi level

resides inside one or more permitted bands in a metal or semimetal. In semimetals, the bands are typically designated as "conduction bands" or "valence bands," contingent upon whether charge transport is mostly electron-like or hole-like, analogous to semiconductors. In numerous metals, the bands exhibit neither electron-like nor hole-like characteristics, sometimes called "valence bands" due to their composition of valence orbitals [53,54]. The band gaps in a metal's band structure are negligible for low-energy physics as they are too far from the Fermi level. DOS analysis can elucidate the alterations in electrical structure induced by external pressure, for instance. Given an energy level, a high density indicates that numerous states are available for occupation[54]. DOS provides essential insights on bonding in solids and categorizes materials as metallic, semiconductor, or insulator. Metals and semimetals possess delocalized electrons and lack a band gap between the valence and conduction bands. The differentiation between semiconductors and insulators is a matter of convention. Semiconductors are considered insulators with limited bandgaps. Insulators with a bandgap exceeding 3 eV are not classified as semiconductors and often do not demonstrate semiconductive properties under realistic settings. In a context involving a parabolic relationship, such as that applicable to free electrons or an electron within a solid exhibiting an isotropic parabolic band structure, the energy is expressed as $\varepsilon = \frac{\hbar^2}{2m} K^2$. The densities of the state in three dimensions are as follows:

$$D(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} \quad (3.40)$$

Despite DFT's tendency to consistently underestimate the bandgap in insulators and semiconductors by approximately 30-40%, it accurately reflects the shape of the density of states (DOS). Thus, more precise approaches rely on linear or quadratic interpolations of band energies between reference sites in the Brillouin zone. While widely regarded as popular and dependable, the tetrahedron interpolation method is regrettably incompatible with the Monkhorst-Pack grid of special points. This approach relies on linear interpolation within the parallelepipeds created by the Monkhorst-Pack point set, then employing histogram sampling of the resulting band energy set.

3.7.2. Equilibrium Voltage and Voltage Profile

The overall cell reaction, combining the anode and cathode reactions of a cathode material Na_xA and Na metal anode during the intercalation, can be considered as:



where the cathode material is intercalated from Na_{x_1}A to Na_{x_2}A by inserting $x_2 - x_1$ Na from the Na metal anode. The average equilibrium voltage V referenced to Na/Na^+ is calculated as the reaction Gibbs free energy ΔG_r over the number of Na ions transferred

$$V = -\frac{\Delta G_r}{(x_2 - x_1)F} = -\frac{G(\text{Na}_{x_2}\text{A}) - G(\text{Na}_{x_1}\text{A}) - (x_2 - x_1)G\text{Na}}{(x_2 - x_1)F} \quad (3.42)$$

where G refers to the Gibbs free energy of the corresponding phase and F is the Faraday constant. In most current first principles computation studies [55,56], ΔG_r is approximated by the reaction internal energy (equation 3.21) calculated at 0 K, as the contributions from entropy and volume changes are small at low temperatures and often canceled out. Using internal energies from static first principles computation, the equilibrium voltage is calculated as:

$$V = - \frac{E(\text{Na}_{x_2}\text{A}) - E(\text{Na}_{x_1}\text{A}) - (x_2 - x_1)E_{\text{Na}}}{(x_2 - x_1)F} \quad (3.43)$$

where internal energies E of Na_{x_2}A , Na_{x_1}A and bulk Na are from first-principles calculations at 0 K. The electrode materials, for example, layered Na transition metal oxides Na_xMO_2 [57,58] and Na-based alloys, may exhibit stable phases at their intermediate Na concentrations. As a result, there may be multiple voltage plateaus during electrochemical cycling. The equilibrium voltage between each pair of adjacent intermediate stable phases can be calculated using equation (3.22), and the voltage profiles as a function of Na concentrations can be constructed from these voltages. Therefore, to construct the voltage profile, one needs to identify the intermediate stable phases of an electrode as a function of Na concentrations.

3.7.3. Phase Stability and Na-ion Ordering

First-principle computation has been widely used in identifying and predicting the intermediate stable phases as a function of Na concentration in parallel with direct experimental characterizations [59]. For example, multiple intermediate phases such as NaPb_3 , NaPb , Na_5Pb_2 , and $\text{Na}_{15}\text{Pb}_4$, can form in Na–Pb alloying electrode [59]. The layered oxides Na_xMnO_2 as cathode materials for NIBs are known to exhibit several stable intermediate states with different Na-vacancy orderings at different Na concentrations x [56,60]. In these intercalation compounds only a fraction of Na sites is occupied, leading to many possible configurations of Na ions and vacancies.

To identify these different Na orderings, computation studies are often performed, first to enumerate many different Na vacancy configurations and then to identify the structures with the lowest energy. Given many possible configurations, a common practice is to first rank the enumerated configurations by electrostatic energy obtained from pre-assumed atomic charges [60], as physically stable structures are unlikely to

have high electrostatic energy, and then to perform DFT calculations on a fraction (often ≈ 10 – 100) of those configurations with the lowest electrostatic energies. The structures with the lowest DFT energies for each composition are then identified. To compare the relative stability of these configurations, the formation energy of the given Na_xMnO_2 composition can be calculated as:

$$E_f = E(\text{Na}_x\text{MnO}_2) - xE(\text{Na}) - (1 - x)E(\text{MnO}_2) \quad (3.44)$$

referencing the intercalated NaMnO_2 and de-intercalated MnO_2 phases. The convex hull of the formation energies of all these structures is constructed as a function of Na concentrations x . The thermodynamically stable phases are identified from the energy convex hull. All stable phases identified are based on static first-principles calculations corresponding to 0 K ground states, and so are the calculated voltage profiles.

3.7.4. Phase Stability and Voltage Profile at Finite Temperatures

Monte Carlo (MC) modelling can evaluate structures and energies at finite temperatures by including the configurational entropy contribution [61]. In MC simulation, many energy evaluations often based on the cluster expansion approach are sampled for different configurations [61,62]. The cluster expansion method provides a lattice-based Hamiltonian fitted to DFT energies and is significantly more efficient in computation costs. Based on the cluster-expansion Hamiltonian, MC modelling can study Na orderings at finite temperatures and obtain finite-temperature phase diagrams.

3.7.5. Elastic Properties

The elastic properties of a solid are important to understanding its mechanical properties and thermodynamic behaviour. From the elastic constants, we can understand the bonding characteristic and describe the response when external forces

are applied to materials [22]. NaMnO_2 is a monoclinic structure with five independent elastic constants, i.e., C_{11} , C_{12} , C_{13} , C_{33} , and C_{44} . For the crystals that have different mechanical stability criteria, the monoclinic crystal mechanical stability criterion can be expressed as [23]

$$\begin{aligned} C_{11} > 0, C_{44} > 0, C_{11} - C_{22} > 0, \\ (C_{11} + C_{12})C_{33} > C_{13}^2. \end{aligned} \quad (3.45)$$

Monoclinic crystal has a Born mechanical stability criterion that can be expressed as:

$$\begin{aligned} C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0 \\ C_{11}C_{22} > C_{12}^2, C_{11}C_{33} > C_{13}^2, C_{22}C_{33} > C_{23}^2 \text{ and} \\ C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} > C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \end{aligned} \quad (3.46)$$

The Born mechanical stability criteria for orthorhombic systems are as follows:

$$\begin{aligned} (C_{11} + C_{12}) > 0, (C_{11} + C_{33} + 2C_{13}) > 0 \\ (2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0, \\ C_{11} > 0, C_{33} > 0, C_{44} > 0 \\ \text{and } C_{44} > 0 \end{aligned} \quad (3.47)$$

These conditions also give a limit to the value of bulk moduli, which should be between C_{11} and C_{12} .

Elastic constants, bulk moduli (B) and shear moduli (G) of the hexagonal, monoclinic and orthorhombic crystals can be calculated by following Voigt–Reuss–Hill (VRH) approximation. The expressions of bulk moduli (B_V , B_R , B) and shear moduli (G_V , G_R , G) are [23]:

$$B_V = \frac{2}{9} \left(C_{11} + C_{12} + 2C_{13} + \frac{C_{33}}{2} \right) \quad (3.48)$$

$$B_R = \frac{1}{(2S_{11} + S_{33}) + 2(S_{12} + 2S_{13})} \quad (3.49)$$

$$G_V = \frac{1}{15} (2C_{11} + C_{33} - C_{12} - 2C_{13}) + \frac{1}{5} (2C_{44} + C_{66}) \quad (3.50)$$

$$G_R = \frac{15}{4(2S_{11} + S_{33}) - (S_{12} + S_{13}) + (S_{44} + S_{66})} \quad (3.51)$$

where S_{ij} is the elastic compliance constant.

$$B = \frac{1}{2} (B_V + B_R), \quad G = \frac{1}{2} (G_V + G_R) \quad (3.52)$$

Meanwhile, Young's moduli γ and averaged compressibility (β) can be calculated by using the following equation:

$$\gamma = \frac{9BG}{3B+G}, \quad \beta = \frac{1}{B} \quad (3.53)$$

Bulk moduli describe the resistance to volume change and provides the response to hydrostatic pressure. Shear moduli evaluate the resistance to plastic deformation of polycrystalline materials. Young's moduli usually provide a measurement of the stiffness of a material, i.e., the larger the value of the shear moduli, the stiffer the material [22,23].

3.8. Thermodynamic Properties

The Debye temperature (θ_D) from the average sound velocity (v_m) using the equation [63]:

$$\theta_D = \frac{h}{k_B} \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} v_m \quad (14)$$

where h and k_B are the Planck's and Boltzmann's constants, respectively, and is the atomic volume. The average sound velocity in polycrystalline systems v_m , is evaluated by the expression:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-\frac{1}{3}} \quad (15)$$

where v_t and v_l are the mean longitudinal and transverse sound velocities, which can be related by the shear and bulk moduli from Navier's equations:

$$v_t = \left(\frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}} \quad (16)$$

$$v_l = \left(\frac{G}{\rho} \right)^{\frac{1}{2}} \quad (17)$$

3.9. Computer Codes

3.9.1. Vienna Ab initio Simulation Package

The Vienna Ab initio Simulation Package (VASP) is a plane-wave code for ab initio density-functional calculations. It employs the projector-augmented wave method to accurately describe the electron-ion interaction, matching the precision of advanced all-electron codes. VASP uses fast iterative techniques for the diagonalization of the density functional theory Hamiltonian and optimized charge-mixing routines. These methods ensure a stable and accurate solution of the Kohn-Sham equations and favorable scaling of computational effort with system size [64,65].

VASP allows total-energy calculations, structural optimizations for systems with thousands of atoms, and ab initio molecular dynamics simulations for ensembles with a few hundred atoms extending over several tens of picoseconds. It has applications in various fields, including structure and phase stability, mechanical and dynamical properties, liquids, glasses and quasicrystals, magnetism and magnetic nanostructures, semiconductors and insulators, surfaces, interfaces, thin films, chemical reactions, and catalysis. Additionally, VASP supports different levels of exchange-correlation functionals and various post-DFT approaches, enabling the calculation of a wide range of material properties [64,65].

3.9.2. MedeA UNCLE

The MedeA UNCLE package allows you to set up, construct, and automatically converge a cluster expansion for bulk or surface systems with partial disorder on some or all sublattices. Accurate *ab initio* calculations of a relatively small number of supercells form the basis on which the effective cluster interactions are determined. MedeA UNCLE can be applied to arbitrary lattice types and multi-component systems.

It automatically performs ground-state searches and applies genetic algorithms or compressive sensing to explore configuration space. The derived effective cluster interactions map the ab initio results onto a much simpler Hamiltonian, enabling large-scale Monte Carlo simulations on systems with up to millions of atoms [66].

MedeA UNCLE consolidates recent advances in the methodology and incorporates new developments in the formalism itself. A core goal of the package is to reduce the need for user intervention, automating the method to minimize human error and judgment. The package extends the standard cluster expansion formalism to more complex cases, such as ternary compounds and surfaces, including adsorption and inequivalent sites [66,67].

REFERENCES

1. Nalewajski, R. F., & Parr, R. G. (1982). Legendre transforms and Maxwell relations in density functional theory. *The Journal of Chemical Physics*, 77(1), 399-407.
2. Pan, G., Jing, W., Qing-Ju, L., & Wen-Fang, Z. (2010). First-principles study on anatase TiO₂ codoped with nitrogen and praseodymium. *Chinese Physics B*, 19(8), 087103
3. Jensen, F. (2013). Atomic orbital basis sets. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 3(3), 273-295.
4. Davidson, E. R., & Feller, D. (1986). Basis set selection for molecular calculations. *Chemical Reviews*, 86(4), 681-696.
5. Marcano, E. (2018). DFT Study of Anthocyanidin and Anthocyanin Pigments for Dye Sensitized Solar Cells: Electron Injecting from the Excited States and Adsorption onto TiO₂ (Anatase) Surface. *Energy Harvesting and Systems*, 5(1-2), 29-38.
6. Ditchfield, R. H. W. J., Hehre, W. J., & Pople, J. A. (1971). Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules. *Chemical Physics*, 54(2), 724-728.
7. Schwerdtfeger, P. (2011). The pseudopotential approximation in electronic structure theory. *ChemPhysChem*, 12(17), 3143-3155.
8. Louie, S. G., Froyen, S., & Cohen, M. L. (1982). Nonlinear ionic pseudopotentials in spin-density-functional calculations. *Physical Review B*, 26(4), 1738.

9. Reis, C. L., Pacheco, J. M., & Martins, J. L. (2003). First-principles norm-conserving pseudopotential with explicit incorporation of semicore states. *Physical Review B*, 68(15), 155111.
10. Kohn, W., & Sham, L. J. (1965). *Phys. Rev. A. Self-Consistent Equations Including Exchange and Correlation Effects*, 140, A1133-A1138.
11. Liechtenstein, A. I., Anisimov, V. I., & Zaanen, J. (1995). Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators. *Physical Review B*, 52(8), R5467.
12. Perdew, J. P., Burke, K., & Wang, Y. (1996). Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Physical Review B*, 54(23), 16533
13. Zhou, F., Cococcioni, M., Marianetti, C. A., Morgan, D., & Ceder, G. (2004). First-principles prediction of redox potentials in transition-metal compounds with LDA+ U. *Physical Review B*, 70(23), 235121.
14. Wang, L., Maxisch, T., & Ceder, G. (2006). Oxidation energies of transition metal oxides within the GGA+ U framework. *Physical Review B*, 73(19), 195107.
15. y de Dompablo, M. A., Van der Ven, A., & Ceder, G. (2002). First-principles calculations of lithium ordering and phase stability on Li_xNiO_2 . *Physical Review B*, 66(6), 064112.
16. Deng, Z., Mo, Y., & Ong, S. P. (2016). Computational studies of solid-state alkali conduction in rechargeable alkali-ion batteries. *NPG Asia Materials*, 8(3), e254-e254.

17. Henkelman, G., Uberuaga, B. P., & Jónsson, H. (2000). A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics*, 113(22), 9901-9904.
18. Matts, I. L., Dacek, S., Pietrzak, T. K., Malik, R., & Ceder, G. (2015). Explaining performance-limiting mechanisms in fluorophosphate Na-ion battery cathodes through inactive transition-metal mixing and first-principles mobility calculations. *Chemistry of Materials*, 27(17), 6008-6015.
19. Mo, Y., Ong, S. P., & Ceder, G. (2014). Insights into diffusion mechanisms in P2 layered oxide materials by first-principles calculations. *Chemistry of Materials*, 26(18), 5208-5214.
20. Urban, A., Seo, D. H., & Ceder, G. (2016). Computational understanding of Li-ion batteries. *npj Computational Materials*, 2(1), 1-13.
21. Bai, Q., Yang, L., Chen, H., & Mo, Y. (2018). Computational studies of electrode materials in sodium-ion batteries. *Advanced Energy Materials*, 8(17), 1702998.
22. Li, X. H., Xing, C. H., Cui, H. L., & Zhang, R. Z. (2019). Elastic and acoustical properties of Cr_3AlB_4 under pressure. *Journal of Physics and Chemistry of Solids*, 126, 65-71.
23. Shao, Y., & Duan, W. (2020). First-principles study of mechanical and electronic properties of Lu_2SnC under pressure. *Journal of Applied Physics*, 127(15), 155902.
24. Clark, S. J., Segall, M. D., Pickard, C. J., Hasnip, P. J., Probert, M. I., Refson, K., & Payne, M. C. (2005). First principles methods using CASTEP. *Zeitschrift für Kristallographie-Crystalline Materials*, 220(5-6), 567-570.

25. Hamann, D. R. (2013). Optimized norm-conserving Vanderbilt pseudopotentials. *Physical Review B-Condensed Matter and Materials Physics*, 88(8), 085117.
26. Lin, J. S., Qteish, A., Payne, M. C., & Heine, V. (1993). Optimized and transferable nonlocal separable ab initio pseudopotentials. *Physical Review B*, 47(8), 4174.
27. Borlido, P., Doumont, J., Tran, F., Marques, M. A., & Botti, S. (2020). Validation of pseudopotential calculations for the electronic band gap of solids. *Journal of chemical theory and computation*, 16(6), 3620-3627.
28. Wang, Y., Wisesa, P., Balasubramanian, A., Dwaraknath, S., & Mueller, T. (2021). Rapid generation of optimal generalized Monkhorst-Pack grids. *Computational Materials Science*, 187, 110100.
29. Hammer, B., Jacobsen, K. W., Milman, V., & Payne, M. C. (1992). Stacking fault energies in aluminium. *Journal of Physics: Condensed Matter*, 4(50), 10453.
30. Löwdin, P. O. (1962). Band theory, valence bond, and tight-binding calculations. *Journal of Applied Physics*, 33(1), 251-280.
31. Bogoliubov, N. N., Born, M., Green, H. S., Kirkwood, J. G., & Yvon, J. (1946). The BBGKY hierarchy: A set of equations describing the dynamics of a system of many interacting particles. *Journal of Physics USSR*, 10(3), 256-270.
32. Gaspard, P., & Cyrot-Lackmann, F. (1973). Cluster expansions and the partition function of statistical field theory. *Journal of Statistical Physics*, 7(4), 339-352.

33. Sánchez, J. M., Ducastelle, F., & Gratias, D. (1984). Generalized cluster description of multicomponent systems. *Physica A: Statistical Mechanics and its Applications*, 128(1-2), 334-350.
34. Zunger, A., Wei, S. H., Ferreira, L. G., & Bernard, J. E. (1990). Special quasirandom structures. *Physical Review Letters*, 65(3), 353-356.
35. de Fontaine, D. (1994). Cluster approach to order-disorder transformations in alloys. *Solid State Physics*, 47, 33-176.
36. J. Sanchez, F. Ducastelle, and D. Gratias, "Generalized cluster description of multicomponent systems", *Physica A: Statistical Mechanics and its Applications* 128, no. 1-2 (November 1984): 334-350
37. Lerch, D., Wieckhorst, O., Hart, G. L., Forcade, R. W., & Müller, S. (2009). UNCLE: a code for constructing cluster expansions for arbitrary lattices with minimal user-input. *Modelling and Simulation in Materials Science and Engineering*, 17(5), 055003.
38. Stefan Müller, "Bulk and Surface Ordering Phenomena in Binary Metal Alloys", *Journal of Physics: Condensed Matter* 15, no. 34 (August 15, 2003): R1429-R1500.
39. Hart, G. L., & Forcade, R. W. (2008). Algorithm for generating derivative structures. *Physical Review B—Condensed Matter and Materials Physics*, 77(22), 224115.
40. Hart, G. L., & Forcade, R. W. (2009). Generating derivative structures from multilattices: Algorithm and application to hcp alloys. *Physical Review B—Condensed Matter and Materials Physics*, 80(1), 014120.
41. Seko, A., Koyama, Y., & Tanaka, I. (2009). Cluster expansion method for multicomponent systems based on optimal selection of structures for

- density-functional theory calculations. *Physical Review B—Condensed Matter and Materials Physics*, 80(16), 165122.
42. Chang, J. H., Kleiven, D., Melander, M., Akola, J., Garcia-Lastra, J. M., & Vegge, T. (2019). CLEASE: a versatile and user-friendly implementation of cluster expansion method. *Journal of Physics: Condensed Matter*, 31(32), 325901.
 43. Hart, G. L., Blum, V., Walorski, M. J., & Zunger, A. (2005). Evolutionary approach for determining first-principles Hamiltonians. *Nature Materials*, 4(5), 391-394.
 44. Collins, C., Dyer, M. S., Pitcher, M. J., Whitehead, G. F. S., Zanella, M., Mandal, P., ... & Rosseinsky, M. J. (2017). Accelerated discovery of two crystal structure types in a complex inorganic phase field. *Nature*, 546(7657), 280-284.
 45. Chang, J. H., Kleiven, D., Melander, M., Akola, J., Garcia-Lastra, J. M., & Vegge, T. (2019). CLEASE: a versatile and user-friendly implementation of cluster expansion method. *Journal of Physics: Condensed Matter*, 31(32), 325901.
 46. van de Walle, A., & Ceder, G. (2002). Automating first-principles phase diagram calculations. *Journal of Phase Equilibria*, 23(4), 348.
 47. Høyvik, I. M., Kristensen, K., Jansik, B., & Jørgensen, P. (2012). The divide-expand-consolidate family of coupled cluster methods: Numerical illustrations using second order Møller-Plesset perturbation theory. *The Journal of Chemical Physics*, 136(1).
 48. Ångqvist, M., Muñoz, W. A., Rahm, J. M., Fransson, E., Durniak, C., Rozyczko, P., ... & Erhart, P. (2019). ICET—a Python library for constructing

- and sampling alloy cluster expansions. *Advanced Theory and Simulations*, 2(7), 1900015.
49. Kadkhodaei, S., & Muñoz, J. A. (2021). Cluster expansion of alloy theory: a review of historical development and modern innovations. *JOM*, 73(11), 3326-3346.
 50. Malatji, K. T. (2019). Computer simulation studies of spinel LiMn_2O_4 and spinel $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 2$) (*Doctoral dissertation*).
 51. Malatji, K. T., Santos-Carballal, D., Terranova, U., Ngoepe, P. E., & de Leeuw, N. H. (2021). Controlling the Lithium Intercalation Voltage in the Li $(\text{Mn}_{1-x}\text{Ni}_x)\text{O}_4$ Spinel via Tuning of the Ni Concentration: a Density Functional Theory Study. *South African Journal of Chemistry*, 74, 3-7.
 52. Giustino, F. (2014). *Materials modelling using density functional theory: properties and predictions*. Oxford University Press.
 53. Hafner, J., Wolverton, C., & Ceder, G. (2006). Toward computational materials design: the impact of density functional theory on materials research. *MRS bulletin*, 31(9), 659-668.
 54. Singh, S., Chopra, M., & de Pablo, J. J. (2012). Density of states-based molecular simulations. *Annual Review of Chemical and Biomolecular Engineering*, 3(1), 369-394.
 55. Payne, M. C., Teter, M. P., Allan, D. C., Arias, T. A., & Joannopoulos, A. J. (1992). Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. *Reviews of modern physics*, 64(4), 1045.
 56. Ong, S. P., Chevrier, V. L., Hautier, G., Jain, A., Moore, C., Kim, S., ... & Ceder, G. (2011). Voltage, stability and diffusion barrier differences between

- sodium-ion and lithium-ion intercalation materials. *Energy & Environmental Science*, 4(9), 3680-3688.
57. Urban, A., Seo, D. H., & Ceder, G. (2016). Computational understanding of Li-ion batteries. *npj Computational Materials*, 2(1), 1-13.
 58. Toumar, A. J., Ong, S. P., Richards, W. D., Dacek, S., & Ceder, G. (2015). Vacancy ordering in O 3-type layered metal oxide sodium-ion battery cathodes. *Physical Review Applied*, 4(6), 064002.
 59. Meng, Y. S., Hinuma, Y., & Ceder, G. (2008). An investigation of the sodium patterning in Na_xCoO_2 ($0.5 \leq x \leq 1$) by density functional theory methods. *The Journal of chemical physics*, 128(10), 104708.
 60. Chevrier, V. L., & Ceder, G. (2011). Challenges for Na-ion negative electrodes. *Journal of The Electrochemical Society*, 158(9), A1011.
 61. Yahia, M. B., Lemoigno, F., Rousse, G., Boucher, F., Tarascon, J. M., & Doublet, M. L. (2012). Origin of the 3.6 V to 3.9 V voltage increase in the LiFeSO_4 F cathodes for Li-ion batteries. *Energy & Environmental Science*, 5(11), 9584-9594.
 62. Hinuma, Y., Meng, Y. S., & Ceder, G. (2008). Temperature-concentration phase diagram of $\text{P2-Na}_x\text{CoO}_2$ from first-principles calculations. *Physical Review B*, 77(22), 224111.
 63. Dima, R. S., Maleka, P. M., Maluta, N. E., & Maphanga, R. R. (2022). Structural, electronic, mechanical, and thermodynamic properties of na deintercalation from olivine NaMnPO_4 : first-principles study. *Materials*, 15(15), 5280.

64. Hafner, J. (2008). Ab-initio simulations of materials using VASP: Density-functional theory and beyond. *Journal of Computational Chemistry*, 29(13), 2044-2078.
65. Marsman, M., Grüneis, A., Paier, J., & Kresse, G. (2009). Second-order Möller–Plesset perturbation theory applied to extended systems. I. Within the projector-augmented-wave formalism using a plane wave basis set. *The Journal of Chemical Physics*, 130(18), 184103.
66. Materials Design Inc. (2023). MedeA UNCLE: Explore phase stability, bridge the length scales. *Materials Design Info*.
67. Lerch, D., Wieckhorst, O., Hart, G. L. W., & Forcade, R. W. (2009). UNCLE: A code for constructing cluster expansions for arbitrary lattices with minimal user

CHAPTER 4

4. Random Substitution of Ti and Zn into NaMnO₂

4.1 Introduction

Doping of semiconducting material with a foreign element or impurity has been used to improve materials' performance, mainly by controlling the band gap size, volume expansion and compression, and improving the electrical conductivity of the material [1]. The most popular doping method in semiconductors involves substitutional doping; this method can be applied in two ways, that is, random and controlled substitution [2]. This chapter presented first-principle DFT calculations of Ti-doped NaMnO₂ using the random substitution approach (i.e., doping in this context refers to substitution of 50% of Mn atoms by Ti or Zn atoms). Random substitution doping involves the replacement of a specific concentration from the parent structure and adds the same concentration of a dopant or an impurity element. Previously, Sukkabot employed substitutional doping to investigate the electronic properties of monoclinic NaMnO₂ doped with *Cr*, *Fe*, and *V* atoms to improve electrochemical performance [3]. The results showed that the dopants induced the expansion of volumes. The current study further reported that the lowest conduction band and highest valence band are primarily from the *d* orbital of the Mn atom and transition-metal dopants responsible for the electronic conductivity. The Na(Mn, Fe)O₂ system was found to be a semiconductor with a reduced band gap while *Cr* and *V* doping in Na(Mn, Cr)O₂ and Na(Mn, V)O₂ compounds were found to be half-metallic. This chapter discussed the random substitution doping of NaMnO₂ with titanium and zinc. Random substitution involves the replacement of host atoms in a crystalline material by foreign atoms at arbitrary positions. This technique is prevalent in semiconductors and solid-state materials to modify their electrical, optical,

and structural characteristics. Dopant atoms can introduce charge carriers, such as electrons or holes, or alter the material's band structure, thereby enhancing conductivity or other beneficial properties. If substitution occurs randomly, it may disrupt certain local electronic environments, which can subsequently affect the material's overall behaviour. The calculated results regarding the structural, electronic, mechanical, and thermodynamic properties of NaMnO_2 doped with Ti and Zn are presented in this chapter.

4.2 Computational Method

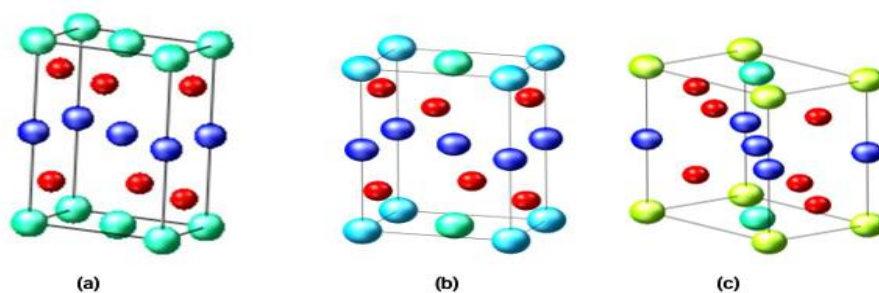
All density functional theory calculations were performed using the Vienna ab initio simulation package [4]. The program was used for all the calculations based on DFT. A spin-polarised generalised gradient approximation was used to solve the Kohn–Sham equations with the Perdew–Burke–Ernzerhof functional exchange-correlation functional with plane-wave pseudopotential. Geometry optimization was performed for the ground state energy of $2 \times 1 \times 1$ NaMnO_2 . The plane wave cutoff energy of 520 eV and the Monkhorst-Pack scheme were used, with $2 \times 2 \times 2$ and $4 \times 4 \times 4$ k-point meshes for bulk structure and supercell, respectively. The random substitution doping technique was used to introduce Ti and Zn atoms into the $2 \times 1 \times 1$ NaMnO_2 supercell, and subsequently, calculations were performed to determine the structural, mechanical and electronic properties of the bulk structures of $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, and $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ as well as $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $2 \times 1 \times 1$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ $2 \times 1 \times 1$ supercells (where $x = 1, 0.75, 0.5, 0.25, 0$). The de-intercalation process was done in four stages, where 27% of Na was removed from the $2 \times 1 \times 1$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ $2 \times 1 \times 1$ supercells until the systems became fully de-intercalated.

4.3. Results and Discussion

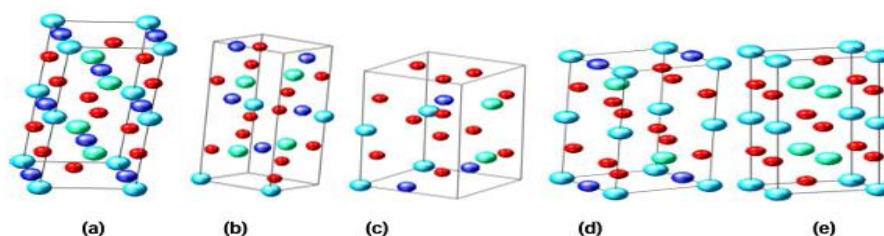
4.3.1 Structural Properties

The calculated structural properties of NaMnO_2 are listed in Table 1, and the calculated lattice parameters are consistent with the experimental values, within a 0.6% deviation from both experimental [5] and theoretical [6] results, indicating that the calculation methods are reasonable. Although the calculated cell volume deviation was 2.59% and 4.09% of the experimental and theoretical reported values, respectively, is still within an acceptable percentage error for DFT calculations [4].

Bulk Structures



2 x 1 x 1 $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercell and the de-intercalated structures



2 x 1 x 1 $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell and the de-intercalated structures

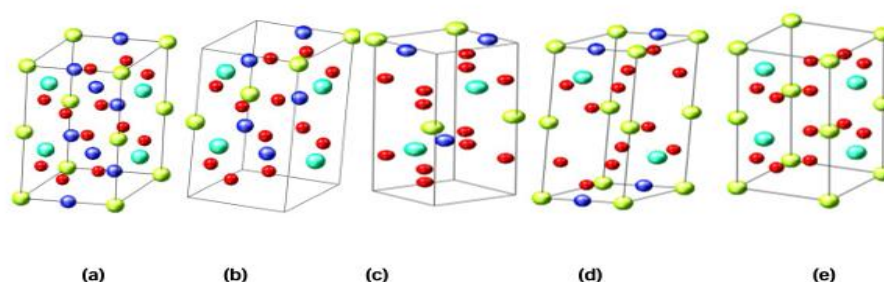


Figure 4. 1 Spin-polarized crystallographic relaxed structures of $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, and $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$

From figure 4.1, the blue balls represent sodium (Na), green balls imply manganese (Mn), red balls indicate oxygen (O), sky blue balls denote titanium (Ti), and lime balls represent zinc (Zn).

Table 4. 1: Calculated structural parameters of NaMnO₂ compared with literature results.

	Experimental	Literature	This work	Deviation	
	[5]	[6]		(%)	
				Experimental	Literature
a (Å)	5.63	5.71	5.131	0.499	0.579
b (Å)	2.86	2.88	2.854	0.006	0.026
c (Å)	5.77	5.74	5.672	0.098	0.068
Volume (Å³)	--	87.08	83.086	--	3.994

Table 4.1 indicates a contraction in the volume for this work, exhibiting a deviation of 3,994%. This phenomenon arises because GGA-PBE tends to overestimate the lattice parameter in most instances. Such overestimation also affects the binding energy, resulting in marginally larger equilibrium atomic separations relative to experimental values. DFT calculations employing GGA functionals typically yield larger lattice constants than those observed experimentally.

Table 4. 2: Lattice parameters of the NaMnO_2 , $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2X\ 1X\ 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercells during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).

	a (Å)	b (Å)	c (Å)	Volume(Å ³)
BULK				
NaMnO_2	5.131	2.854	5.672	83.086
$\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	5.488	3.046	6.446	90.152
SUPERCELL				
$\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	10.981	3.048	6.443	180.376
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	10.806	2.988	6.325	180.127
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	10.871	2.922	6.358	175.257
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	10.131	3.007	6.603	167.988
$\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	10.159	2.944	6.110	152.914

The lattice parameters and volumes were clearly altered by the dopants because of the difference in atomic radius between the Mn host and the doping element, Ti. The lattice parameters of the Ti-doped system are higher than those of the pure system, resulting in the expansion of the volume in the presence of the dopants. Stretching of the lattice parameters and volume expansion were again observed when the supercell was computed.

Table 4. 3: Lattice parameters of NaMnO_2 , $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2X\ 1X\ 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).

	a (Å)	b (Å)	c (Å)	Volume (Å ³)
BULK				
NaMnO_2	5.131	2.854	5.672	83.086
$\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	5.404	3.055	6.421	88.839
SUPERCCELL				
$\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	10.798	3.055	6.421	177.581
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	10.702	3.004	6.517	178.542
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	10.647	2.966	6.322	178.666
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	10.965	2.916	6.634	181.515
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	11.542	2.871	6.145	172.563

The change in lattice parameters and volume is observed after, Mn a certain concentration of Mn was replaced by the same concentration of Zn and during Na extraction, as was observed in the Ti-doped system, with the significant stretch in the lattice parameter observed on the lattice constant, a . In contrast, lattice constants b and c are slightly stretched, and in the case of $\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, the lattice constant, c is compressed.

Dopants can make the volume larger, as a result widening the Na-ion diffusion channel and improving the electronic conductivity as reported previously [3,5]. Both Ti- and Zn-doped systems show the stretching in lattice parameters and volume expansion of 90.152 Å³ and 88.839 Å³, respectively, before de-intercalation. The Ti-doped system's lattice parameters slightly contract upon Na extraction. This small contraction in the volume results in the fully de-intercalated system having the most smaller diffusion

channel while the fully intercalated has the biggest. In the case of a Zn-doped system, the volume expands during each de-intercalation stage and only drops when the system is fully de-intercalated. Hence, the diffusion channel widens at each de-intercalated stage and decreases when the system is fully de-intercalated.

4.3.2 Electronic Properties

4.3.2.1 Density of States for NaMnO₂, Ti or Zn Doped NaMnO₂ Bulk and NaMnO₂ 2 x 1 x 1 Supercell

The density of states (DOS) calculations was computed using the spin-polarized PBE-GGA functional. The spin-up states are displayed on the positive scale, whereas the lower spin states are seen on the negative scale of the DOS plot. Subsequently, the total contributions of all atoms in the structure are indicated by the total density of states (TDOS), whereas the partial density of states (PDOS) indicates the contribution of individual atoms. The Fermi level (E_F) is set to zero for all plots. The concept of Fermi level and energy band gaps is necessary to understand the stability of the system, where the shift of the E_F concerning the band gap plays an essential role in stability and changes in coordination within the system.

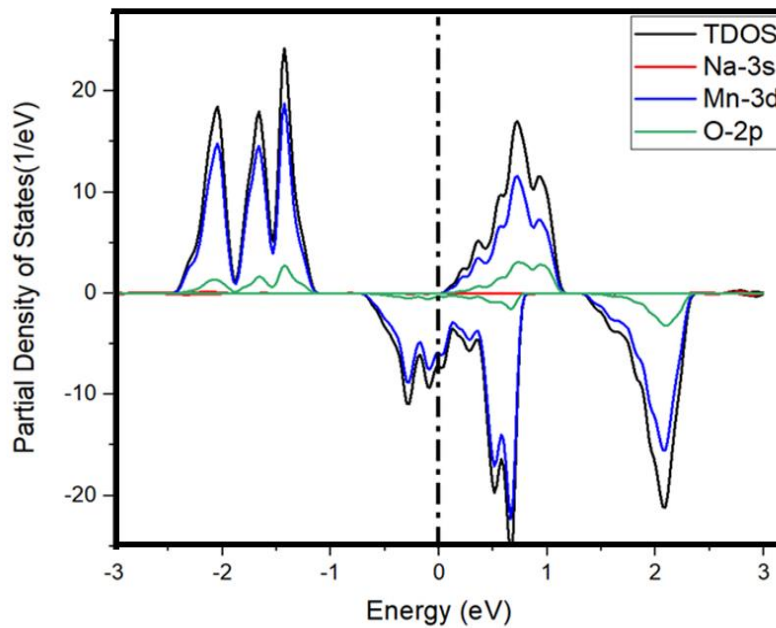


Figure 4.2: Spin-polarized DOS near the Fermi level of bulk NaMnO₂ material.

Figure 4.2 shows the spin-polarized density of monoclinic NaMnO₂; it is evident that the spin-up and spin-down states are fully occupied, characterising the semiconducting behaviour of the system. The findings are consistent with those reported in the literature [6]. The figure shows that O-2p orbitals mainly contribute to the valence band, interacting with Mn-3d states, while Na-3s have minimal impact. The total density of states (TDOS) suggests a clear band gap. The PDOS of NaMnO₂ is primarily dominated by Mn-3d orbitals, which contribute significantly near the Fermi level.

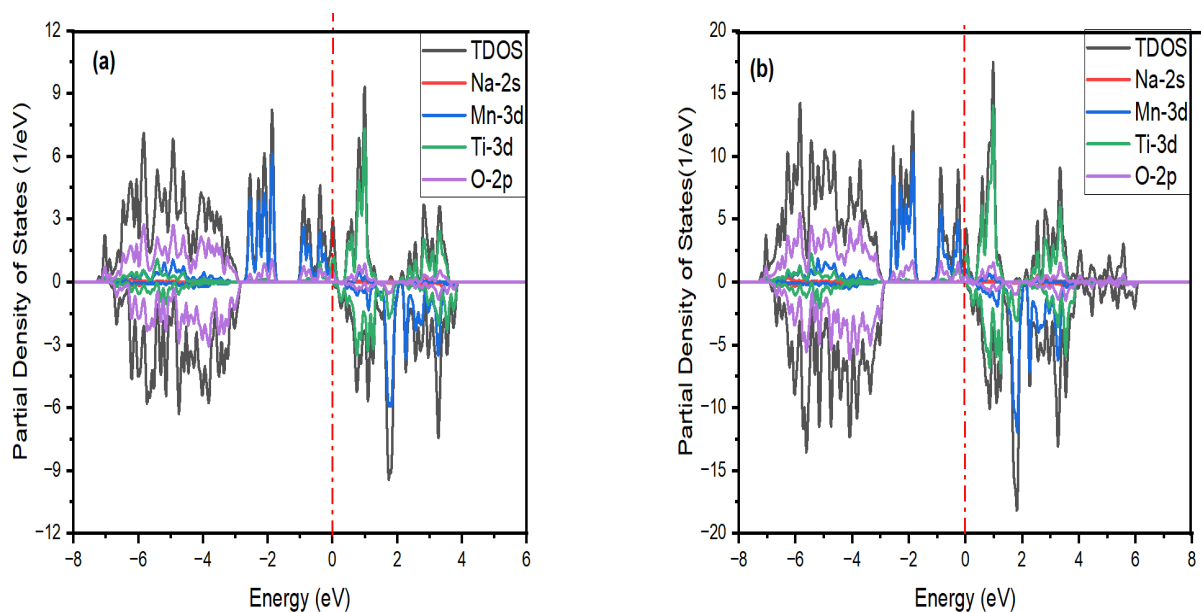


Figure 4. 2: Spin-polarized PDOS of the (a) NaMn_{0.5}Ti_{0.5}O₂ bulk structure and (b) 2x 1x 1 NaMn_{0.5}Ti_{0.5}O₂ supercell.

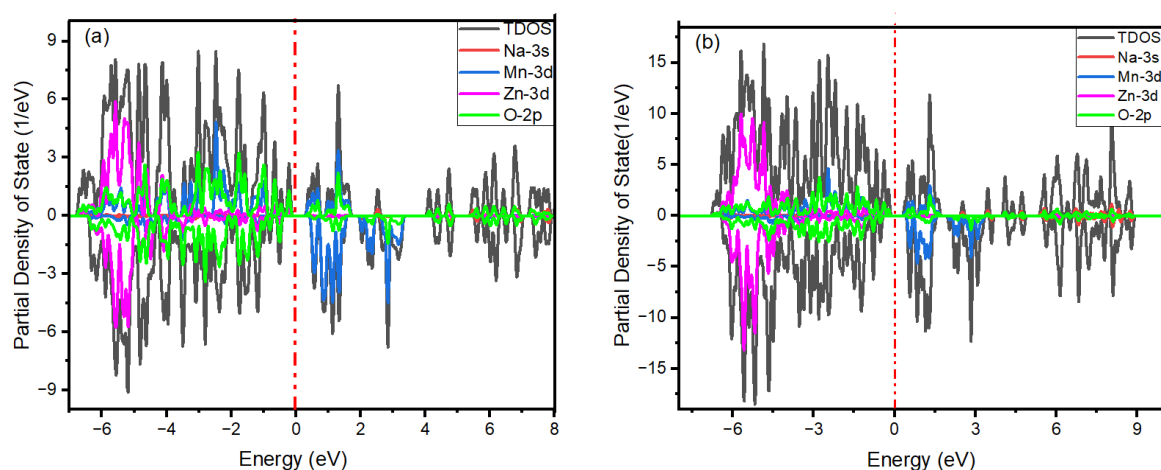


Figure 4. 3: Spin-polarized PDOS of the (a) NaMn_{0.5}Zn_{0.5}O₂ bulk structure and (b) 2x 1x 1 NaMn_{0.5}Zn_{0.5}O₂ supercell.

Figure 4.3 illustrates the spin-polarized total density of states (TDOS) and the partial density of states (PDOS) for both the bulk structure and the 2x 1 x 1 supercell of NaMn_{0.5}Ti_{0.5}O₂. The observed asymmetry in the spin-polarized density of states confirms the existence of magnetism in the doped systems. Doping of NaMnO₂ with Ti creates localised dopant states at the Fermi level, primarily associated with the 3d

orbital of Ti, as demonstrated by the PDOS analysis. This phenomenon arises from the hybridization of the $3d$ orbitals of the dopant Ti and Mn atoms with the $2p$ orbitals of oxygen, referred to as $p-d$ exchange hybridization. Hybridization significantly influences the electronic and magnetic properties of the material. The conduction band minimum (CBM) and valence band maximum (VBM) are primarily influenced by Mn and Ti atoms, which enhance electronic conductivity in the doped structure.

The electronic density of states for $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, derived from spin-polarized DFT calculations is presented in Figure 4.4. Similar to Ti-doped systems, the Zn-doped bulk $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and the $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell exhibit semiconducting characteristics. The band gap is reduced in the doped bulk structure relative to the undoped system, presumably due to the creation of localised states by the Zn dopant adjacent to the valence band. The $2 \times 1 \times 1$ supercell exhibits a larger band gap than the doped bulk structure, likely due to additional structural distortions and enhanced atomic interactions arising from the supercell formation. The Zn dopant has a more pronounced effect on the valence band states than on the conduction band, modifying the electronic structure while maintaining the material's semiconducting characteristics.

4.3.2.2 Energy Band Gap

Table 4.4 depicts the effect of Ti doping on NaMnO_2 system behaviour during de-intercalation. The behaviour changes from semiconductor to half-metallic when doped with Ti, before de-intercalation. The system returns to a semiconductor state upon the extraction of 25% and 50% Na concentration. Then the system changes to a metallic behaviour after removing 75% concentration of Na, while a fully de-intercalated system returns to depicting semiconducting characteristics.

Table 4. 4: Calculated energy band gap of NaMnO_2 , $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercell during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).

	Energy Gap (eV)	Band Material Type
BULK		
NaMnO_2	1.024	Semiconductor
$\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.928	Half-metallic
SUPERCELL		
$\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	2.988	Half-metallic
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.165	Semiconductor
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.415	Semiconductor
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.000	Metallic
$\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	1.137	Semiconductor

Table 4. 5: Calculated energy band gap of NaMnO_2 , $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell during Na extraction after relaxation ($x = 1, 0.75, 0.5, 0.25, 0$).

	Energy Gap (eV)	Band Material Type
BULK		
NaMnO_2	1.024	Semiconductor
$\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.633	Semiconductor
SUPERCCELL		
$\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	2.063	Semiconductor
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	1.712	Half-metallic
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.059	Semiconductor
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.003	Half-metallic
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.118	Semiconductor

Table 4.5 shows the calculated energy band gap and behaviour of NaMnO_2 , bulk $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell as well as de-intercalated systems. The introduction of Zn into NaMnO_2 reduces the band gap, while the creation of a supercell leads to an increase, all while maintaining semiconducting behaviour after de-intercalation. $\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ exhibit half-metallic behaviour with a diminished band gap. In contrast, the other de-intercalation phases, $\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, retain semiconductor properties but possess smaller band gaps relative to the fully de-intercalated state. Both Ti and Zn reduce the band gap as the system transitions from semiconductor to half-metallic and metallic states throughout various de-intercalation stages.

4.3.2.3 Density of States for De-Intercalated Systems

The system behaviour is characterised by the states appearing on the spin-up and spin-down states as firstly discussed in subsection 4.3.2. Figure 4.4 below illustrates the calculated total and partial densities of states for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, a $2 \times 1 \times 1$ supercell of $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, and associated various de-intercalated systems. For all the systems, as per usual the Fermi level is positioned at the edge of the uppermost valence band, indicating their electronic states.

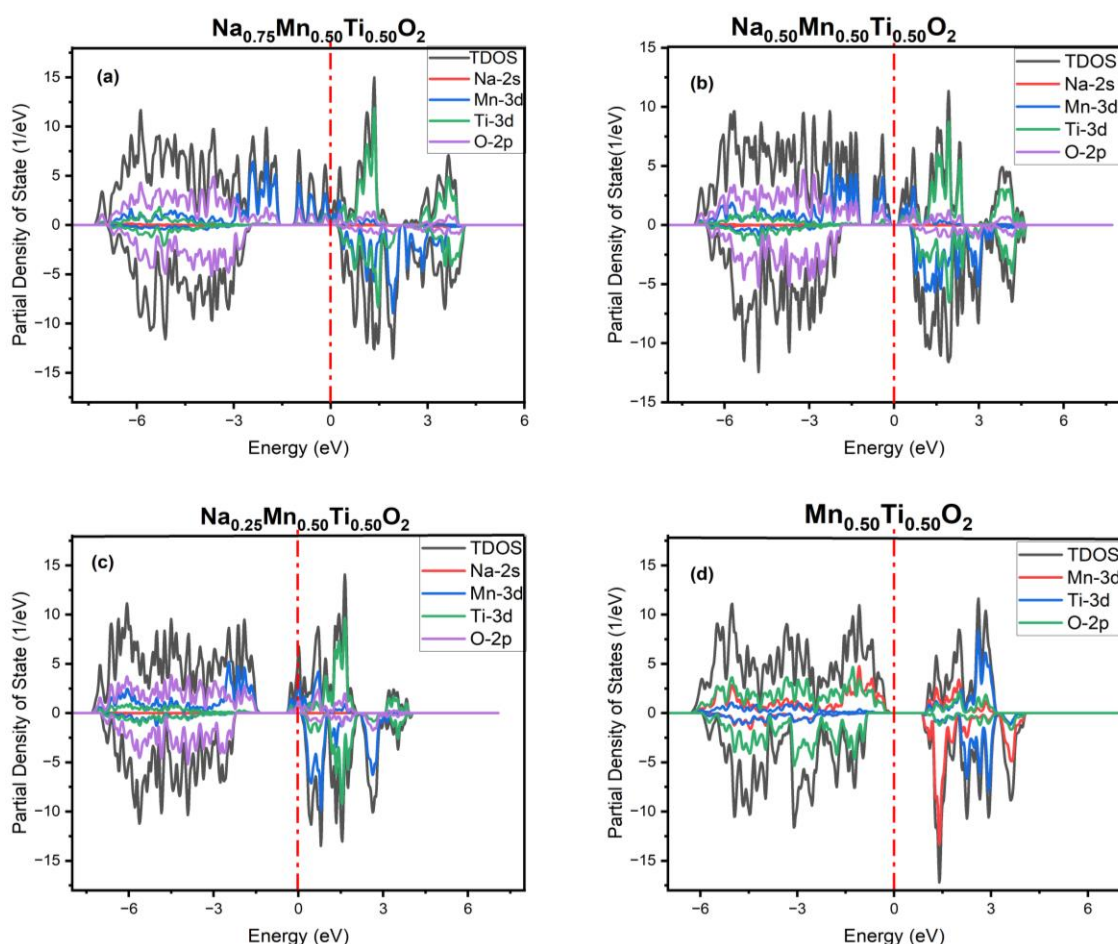


Figure 4. 4: Spin-polarized PDOS of $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercell (a) $x = 0.75$, (b) $x = 0.5$, (c) $x = 0.25$, (d) $x = 0$.

During extraction, the O-2*p*, Mn-3*d*, and Ti-3*d* states slightly cross the Fermi level, as illustrated in Figure 4.5. The up-spin and down-spin states in Figure 4.5(a) and 4.5(b) are fully occupied, characterising the semiconducting behaviour, with band gaps of 0.165 eV and 0.416 eV for Na_{0.75}Mn_{0.5}Ti_{0.5}O₂ and Na_{0.5}Mn_{0.5}Ti_{0.5}O₂, respectively, while the PDOS depicted in Figure 4.5(c) shows the spin-up states that are partially occupied and thus becomes metallic, whereas the spin-down states are completely filled and present the semiconducting behaviour, resulting in the compound Na_{0.25}Mn_{0.5}Ti_{0.5}O₂ depicting the half-metallic behaviour. Lastly, a fully de-intercalated Mn_{0.5}Ti_{0.5}O₂ compound returns back to showing semiconducting characteristics.

The partial density of state calculations reveal that the intrinsic NaMnZnO₂ system maintains its semiconducting nature even when a dopant is introduced. However, this semiconducting behaviour is altered during the de-intercalation process. Specifically, in the first de-intercalation step, where 25% of the sodium (Na) atoms are removed, the system's behaviour transitions from semiconducting to half-metallic behaviour. This significant change highlights the sensitivity of the electronic properties to the sodium content in the material.

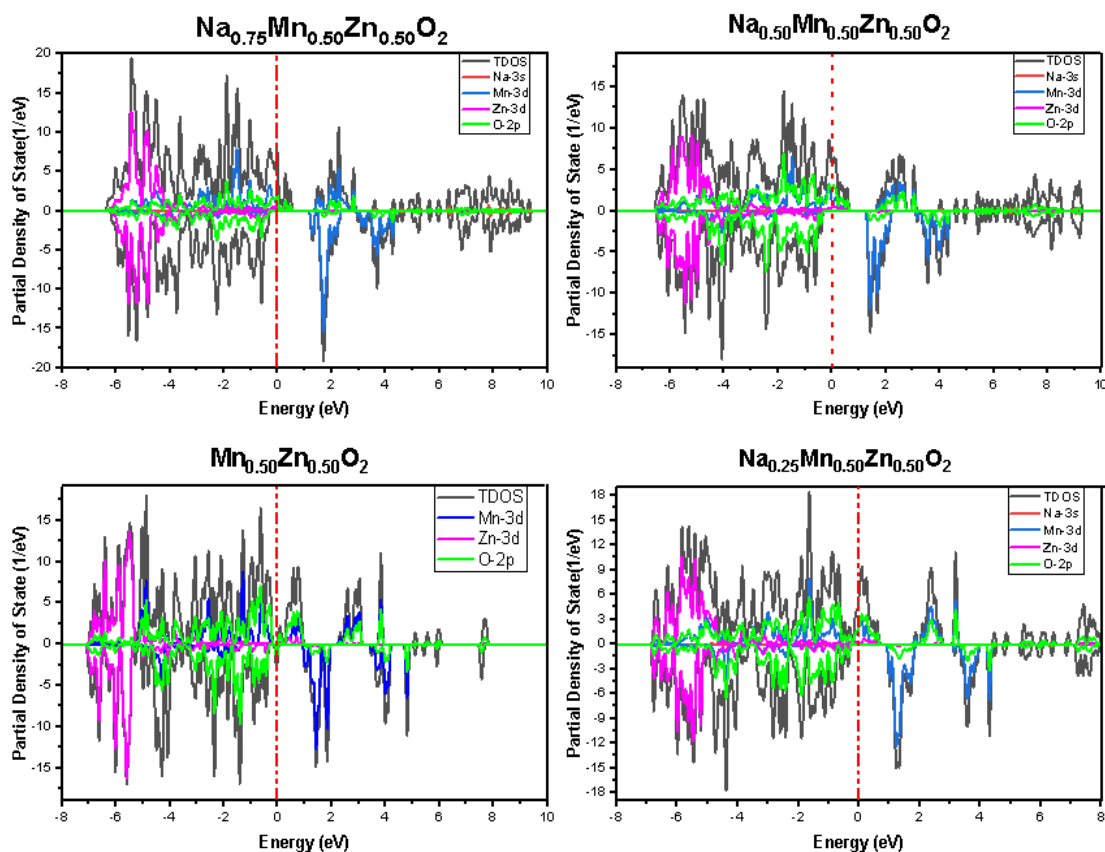


Figure 4. 5: Spin-polarized PDOS of $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell (a) $x = 0.75$, (b) $x = 0.5$, (c) $x = 0.25$, (d) $x = 0$.

Figure 4.6 also illustrates the impact of progressive sodium de-intercalation on the electronic properties of NaMnZnO_2 -based systems. In the 2nd, 3rd, and 4th de-intercalation steps, corresponding to the removal of 50%, 75%, and 100% of Na, the spin-up PDOS becomes filled. This indicates that these systems retain their semiconducting nature despite significant changes in Na concentration. For the $\text{Na}_{0.25}\text{MnZnO}_2$ and MnZnO_2 systems, the states originating from the O-2p, Mn-3d, and Zn-3d orbitals intersect the Fermi level. This intersection suggests a mixing of these states at the Fermi level, contributing to the overall semiconducting behaviour. In the $\text{Na}_{0.50}\text{MnZnO}_2$ system, only the O-2p and Zn-3d states cross the Fermi level, indicating a slight shift in electronic structure but still maintaining semiconductor characteristics.

The $\text{Na}_{0.75}\text{MnZnO}_2$ system presents a unique scenario where the spin-up states are partially occupied, leading to a metallic behaviour. Conversely, the spin-down states remain fully occupied and semiconducting. This disparity between spin states results in half-metallic behaviour, where the material exhibits metallic properties for one spin channel and semiconducting properties for the opposite spin channel.

4.3.3. Voltages/Redox Potential and Formation Energy

The energy change of the individual Na atom at each de-intercalation stage of the NaMnO_2 . The energy change is calculated using the analytical expression:

$$\Delta E = E[\text{Na}_{x-y}\text{MnO}_2] + yE(\text{Na}) - E[\text{Na}_x\text{MnO}_2] \quad (4.1)$$

where ΔE is the energy change of the process that, $y(\text{Na})$ atoms are extracted between the NaMnO_2 layers, $E[\text{Na}_{x-y}\text{MnO}_2]$, $E(\text{Na})$ and $E(\text{Na}_x\text{MnO}_2)$ are the energy of $[\text{Na}_{x-y}]$, Na metal and Na_xMnO_2 . Accordingly, the cathode voltage could be calculated by [7]:

$$U = \frac{\Delta E}{ye} \quad (4.2)$$

where U is the cathode voltage, e is the absolute value of the electron charge and y is the number of the extracted Na atom [7]. To understand the formation of solid solutions of Na removal Na_xMnO_2 , the formation energy per unit of formula was calculated using the expression:

$$\text{FE} = E[\text{Na}_x\text{MnO}_2] - x \times E[\text{NaMnO}_2] - (1 - x)E[\text{MnO}_2] \quad (4.3)$$

where $E[\text{Na}_x(\text{Mn}, \text{Ti})\text{O}_2]$ is the energy of the partially deintercalated material and $E[\text{Na}(\text{Mn}, \text{Ti})\text{O}_2]$ and $E[(\text{Mn}, \text{Ti})\text{O}_2]$ are the energies in its original condition and totally deintercalated structures, respectively.

Table 4. 6: Cathode voltage/redox potential and formation energy for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$).

	Voltage (V)	Formation Energy(eV)
$\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	-----	-1648.73
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	4.132	-3208.95
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3.896	-1527.70
Units$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3.727	-2849.06
$\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3.410	-1305.28

For the $\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ systems, the predicted formation energies are found to be -1648.73 eV, -3208.95 eV, -1527.70 eV, -2849.06 eV and -1305.28 eV, respectively, as shown in Table 4.6. The formation energy of the intercalation systems was found to be negative for all materials. This negative value indicates that these materials are predicted to form a stable solid solution, signifying that the intercalation process is thermodynamically favourable. Consequently, these materials are likely to exhibit good chemical stability and homogeneity, making them promising candidates for applications in energy storage and conversion technologies.

Table 4. 7: Cathode voltage/redox potential and formation energy for $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$).

	Voltage (V)	Formation Energy (eV)
$\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	-----	-1127.284
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	2.221	-2074.865
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	3.548	-1778.782
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	4.040	-1459.448
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	4.337	-1108.467

Table 4.7 provides the formation energy values for the 2 X 1 X 1 $\text{Na}_x\text{MnZnO}_2$ de-intercalated systems. On analysing the data, we observed that the formation energy is negative for all de-intercalated phases, which strongly suggests that these materials can form stable solid solutions. This negative formation energy is a clear indication that the intercalation and subsequent de-intercalation processes are thermodynamically favourable, ensuring the structural and chemical stability of these materials.

Among the various compositions studied, $\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ exhibited the most negative formation energy, highlighting it as the most thermodynamically stable compound within the series. This exceptional stability is crucial for practical applications, as it implies enhanced durability and performance of the material when used as a cathode in sodium-ion batteries.

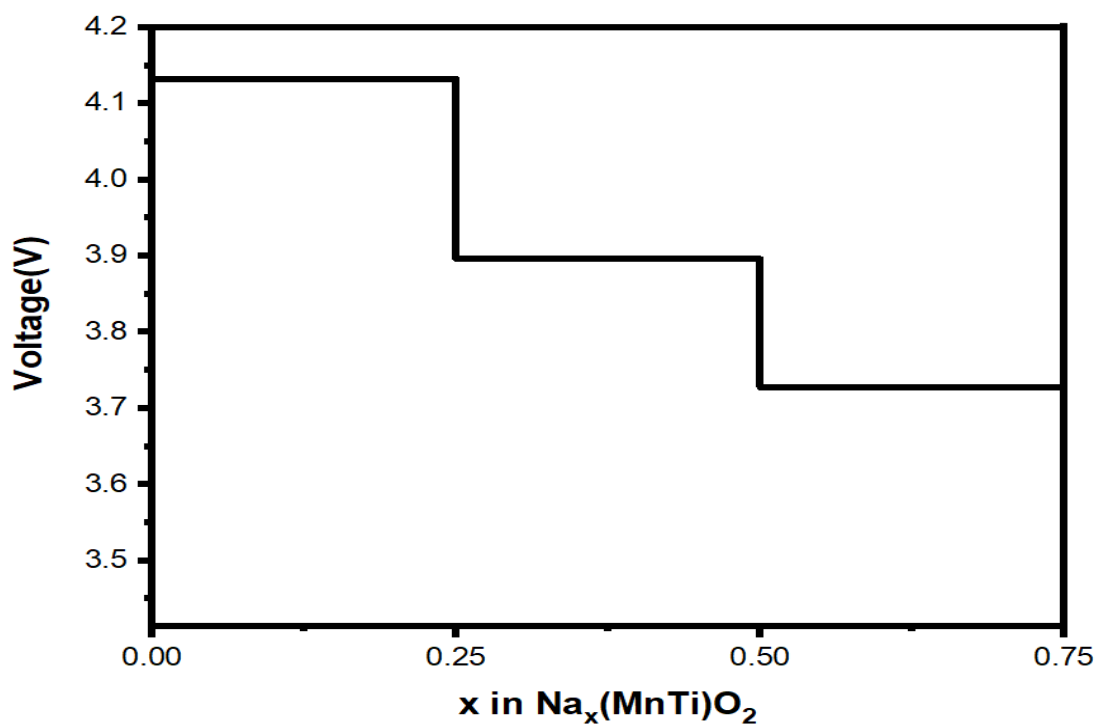


Figure 4. 6: Deintercalation potentials (V) for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$)

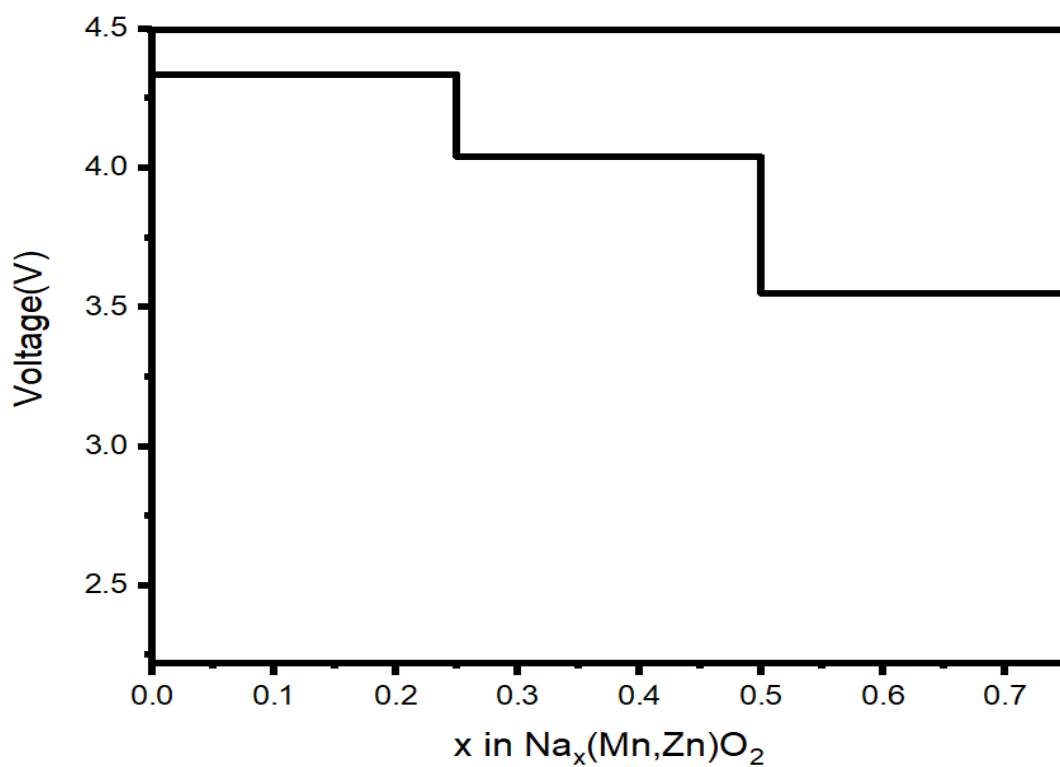


Figure 4. 7: Deintercalation potentials (V) for $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$).

The de-intercalation potentials for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ are presented in Table 4.6 and illustrated in Figure 4.7, with values spanning from 3.410 V to 4.132 V. This range indicates a high voltage window, suggesting that the material possesses significant potential as a cathode for sodium-ion batteries. The high-voltage range significantly enhances energy-density and efficiency, essential characteristics for advanced energy storage technologies. The results correspond with the research of Dima *et al* [7], highlighting the necessity of high-voltage cathode materials to achieve elevated energy densities in rechargeable batteries [7]. The stability of the voltage range highlights the material's potential for long-term cycling stability, an essential consideration for practical applications. The de-intercalation potentials for $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, as indicated in Table 4.7 and Figure 4.8, range from 2.221 V to 4.337 V. This broad voltage range indicates that $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ serves as a versatile cathode material. The lower end of the range at 2.221 V, signifies enhanced energy efficiency in the de-intercalation process, leading to reduced energy loss. Meanwhile, the upper end at 4.337 V indicates the potential for high energy-density. These dual benefits render the material highly appropriate for various SIB applications.

These findings align with earlier research conducted by Yabuuchi *et al.* [8]., who reported experimental de-intercalation voltages ranging from approximately 2.0 V to 4.3 V, depending on the specific material composition and structure. For instance, the layered oxides P2-type $\text{Na}_{2/3}[\text{Fe}_{1/2} \text{Mn}_{1/2}]\text{O}_2$ exhibited average operating voltages around 3.0 V, while $\text{Na}_{0.70}\text{MnO}_2$ demonstrated a higher voltage of 4.0 V. Similarly, Zhang *et al* [9] reported that NaCoO_2 has an average deintercalation voltage of about 3.0 V, which aligns well with the voltage profiles obtained in this study and corroborates the experimental observations by Yabuuchi *et al.* Both $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ exhibits properties that render them suitable as cathode materials for

sodium-ion batteries. Their voltage ranges correspond well to the specifications for high energy-density and efficiency.

4.3.4. Mechanical Properties

NaMnO_2 crystalizes into a monoclinic phase, therefore, there are nine independent elastic constants, i.e., C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} and C_{66} . For the monoclinic crystal, the mechanical stability criterion can be expressed by analytical expression presented in equation 3.46 in chapter 3.

Table 4. 8: Elastic constants (C_{ij}) for $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
BULK									
NaMnO_2	119.15	50.44	45.01	321.88	39.72	163.13	61.44	52.21	59.97
$\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	191.96	80.93	53.20	266.44	59.00	190.85	50.31	40.98	62.95
SUPERCCELL									
$\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	195.40	68.44	50.36	243.84	44.15	183.62	46.16	43.78	62.91
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	160.42	68.25	24.22	301.40	31.43	142.13	33.22	22.70	59.45
$\text{Na}_{0.50}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	147.21	59.17	31.01	320.03	18.26	84.84	17.84	18.34	77.74
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	266.99	67.48	21.26	260.63	15.66	54.62	10.73	15.41	76.09
$\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	279.77	51.50	6.34	309.47	4.20	11.92	14.58	23.45	115.63

Table 4. 9: Elastic constants (C_{ij}) for $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
BULK									
NaMnO_2	119.15	50.44	45.01	321.88	39.72	163.13	61.44	52.21	59.97
$\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	184.63	55.87	40.04	231.62	13.74	144.82	43.90	32.35	45.60
SUPERCELL									
$\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	185.92	54.70	38.96	235.46	18.84	158.05	43.79	31.44	46.14
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	129.94	50.91	21.07	235.97	22.35	117.06	26.07	25.27	45.34
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	122.74	53.75	23.10	235.80	11.28	89.40	12.72	16.39	51.14
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	58.75	45.40	8.26	239.53	3.93	31.82	7.26	12.64	64.65
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	11.04	28.69	1.22	269.44	4.57	14.72	2.88	9.89	80.12

The results in Tables 4.8 and 4.9 show that the mechanical stability criterion for the monoclinic crystal has been satisfied by all the systems. Hence, the crystal structures investigated in this study are mechanically stable during and after Na extraction, this holds true in all the crystal structures including the fully deintercalated structure. The findings suggest that both $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$) can be fully deintercalated and still maintain their mechanical stability.

The bulk, shear, and Young's moduli of the $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25$) structures are relatively large as shown in Table 4.10, which implies hardness, excellent resistance to volume change, deformation, and stiffness, respectively. In addition, the Pugh ductility and brittleness criterion was investigated. The bulk-to-shear modulus, (B/G) ratio for polycrystalline phases can be calculated, knowing that the shear modulus represents the resistance to plastic deformation, and the bulk

modulus represents the resistance to fracture [10,11]. Brittleness is associated with a low B/G value, while ductility is associated with a high B/G value. The value of 1.75 is the critical number that distinguishes ductility from brittleness. Because B/G is greater than 1.75, the structures of the $\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_{0.50}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ are ductile, which implies that these materials can bend without deformation, resulting in fewer cracks to no cracks during battery operation. At the same time, $\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ give the brittle behaviour as its B/G values is 1.072 which is less than 1.75, the ductility and brittleness behaviour has also been complemented by the calculated Poisson ratio as shown in Table 4.10, wherein the $\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{Na}_{0.50}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ systems have Poisons ratio greater than 0.25 showing ductile behaviour and in agreement with the Pugh's ratio. The Poisson ratio value of 0.144 for a fully de-intercalated $\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ suggests that the material is brittle unlike the others.

Table 4. 10: Bulk, shear and Young's moduli, Poisson's and Pugh's ratio for $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

	B_H	G_H	E_H	Poisson's Ratio	Pugh's Ratio
BULK					
NaMnO_2	85.92	59.48	144.97	0.219	1.445
$\text{Na Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	112.71	58.52	149.64	0.2787	1.9260
SUPERCCELL					
$\text{Na}_1 \text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	104.25	58.82	148.50	0.2626	1.7725
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	73.81	41.15	103.92	0.2649	1.7937
$\text{Na}_{0.50}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	88.19	48.49	122.87	0.2677	1.8188
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	66.98	37.62	94.96	0.2634	1.7798
$\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	46.11	43.00	97.04	0.1443	1.0723

Table 4. 11: Bulk, shear and Young's moduli, Poisson's and Pugh's ratio for $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $2 \times 1 \times 1 \text{ Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

	B_H	G_H	E_H	Poisson's Ratio	Pugh's Ratio
BULK					
NaMnO_2	85.92	59.48	144.97	0.219	1.445
$\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	86.71	72.17	79.44	0.243	1.614
SUPERCELL					
$\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	89.39	50.60	127.06	0.256	1.718
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	70.12	40.82	102.53	0.256	1.718
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	63.40	31.69	81.20	0.286	2.000
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	36.74	23.81	58.58	0.234	1.543
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	23.36	18.65	43.49	0.185	0.125

Table 4.11 shows the bulk, shear, and Young's moduli of $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ of monoclinic crystal structure. Where B, G, and E are the bulk, shear, and Young's moduli, respectively, while H signifies Hill bound. It can be seen from the findings that the calculated bulk-to-shear modulus (B/G) ratio for the investigated systems $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$) gives evident that the investigated material behaves differently at different de-intercalation stages. For the second stage de-intercalated system, where 50% of Na was removed, the B/G ratio of 2.00 was obtained. On the other hand, the crystal structures of the $\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, $\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, $\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ structures are predicted to have B/G ratio of less than 1.75 suggesting that these systems are ductile, can bend without deformation, and can experience fewer cracks to no cracks during battery operation.

Anisotropy refers to the directional dependence of a property, meaning that the properties of the crystal may vary with direction. In monoclinic crystals, there are three crystallographic axes, namely, two equivalent short axes (A_1 and A_2) in the plane of the hexagon and a longer axis (A_3) perpendicular to the plane. For monoclinic crystal systems, anisotropy arises from shear as well as from the anisotropy of the linear bulk modulus. The shear anisotropy factors are given by the expression [12,13]:

$$A_1 = \frac{4C_{44}}{C_{11}+C_{33}-2C_{13}} \quad (4.4)$$

$$A_2 = \frac{4C_{55}}{C_{22}+C_{33}-2C_{23}} \quad (4.5)$$

$$A_3 = \frac{4C_{66}}{C_{11}+C_{22}-2C_{12}} \quad (4.6)$$

By introducing a comprehensive concept, Chung and Buessem pioneered a more encompassing approach to quantifying elastic anisotropy. Their approach involves measuring the percentage anisotropy in compressibility and shear properties [14]. This innovative approach expands the scope of understanding and characterising elastic anisotropy, providing a more thorough and nuanced perspective on the material's response to various stress conditions. By considering both compressibility and shear, the approach of Chung and Buessem's allows for a more holistic assessment of how materials deform and respond to external forces in different directions, the compressibility and shear. According to Chung and Buessem approach the two parameters (anisotropy in compressibility and shear moduli) are defined using the relations [14,15]:

$$A_B = \frac{B_V - B_R}{B_V + B_R} \quad (4.7)$$

$$A_G = \frac{G_V - G_R}{G_V + G_R} \quad (4.8)$$

where A_G is Shear asymmetry index, G_V is Shear Modulus in vertical direction and G_r is Shear modulus in the radial direction.

Table 4. 12: Anisotropy in shear elastic factor (A_i , with $i = 1,2,3$) and anisotropy in compressibility and shear moduli (A_B and A_G in %) for de-intercalated $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$.

	A_1	A_2	A_3	A_B	A_G
BULK					
NaMnO_2	1.278	0.514	0.705	0.131	0.110
$\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.728	0.483	0.849	0.020	0.046
SUPERCCELL					
$\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.662	0.516	0.832	0.011	0.041
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.523	0.239	0.731	0.073	0.145
$\text{Na}_{0.50}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.420	0.199	0.891	0.157	0.272
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.153	0.217	0.775	0.319	0.390
$\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	0.291	0.299	0.957	0.747	0.550

A_1 , A_2 , and A_3 give the degree of anisotropy in the bonding between atoms in different planes, which the following three shear anisotropy factors can also describe. A_1 is the shear anisotropy factor defined by the anisotropy for the $\{100\}$ shear planes between $\langle 011 \rangle$ and $\langle 010 \rangle$ directions, A_2 is associated with the $\{010\}$ shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions, while A_3 factor represents shear anisotropy in the $\{001\}$ shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions. For an isotropic crystal, all A_i ($i = 1,2,3$) have unit values. If it is not equal to 1, then the crystals have anisotropy. Deviation of A_i from the unit quantifies the degree of elastic anisotropy.

A_3 is the highest and close to 1, followed by A_1 , while A_2 is the smallest. This means that elastic anisotropic for $\{001\}$ shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions are larger than $\{100\}$ shear planes between $\langle 011 \rangle$ and $\langle 010 \rangle$ directions and $\{010\}$ shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions, except for one system $\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ where A_2 is found to be larger than A_1 .

There is no deviation of A_i ($i = 1, 2$ and 3) from the unit in all calculated systems, as we did not get any value greater than 1. According to Hill [16], the difference between B_V and B_R may be proportional to the degree of elastic anisotropy of the crystal, for compressibility and shear moduli $B_R = B_V$ is related to isotropic elastic constants. Still, a value of 100% is associated with the maximum amount of anisotropy that may be achieved [17,18]. The values of A_B and A_G for all the de-intercalated systems are listed in Table 4.12. When compressibility and shear are considered, these two factors are assigned to zero for the isotropic crystal. The higher the value of these factors, the greater the anisotropy of the crystal. It is apparent from Table 4.12 that anisotropy factors A_B and A_G increase during de-intercalation, suggesting an improvement in isotropy and a reduction in microcracks and dislocation in the charge and discharge process.

The effect of Na de-intercalation on anisotropy factors is essential to determine the susceptibility of cracks during battery operation [19] and reduce micro-cracks and dislocations. The derivation of the anisotropic factor from unity measures elastic anisotropy [20]. For fully intercalated system, $A_1(0.662)$, $A_2(0.516)$, and $A_3(0.832)$, diverge from unity by 33.8%, 48.4%, and 16.8%, respectively, suggesting isotropy characteristics at every de-intercalation step. Both A_1 and A_2 are decreasing while for stages 2 and 4 (at 50% and 100%) of de-interacted process, A_3 increase and convergence to unity. This decrease during de-intercalation suggests mechanical

stability and less chance of performance failure during battery operation. At the same time, the increase in the values of A_3 for 50% and 100% makes the deformation at the de-intercalation stages likely.

Table 4. 13: Anisotropy in the shear elastic factor A_i (with $i = 1,2,3$) and the anisotropy in compressibility and shear moduli (A_B and A_G in %) for de-intercalated $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$.

	A_1	A_2	A_3	A_B	A_G
BULK					
NaMnO_2	1.278	0.514	0.705	0.131	0.110
$\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.658	0.353	0.592	0.028	0.950
SUPERCCELL					
$\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.509	0.334	0.687	0.092	0.107
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.307	0.217	0.815	0.064	0.109
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.392	0.192	1.246	0.094	0.263
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.494	0.144	1.436	0.347	0.473
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	0.704	0.371	0.599	0.732	0.929

Table 4.13 shows anisotropy in the shear elastic factor (A_i with $i = 1,2,3$) and anisotropy in compressibility and shear moduli (A_B and A_G) for de-intercalated $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$. A_3 was found to be the highest and close to 1, followed by A_1 while A_2 is the smallest. This means that elastic anisotropic for $\{001\}$ shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions are larger than $\{100\}$ shear planes between $\langle 011 \rangle$ and $\langle 010 \rangle$ directions and $\{010\}$ shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions. The divergence is then observed in the case of $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ with the fully intercalated system showing $A_1(0.509)$, giving the divergence of 49.1 % from unity. When 75% Na de-intercalation the anisotropy shows $A_1(0.494)$ with a divergency percentage of 50.6%.

This indicates a minimal convergence to unity. However, for 50% and 25% sodium de-intercalated, A_3 gives the anisotropy of 1.246 and 1.436, respectively, which exceeds the unity by 24.6% and 43.6%, respectively. This indicates that $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ becomes structurally unstable with decreasing sodium concentration, although it provides higher energy density.

$\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ shows a reduction in divergence from unity in all anisotropy metrics, indicating enhanced structural stability during cycling. $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ exhibits increased anisotropy with reduced sodium content, potentially compromising stability while enhancing energy density. The findings are consistent with the existing literature, including the studies by Yabuuchi *et al.* [8], highlighting the importance of compositional tuning in the enhancement of cathode materials for SIBs. De-intercalations of Na tend to raise A_B and A_G values, suggesting an improvement in isotropy and a reduction in microcracks and dislocations during charging and discharging process. In all stages of de-intercalation, the proportion of shear modulus anisotropy A_G is lower than the percentage of bulk modulus anisotropy A_B for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$. For $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$, the trend cannot be defined as the values of A_B are larger than A_G in some fully intercalated and fully de-intercalated, while A_G becomes larger than A_B in the 25%, 50% and 75% de-intercalated.

4.3.5. Thermodynamic Properties

Table 4.14: shows the calculated volumetric density, sound velocities, and Debye temperature as a function of Na removal for $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$). The calculated debye temperature θ_D for $\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ was found to be 572.7 K.

Table 4. 14: Calculated volumetric density, sound velocities, and Debye temperature for $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$.

	ρ	v_t	v_l	v_m	θ_D
BULK					
NaMnO_2	4037	3849	6416	4258	563.8
$\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3919	3868	6983	4309	571.8
SUPERCELL					
$\text{Na}_1\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3918	3879	6837	4313	572.7
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3711	3604	6398	4009	522.3
$\text{Na}_{0.50}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3597	3371	5961	3749	481.8
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3525	3273	5774	3639	461,1
$\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$	3623	3453	5356	3790	482.4

Na de-intercalation results in a monotonic drop in all sound velocities as well as the θ_D for all the systems. Considering that the Debye temperature (θ_D) in a solid may be used to define its covalent strength, the drop in θ_D as a result of sodium (Na) de-

intercalation indicates that the covalent strength of NaMnTiO_2 decreases with each de-intercalation step. Although the thermal conductivity of a material generally increases with rising θ_D , our results showed only a modest drop in θ_D . This suggests that the thermal conductivity of NaMnTiO_2 was maintained after Na de-intercalation. Notably, during the fourth step of Na deintercalation, there was an increase in volumetric density, sound velocities, and Debye temperature, with the latter calculated to be 482.4 K. These observations imply that despite the deintercalation process, the material retains significant thermal and mechanical properties, underscoring its robustness in potential applications.

The sound velocities of monoclinic crystals in the principal direction have been calculated and listed in Table 4.14, v_l and v_t are longitudinal and transverse sound velocities, ρ is the density.

Table 4. 15: Calculated volumetric density, sound velocities, and Debye temperature for $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$.

	ρ	v_t	v_l	v_m	θ_D
BULK					
NaMnO_2	4037	3849	6416	4258	563.8
$\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	4305	3359	5766	3726	499.4
SUPERCELL					
$\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	4307	3379	5903	3754	505.8
$\text{Na}_{0.75}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	4070	3067	5357	3407	453.9
$\text{Na}_{0.5}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	3853	2822	5152	3146	405.2
$\text{Na}_{0.25}\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	3583	2489	4221	2758	349.1
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$	3547	1497	2408	1650	268.4

It is apparent that the system with a small density of ρ and large elastic constants has large value of directional v_l and v_t . Also, it can be found that the longitudinal waves of all systems are fastest along the [0 0 1] direction. Anisotropy in the sound velocities suggests the anisotropy of these crystals.

Table 4.15 shows that $\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ exhibits the highest density of 4307 amongst all other systems, indicating stability and high energy density. At the same time, the lowest density is found to be 3547 for $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$. Also, $\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ has the highest sound velocities, with $v_t = 3379$ m/s, $v_l = 5903$ m/s, and $v_m = 3754$ m/s, suggesting that the material is stiffer. In contrast, $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ has the lowest sound

velocity values indicating mechanical resilience or lower stiffness. The trend continues with the Debye temperature, which is found to have an immense value for $\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ (505,8) and lowest for $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ (268.4) with larger values indicating that the system has superior thermal stability. The compound $\text{Na}_1\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ was found to be the most stable during charge/discharge stage, providing a good balance of high density, mechanical stiffness, and thermal stability. The other de-intercalation stages are still viable in battery applications since the charge and discharge continue during battery operation.

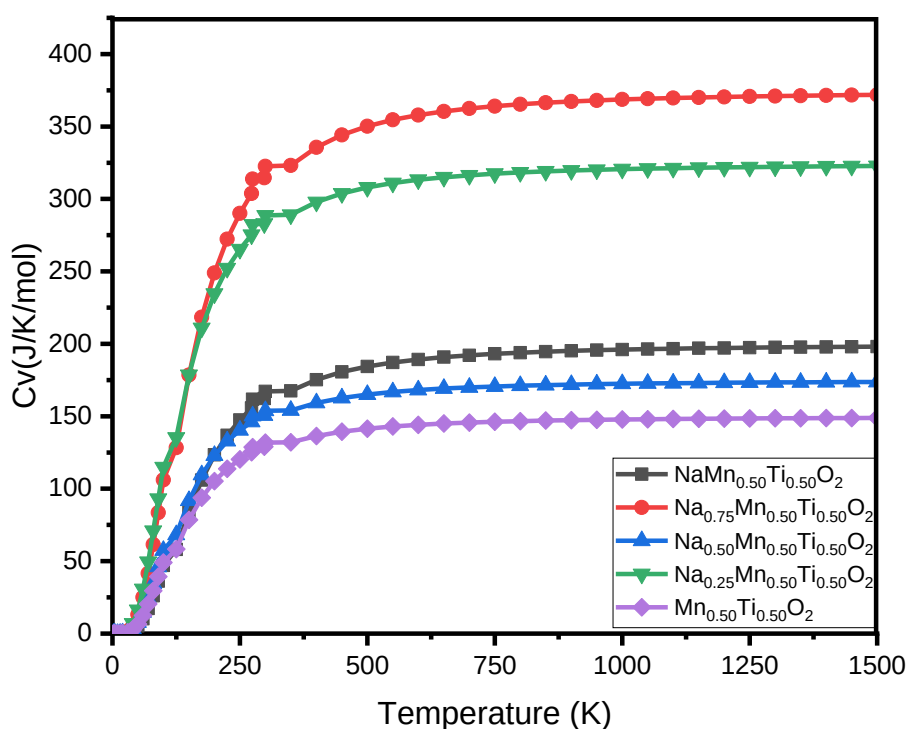


Figure 4. 8: Temperature versus specific heat at constant volume (C_v) for $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

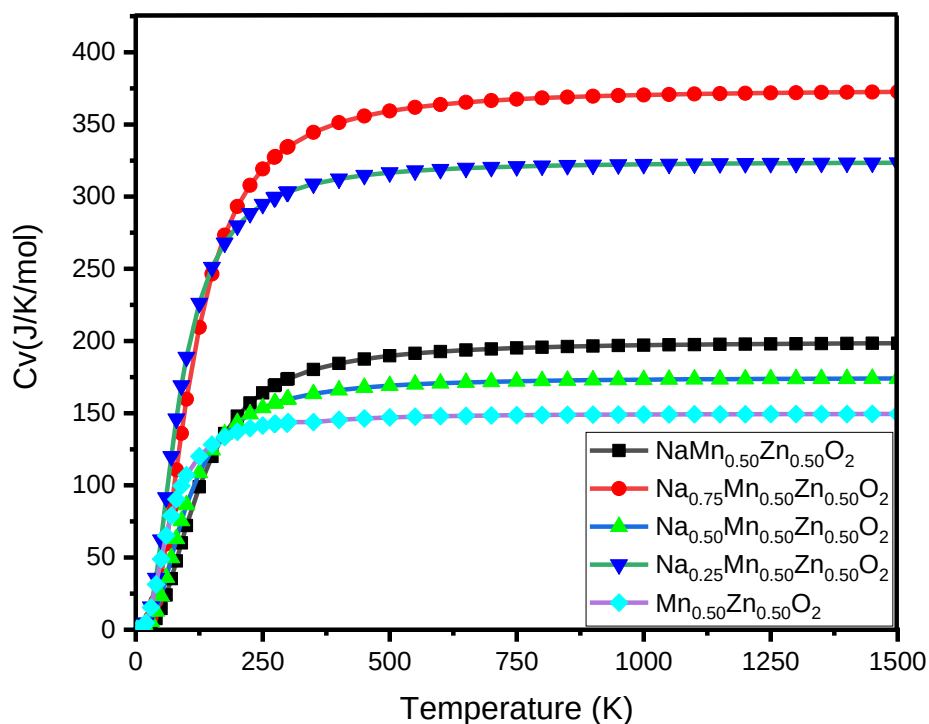


Figure 4. 9: Temperature versus specific heat at constant volume (C_v) for $2 \times 1 \times 1$ $\text{NaMn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

Thermodynamic parameters such as specific heat (C_v) at constant volume and entropy were calculated at a pressure of 0 GPa and temperatures ranging from 0 to 1500 K to investigate the thermodynamic properties of de-intercalated materials. Figures 4.9 and 4.10 illustrate the influence of temperature on C_v for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$, while in $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$. At low temperatures, the rate of increase in specific heat is rapid for all de-intercalation phases, irrespective of the de-intercalation stage. As the differences in phonon modes contribute to the thermal properties of the material, reflecting changes in lattice dynamics influenced by sodium content. At high temperatures, the specific heat values of all de-intercalation stages approach the classical asymptotic limit, known as the Dulong-Petit law [21,22].

At higher temperatures, C_V for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and their de-intercalated systems reach saturation point, constant specific heat at high temperatures due to the complete excitation of vibrational modes in the lattice as per the classical asymptotic limit. The 25% de-intercalated system exhibits the highest C_V of all doped systems, followed by the 75% de-intercalated system, then fully de-intercalated for both $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$. Higher specific heat in de-intercalated states implies better heat absorption and dissipation capabilities, which improves thermal stability during battery operation.

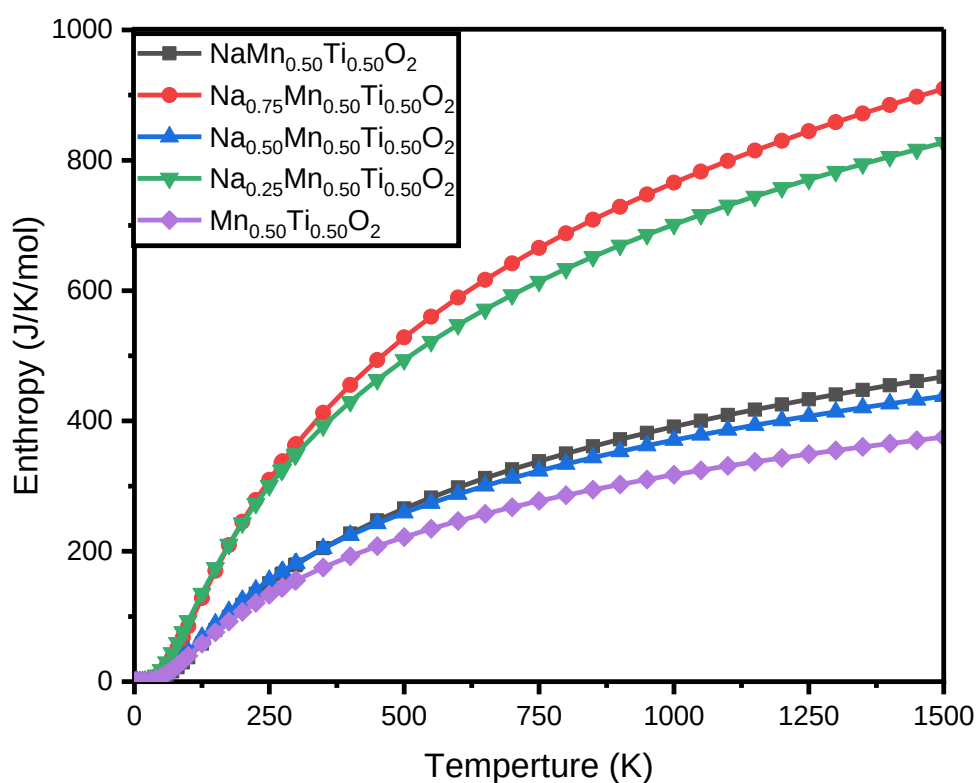


Figure 4. 10: Entropy versus Temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

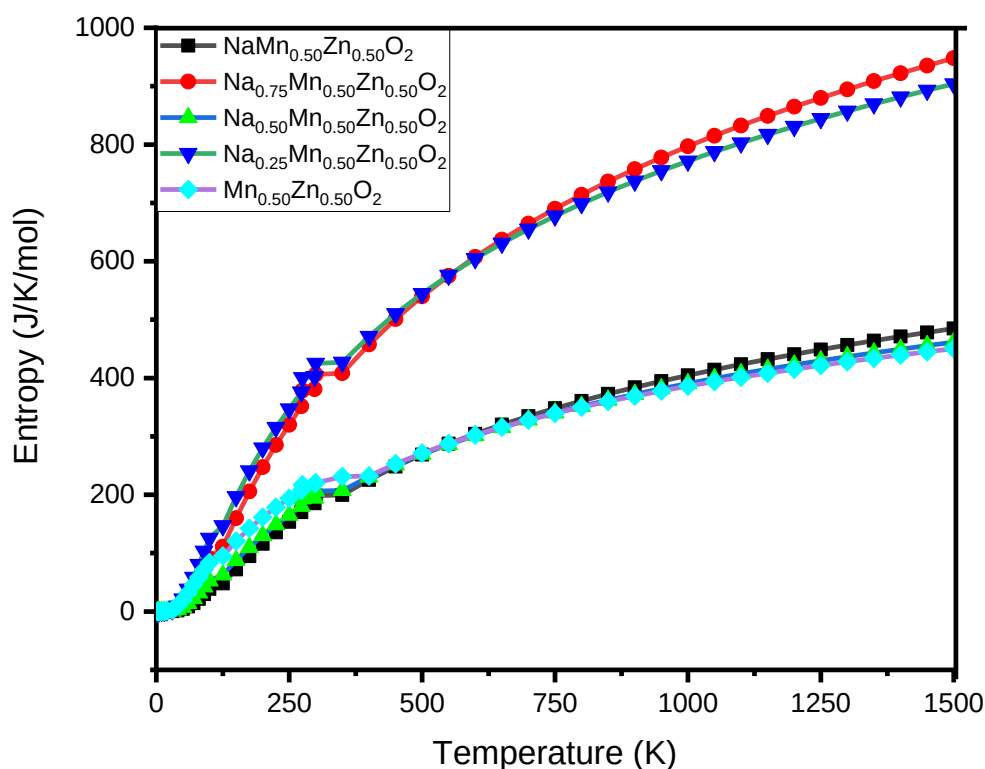


Figure 4. 11: Entropy versus Temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

The plots of entropy as a function of temperature for $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ are shown in Figures 4.11 and 4.12, respectively. For all de-intercalated stages, entropy, which is a measure of disorder, has risen with temperature, suggesting stronger lattice vibrations and configurational entropy at higher temperatures. The 25% and 75% de-intercalated systems exhibit the highest entropy values across all temperature ranges for all systems under investigation, indicating that they experience the most substantial structural and vibrational changes when heated. This implies that materials may release significant heat during cycling, which may affect battery safety and performance. The alternative system is preferred for applications that need a high temperature operation or prolonged cycling stability

because it exhibits modest increments in entropy, representing more structural rigidity and less sensitivity to temperature-induced disorder.

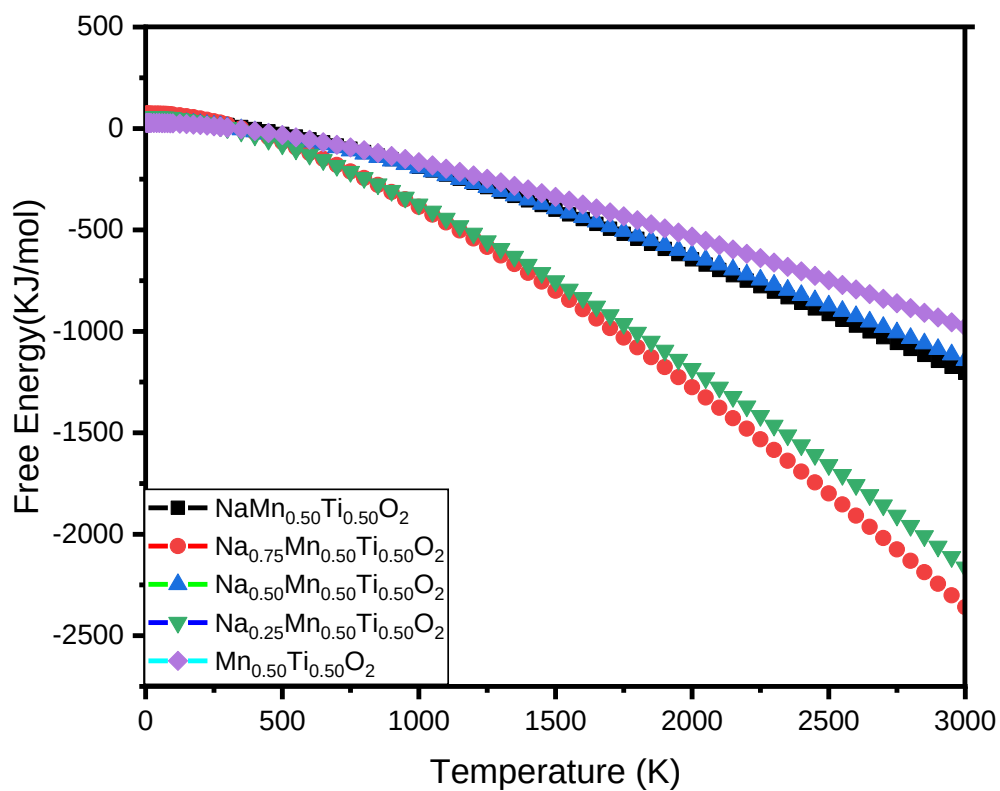


Figure 4. 12: Free energy versus temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

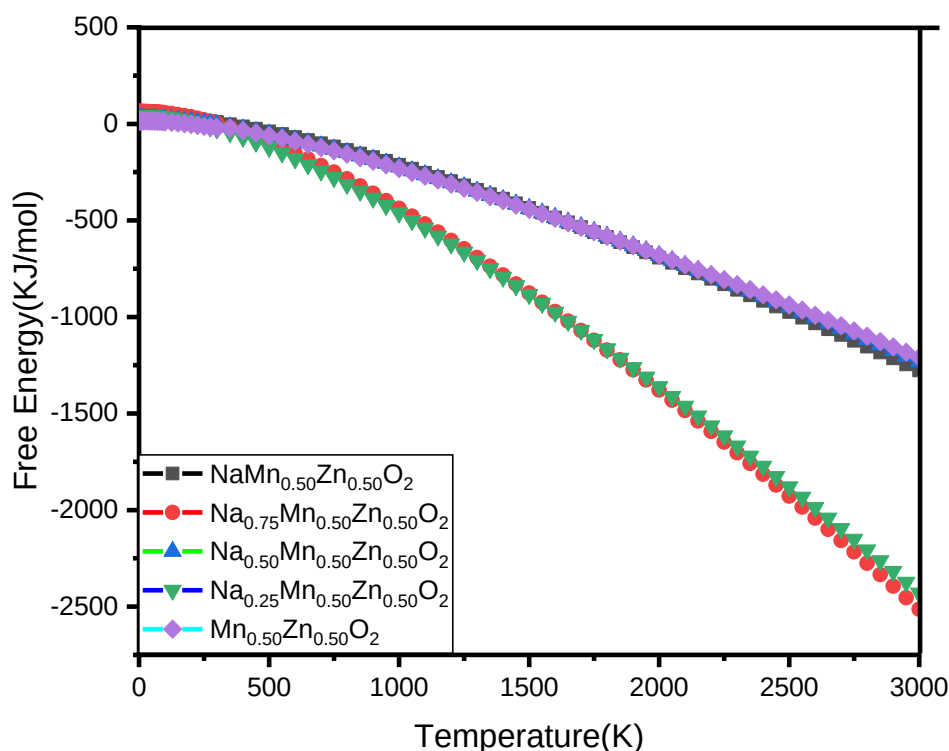


Figure 4. 13: Free energy versus Temperature for $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ ($x = 1, 0.75, 0.5, 0.25, 0$).

The Helmholtz free energy is a crucial factor in assessing the stability of a structure. A structure with a lower Helmholtz free energy is deemed stable. At low temperatures, the fluctuation of free energy in relation to temperature and the variation of heat capacity (C_v) with temperature. Figures 4.13 and 4.14 illustrate that the augmentation of free energy is substantial across all intercalation phases, but it increasingly becomes negative during all de-intercalation phases, leading to enhanced stability of the de-intercalated system. With rising temperature, the free energy diminishes for all de-intercalated systems, signifying enhanced thermodynamic favorability of the de-intercalated states at higher temperatures. The 25% and 75% de-intercalated systems of $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$. exhibit the highest negative values, underscoring their stability at elevated temperature settings. The thermodynamic

favorability of de-sodiated states at high temperatures indicates that these materials may remain stable during elevated-temperature battery operation, thereby minimizing the danger of structural damage. Moreover, the incremental decrease in free energy with temperature facilitates seamless phase transitions during cycling. De-intercalated systems of $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ at 25% and 75% may provide an equilibrium between energy density and thermal stability.

4.4. SUMMARY

A first-principle density functional theory approach was successfully applied to investigate the effect of transition metal dopants on the structural, electronic, and mechanical properties of NaMnO_2 doped with Ti and Zn. The properties investigation was focused on $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ bulk's structures, and the 2 X 1 X 1 $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ supercells as a cathode material also the and the effect of Na-ion de-intercalation on the 2 X 1 X 1 $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and 2 X 1 X 1 $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercells. The dopants alter the lattice parameters and volumes as a result of the difference in atomic radius between the Mn host and the doping elements, Ti and Zn. The expansion of the volumes induced by the dopant is observed, which widens the Na-ion diffusion channel and thus improves the electronic conductivity. Our results show that the spin-up and spin-down states in $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ bulks structure and 2 X 1 X 1 $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and 2 X 1 X 1 $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercells are not symmetric, showing magnetism. In the case of de-intercalation, it is demonstrated that the compounds become more metallic as the number of Na atoms extracted increases; hence, the compound charge carrier density increases, and as a result, the electronic conductivity improves. The calculated elastic constants

suggested mechanical stability for this compound, since all de-intercalated systems' stability criteria were satisfied. All de-intercalated systems were ductile except the fully de-intercalated system MnO_2 , which was brittle according to the Pugh criterion of ductility and brittleness. The voltage window of 3.410 V and 4.132 V was obtained for the Ti doped system, while the Zn voltage windows of 2.221 and 4.337 V were obtained. This calculated voltage is consistent with the voltage window of 3.54–2.52 V reported previously in literature. The calculated formation energy values were negative, symbolising the prediction of a solid possessed by the material. The thermodynamics properties of the doped system investigated in this study show that these materials (2 X 1 X 1 $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and 2 X 1 X 1 $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$) remain stable during elevated temperature battery operation, thus minimising the risk of structural damage.

REFERENCES

1. Scaccabarozzi, A. D., Basu, A., Aniés, F., Liu, J., Zapata-Arteaga, O., Warren, R., ... & Anthopoulos, T. D. (2021). Doping approaches for organic semiconductors. *Chemical Reviews*, 122(4), 4420-4492.
2. Wei, X., Zhang, P., Xu, T., Zhou, H., Bai, Y., & Chen, Q. (2022). Chemical approaches for electronic doping in photovoltaic materials beyond crystalline silicon. *Chemical Society Reviews*, 51(24), 10016-10063.
3. Sukkabot, W. (2020). First-principles calculations of the monoclinic transition-metal doped NaMnO₂ cathode material. *Philosophical Magazine*, 100(7), 917-926.
4. Kresse, G., & Hafner, J. (1993). Ab initio molecular dynamics for liquid metals. *Physical Review B*, 47(1), 558.
5. Jo, I. H., Ryu, H. S., Gu, D. G., Park, J. S., Ahn, I. S., Ahn, H. J., & Kim, K. W. (2014). The effect of electrolyte on the electrochemical properties of Na/ α -NaMnO₂ batteries. *Materials Research Bulletin*, 58, 74-77.
6. Zhang, R., Lu, Z., Yang, Y., & Shi, W. (2018). First-principles investigation of the monoclinic NaMnO₂ cathode material for rechargeable Na-ion batteries. *Current Applied Physics*, 18(11), 1431-1435.
7. Dima, R. S., Maleka, P. M., Maluta, N. E., & Maphanga, R. R. (2022). Structural, electronic, mechanical, and thermodynamic properties of Na-deintercalation from olivine NaMnPO₄: First-principles study. *Materials*, 15(15), 5280.
8. Yabuuchi, N., Kubota, K., Dahbi, M., & Komaba, S. (2014). Research development on sodium-ion batteries. *Chemical Reviews*, 114(23), 11636-11682.

9. Zhang, Y., Liu, Y., Li, X., Zhang, Y., & Guo, H. (2015). First-principles investigation on structural and electrochemical properties of NaCoO_2 for rechargeable Na-ion batteries. *Journal of Power Sources*, 274, 1217–1223.
10. Yousuf, S., & Gupta, D. C. (2018). Insight into half-metallicity, spin-polarization and mechanical properties of L21 structured MnY_2Z (Z= Al, Si, Ga, Ge, Sn, Sb) Heusler alloys. *Journal of Alloys and Compounds*, 735, 1245-1252.
11. He, X., Shen, H., Wang, W., Wang, Z., Zhang, B., & Li, X. (2013). The mechanical and thermo-physical properties and electronic structures of SnS and SnSe in orthorhombic structure. *Journal of Alloys and Compounds*, 556, 86-93.
12. Biedermann, A. R. (2018). Magnetic anisotropy in single crystals: A review. *Geosciences*, 8(8), 302.
13. Mohamed, R. M., Mishra, M. K., Al-Harbi, L. M., Al-Ghamdi, M. S., & Ramamurty, U. (2015). Anisotropy in the mechanical properties of organic crystals: temperature dependence. *RSC Advances*, 5(79), 64156-64162.
14. Chung, D.H., & Buessem, W.R. (1967). The Voigt-Reuss-Hill Approximation and Elastic Anisotropy of Polycrystalline MgO , CaF_2 , $\beta\text{-ZnS}$, ZnSe , and CdTe . *Journal of Applied Physics*, 38(6), 2535.
15. Chung, D. H., & Buessem, W. R. (1967). The elastic anisotropy of crystals. *Journal of Applied Physics*, 38(5), 2010-2012.
16. Hong, D., Zeng, W., Liu, F. S., Tang, B., & Liu, Q. J. (2019). Structural, electronic, elastic and mechanical properties of NbC-based compounds: First-principles calculations. *Physica B: Condensed Matter*, 558, 100-108.

17. Erum, N., & Iqbal, M. A. (2017). Study of pressure variation effect on structural, opto-electronic, elastic, mechanical, and thermodynamic properties of SrLiF_3 . *Physica B: Condensed Matter*, 525, 60-69.
18. Di Chen, D. I. (2012). Microscopic investigations of degradation in lithium-ion batteries. (Doctoral dissertation, Karlsruhe Institute of Technology).
19. Shikder, M. R. A. (2022). *Battery Material Characterization Using On-Chip Electrochemical Platforms* (Doctoral dissertation, University of Illinois at Chicago).
20. Daoud, S., Bioud, N., & Lebga, N. (2013). Elastic and piezoelectric properties, sound velocity and Debye temperature of (B3) boron–bismuth compound under pressure. *Pramana*, 81, 885-892.
21. Rugut, E. K., Maluta, N. E., Maphanga, R. R., Mapasha, R. E., & Kirui, J. K. (2024). A density functional theory insight into structural, mechanical, and optical properties of $\text{Rb}_2\text{LiTiF}_6$ double perovskite. *Advanced Engineering Materials*, 26(5), 2300995.
22. Hermann, A. (2013, June). Tuning dimensionality in binary Li-B compounds and evaluating thermodynamic vs kinetic stability under pressure. In *APS Shock Compression of Condensed Matter Meeting Abstracts* (pp. B3-003).

CHAPTER 5

5. Predicted Ti Doped NaMnO₂ Structures Using Cluster Expansion Approach

5.1 Introduction

The cluster expansion (CE) method represents a coarse graining of the material properties of multicomponent crystals based on the possible configurations of species over the sites of an underlying disordered crystal structure. A combination of the CE method and Monte Carlo (MC) analysis have become a standard computational tool for calculating the thermodynamic properties of crystalline materials with site disorder [1–4]. By representing the formation energy in terms of atomic configurations, thermodynamic properties can be calculated by sampling finite-temperature states in MC simulations [3–6]. The CE method was initially proposed for the study of metallic alloys [7], subsequently extended to multi-sublattice systems [3,8] and eventually introduced into the study of oxides and ionic materials [9]. The method has seen continuous and increasing use in the study of the configuration-dependent properties of crystalline materials. Furthermore, the methodology has also been actively and successfully used in the study of ionic materials. Theoretically, the CE method can represent functions over a configuration space of arbitrary dimension. Several complexities arise when CE models are fitted to materials with high-dimensional configuration spaces. The most significant complexity comprises the increasing gap between the polynomial growth in the number of expansion basis functions within fixed radial cutoffs and the number and supercell size of training structures needed for successful training. It is worth noting that first-principles calculations used for training cluster expansions become more involved as the complexity in the physical interactions among components increases [10,11]. This study used the cluster

expansion method to predict the stable structure of NaMnO_2 doped with Ti with different concentrations in the Mn atom and the transition metal dopant Ti. The predicted stable structures were then simulated employing first-principle DFT to elucidate their structural, electronic, mechanical, and thermodynamic properties.

5.2 Computational Method

All density functional theory calculations were performed using VASP code of MedeA as introduced in chapter 3 and the Universal Cluster Expansion (UNCLE) module was used for structural prediction. Theoretical background of cluster expansion approach is presented in detail in chapter 3. Combining these two methods enables high quality structure prediction while maintaining the predictive power and accuracy of the first-principle density functional theory method. The predicted structures were optimized with VASP code employing the projector augmented wave pseudopotential based on DFT. The exchange-correlation functional in the generalized gradient approximation was used to solve the Kohn–Sham equations with the Perdew Burke Ernzerhof approximation. Geometry optimization for the ground state energy of the predicted structures was performed using different convergence parameters since the predicted structures are different and found to converge at different cutoff energy and k-point mesh. Tolerance for the self-consistence field of 1×10^{-6} eV was applied in all calculations and the maximum displacement of 0.015 Å. Spin-polarized (i.e., spin-up and spin-down) calculations were performed to find electronic properties using the tetrahedron method with Blöch corrections smearing, while mechanical properties of the predicted structures were calculated using a strain of 0.005.

5.3 Structure Prediction

The cluster expansion method determines stable multi-component crystal structures. It ranks metastable structures by the enthalpy of formation while maintaining the

predictive power and accuracy of first-principles density functional methods. The technique determines stable multi-component crystal structures and ranks metastable structures by the enthalpy of formation. This fitting scheme ran for a maximum number of iterations, adding five structures in each iteration, and starting from an initial training set of five structures. Iterations continue until the energies of all structures are predicted by the cluster expansion, which is higher than the energy calculated for the structure of the ground state line at each sampled concentration. Iterations continued until 95% of the standard deviation of the structures was within 5 meV of the cross-validation score (CVS). Therefore, the CVS indicates how well the energies of the structures of the stable phases in the training set compare with each other. However, systematic errors will not be displayed.

Lastly, the properties of all structures identified on the binary diagram are characterized by calculating heats of formation, elastic properties to determine mechanical properties, electronic stability from their density of states, and thermodynamic properties of the generated structures of stable phases. Figure 5 shows an isotropic volume optimization binary ground state diagram with a non-magnetic structure. This is an alternative to full structural optimization, instead only the volume of the structure is optimized isotropically at distinct stages. Then, to counter the anomalous DFT total energy values, we increased the accuracy of the VASP flowchart by increasing the planewave basis cut-off from 300 to 400 eV. In the GGA stage, the k-spacing was decreased from 0.5 to 0.35 in the second minimisation stage. The isotropic volume optimization calculations yielded miscible constituents, as shown in Figure 5. The plot indicates that the generated phases close to the ground state with the lowest formation energy at a given concentration should be stable. The highlighted red line corresponds to density functional theory ground state systems,

and the DFT ground state line structures are thermodynamically stable. The binary diagram produced 34 new structures of stable phases, of which only four are stable. All the stable structures obtained from the binary diagram in Figure 5.1 have the same different space group, different lattice parameters and different energy of formation. The isotropically optimized structures have a cross-validation score of 1.7 meV, indicating a good cluster expansion because it has CVS less than 5 meV per active position. Figure 5.1 shows a fully optimized binary ground state diagram of $\text{Na}(\text{Mn,Ti})\text{O}_2$.

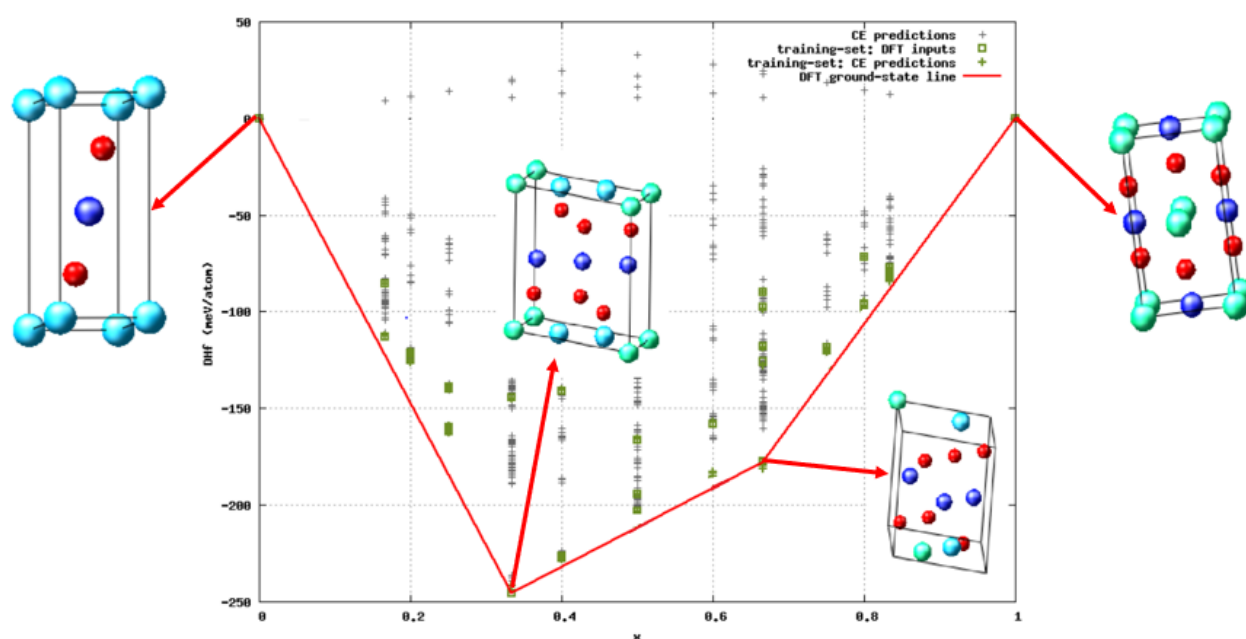


Figure 5. 1: An isotropic volume optimized binary ground state diagram of $\text{Na}(\text{Mn,Ti})\text{O}_2$ with a cross-validation score of 1.7 meV.

From the predicted stable structures shown in Figure 5.1, the undoped system NaMnO_2 is randomly mixed to produce the stable phases, which are also predicted as stable structures on the DFT ground state line. In an anisotropic volume-optimized

binary ground-state diagram, presents several theoretical and computational methods applied to forecast characteristics and stability of materials. Based on a statistical model educated on first-principles data, CE prediction also known as Cluster Expansion prediction which represents the projected formation energies. DFT input, then, is the first structures and formation energies derived from Density Functional Theory (DFT) calculations. Direct from DFT, DFT Ground-State Line shows the most stable structures at given compositions. Training CE guarantees correct material behaviour by specifying the dataset used to create the cluster expansion model. The other stable predicted structures are $\text{NaTiMn}_2\text{O}_2$, $\text{NaTi}_2\text{MnO}_2$, and NaTiO_2 and their calculated properties are discussed in the next sections. from the predicted structures, blue balls denote sodium (Na), the green balls signify manganese (Mn), the red balls indicate oxygen (O), and the sky-blue balls represent Titanium (Ti).

5.4 Structural Properties

The evaluation of lattice parameters and volume change upon the addition of Ti dopant has been conducted to identify the cathode material with optimal electrochemical characteristics. The calculated structural properties are presented in Table 5.1.

Table 5. 1: Structural properties for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE predicted stable structures.

	NaTiO_2	$\text{NaTi}_2\text{MnO}_2$	$\text{NaTiMn}_2\text{O}_2$	NaMnO_2
a (Å)	4.998	5.108	5.083	5.122
b (Å)	2.998	5.755	5.698	2.925
c (Å)	5.803	5.108	5.082	5.619
Volume (Å ³)	86.907	150.158	121.783	79.869
Space group	C2/m	P-1	C2/m	C2/m

The dopants alter the lattice parameters and volumes because of the difference in the atomic radius between the Mn host and the Ti dopant. The results show that the lattice constants a and b for the $\text{NaTiMn}_2\text{O}_2$ and $\text{NaTi}_2\text{MnO}_2$ systems stretch, while the lattice constant c contracts. When Mn is fully replaced with Ti (NaTiO_2), all lattice parameters are slightly stretched compared to those of the NaMnO_2 parent structure. It is evident that the lattice constant c stretches more and has a bigger value than the predicted parent structure NaMnO_2 . Stretching in lattice parameters due to the effect of the Ti dopant, results in volume expansion. This volumetric expansion by dopants can widen the Na-ion diffusion channel and thus improve electronic conductivity [12]. We compared the calculated lattice parameters obtained from the predicted structures and the parent structure NaMnO_2 , and we observed an increase in the lattice parameters and volume of the system with Ti-dopant. The combination of Mn and Ti predicted stable structures with larger volume compared to parent structures, implying that the doped systems have larger diffusion channels. A complete removal of Mn results in a small volume but not smaller than the one for parent structure NaMnO_2 , there is no literature reporting the completely substitution of Mn by Ti, The increase in volume and lattice parameters upon the addition of Ti concentration to NaMnO_2 aligns with prior research by Sukkatbot[13], which documented the effects of transition-metal doping on NaMnO_2 , indicating a rise in lattice parameter values and volume. The predicted structures show different space groups, $\text{NaTi}_2\text{MnO}_2$ is P-1 triclinic space group which is known for generating distortions that may compromise performance, while others are C2/m. The frequency of C2/m implies a monoclinic structure that allows effective Na^+ ion mobility and preserves structural integrity [14]. The constant frequency of C2/m emphasizes its importance in maintaining favourable electrochemical properties.

5.5 Electronic Properties

The density of states describes the number of different states at a particular energy level that electrons can occupy. It allows one to determine the general distribution of states as a function of energy and stability of the material and also allows one to evaluate the nature of the material. A high density of states at a specific energy level means that many states are available for occupation. A zero DOS means that no states can be occupied at that energy level. In semiconductors and insulators, the gap is present, which happens to be larger for insulators. In metals, the occupied and unoccupied orbitals overlap; therefore, no gap between the bands is observed.

The spin-polarized total density of states and partial density of states in the CE predicted structures NaMnO_2 , NaTiO_2 , $\text{NaTiMn}_2\text{O}_2$, and $\text{NaTi}_2\text{MnO}_2$ are plotted in Figure 5.2. The spin-up states are represented on the positive axis, whilst the lower spin states are depicted on the negative axis of the DOS plot. The upper plots indicate the total densities of states, and the lower plots show partial densities of Ti doped NaMnO_2 . The TDOS indicates the total contributions of all atoms in the structure, while the PDOS indicates contribution by individual atoms.

The band gap of the NaMnO_2 compound is reduced by the Ti dopants, except on the $\text{NaTiMn}_2\text{O}_2$ system, as shown in Table 5.2. The systems become more metallic as the concentration of Ti-dopant increases. This gives evidence that the electronic conductivity can be improved by transition-metal doping in NaMnO_2 .

Table 5. 2: Calculated energy band gap for Na(Mn,Ti)O₂ CE predicted stable structures.

	Energy Band Gap (eV)	Material Type
NaTiO₂	0.000	metallic
NaTi₂MnO₂	0.583	Half-Metallic
NaTiMn₂O₂	1.414	Semiconductor
NaMnO₂	1.069	Semiconductor

Ti dopants introduce a band gap of NaMnO₂ that affects While displaying a larger band gap (1.414 eV) than the parent compound (1.069 eV), NaMnO₂ itself is a magnetic semiconductor and Ti-doped NaMnO₂ (NaTiMn₂) retains this magnetic semiconducting characteristic. But as the Ti concentration rises, the band gap closes as shown in NaTi₂MnO₂ (0.583 eV), which changes into a half-metallic ferromagnet. This quality points to possible uses improving charge storage and cycling stability. Conversely, NaTiO₂ shows metallic behaviour with a zero band gap, so offering outstanding electronic conductivity and quick charge transfer. This suggests that a useful approach for adjusting the electrical characteristics and raising conductivity in these materials is doping with Ti.

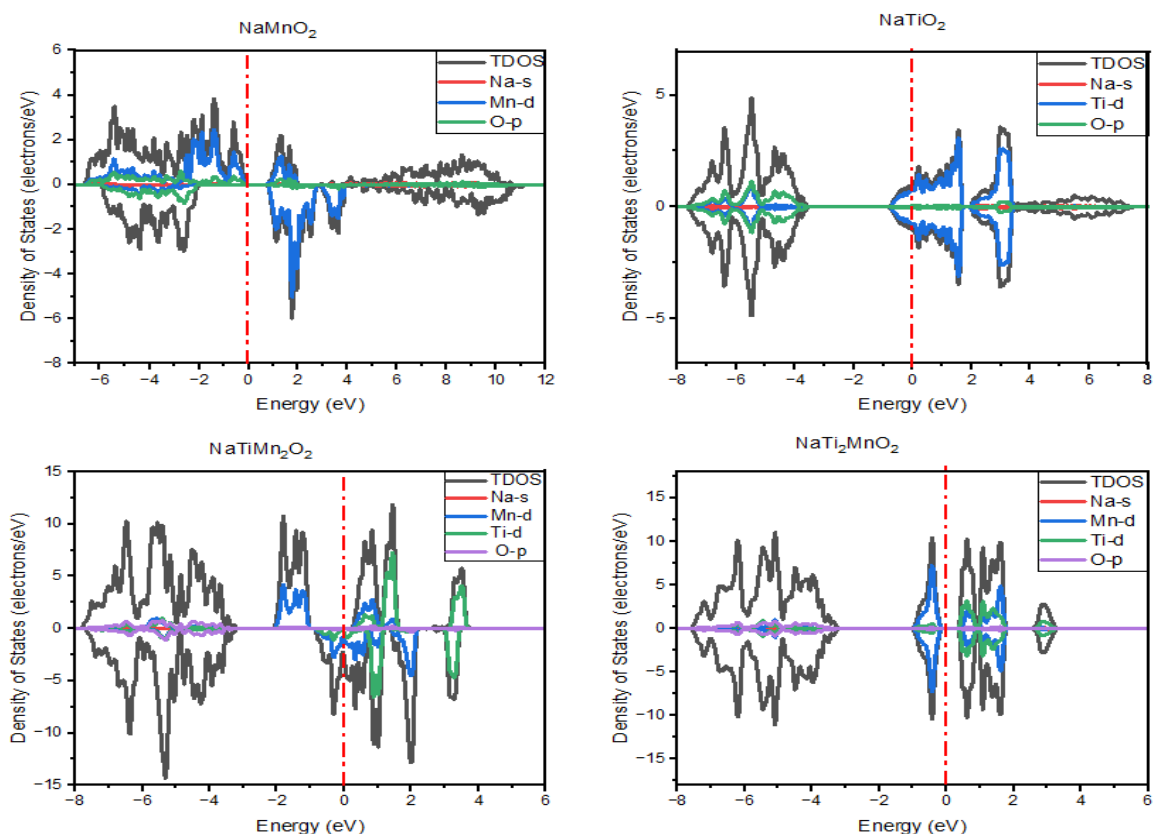


Figure 5. 2: Spin-polarized DOS for Na(Mn,Ti)O₂ CE predicted stable structures.

Figure 5.2 shows that the spin-polarized density of states is not symmetric for all the systems, indicating the magnetism characteristics. The introduction of Ti into NaMnO₂ forms new states at the Fermi level. Figure 5.2 shows that the *d* orbital of the transition metals contributes to these states near the Fermi level. The up-spin and down-spin states in NaMnO₂ and NaTiMn₂O₂ are fully occupied, which results in the compounds keeping their semiconducting characteristics, while for NaTi₂MnO₂ the spin-up states are partially occupied and thus depicting metallic behaviour. In contrast, the spin-down states are filled and present the semiconducting behaviour, which results in the compound being half-metallic and metallic for NaTi₂MnO₂ and NaTiO₂, respectively. The predicted structures indicate that metallicity rises as Ti concentration increases. The integration of Ti leads to the development of new states near and at the Fermi

level for all the structures with a given concentration of Ti, where O-p and Ti-d states overlap with the Fermi level. In contrast, Mn-d states closely approach the Fermi level. Ti dopant significantly contributes more towards the formation of states in the conduction band for both spin-up and spin-down electrons. Mn-*d* states appear more on the conduction band and less on the valence band for NaTiMn₂O₂ and NaTi₂MnO₂ structures. Oxygen contributes to both the valence and conduction bands.

5.6 Mechanical Properties

Calculating elasticity is essential to understand solids' mechanical stability and elastic properties. The calculations were performed at 0K temperature since temperature-related differences in the C_{ij} are likely to be at a minimum. The compound NaMnO₂ crystallizes into a monoclinic structure with nine independent elastic constants, C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} and C_{55} used to determine the mechanical stability. The criteria for mechanical stability for a monoclinic system defined in chapter 3.

Table 5. 3: Elastic constant (C_{ij}) for Na(Mn,Ti)O₂ CE-predicted stable structures.

	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}
NaTiO₂	288.63	74.51	59.54	282.09	62.58	234.05	82.93	81.96
NaTi₂MnO₂	199.52	46.06	65.95	196.67	70.35	241.74	77.63	78.60
NaTiMn₂O₂	274.94	78.00	81.73	220.65	85.54	257.06	69.98	74.86
NaMnO₂	102.98	49.27	34.31	322.00	36.66	146.50	54.05	50.05

The calculated elastic constants presented in Table 5.3 shows that all the stability conditions for a monoclinic system have been satisfied, suggesting that all the predicted structures are mechanically stable. The bulk and Young's moduli determine the hardness and stiffness of the material, respectively, while shear determines the resistance to deformation under shear stress. The bulk modulus also measures the

resistance to volume change under pressure. The calculated C_{11} , C_{22} , and C_{33} values are much larger than C_{44} and C_{55} for $\text{NaTiMn}_2\text{O}_2$, $\text{NaTi}_2\text{MnO}_2$, and NaTiO_2 , implying that the predicted Ti doped structures have strong directional resistance to linear compressions against uniaxial pressures but limited resistance to shear deformations. Unfortunately, no experimental data or other theoretical conclusions available for these predicted structures to compare. We hope that these findings will be useful in future experiments.

Table 5. 4: Bulk, shear, and Young's modulus, and Poisson's ratio for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ CE-predicted stable structures

	B_H	G_H	E_H	Poisson's Ratio	Pugh's Ratio
NaTiO_2	131.245	90.545	49.077	1.450	0.221
$\text{NaTi}_2\text{MnO}_2$	109.48	73.745	40.293	1.485	0.213
$\text{NaTiMn}_2\text{O}_2$	143.600	80.980	45.444	1.773	0.225
NaMnO_2	79.675	56.675	30.542	1.406	0.262

Shear modulus evaluates the resistance to plastic deformation of polycrystalline materials. Young's modulus usually provide a measurement of stiffness for a material, that is, the higher the value of the shear moduli, the stiffer the material. The bulk, shear, and Young's moduli of $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ structures are relatively large, as shown in Table 5.4 implying hardness, great resistance to volume change, deformation, and stiffness, respectively. In addition, the Pugh ductility and brittleness criterion is investigated. The bulk-to-shear modulus (B/G) ratio for polycrystalline phases is calculated with the knowledge that the shear modulus represents the resistance to plastic deformation and the bulk modulus represents the resistance to fracture. Brittleness is related to a

low B/G value, whereas ductility is related to a high B/G value. The value 1.75 is the critical number that distinguishes ductility from brittleness. The results show that NaTiMn₂O₂ is ductile with a Pugh's ratio of 1.773, which is bigger than the critical value, suggesting that NaTiMn₂O₂ can bend without deformation, resulting in fewer cracks during battery operation. The other three system, NaTiO₂, NaTi₂MnO₂, and NaMnO₂ are both predicted to be brittle. The Poisson's ratios of all the predicted structures show brittle behaviour, with NaTiO₂ exhibiting 2.9%, NaTi₂MnO₂ showing 3.7%, and NaTiMn₂O₂ exhibiting 2,5% less than the critical poison ratio value of 0.25, while the parent structure NaMnO₂ shows the Poisson ratio of 0.262, which is greater than 0.25 and hence ductile.

Table 5. 5: Anisotropy in the shear elastic factor (A_i with $i = 1,2,3$) and anisotropy in compressibility and shear moduli (A_B and A_G) for Na(Mn,Ti)O₂ CE-predicted stable structures.

	A_1	A_2	A_3	A_B	A_G
NaTiO₂	0.517	0.839	0.969	0.007	0,038
NaTi₂MnO₂	0.630	1.056	0.982	0.018	0.038
NaTiMn₂O₂	0.402	0.977	1.105	0.006	0.048
NaMnO₂	0.680	0.484	0.732	0.132	0.109

Table 5.5 shows the anisotropy in the shear elastic factor for NaTiO₂, NaTi₂MnO₂, NaTiMn₂O₂, and NaMnO₂ CE predicted structures. Anisotropy A_3 is the highest and close to 1, followed by A_2 while A_1 is the smallest. This means that elastic anisotropic for {001} shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions are larger than {100} shear planes between $\langle 011 \rangle$ and $\langle 010 \rangle$ directions and {010} shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions, except for one system NaTi₂MnO₂ where A_2 is larger than A_3 . For all

Ti doped NaMnO_2 systems, A_1 is predicted to be the smallest, which implies that this system has preferred direction for deformation, which could affect the stability during battery operation.

The assessment of elastic anisotropy was conducted by examining the deviation of anisotropic factors from unity. It is determined that NaTiO_2 deviates from unity by 48.3% (A_1), 16.1% (A_2), and 3.1% (A_3). $\text{NaTi}_2\text{MnO}_2$ shows divergence with A_1 at 37.0% and A_3 at 1.8%, while A_2 (5.6%) exceeds unity, with $A_2=1.056$, indicating an enhancement in structural, mechanical, or physical anisotropy. The anisotropy of $\text{NaTiMn}_2\text{O}_2$ approaches unity, with A_1 at 59.8% and A_2 at 2.3%, while A_3 surpasses unity by approximately 10.5%, yielding a value of $A_3 = 1.105$. The parent structure NaMnO_2 exhibits deviations from unity with A_1 (32%), A_2 (51.6%), and A_3 (26.8%). All predicted structures demonstrate slight divergences from unity, indicating minor directional variations in ion transport, electronic conductivity, or mechanical stability. This behaviour facilitates efficient charge and discharge performance while preserving structural stability.

5.7 Thermodynamic Properties

The sound velocities of monoclinic crystals in the principal direction are listed in Table 5.6.

Table 5. 6: Calculated, volumetric density sound velocities and Debye temperature for Na(Mn,Ti)O₂ CE predicted stable structures.

	$\rho(\text{kg/m}^3)$	$v_t(\text{m/s})$	$v_l(\text{m/s})$	$v_m(\text{m/s})$	$\theta_D (K)$
NaTiO₂	3962	4569	7711	5060	681.9
NaTi₂MnO₂	4216	4188	7031	4637	632.6
NaTiMn₂O₂	4400	4290	7561	4770	655.9
NaMnO₂	4604	4340	6970	4783	662.4

The density of the materials varies between 3962 and 4604 kg/m³. A more compact and stable crystal structure is often linked to increased densities, enhancing a material's ability to maintain structural integrity throughout cycling. Among the predicted structures, NaMnO₂ exhibited the highest density, suggesting its potential for enhanced structural robustness.

The longitudinal (v_l) and transverse (v_t) sound velocities, which indicate the speed at which sound waves propagate through the material, are determined, and presented in Table 6.6. Higher velocity values suggest increased stiffness and mechanical strength of the material. The maximum longitudinal velocity of 7711 m/s observed in the case of NaTiO₂ material indicates a robust lattice structure demonstrating enhanced mechanical deformation resistance during battery operation. In contrast, NaTi₂MnO₂ shows the lowest transverse velocity at 4188 m/s and a longitudinal velocity of 7031

m/s, suggesting a less rigid structure that may affect its mechanical stability under operational stress, potentially resulting in quicker degradation relative to other predicted structures. The mean sound velocity (v_m) offers an average assessment of the acoustic characteristics of the material, indicating its stiffness. The values range from 4637 m/s to 5060 m/s, with NaTiO_2 exhibiting the highest mean sound velocity of 5060 m/s. This suggests enhanced mechanical stability and contributes to its durability as a cathode material.

The Debye temperature (θ_D) relates to the vibrational characteristics of the crystal lattice. Elevated θ_D values indicate a more rigid lattice, which suggests enhanced thermal stability and a reduced tendency for thermal expansion, both of which are crucial elements for battery performance across different temperatures. NaTiO_2 exhibits a Debye temperature of 681.9 K, suggesting its potential for enhanced performance at higher temperatures while preserving structural integrity and electrochemical functionality across a broader temperature spectrum. In contrast, $\text{NaTi}_2\text{MnO}_2$ exhibits the lowest Debye temperature at 632.6 K, rendering it more vulnerable to thermal degradation and possibly constraining its efficacy in high-temperature applications. In summary, NaTiO_2 demonstrates the most favourable mechanical and thermal characteristics among the materials evaluated, whereas NaMnO_2 also shows significant potential owing to its elevated density and sound velocities. Meanwhile, $\text{NaTi}_2\text{MnO}_2$ may necessitate further examination concerning its long-term stability in operational environments.

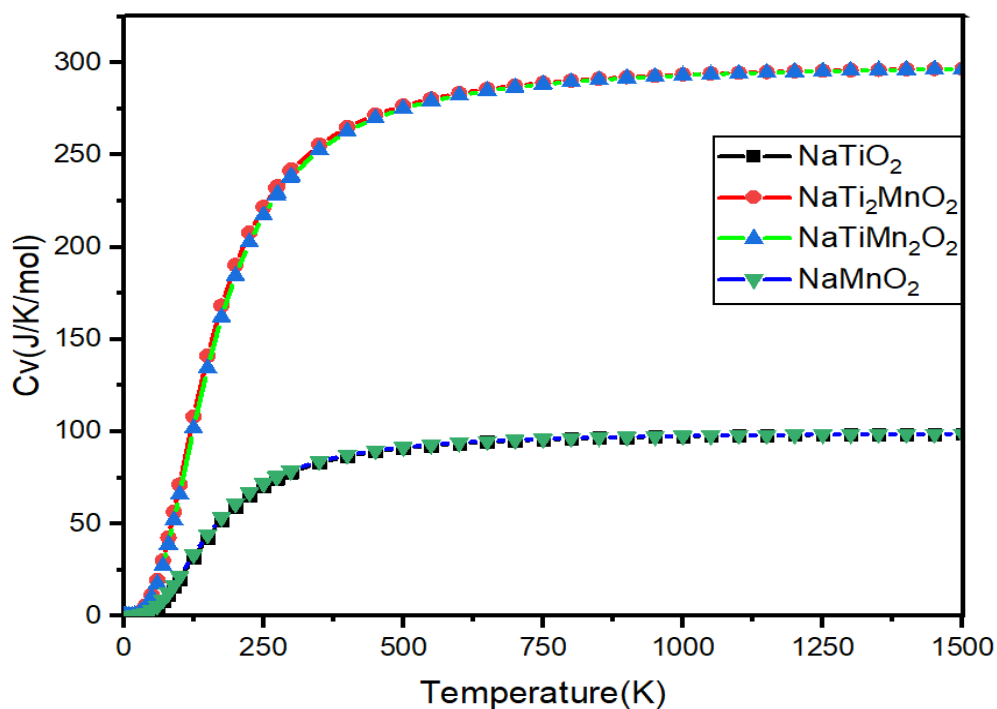


Figure 5. 3: Specific heat vs. temperature for Na(Mn,Ti)O₂ CE predicted stable structures.

The thermodynamic properties, namely, specific heat, entropy, and free energy as a function of temperature for CE predicted Na(Mn,Ti)O₂ structures, are plotted in Figures 5.3, 5.4, and 5.5, respectively. The findings suggest that these thermodynamic properties are highly dependent on temperature.

Regardless of the Ti concentration, Figure 5.3 clearly shows that the specific heat (C_v) rises sharply at low temperatures for all systems. Because there is less thermal energy available at lower temperatures where even tiny amounts of heat input can considerably enhance the internal energy of the material, this quick increase in C_v aligns with the Debye heat capacity model, which predicts that phonon contributions will cause C_v to depend strongly on temperature ranges. The C_v values for every Ti concentration progressively become closer to the traditional asymptotic limit as the temperature rises, matching the Dulong-Petit rule. In contrast, the free energy

stabilises, and the system approaches a more constant and predictable state as the temperature increases. This is especially important for applications involving high temperatures since those applications depend on materials maintaining their structural and thermodynamic stability.

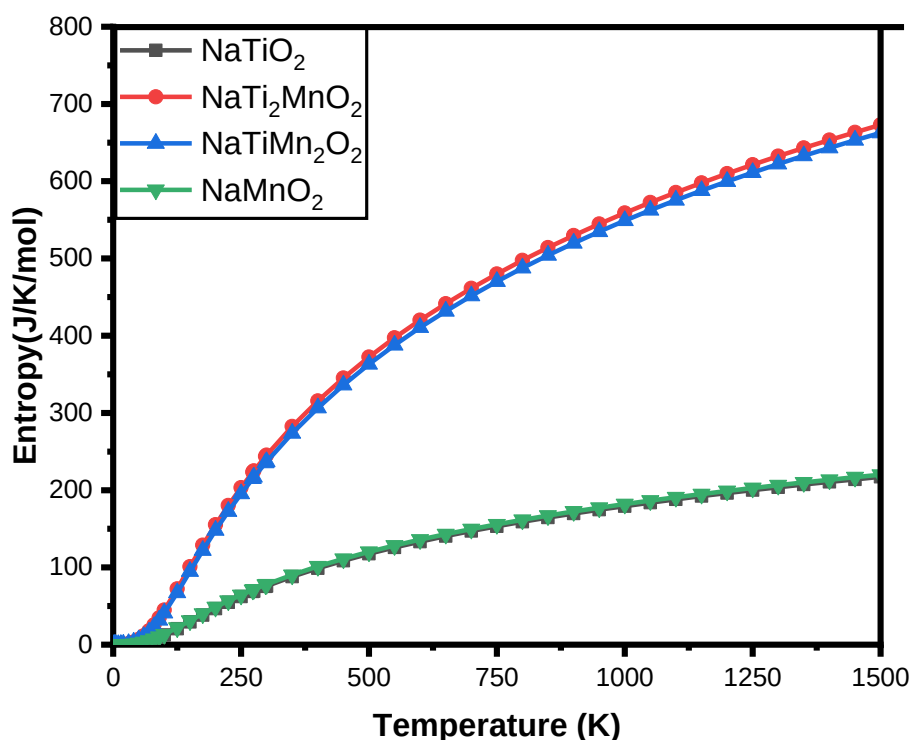


Figure 5. 4: Entropy vs. temperature for Na(MnTi)O₂ CE predicted stable structures.

Figure 5.4 shows computed entropy values and demonstrate a notable temperature sensitivity. Entropy shows how a system moves from a more ordered state to a less ordered state as temperature rises. The results show that at low temperatures of up to 120 K, the entropy increases gradually. This is consistent with how entropy is supposed to behave; thus, material's disorder increases as the temperature is increased. The predicted structures NaTi₂MnO₂ and NaTiMn₂O₂ exhibit a quick increase with rising temperature, whereas NaMnO₂ and NaTiO₂ have a more gradual

increase. This increase signifies heightened disorder at elevated temperatures. The presence of Ti demonstrates increased entropy, indicating enhanced configurational and vibrational contributions, which lead to improved ionic diffusion.

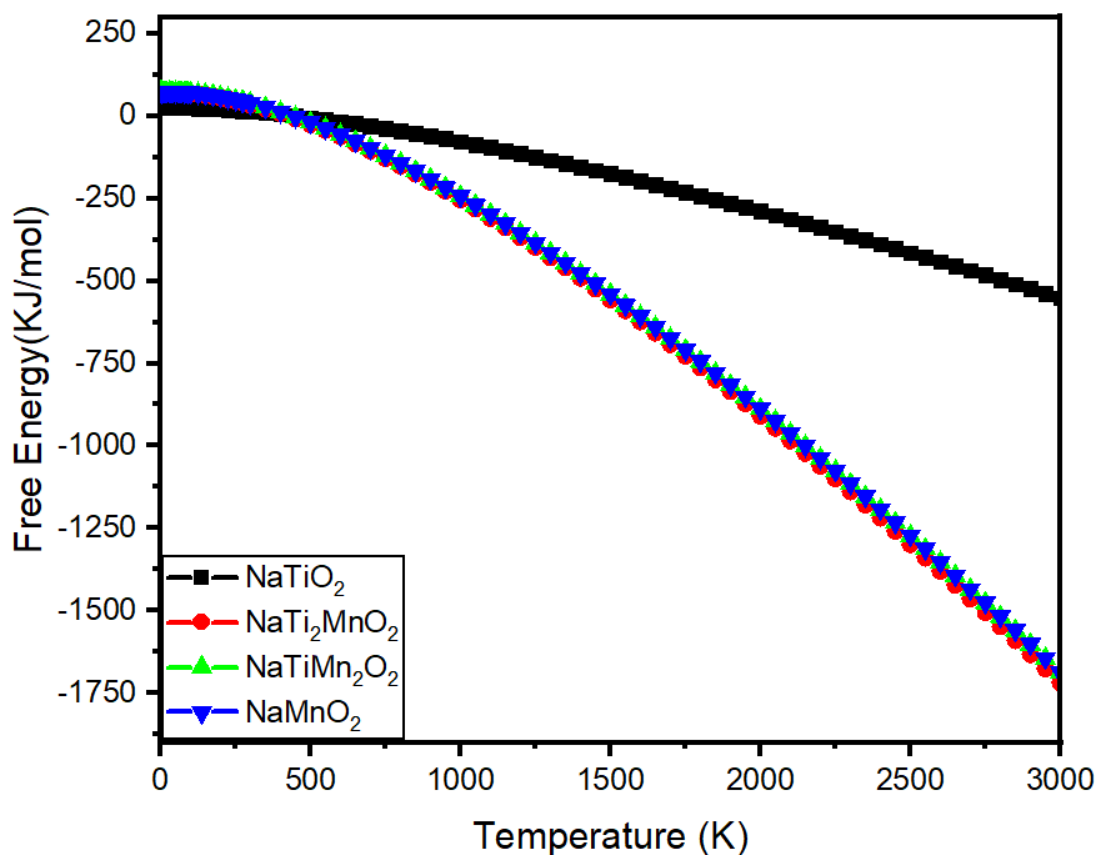


Figure 5. 5: Free energy vs. temperature of Na(Mn,Ti)O₂ CE predicted stable structures.

Figure 5.5 illustrates the Helmholtz free energy for the predicted new structures, NaTiO₂, NaTi₂MnO₂, NaTiMn₂O₂, and NaMnO₂, indicating a rapid drop in free energy with increasing temperature. This indicates that the investigated systems are thermodynamically stable phases at high temperatures; hence, there is evidence of reduced structural breakdown during battery operation since the material free energy is not rising with temperature increase.

5.8 Summary

First-principle density functional theory and cluster expansion approaches were combined to investigate the ground state search and phase stability of Ti doped NaMnO_2 . Employing both methods maintains the predictive power and accuracy of the first-principles DFT while searching for new configurations. The predicted structures have a cross-validation score of 1.7 meV. The results showed that the lattice parameters expand when Ti atom is introduced to the system, causing the volume to expand, which results in the widening of the Na ion diffusion channels. The calculated energy band gap reduces as the concentration of Ti increases, suggesting improved conductivity of the material. The results of elastic constants and mechanical properties show that all the predicted structures satisfy the stability criteria and are thermodynamically stable, according to the Pugh criterion of ductility and brittleness. The findings showed that $\text{NaTiMn}_2\text{O}_2$ is ductile and able to bend without deformation, implying that it can be used in battery applications and not crack during operation, while the other structures $\text{NaTi}_2\text{MnO}_2$, $\text{NaTiMn}_2\text{O}_2$ and NaMnO_2 are predicted to be brittle. The calculated sound velocities in this study suggests that mechanical stability improvement and contributes to structural durability as a cathode material, The thermodynamic properties revealed that the θ_D decreases as the concentration of Mn is reduced, with NaMnO_2 having the highest value and NaTiO_2 with the lowest value, While the free energy demonstrates that the material is thermodynamical stable, the entropy rise with temperature increase suggests significant ion mobility and reversible electrochemical reaction which gives clear indication of ion diffusion during charge and discharge.

REFERENCES

1. A. Walle and G. Ceder, Automating first-principles phase diagram calculations, *Phase Equilibria and Diffusion*.23, 348 (2002).
2. Ruban, A. V., & Abrikosov, I. A. (2008). Configurational thermodynamics of alloys from first principles: Effective cluster interactions. *Reports on Progress in Physics*, 71(4), 046501.
3. Van De Walle, A. (2009). Multicomponent Mult sublattice alloys, non-configurational entropy and other additions to the Alloy Theoretic Automated Toolkit. *Calphad*, 33(2), 266-278.
4. Widom, M. (2018). Modeling the structure and thermodynamics of high-entropy alloys. *Journal of Materials Research*, 33(19), 2881-2898.
5. Van der Ven, A., Thomas, J. C., Puchala, B., & Natarajan, A. R. (2018). First-principles statistical mechanics of multicomponent crystals. *Annual Review of Materials Research*, 48(1), 27-55.
6. Van der Ven, A., Thomas, J. C., Xu, Q., & Bhattacharya, J. (2010). Linking the electronic structure of solids to their thermodynamic and kinetic properties. *Mathematics and computers in simulation*, 80(7), 1393-1410.
7. Sanchez, J. M., Ducastelle, F., & Gratias, D. (1984). Generalized cluster description of multicomponent systems. *Physica A: Statistical Mechanics and its Applications*, 128(1-2), 334-350.
8. Sanchez, J. M. "Cluster expansions and the configurational energy of alloys." *Physical Review B* 48, no. 18 (1993): 14013.
9. Ceder, G., Garbulsky, G. D., & Tepesch, P. D. (1995). Convergent real-space cluster expansion for configurational disorder in ionic systems. *Physical Review B*, 51(17), 11257.

10. Barroso-Luque, L., Zhong, P., Yang, J. H., Xie, F., Chen, T., Ouyang, B., & Ceder, G. (2022). Cluster expansions of multicomponent ionic materials: Formalism and methodology. *Physical Review B*, 106(14), 144202.
11. Yang, J. H., Chen, T., Barroso-Luque, L., Jadidi, Z., & Ceder, G. (2022). Approaches for handling high-dimensional cluster expansions of ionic systems. *npj Computational Materials*, 8(1), 133.
12. Huang, L., Cheng, J., Li, X., & Wang, B. (2015). Electrode nanomaterials for room temperature sodium-ion batteries: a review. *Journal of Nanoscience and Nanotechnology*, 15(9), 6295-6307.
13. Sukkabot, W. (2020). First-principles calculations of the monoclinic transition-metal doped NaMnO₂ cathode material. *Philosophical Magazine*, 100(7), 917-926.
14. Aslfattahi, N., Samylingam, L., Kiai, M. S., Kadirgama, K., Kulish, V., Schmirler, M., & Said, Z. (2023). State-of-the-art review on electrolytes for sodium-ion batteries: Potential recent progress and technical challenges. *Journal of Energy Storage*, 72, 108781.

CHAPTER 6

6. Predicted Zn Doped NaMnO₂ Structures Using Cluster Expansion Approach

6.1 Introduction

This chapter presented similar study that is presented in chapter 5. In this chapter, NaMnO₂ is doped with Zn using cluster expansion approach to predict the most stable phases at various concentrations of Mn and Zn atoms. The structural, electronic, mechanical, and thermodynamic properties of the predicted stable structures are then investigated using density functional theory to evaluate their potential as sodium-ion battery materials.

6.2 Computational Method

Computational details that were followed are presented in chapter 5, section 5.2. The flowchart utilised in UNCLE code facilitated cluster expansion calculations through a genetic algorithm methodology. The flow chart commences by optimising the structures of the training set concerning atomic positions, cell volume, and cell shape utilising VASP 5.4 with a GGA exchange-correlation functional.

6.3 Structure Prediction

Details on structure prediction are the same as those of Ti doped NaMnO₂ as presented in section 5.3 in chapter 5. Figure 6.1 depicts a binary ground state diagram for isotropic volume optimization with a non-magnetic construction. The isotropic volume optimization computation indicates that the components are miscible, as illustrated in Figure 6.1 This indicates that the phases formed around the ground states with minimal concentration should be stable. The emphasized red line represents density functional theory ground state systems, and the DFT ground state line structures exhibit thermodynamic stability.

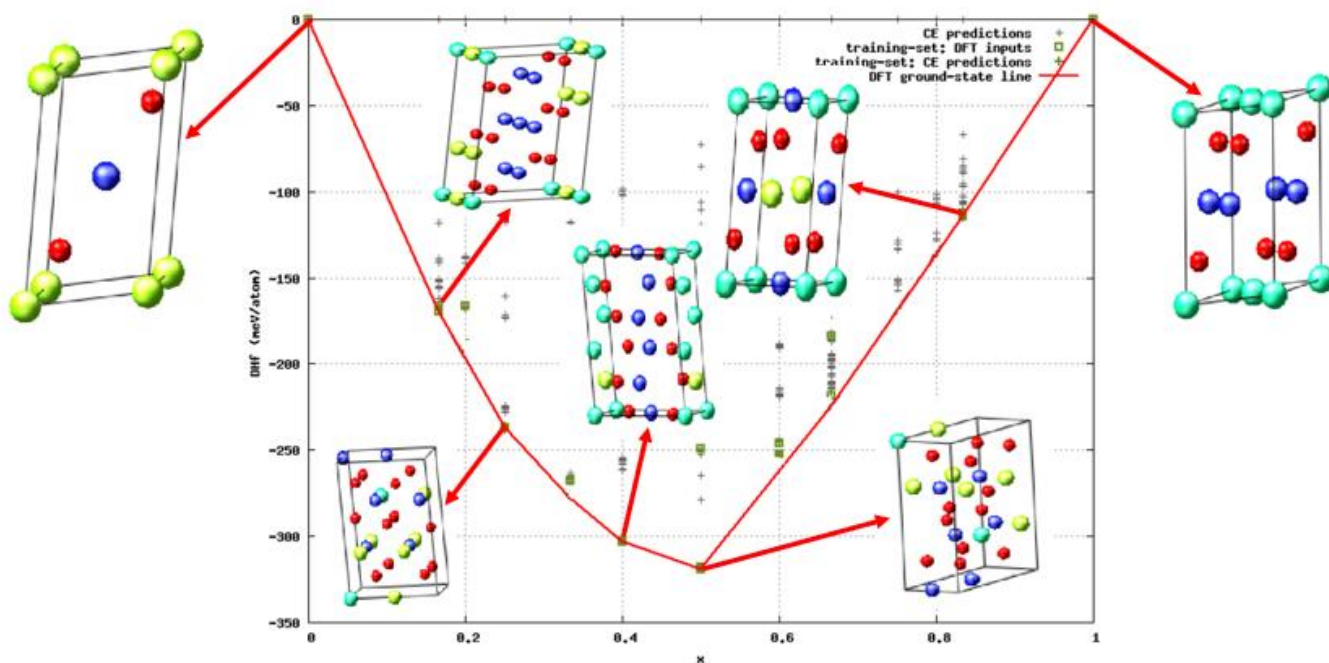


Figure 6. 1: An isotropic volume optimized binary ground state diagram of $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ with a cross-validation score of 1.9 meV

The binary diagram generated 65 new stable phase structures, of which only seven are stable, from the predicted structures, blue balls denote sodium (Na), the green balls signify manganese (Mn), the red balls indicate oxygen (O), and the lime balls represent zinc (Zn). The stable structures derived from the binary diagram in Figure 6.1 exhibit different space groups, varying lattice parameters, Wyckoff locations, and disparate formation energies. The isotropically optimized structures exhibit a cross-validation score of 1.9 meV, signifying an effective cluster expansion, as their CVs is below 5 meV per active position.

6.4 Structural Properties

The calculated structural properties are shown in Table 6.1, along with their associated structures as predicted by cluster expansion. The predicted structures undergo geometry optimization, to determine their equilibrium state and relaxed internal lattice parameters.

Table 6. 1: Lattice parameters of Na(Mn,Zn)O₂ CE-predicted stable structures

	a (Å)	b (Å)	c (Å)	Volume (Å³)	Space group
NaZnO₂	4.979	3.240	5.593	90.226	C2/m
Na₃Mn₂ZnO₆	5.222	5.685	5.222	129.091	P-1
Na₆MnZn₅O₁₂	5.603	6.105	8.286	264.891	C2/m
Na₆Mn₂Zn₄O₁₂	6.393	6.146	8.107	260.295	C2/c
Na₂MnZnO₄	2.993	5.646	5.368	85.581	C2/m
Na₅Mn₄ZnO₁₀	5.567	7.847	5.756	218.788	P-1
NaMnO₂	5.878	2.257	5.587	76.234	C2/m

The calculated lattice parameters obtained from a conventional structure and doped structures using a GGA-PBE approximation were previously reported by Su *et al*[1]. The study indicates that doping NaMnO₂ modifies the lattice parameters; specifically, the parameters a and c rise with the addition of dopants, whereas parameter b experiences a slight decrease, resulting in an overall increase in volume [1]. Our work reveals an augmentation in the lattice parameters and volume with an increase in Zn content. The modification of the lattice parameters in the presence of Zn is distinctly observable in Table 7.1 and aligns with the trends in the existing literature [1]. This alteration is due to the different atomic radius between the Mn host and the transition metal dopant Zn. Overall, the volume expansion is evident in the presence of Zn. Hence, the diffusion channels of the Zn containing predicted structure are widened compared to undoped structure, thus, improving the material's conductivity [2]. Different space groups specify atomic symmetry and impact ion transport,

conductivity, and phase stability. Commonly seen monoclinic space group C2/m with mirror plane symmetry supports stable Na⁺ intercalation. With least symmetry, P-1 is a triclinic space group that can cause structural distortions influencing performance. Another monoclinic space group, C2/c, has glide plane symmetry, therefore influencing ion mobility and phase transitions. The predominance of C2/m implies it is fundamental for structural stability and electrochemical activity.

6.5 Electronic Properties

A basic understanding of the electronic structure of the cathode material is of utmost importance in developing advanced cathode materials since it underlines the electrochemical behaviour of the battery. The electronic density of states along high-symmetry lines in the Brillouin zone for both spin-up and spin-down configurations were calculated to determine the electronic properties of CE predicted stable structures. The top of the valence band is taken as the zero of energy in band structure plots, while the Fermi energy is used as the zero of the energy scale in the density of states plots. The band gap value and the location of the Fermi level provides the details on the behaviour of the predicted structures.

Table 6. 2: Energy gap of Na(Mn,Zn)O₂ CE predicted stable structures

	Energy Band Gap (eV)	Material Type
NaZnO₂	0.001	Metallic
Na₃Mn₂ZnO₆	1.239	Half-metallic
Na₆MnZn₅O₁₂	0.000	Metallic
Na₆Mn₂Zn₄O₁₂	1.779	Half-metallic
Na₂MnZnO₄	0.546	Semiconductor
Na₅Mn₄ZnO₁₀	1.088	Half-metallic
NaMnO₂	1.069	Semiconductor

The spin-polarized partial densities of states of NaMnO₂ doped with Zn Cluster expansion predicted stable structures are shown in Figure 6.2.

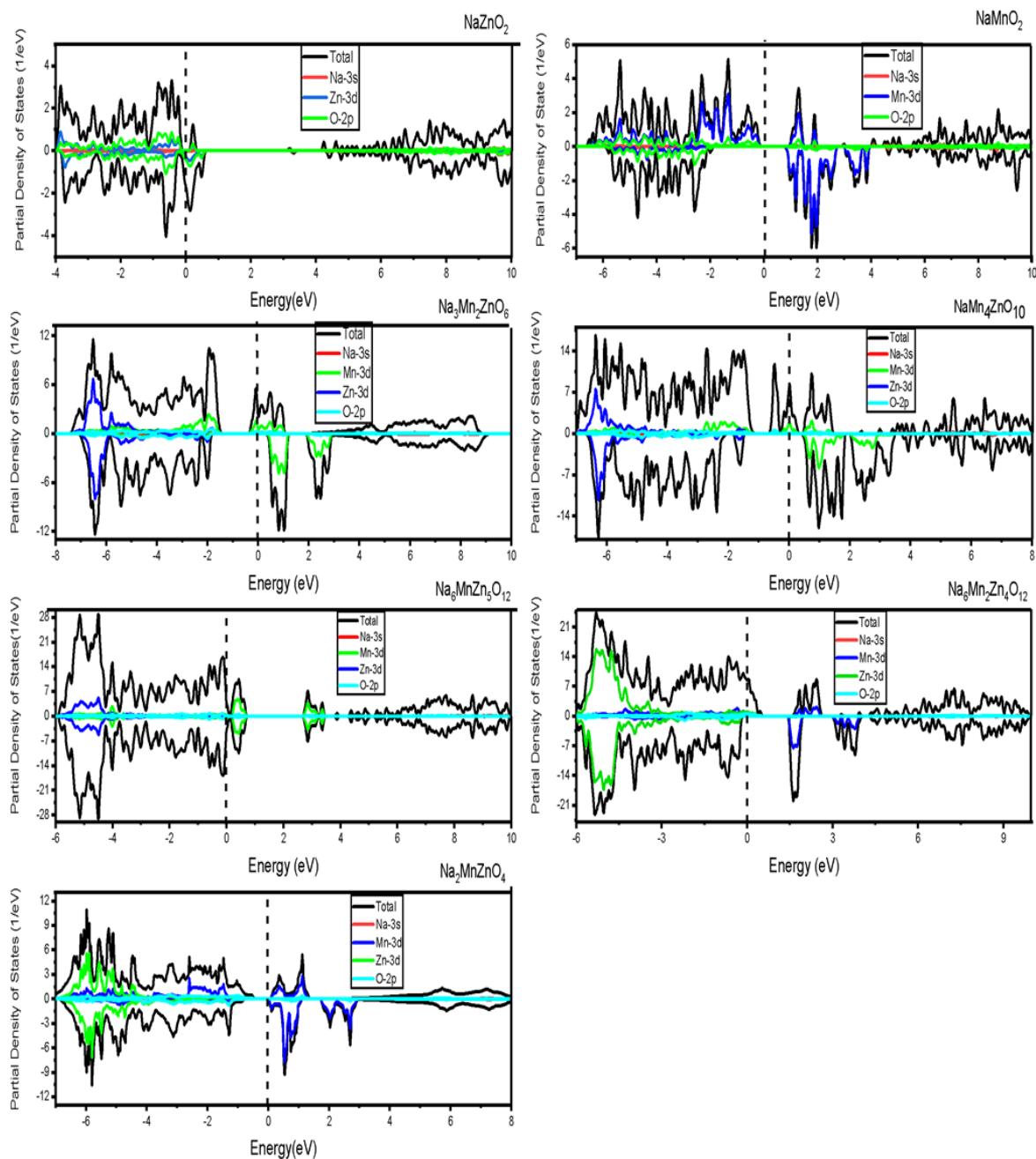


Figure 6. 2: Spin-polarized DOS for Na(Mn,Zn)O₂ CE predicted stable structures.

For Zn doped NaMnO₂ predicted structures, the electronic partial density of states plots is shown in Figure 6.2, and the behaviour of each predicted structure is tabulated in Table 6.2. It is revealed in the table that the predicted structures are of several types. There are half-metallic systems with a smaller energy band gap, metallic systems with a reduced energy band gap as Zn is introduced into NaMnO₂ and semiconducting

doped systems ($\text{Na}_2\text{MnZnO}_4$). The parent structure NaMnO_2 kept its semiconducting behaviour as observed in the previous two chapters. This points out that the electronic conductivity can be improved by transition metal doping. From the PDOS graph, it is shown that the partial density of states underlines that the states near the Fermi level are contributed from the d orbital of the transition metals, with the Mn- $3d$, Zn- $3d$, and O- $2p$ orbitals as the major contributors for both the valence and conduction bands. Also, there is DOS hybridization between Mn- $3d$ and O- $2p$ on the valence band and hybridization between Zn- $3d$ and O- $2p$ on the conduction band for $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$ and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ CE predicted structures. Moreover, there is a superior contribution from Mn- $3d$, Zn- $3d$, and O- $2p$ states in the total density of states. The conduction band minima and valence band maxima are mostly contributed by Mn- $3d$ and Zn- $3d$ atoms and transition-metal dopants, which are responsible for electronic conductivity. The spin-up and spin-down states in NaMnO_2 and $\text{Na}_2\text{MnZnO}_4$ are fully occupied, characterising the semiconducting characteristics. In $\text{Na}_6\text{MnZn}_5\text{O}_{12}$ and NaZnO_2 , the spin-up states are partially occupied and thus metallic behaviour. This behaviour possesses the free electrons that contribute to the high electrical conductivity of the predicted structures. In contrast, the spin-down states for $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ are filled and present the semiconducting behaviour. These compounds characterise the half-metallic performance and function as a conductor for electrons of the one spin direction and insulator-semiconductor for the other spin direction.

6.6 Mechanical Properties

As mentioned previously, NaMnO_2 exhibits a monoclinic structure and has nine independent elastic constants, i.e., C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} and C_{66} . The elastic properties of a solid are important to understand its mechanical properties. The

mechanical stability criterion expressed by equation 3.23 for the monoclinic crystal must be fulfilled to a system considered mechanically stable.

Table 6. 3: Elastic constants (C_{ij}) for $\text{Na}(\text{Mn,Zn})\text{O}_2$ CE-predicted stable structures

	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
NaZnO_2	101.28	56.43	51.82	172.56	57.63	159.31	55.26	47.04	51.04
$\text{Na}_3\text{Mn}_2\text{ZnO}_6$	206.65	88.35	52.53	249.22	52.20	194.56	47.40	56.58	44.20
$\text{Na}_6\text{MnZn}_5\text{O}_{12}$	155.44	72.39	45.84	199.50	45.67	164.15	41.81	50.38	49.62
$\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$	204.72	88.54	52.79	249	53.56	196.75	49.61	56.12	47.91
$\text{Na}_2\text{MnZnO}_4$	210.94	69.75	58.31	247.49	45.08	197.01	61.85	40.36	69.81
$\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$	159.59	73.43	50.50	286.00	54.11	185.76	46.94	53.49	63.21
NaMnO_2	119.15	50.44	45.01	321.88	39.72	163.13	61.44	52.21	59.97

Table 6.4. illustrates that elastic constants are all positive and satisfy the conditions of mechanical stability. Thus, the predicted structures are mechanically stable. These conditions also give a limit to the value of bulk moduli, which should be between C_{11} and C_{12} .

Table 6. 4: Bulk, shear and Young's moduli, Poisson's and Pugh's ratio for Na(Mn,Zn)O₂ CE-predicted stable structures.

	B_H	G_H	E_H	Poisson's Ratio	Pugh's Ratio
NaZnO₂	77.30	45.97	115.07	0.252	1.681
Na₃Mn₂ZnO₆	113.81	57.54	147.72	0.284	1.978
Na₆MnZn₅O₁₂	93.10	51.04	129.46	0.268	1.824
Na₆Mn₂Zn₄O₁₂	114.18	59.17	151.36	0.279	1.930
Na₂MnZnO₄	108.15	63.42	159.15	0.255	1.705
Na₅Mn₄ZnO₁₀	105.15	60.50	152.28	0.259	1.738
NaMnO₂	85.92	59.48	144.97	0.219	1.445

The hardness of a material correlates with its bulk and shear moduli; thus, hard solids can be identified by examining materials with high bulk and shear moduli, as evidenced by the table indicating that $B_H > G_H$. The Pugh ductility and brittleness criterion was also assessed. The value 1.75 is the critical number that distinguishes ductility from brittleness. Because B_H/G_H is greater than 1.75, the predicted structures, Na₃Mn₂ZnO₆, Na₆MnZn₅O₁₂, Na₆Mn₂Zn₄O₁₂, Na₂MnZnO₄, and Na₅Mn₄ZnO₁₀ structures are ductile, which implies that these materials can bend without deformation, resulting in fewer cracks during battery operation. This behaviour is again supported by looking at the value of Poisson's ratio which can distinguish the brittleness and ductility of the material. The dividing line between the brittle material and the ductile material is 0.25. When Poisson's ratio is less than 0.25, the material is brittle, while they are ductile if Poisson's ratio is greater than 0.25. The Poisson ratio of NaZnO₂, Na₃Mn₂ZnO₆, Na₆MnZn₅O₁₂, Na₆Mn₂Zn₄O₁₂, Na₂MnZnO₄, and Na₅Mn₄ZnO₁₀ is greater than 0.25, suggesting that all these predicted structures are

ductile except NaMnO_2 . Poisson's and Pugh's ratio give the consistent behaviour for the predicted structures.

Elastic anisotropy of crystals has an important implication in engineering and science because it is strongly related to the possibility of microcracks in the material. The difference between the two elastic constants, C_{11} and C_{33} , illustrates the conditions of elastic anisotropy of the crystal and can be determined by equations 4.6.4 and 4.6.5.

Table 6. 5: Anisotropy in the shear elastic factor (A_i with $i = 1,2,3$) and anisotropy in compressibility and shear moduli (A_B and A_G) for $\text{Na}(\text{Mn,Zn})\text{O}_2$ CE-predicted stable structures.

	A_1	A_2	A_3	A_B	A_G
NaZnO_2	1.408	0.869	1.268	0.099	0.051
$\text{Na}_3\text{Mn}_2\text{ZnO}_6$	0.640	0.666	.0.633	0.012	0.045
$\text{Na}_6\text{MnZn}_5\text{O}_{12}$	0.751	0.740	0.876	0.011	0.020
$\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$	0.671	0.664	0.693	0.080	0.045
$\text{Na}_2\text{MnZnO}_4$	0.849	0.456	0.870	0.029	0.050
$\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$	0.768	0.589	0.846	0.043	0.041
NaMnO_2	1.278	0.514	0.705	0.131	0.110

The values of A_1 , A_2 , and A_3 for the Zn doped NaMnO_2 predicted structures are uniform, indicating isotropic characteristics. The systems $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$, and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ exhibit minor departures from unity, while A_1 and A_3 for NaZnO_2 and A_1 for NaMnO_2 had the most significant deviation from unity. The projected structures for NaMnO_2 doped with Zn exhibit a decline in A_B and A_G values with increasing Zn concentration, indicating a drop in isotropy that may lead to micro-cracks and dislocations during the charge/discharge cycle. The proportion of

shear modulus anisotropy, A_G exceeds the percentage of bulk modulus anisotropy A_B for the compounds $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$, and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$. The system NaZnO_2 has an anisotropy factor exceeding unity, with A_1 and A_3 surpassing unity by 40.8% and 26.8%, respectively, indicating enhanced directional bonding and increased stiffness. An identical pattern is observed in NaMnO_2 , with the anisotropy factor A_1 exceeding unity by 27.8%. The alternative anticipated structure exhibits anisotropic components that slightly deviate from the unit, implying uniform mechanical properties in all directions. This is essential for long-term cycling stability and positively influences sodium diffusion channels, battery stability, and performance during daily use.

6.7 Thermodynamic Properties

The calculated volumetric density, sound velocities, and Debye temperature of the CE-predicted structure are listed in Table 6.6.

Table 6. 6: Calculated volumetric density longitudinal sound velocities and Debye temperature θ_D for Na(Mn,Zn)O₂ CE-predicted stable structures.

	$\rho(\text{kg/m}^3)$	$v_t(\text{m/s})$	$v_l(\text{m/s})$	$v_m(\text{m/s})$	$\theta_D (K)$
NaZnO₂	4352	3250	5644	3609	476.3
Na₃Mn₂ZnO₆	4371	3628	6602	4044	545.2
Na₆MnZn₅O₁₂	4462	3381	6007	3762	503.1
Na₆Mn₂Zn₄O₁₂	4376	3677	6642	4096	552.5
Na₂MnZnO₄	4469	3764	6561	4181	565.3
NaMn₄ZnO₁₀	4251	3773	6613	4193	562.3
NaMnO₂	4037	3849	6416	4258	563.8

The structures of Zn doped NaMnO₂ exhibit calculated density ranging from 4037 to 4469 kg/m³, as detailed in Table 6.6. These elevated values suggest these materials are stable and can maintain their form during battery operation. The velocity of sound waves traveling through the material was measured and is presented in Table 6.6 as the longitudinal (v_l) and transverse (v_t) sound velocities. The table indicates that Zn doped NaMnO₂ predicted structures exhibit elevated velocities, suggesting increased stiffness and mechanical stability. The longitudinal velocity values further demonstrate that these predicted structures possess greater strength and enhanced resistance to

mechanical deformation during battery operation, as evidenced by the higher longitudinal velocity values.

Given that the Debye temperature in a solid can indicate its covalent strength, the values derived for the lattice imply a more rigid structure, suggesting enhanced thermal stability and a reduced probability of thermal expansion both crucial elements for battery performance across different temperatures. The maximum Debye temperature recorded was 565.3 kg/m^3 for $\text{Na}_2\text{MnZnO}_4$, indicating that $\text{Na}_2\text{MnZnO}_4$ has the potential to excel at elevated temperatures by preserving its structural integrity and electrochemical performance across a broader temperature spectrum. The minimum value of 476.3 kg/m^3 was recorded for NaZnO_2 , suggests a higher susceptibility to thermal degradation, which could restrict its effectiveness in high-temperature settings.

To assess the thermal behaviour of various materials within this temperature range, it is essential to examine their thermodynamic properties, including specific heat at constant temperature (C_V). Calculations of free energy and entropy at 0 GPa pressure across a temperature range of 0 to 1500 K were conducted. The thermodynamic properties of electrode materials in a sodium-ion battery are the primary focus of our investigation [8]. This study examines thermodynamic quantities, including Helmholtz free energy, entropy, and specific heat capacity, as they relate to temperature. Thermodynamic properties results obtained for Zn doped NaMnO_2 predicted structures are illustrated in Figures 6.2, to 6.4.

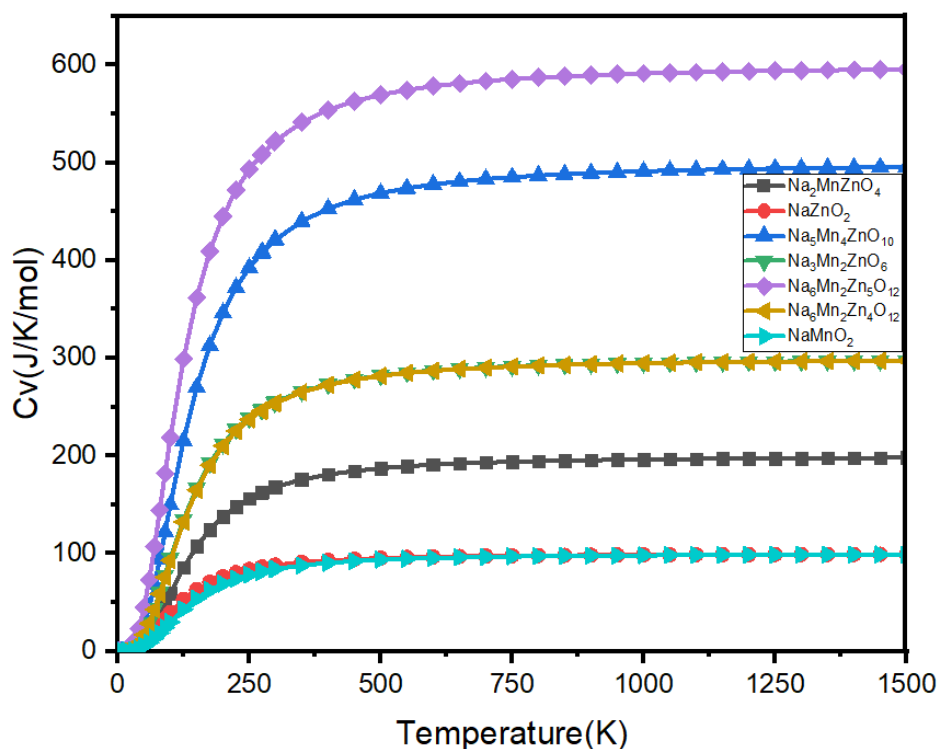


Figure 6. 3: Specific heat vs. temperature for CE-predicted $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ structure.

Figure 6.3 depicts the specific heat at constant volume demonstrating a considerable correlation between temperature and C_v . At low temperatures, the rate of growth in C_v is swift for all predicted structures. At elevated temperatures, the C_v values of all structures converge towards the traditional asymptotic limit. The specific heat capacity rises with increasing temperature and reaches a saturation point as the temperature continues to escalate.

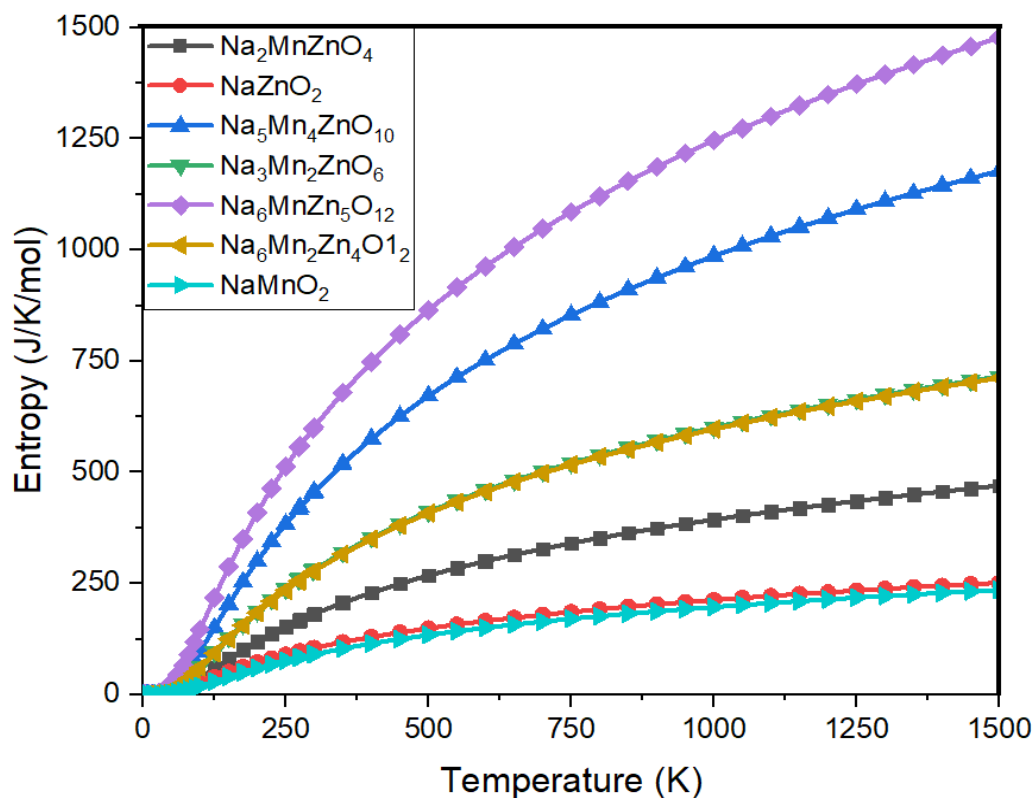


Figure 6. 4: Entropy vs. temperature for CE predicted $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ structure.

At a temperature of 375 K, Figure 6.4 illustrates the entropy of the newly predicted structures of Zn doped NaMnO_2 . The predicted structures exhibit a swift increase in entropy values with rising temperature, indicating the material's thermal stability, and enhancing its ionic diffusion pathways.

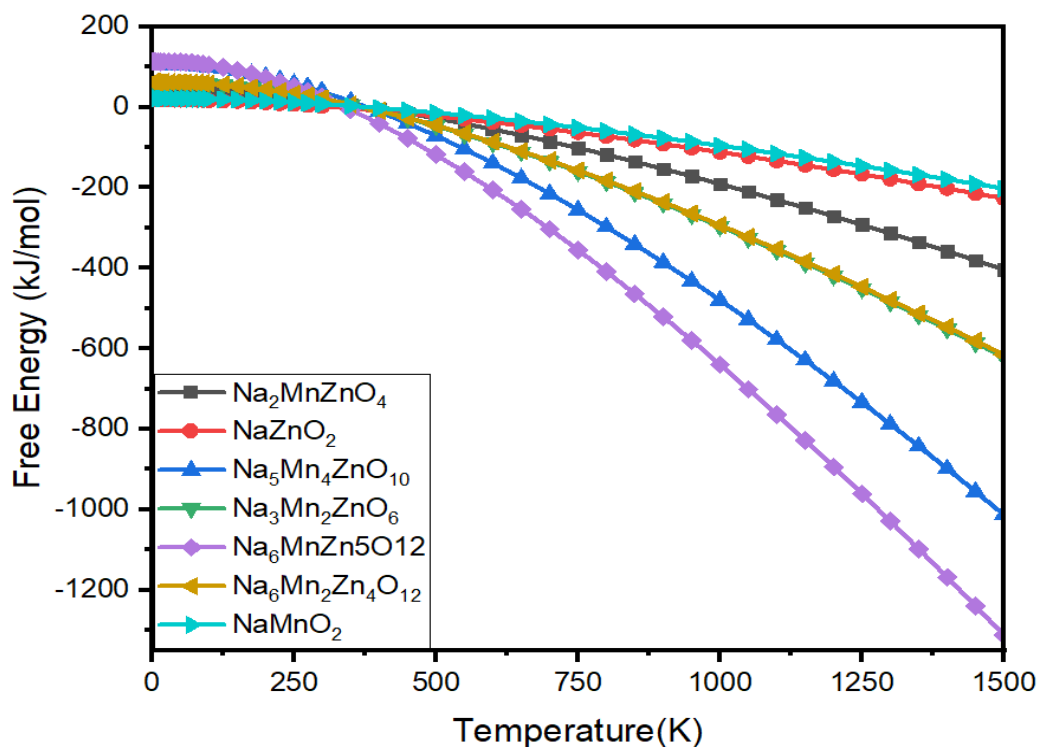


Figure 6. 5: Free energy vs. Temperature for CE-predicted $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$ structure.

The Helmholtz free energy of the predicted structure was examined, revealing that the free energy diminishes as temperature rises. The Helmholtz free energy is a crucial measure for evaluating the stability of a structure. A structure with a reduced Helmholtz free energy is considered stable [9,10]. Figure 6.5 demonstrates that the computed Helmholtz free energy for Zn doped NaMnO_2 has a greater negative trend at temperatures over 250 K, while NaMnO_2 and NaZnO_2 exhibit fewer negative values compared to other structures. Consequently, Figure 6.5 demonstrates that all Zn doped NaMnO_2 predicted structures exhibit thermodynamic stability, with $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$, and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ displaying greater stability as their thermodynamic free energy properties become increasingly unfavourable with rising temperatures, in contrast to NaMnO_2 and NaZnO_2 .

6.8 Summary

The cluster expansion approach has been successfully used to predict the stable structures of Zn doped NaMnO_2 . The results demonstrate a cross-validation score of less than 5 meV. Expansion in the lattice parameters when adding Zn concentration to NaMnO_2 causes the volumetric expansion, which results in a wider diffusion channel. The calculated energy band gap values of Zn containing predicted structures are lower than that of the parent structure (NaMnO_2), implying enhanced conductivity of the materials. The mechanical properties results show that all the predicted structures satisfied the Born stability criteria for monoclinic structure and are mechanically stable. According to the Pugh criterion of ductility and brittleness, the predicted structures, $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$ and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ structures are ductile, which implies that these materials can bend without deformation, resulting in fewer cracks during battery operation. The Poisson ratio analysis of $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$ and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ shows values greater than 0.25, implying that the predicted structures are ductile. The Poisson and Pugh ratios demonstrate consistent characteristics for the predicted structures. Thermodynamic properties showed that NaZnO_2 , $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$, and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ have lower Debye temperature than that of the parent structure. However, $\text{Na}_2\text{MnZnO}_4$ compound has the highest Debye temperature, suggesting highest thermal conductivity followed by the parent structure.

REFERENCES

1. Su, Jingcang, Yong Pei, Zhenhua Yang, and Xianyou Wang. "First-principles investigation on crybeen stal, electronic structures and Diffusion barriers of $\text{NaNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for advanced rechargeable Na-ion batteries." *Computational Materials Science* 98 (2015): 304-310
2. Sukkabot, W. (2020). First-principles calculations of the monoclinic transition-metal doped NaMnO_2 cathode material. *Philosophical Magazine*, 100(7), 917-926.
3. Voigt, W. (1928). *Lehrbuch der Kristallphysik*, Leipzig Germany.
4. Reuss, A. J. Z. A. M. M. (1929). Calculation of the flow limits of mixed crystals on the basis of the plasticity of monocrystals. *Applied Mathematics and Mechanics*, 9(1), 49-58.
5. Hill, R. (1952). The elastic behaviour of a crystalline aggregate. *Proceedings of the Physical Society. Section A*, 65(5), 349.
6. Shao, Y., & Duan, W. (2020). First-principles study of mechanical and electronic properties of Lu_2SnC under pressure. *Journal of Applied Physics*, 127(15)
7. Romero, M., & Escamilla, R. (2012). First-principles calculations of structural, elastic and electronic properties of Nb_2SnC under pressure. *Computational Materials Science*, 55, 142-146.
8. Liu, B., Wang, H. W., & Ouyang, C. Y. (2017). Vibrational and Thermodynamic Properties of Layered $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$ (M= Mn, Co) Cathode Materials for Li-Ion Batteries. *International Journal of Electrochemical Science*, 12(4), 2963-2972.
9. Aarifeen, N. U., & Afaq, A. (2017). Thermodynamic properties of ZnSe under pressure and with temperature. *Chinese Physics B*, 26(9), 093105

10. Bussi, G., & Branduardi, D. (2015). Free-energy calculations with metadynamics: Theory and practice. *Reviews in Computational Chemistry Volume 28*, 1-49.

CHAPTER 7

CONCLUSION

First principle calculations based on density function theory used to carry out the structural, electronic, mechanical and Thermodynamics properties of $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ bulk structures, and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercells as cathode materials for sodium-ion batteries, the structural doping by Ti and Zn were done using random substitution doping technique. We also used the first-principle simulations to investigate the consequences of Na^+ on the $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercells. The dopants (Ti and Zn) change the lattice parameters and volumes for the doped systems because their atomic radii are different from the host Mn (The atomic radii of Mn, Ti, and Zn are not all the same). All the doped systems exhibit dopant-induced volume expansion, which widens the Na^+ diffusion channel wider and enhances the materials' conductivity. The introduction of impurities leads to structural changes that affect Na^+ mobility. Wider diffusion channels decrease the activation energy barrier for Na^+ transport, allowing for quicker ion migration through the host lattice. This improved Na^+ mobility enhances the rate capability of the cathode material and enables more efficient charge/discharge dynamics. The spin-polarized total and partial density of states (TDOS and PDOS) reveal a clear asymmetry between spin-up and spin-down channels, confirming half-metallic behavior and intrinsic magnetism in Ti-doped NaMnO_2 systems. The PDOS analysis attributes this magnetism to the hybridization of Ti and Mn 3d orbitals with O 2p states, which introduces localized electronic states at the Fermi level. These electronic and magnetic modifications, driven by p–d exchange interactions, enhance the material's conductivity and make it a promising candidate for multifunctional sodium-ion battery applications. This observation also applies to the $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ bulk structure and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercell. In this study, we investigated various properties of the materials, including the voltage window which reflects their dynamic response during the charge and discharge processes. For the Ti-doped system, we found that the voltage window ranges from 3.410 V to 4.132 V. In contrast, the voltage window for the Zn-doped system ranges from 2.221 V to 4.337 V. These ranges represent the operating voltages during sodium extraction and insertion, highlighting the electrochemical behavior under cycling conditions. Notably, the

voltage profile reported by Zhang *et al.* for a related system spans from 3.54 V to 2.52 V, which is comparable to our findings. Additionally, the negative formation energy values calculated for these doped systems suggest thermodynamic stability, further strengthening their potential as candidate cathode materials. The calculated elastic constants for the $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ bulk structures, as well as the $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ supercells, indicate mechanical stability for this compound. However, the fully de-intercalated system (MnO_2) indicate that it is not stable and cannot be fully de-intercalated, this is show but Pugh less than 1.75 and poisson ration below 0.25. negative, symbolizsng the prediction of a solid possessed by the material. The material investigated found to be thermodynamical stable, with thermodynamics properties of $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $2 \times 1 \times 1$ $\text{Na}_x\text{Mn}_{0.5}\text{Zn}_{0.5}\text{O}_2$ remain stable during elevated temperature battery operation, thus minimising the risk of structural damage. hence the search for a proper concentration of Ti and Zn to be added to the NaMnO_2 was looked at using the cluster expansion approach. The UNCLE code implemented the cluster expansion formalism to investigate $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ and $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$. We used this method to find stable multi-component crystal structures and rank metastable structures based on the enthalpy of formation. It works just as well and accurately as first-principles density functional methods. The ground state phase diagram generated various structures with different concentrations and symmetries. The isotropically volume-optimized and fully optimized structures produced the cross-validation score of 1.7 meV and 1.9 meV for $\text{Na}(\text{Mn},\text{Ti})\text{O}_2$ and $\text{Na}(\text{Mn},\text{Zn})\text{O}_2$, respectively, which is an indication of a favourable cluster expansion since it is less than 5 meV per active position. We figured out the structural, electronic, mechanical and Thermodynamics properties of all the structures, we found on the isotropically optimized volume and fully optimized binary diagram to show how stable they are. In the presence of a dopant, the lattice parameters stretch, causing the volume to expand and widening the Na-diffusion channel of all the CE-predicted structures. The band gap gets smaller as the amount of Ti increases, as shown by the electronic properties analysis. Similarly, for Zn-based predicted structures, the band gap was smaller than that of the parent structure, which means that the doped material is more of the conductor. We investigated the mechanical properties by measuring the elastic constants. The results showed that all the predicted structures met the stability requirements for monoclinic structures. Pugh and poisson criteria of ductility and brittleness shows that the CE-Predicted structures for

Ti-doped systems, indicate that $\text{NaTiMn}_2\text{O}_2$ is ductile and able to bend without deformation, implying that it can be used in battery applications and cannot crack during operation while the other structures $\text{NaTi}_2\text{MnO}_2$, $\text{NaTiMn}_2\text{O}_6$ and NaMnO_2 are both brittle, for Zn-doped systems $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$ and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ structures found to be ductile, which implies that these materials can bend without deformation, resulting in fewer cracks during battery operation, while the Poisson ratio analysis of $\text{Na}_3\text{Mn}_2\text{ZnO}_6$, $\text{Na}_6\text{MnZn}_5\text{O}_{12}$, $\text{Na}_6\text{Mn}_2\text{Zn}_4\text{O}_{12}$, $\text{Na}_2\text{MnZnO}_4$ and $\text{Na}_5\text{Mn}_4\text{ZnO}_{10}$ shows values greater than 0.26 which shows that these predicted structures are ductile. The Poisson and Pugh ratios demonstrate the same behaviour for the predicted structures. The thermodynamic analysis of the investigated materials shows a strong dependence on temperature, so influencing important parameters including specific heat, entropy, and free energy. At low temperatures, the particular specific heat (C_v) at higher temperatures it corresponds with the Dulong-Petit rule. Especially in the systems that were doped with Ti, entropy increases with temperature indicate greater disorder and enhanced ionic transport. The observed decrease in Helmholtz free energy with rising temperature confirms the thermodynamic stability of the expected structures, therefore making them suitable for high temperature uses.