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**STRUCTURAL, THERMODYNAMIC, ELECTRONIC,
AND MECHANICAL PROPERTIES OF CALCIUM
MANGANESE OXIDE POLYMORPHS FOR
APPLICATION AS CATHODE MATERIAL IN
CALCIUM ION BATTERIES**

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**A dissertation submitted to Faculty of Science and Agriculture of the University of
Fort Hare in fulfilment of a Master of Science Degree in Physics**

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Declaration

I, ROBERTS OSWALD, declare that this dissertation submitted to the Faculty of Science and Agriculture in the University of Fort Hare in fulfilment of a Master of Science degree in Physics (Material Science) hasn't been submitted to any University or institution and that it is my research and that all material contained therein has been duly recognised.



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Dedications

This dissertation is dedicated to my family, comprised of my father, Samson Roberts, my mother, Sophie Roberts, and my brother, Torrelido Roberts.



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I want to thank the forefathers of science who came before us and paved the way. I would also like to thank my supervisor, Dr. NL Lethole, for the support throughout this project and for not giving up on me even when I seem down/ uncooperative. I would like to also extend my gratitude to the staff members of the Department of Physics and the entire community of the University of Fort Hare. The Centre of High-Performance Computing (CHPC) is also appreciated for providing computational resources and simulation code to perform the calculations of this study.



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Table of Contents

Declaration	i
Dedications.....	ii
Acknowledgements	iii
Abbreviations	x
Abstract	xii
Chapter 1	1
1.1. Introduction.....	1
1.2. Problem Statement and Rationale.....	4
1.3. Aims and Objectives	6
1.4. Outline of the Study	7
Chapter 2	9
2.1. Literature Review.....	9
2.2. Theoretical Background of the Calculated Properties	12
2.2.1. Lattice Parameters.....	12
2.2.2. Heats of Formation	13
2.2.3. Density of States (DOS).....	14
2.2.4. Elasticity	14
Chapter 3	19
Method	19
3.1. Density Functional Theory (DFT)	19
3.2. Exchange-Correlation (XC) Functional.....	22
3.2.1. Local Density Approximation (LDA).....	23
3.2.2. Generalised Gradient Approximation (GGA)	25
3.3. Density Functional Theory with Hubbard Correction (DFT+ <i>U</i>).....	26
3.4. Plane-wave Pseudopotential Method (PWP).....	28
3.3.1. Pseudopotentials	28

3.3.2. Ultrasoft Pseudopotentials	29
3.5. CAmbridge Serial Total Energy Package (CASTEP) Code	30
3.6. Methodology	31
Chapter 4.....	33
Results and Discussions	33
4.1. Convergence Test.....	33
4.2. Determination of Hubbard <i>U</i> Correction	34
4.3. Structural Properties.....	35
4.4. Thermodynamic Properties.....	36
4.5. Electronic Properties	36
4.6. Mechanical Properties.....	39
Chapter 5.....	44
Conclusion.....	44
Appendices.....	57
Conference attendance	57
Publications	57



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List of Figures

Figure 2.1 Schematic representation of atomic arrangement for (a) Fd3m-CaMn ₂ O ₄ , (b) Pbcm-CaMn ₂ O ₄ and (c) Pnma-CaMn ₂ O ₄	12
Figure 3.1 Basic chart of a DFT calculation:	21
Figure 4.1 Total energy vs Cut-Off energy for (a) Fd3m-CaMn ₂ O ₄ , (b) Pbcm-CaMn ₂ O ₄ , and (c) Pnma-CaMn ₂ O ₄	34
Figure 4.2 Total density of states for Fd3m-CaMn ₂ O ₄ , Pbcm-CaMn ₂ O ₄ and Pnma-CaMn ₂ O ₄ . Fermi level is used as zero on the energy level	37
Figure 4.3 (a) Fd3m-CaMn ₂ O ₄ , (b) Pbcm-CaMn ₂ O ₄ and (c) Pnma-CaMn ₂ O ₄ . The Fermi energy is used as zero on the energy scale.	38



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List of Tables

Table 4.1 Cut-off and total energies for Fd3m-CaMn ₂ O ₄ , Pbcm-CaMn ₂ O ₄ , and Pnma-CaMn ₂ O ₄	33
Table 4.2 Ueff values vs lattice parameters for Pbcm-CaMn ₂ O ₄	34
Table 4.3 Calculated equilibrium lattice parameters, unit cell volume and enthalpy of formation for Fd3m-CaMn ₂ O ₄ , Pbcm-CaMn ₂ O ₄ and Pnma-CaMn ₂ O ₄ . Experimental data is also given where available.	35
Table 4.4 The computed elastic constants, Moduli, Pugh ratio, Poisson ratio, Hardness, Universal Anisotropy Index and Debye temperature for Fd3m-CaMn ₂ O ₄ , Pbcm-CaMn ₂ O ₄ and Pnma-CaMn ₂ O ₄	40



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List of Equations

Equation 2.1	13
Equation 2.2 heats of formation	13
Equation 2.3	14
Equation 2.4 Density of States	14
Equation 2.5 Stress-strain Relationship.....	15
Equation 2.6 Stress components in terms of elastic and strain components	15
Equation 2.7 Stability criteria for cubic system	16
Equation 2.8 Elastic moduli for cubic crystal.....	16
Equation 2.9 Mechanical stability conditions for orthorhombic crystals.....	17
Equation 2.10 Bulk modulus (B) for orthorhombic system	17
Equation 2.11 Shear modulus (G) for orthorhombic system.....	17
Equation 2.12 Young's modulus (E).....	18
Equation 2.13 Coefficients for inverse matrix S for orthorhombic system.....	18
Equation 3.1 Hohenberg-Kohn free energy functional.....	19
Equation 3.2 Electrostatic energy	20
Equation 3.3 KS equation from SE	20
Equation 3.4 KS equation for Kinetic energy.....	20
Equation 3.5 KS equation for effective potential	20
Equation 3.6 KS equation for electrostatic potential	21
Equation 3.7 KS equation for XC potential.....	21
Equation 3.8 wave function	21
Equation 3.9 cut-off energy	21
Equation 3.10 XC energy	23
Equation 3.11 XC energy Functional	23
Equation 3.12 Unity.....	23
Equation 3.13 Exchange energy for homogeneous electron gas	23
Equation 3.14 Exchange energy Functional for LDA	24
Equation 3.15 Upper bound Correlation energy Functional for LDA.....	24
Equation 3.16 Lower bound Correlation energy Functional for LDA	24
Equation 3.17 Wigner-Seitz radius.....	24
Equation 3.18 XC energy Functional for LDA	24
Equation 3.19 XC Functional for LDA	25

Equation 3.20 XC potential for LDA	25
Equation 3.21 XC Functional for LSDA	25
Equation 3.22 XC Functional for GGA.....	26
Equation 3.23 XC energy Functional for GGA.....	26
Equation 3.24 Hubbard Hamiltonian.....	27
Equation 3.25 DFT+U functional.....	28
Equation 3.26	29
Equation 4.1 Energy of strained system	39
Equation 4.2 Poisson ratio	42
Equation 4.3 Universal Anisotropy Index	42
Equation 4.4 Debye’s temperature.....	43
Equation 4.5 velocity.....	43



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Abbreviations

AE – All-electron

BZ – Brillouin zone

CASTEP – Cambridge Serial Total Energy Package

CB – Conduction Band

CIBs – Calcium-Ion Batteries

DFT – Density Functional Theory

DFT+U – Density Functional Theory with Hubbard Correction

DOS – Density of States

EVs – Electric vehicles

GGA – Generalized Gradient Approximation

HEVs – Hybrid Electric Vehicle

HF – Hartree-Fock

HOF – Heats of Formation

KS – Kohn-Sham

LAPW – Linearized augmented-plane wave

LDA – Local Density Approximation

LIBs – Lithium-Ion Batteries

LSDA – Local Spin-Density Approximation

NiCd – Nickel-Cadium

NiMH – Nickel Metal Hydride

OTFG – On-The-Fly Generated

PBE – Perdew-Burke-Ernzerhof

PEDs – Portable electronic devices



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PHF – Post-Hartree-Fock

PP - Pseudopotential

PS - Pseudo

PWP – Plane Wave Pseudopotential

QM – Quantum Mechanics

SE - Schrödinger's Equation

SCs - Supercapacitors

SCF - Self-Consistent Field

SIE - Self-Interaction Error

S.G – Space Group

US-PP – Ultrasoft pseudopotential

VB – Valence Band

XC – Exchange-correlation

ZIBs – Zinc-Ion Batteries



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Abstract

The exploration of alternative energy storage battery chemistries has become increasingly crucial in recent years, driven by the anticipated depletion of lithium resources and the high costs associated with Li-ion batteries. In response to these challenges, research on the bivalent Ca-ion has gained traction as a promising alternative for developing new rechargeable battery chemistries. Among the various candidates, CaMn_2O_4 has emerged as a particularly promising option due to its desirable physical and chemical properties. This study employed *ab initio* computational simulations to investigate the structural, thermodynamic, electronic, and mechanical characteristics of three different polymorphs of CaMn_2O_4 : namely $\text{Fd}3\text{m-CaMn}_2\text{O}_4$, $\text{Pbcm-CaMn}_2\text{O}_4$, and $\text{Pnma-CaMn}_2\text{O}_4$ under ambient conditions. The density functional theory (DFT) method, implemented in the CASTEP code, was utilized, with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) and Hubbard U-correction for the exchange-correlation functional. The computed structural lattice parameters demonstrated excellent agreement with experimental data, with a percentage difference of less than 5%, validating the methodology employed. The negative enthalpies of formation indicated that all three CaMn_2O_4 polymorphs are thermodynamically stable and can be feasibly synthesized under ambient conditions. Analysis of the electronic densities of states revealed that $\text{Pnma-CaMn}_2\text{O}_4$ is metallic, while $\text{Fd}3\text{m-CaMn}_2\text{O}_4$ behaves as a semiconductor. Furthermore, the projected intercalation potentials suggest that the Ca ion can be reversibly inserted and removed from Mn_2O_4 . Lastly, the values of elastic constants indicated that the $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Fd}3\text{m-CaMn}_2\text{O}_4$ polymorphs are mechanically stable, meeting the Born stability conditions, while the $\text{Pnma-CaMn}_2\text{O}_4$ may exist only at elevated pressure. This comprehensive study sheds light on the potential of CaMn_2O_4 as a potential cathode material in rechargeable Ca-ion batteries.

Chapter 1

1.1. Introduction

The advancement and proliferation of electronic devices, including laptops, smartphones, tablets, and smartwatches, have heightened the demand for energy sources and storage components [1]. In today's technology-driven society, these portable electronic devices (PEDs) have fuelled the rapid expansion of information processing and sharing. Reliable energy sources and storage components are essential in ensuring the optimal performance of these devices. Energy storage devices play a crucial role in the modern world, as they enable efficient utilization of renewable energy sources and serve as a backup during power outages [2]. Thus, there is a need to intensify research on energy storage devices to enhance the performance and reliability of these systems, ultimately contributing to a more sustainable energy landscape [3]. Furthermore, the research on energy storage devices holds immense potential for advancing the efficiency and sustainability of various industries, including transportation, telecommunications, and grid management [3]. In the transportation sector, for instance, the development of high-performance batteries can enable the widespread adoption of electric vehicles, reducing greenhouse gas emissions and dependence on fossil fuels [4]. Similarly, energy storage devices play a critical role in stabilizing the power grid, enhancing grid resilience, and enabling the seamless integration of intermittent renewable energy sources [4, 5]. Most renewables, such as wind energy, hydropower, and photovoltaics, rely on energy storage devices for a constant supply of energy [2]. There are two most used energy storage devices namely supercapacitors and batteries. Supercapacitors are safe, simple to use, have high power density, quick charge and discharging processes and exceptional cycle stability [6]. However, their low energy density (10 Wh/kg) and high manufacturing cost of supercapacitors currently utilized at the commercial level have limited their widespread application [7, 8]. Rechargeable batteries that can store and release electrical charges as energy for various applications per power demands have been central to clean renewable energy storage for PEDs. A battery with high energy density, high thermal stability, low cost, excellent cycle of life, low ion, fast charging/discharging rates, electronic transport resistance, and environmentally benign is incredibly desirable for application in PEDs and electric vehicles (EVs) [1, 9]. These requirements are essential for ensuring the reliability and economic viability of energy storage systems. Additionally, the integration of renewable energy sources, such as solar and wind power, into the grid necessitates scalable and reliable

energy storage solutions. By addressing these challenges through research and innovation, we can accelerate the transition towards a cleaner and more resilient energy infrastructure [10]. Significant advancements and innovations have been achieved in rechargeable battery technology over the years from the first commercially successful rechargeable battery, the lead-acid battery invented by French physicist Gaston Plante [11] in 1859 to the commonly used battery in the modern era, the Li-ion battery commercialized in 1991 by Sony [12]. Most relevant rechargeable batteries at the commercial level are lead-acid [13, 14, 15], nickel metal hydride (NiMH) [16, 17, 18], nickel-cadmium (NiCd) [19] and Lithium-ion batteries (LIBs). The earliest mobile phone used the Ni-Cd battery with capacity of 500 mAh which took 20 minutes to discharge while in use but took 10 hours to fully charge. Smartphones in 2023 uses a Li-Ion rechargeable battery with 4000+ mAh capacity lasting 1 hours or longer while in use and charges to full in less than an hour [20]. The Lead-acid rechargeable battery had 30-50 Wh.kg⁻¹ gravimetric energy density, short lifetime of about 300-400 cycles and a slow charging rate of 8-16 hours to full [1]. The second generation of battery commercialized successfully was the NiCd invented by Waldemar Jungner in 1899 [19]. The NiCd had a slightly better gravimetric energy density of 40-60 Wh.kg⁻¹, a long lifetime of 1500 cycles which was five times better than the lead-acid battery and a fast charge time of 1 hour, but NiCd batteries had some notable drawbacks. One major issue was their sensitivity to charging practices. They tended to lose their maximum energy capacity if recharged before being fully discharged, a phenomenon often referred to as the "memory effect." This effect could reduce the battery's effective capacity over time. Furthermore, NiCd batteries exhibited a relatively high self-discharge rate, meaning they would gradually lose their charge even when not in use. This characteristic necessitated more frequent recharging or replacement compared to some other battery technologies. The NiMH battery can be considered as the next generation of the NiCd battery because they have similar configurations i.e. same cathode, and electrolyte but different anode [1, 19]. The NiMH battery used a hydrogen absorbing alloy instead of the Cd which improved the gravimetric energy density from 40-60 Wh.kg⁻¹ to 60-120 Wh.kg⁻¹ which is two times higher than lead-acid batteries. However, the self-discharge rate was three times higher than NiCd batteries [1]. LIBs as the dominant technology for use in PEDs. Before being commercialized by Sony it was first built by Michael Stanley Whittingham in 1970 [21]. He used lithium metal and titanium sulphide as electrodes which had no use other than providing a foundation for further work. At the same time, Besenhard et al. [22, 23, 24] proposed the implementation of reversible intercalation in graphite and cathode oxides to be used in building lithium batteries. This was followed by research in the

electrochemical intercalation of lithium in graphite in the late 1970s done by Samar Basu, [25] and in the early 1980's research done by Rachid Yazami [26] demonstrated the reversible electrochemical intercalation of lithium in graphite which helped with the battery cell deterioration rate problem. Many researchers focused on improving the chemistry of LIBs until its commercial release in 1991 [1]. These developments and advancements in battery technology have greatly improved energy storage capabilities for PEDs and hybrid electric vehicles (HEVs). Current batteries for PEDs have a gravimetric energy density of 170-250 Wh.kg⁻¹, a lifespan of 500-2000 cycles and fast charging time. HEV batteries have a capacity of about 8 kWh which can drive over 30 km only using electric power (EVs have batteries with a capacity higher than 18 kWh which can drive for more than 120 km) [9]. However, the current battery technology cannot fully catch up with the rapid growth of PEDs and HEVs due to their short cycle life, high manufacturing cost and limited energy storage capacity, harming the development of PEDs and HEVs [27]. These hindrances inherently depend on the type of cathode (charge host structure) material employed, the electron transfer reactions between the alkali metal atoms and host structure lattice, and their consequent electrochemical insertion/removal voltage of alkali metal atoms [9]. These reactions greatly influence the structural changes and stability of the host material, whose physical and chemical properties significantly affect the electrochemical performance, cycle life, operating voltage, and energy density of the battery [1, 28]. As a result, irrespective of the past and current advances in battery technologies, there remains a need for battery chemistries with high energy density, volumetric power, charge/discharge capacity and adequate insertion/removal potentials. To find such rechargeable batteries two routes were formed, one is to try and improve the current battery technology by finding compatible electrode materials, electrolytes, separators, binders, current collectors, and battery manufacturing techniques to increase energy density, use non-flammable battery components and building solid-state batteries to improve safety. The other approach is finding other battery chemistries which offer better performances. Most tend to lean on finding alternative battery chemistry fearing that the current battery chemistry has reached a bottleneck i.e. no further improvements can be achieved specifically when it comes to increasing energy density [29]. As an alternative to the current battery chemistries, the multivalent (MV) battery chemistry such as that of Ca²⁺ presents a greater potential for future application in calcium ion batteries. The quest for more efficient, energy-dense, and cost-effective battery solutions is still ongoing as no new battery chemistry has yet reached commercial viability. As a result, this work will delve into the prospect of employing CaMn₂O₄ polymorphs as cathode materials in

rechargeable Ca-ion battery chemistries. Herein, the fundamental physical and chemical properties that underline the suitability of CaMn_2O_4 polymorphs as cathode materials in Ca-ion batteries are investigated using computational-based first-principles calculations. These properties include the structural cell parameters that determine volumetric capacity and density; energetic heats of formation, which dictate thermodynamic stability and experimental achievability; elastic constants to mimic the mechanical stability and response of cathode material to field stress and densities of states structure to determine the electronic conductivity. Three CaMn_2O_4 polymorphs distinguished by space groups are considered in this work; these are $Fd3m$, $Pbcm$ and $Pnma$. Several other space groups (S.G) could not be simulated because of limitations on computational resources.

1.2. Problem Statement and Rationale

The widely studied and developed monovalent lithium-ion batteries (LIBs) have been the most efficient and dominant options available in the market for energy storage. A rechargeable lithium-ion battery has four components: electrodes (cathode and anode), electrolytes, and separators. Singly charged lithium ions (Li^+) move back and forth between electrodes passing through the electrolytes during the charge/discharge process [9]. The characteristics of a battery are inherently dependent on the type of cathode (charge host structure) material employed and the electron transfer reactions between the alkali metal atoms and host structure lattice along with their consequent electrochemical insertion/removal voltage of alkali metal atoms [9]. These reactions greatly influence the structural changes and stability of the host material, whose physical and chemical properties significantly affect the electrochemical performance, cycle life, operating voltage, and energy density [1, 28]. LIBs have high specific energy and power, high reliability, reasonable self-discharge rate and relatively fast recharge, and lithium is light and electropositive compared to current commercialized batteries [9, 28]. However, its single charge brings about minimal energy density, raising concerns about the application of these batteries in large-scale industries [4]. LIBs require high initial manufacturing costs and advanced battery management systems, face safety concerns, encounter material bottlenecks, are susceptible to thermal runaway, have limited recovery capabilities, and involve complex recycling processes [9]. Lithium is highly reactive, resulting in technological challenges when building safe battery cells containing lithium [9]. LIBs contain flammable electrolytes, meaning that during improper handling of the battery, the chemical energy in the battery can be released in the form of fire or explosions, which may result in accidental fires [28, 30, 31]. Moreover, the

projected high demand and extensive use of LIBs may lead to the exhaustion of resources and, consequently, increased costs and jeopardise sustainability [1]. To even think about high-energy battery system applications, we must first solve thermal runaway and depletion of lithium or look for alternative solutions. These shortfalls demand more intensified research efforts toward the development of alternative technologies. Possible alternative chemistries researchers are concentrating on are Na-ion, Li-S, Li-air and multivalent (MV) ion technologies. MV battery chemistries such as Mg^{2+} , Zn^{2+} , Ca^{2+} , and Al^{3+} ions present a more significant potential for future applications in battery storage [32]. MV battery chemistries are of great interest since the multivalent ion insertion/extraction is associated with double/triple electron transfer per ion in the intercalation reaction, leading to higher specific energy density and volumetric power than monovalent ions [33, 34]. Calcium ion battery (CIB) chemistry is particularly promising due to calcium being a safe and a high abundance element on the earth's crust only comparable to Mg which Ca: 4.2%, Mg: 2.3%, Li: 0.002% of Earth's crust suggesting low raw material cost. CIB chemistry have negative reduction potential (only 170mV above lithium metal) and high capacity (1340 mAh.g^{-1}) of calcium anodes [35]. CIBs are capable of offering the highest voltage due to the low reduction potential of Ca/Ca^{2+} with -2.9 V (vs standard hydrogen electrode, SHE), which is lower than -2.4 V (vs SHE) for magnesium, -1.7 V (vs SHE) for aluminium, and -0.76 V (vs SHE) for zinc [33, 36], enabling a high energy density with the voltage comparable to that of LIBs. When it comes to ion mobility in liquid electrolytes, Ca^{2+} ions are expected to surpass Mg^{2+} and Al^{3+} ions, attributing this to its charge/radius ratio [37]. Calcium has a density of 1.54 g.cm^{-3} and charge capacity of 1.34 Ah.g^{-1} resulting in a theoretical energy density of 2.06 Ah.cm^{-3} which exceeds 0.97 Ah.cm^{-3} , the energy density achieved by graphite used in LIBs. However, the development of calcium ion battery technology has been greatly impeded by the lack of suitable positive electrode (host structure) materials that will reversibly allow the insertion and removal of Ca^{2+} with high capacity and good electrochemical and electroconductivity performance without structural degradation [2]. The high valency of Ca^{2+} causes slow kinetic diffusion through the cathode material. Thus, using calcium-based cathodes analogous to those commonly used in lithium is not ideal. This is due to the substantial differences in the interactions between a single-charged cation (i.e. Li^+ , Na^+ , K^+) vs a double-charged cation (i.e. Mg^{2+} , Zn^{2+} , Ca^{2+}) and the intercalation host material [38, 39]. Few cathode materials in CIBs have shown good performance in electrochemical test despite efforts in simulations and experiments. These materials are classified into three main types: Prussian blue analogues, layered metal oxides, and chalcogenides materials [40, 41, 42]

which enables facile Ca plating/stripping [34, 43, 44] and fast Ca intercalation into graphite [45]. Metal oxides have been researched as a cathode material because of their high theoretical capacities, suitable voltage platforms, and scalable synthesis with Transitional metal oxides applied in commercial LIBs (LiCoO_2 and LiMn_2O_4) [46]. Transitional metal oxide postspinel structures are classified as crystal structures with low migration barriers, high voltages, and facile transport pathways for calcium ions [47]. Density Functional Theory (DFT) screening has identified transition metal oxides as promising candidates for calcium batteries [48, 49]. As a rich transitional metal, manganese has divalent, trivalent, and tetravalent valence states [50] and exists in a variety of manganese-based compounds such as MnO_2 , MnO , Mn_2O_3 , Mn_3O_4 and CaMn_2O_4 . However, finding a perfectly ideal material for a cathode material is improbable. Manganese oxides suffer from low intrinsic electronic conductivity, formation of secondary products during charge/discharge and manganese dissolution, which can be improved using electrolytes [37, 46]. The search for a suitable cathode material for CIBs is a lengthy process that requires patience and perseverance. While manganese oxide may have some drawbacks, it is important to continue researching and exploring ways to mitigate these limitations. Scientists have been diligently studying various techniques to address the challenges associated with manganese oxides. The identification of a dependable cathode material for CIBs has the potential to revolutionize energy storage technology and significantly enhance its efficiency. The density functional theory (DFT) along with other computational techniques can help with the analysis of cathode materials for CIBs since DFT permits the research of both existing and virtual materials. Various polymorphs of CaMn_2O_4 (Marokite, spinel and CaFe_2O_4 -type) have shown promise to initiate the quest for cathode materials for Ca ion batteries [35].

1.3. Aims and Objectives

The aim of this study is to investigate the structural, thermodynamic, electronic, and mechanical properties of $\text{Fd}3\text{m-CaMn}_2\text{O}_4$, $\text{Pbcm-CaMn}_2\text{O}_4$, and $\text{Pnma-CaMn}_2\text{O}_4$ polymorphs to evaluate their stability.

The objectives of the study are to:

- ❖ optimize the equilibrium cell parameters to determine structural properties,
- ❖ compute the heats of formation to determine thermodynamic stability,
- ❖ simulate the electronic density of states and band structure to determine electronic conductivity,

- ❖ simulate the elastic constants and macroscopic moduli to mimic mechanical stability.

1.4. Outline of the Study

The outline of the dissertation is divided into five chapters as follows:

- ❖ Chapter One: This chapter starts with an introduction that provides the reader with a concise explanation for the pursuit of improved energy storage devices, including an overview of currently commercialized batteries and potential alternative energy storage solutions. The subsequent section, labelled as 1.2 Problem Statement and Rationale, offers a brief discussion on the widely used modern era Lithium-Ion Battery (LIB), highlighting its limitations, and introduces the alternative option of the Calcium-Ion Battery (CIB), along with its advantages and challenges. In section 1.3, we outline the aims and objectives that we aim to accomplish in this study. Finally, section 1.4 serves as an outline of the study, offering readers a preview of what to expect from each chapter.
- ❖ Chapter Two: This chapter is divided into two sections: Literature Review, which provides background information and previous research on the CaMn_2O_4 polymorphs, and an overview of the properties under investigation. These properties include Lattice Parameters, Density of States, Elastic Constants, and Elastic Moduli. The rationale for studying these properties is also briefly discussed.
- ❖ Chapter Three: This chapter delves into the computational method utilized in this study. The first section provides an introduction to Density Functional Theory, with two subsections dedicated to discussing the LDA and GGA approximation methods. Following this, DFT+U is defined, along with the rationale for its preference over its predecessor, DFT. Section 3.3 includes subsections 3.3.1 and 3.3.2, which elaborate on the concept of pseudopotential. The penultimate section offers insights into the CASTEP code employed for computing the properties of the structures under investigation. Lastly, the final section outlines a detailed, step-by-step procedure of the study.
- ❖ Chapter Four: In this chapter, we will explore five key sections. In Section 4.1, we will delve into the convergence test for the cut-off energy and k-points, as well as the determination of Hubbard U correction by comparing the lattice constants for each U . Following this, we will examine the Structural and Thermodynamic Properties of the structures. In the subsequent chapter, we will analyse the electronic properties by

studying the Density of States (DOS) of each structure. Finally, we will investigate the Mechanical Properties by examining the elastic constants, moduli, Pugh ratio, Poisson ratio, universal anisotropy index, and Debye temperature for each structure. This comprehensive analysis will provide valuable insights into how the structures respond to external forces.

- ❖ Chapter Five: This chapter offers a comprehensive summary and conclusions of the study, based on the findings presented in Chapter Four. We will delve into our interpretation of these findings and outline the future work to be pursued as a result of this study. Moreover, the future objectives are listed.



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Chapter 2

2.1. Literature Review

Calcium manganese oxides (CaMn_2O_4) is a naturally occurring mineral discovered in 1963 in Morocco [51] and due to its country of origin, it was consequently named Marokite. Under different ambient and elevated conditions, this mineral crystallises in five (one cubic and four orthorhombic) polymorphs differentiated by space groups. These are marokite $\text{Pbcm-CaMn}_2\text{O}_4$ [35], spinel $\text{Fd3m-CaMn}_2\text{O}_4$, post-spinel $\text{Pnma-CaMn}_2\text{O}_4$, $\text{Pmab-CaMn}_2\text{O}_4$, and $\text{Pbca-CaMn}_2\text{O}_4$. Their ground state cell parameters are as follows: $\text{Pbcm-CaMn}_2\text{O}_4$ ($a = 0.31587 \text{ nm}, b = 0.99937 \text{ nm}, c = 0.96748 \text{ nm}$ [35]), $\text{Pbca-CaMn}_2\text{O}_4$ ($a = 0.62545 \text{ nm}, b = 0.98995 \text{ nm}, c = 0.9627 \text{ nm}$ [52]), $\text{Pnma-CaMn}_2\text{O}_4$ ($a = 0.9675 \text{ nm}, b = 0.3154 \text{ nm}, c = 0.9899 \text{ nm}$ [35]) and $\text{Fd3m-CaMn}_2\text{O}_4$ ($a = b = c = 0.8246 \text{ nm}$).

The electrochemical and structural characteristics of CaMn_2O_4 have been the focus of numerous researchers over the past few decades. This compound has been well-known for its unique magnetic properties, with manganese ions taking on various oxidation states and exhibiting different magnetic behaviours [53]. The marokite $\text{Pbcm-CaMn}_2\text{O}_4$ has been reported to exhibit a significant distortion of the MnO_6 octahedra, indicative of a pronounced Jahn-Teller effect on the Mn^{3+} cations. Furthermore, it shows a dominant antiferromagnetic spin ordering below 225 K along Mn-O bonds, as well as ferromagnetic properties [52, 54]. Khanahmadzadeh et al. [55] successfully synthesized nanoparticles of marokite CaMn_2O_4 through the sol-gel process. Their research revealed that the material possesses a direct band gap value of 1.4 eV, placing it within the range of highly efficient photovoltaic materials, hence it also possesses acceptable photocatalytic activity [55]. Earlier, White et al. [56] experimentally investigated the magnetic, electronic, and thermodynamic properties of single-crystal samples of marokite CaMn_2O_4 and reported that it exhibits long-range antiferromagnetic order below the Neel temperature $T_N = 217.5 \text{ K}$. Moreover, their room-temperature electrical resistivity showed that CaMn_2O_4 is highly electrical insulating. On the contrary, a density functional theory investigation conducted by Arroyo-de Dompablo et al. [35] predicted semiconductor behaviour for CaMn_2O_4 with a band gap of less than 1 eV. Additionally, they found metallic characteristics for the deintercalated Mn_2O_4 , suggesting potential applications of these materials in the electrochemical industry [35].

Recently, much attention has been shifted towards investigating the potential use of CaMn_2O_4 in secondary (i.e. rechargeable) battery technologies, as its magnetic properties could enhance the performance and efficiency of rechargeable batteries. Studies on the structural and electrochemical properties of CaMn_2O_4 are ongoing, with the aim of unlocking its full potential for various technological applications. Arroyo-de Dompablo et al. [35] employed both computational and experimental techniques to investigate the electrochemical behaviour of the spinel, CaFe_2O_4 -type and marokite polymorphs of CaMn_2O_4 . They reported that the marokite- CaMn_2O_4 is capable of sustaining reversible Ca deinsertion reactions in terms of voltage and capacity. It is predicted that half of the calcium will be removed at an average voltage of 3.7 V, resulting in a volume variation of 6%. The spinel and CaFe_2O_4 -type showed an average intercalation voltage of 3.1 V, however, with a significant volume variation of up to 20%. Furthermore, Chando et al. [47] explored CaMn_2O_4 in postspinel phase as an intercalation cathode for CIBs and reported CaMn_2O_4 to cycle at the capacity of 52 mAh/g at a rate of C/33. Moreover, energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and DFT simulations verified calcium cycling. Chando et al. [47] further used cyclic voltammetry (CV) and galvanostatic (GS) cycling to investigate redox activity and identified oxidation potentials at 0.2 and 0.5 V and a broad insertion potential at -1.5 V. Additionally the research reported a rapid increase in charge transfer resistant that builds within the electrode and leads to limited capacities during cycling. They also noticed structural changes of CaMn_2O_4 post charging, and X-ray diffraction (XRD) revealed several features that aligned with DFT calculations made of decalciated CaMn_2O_4 .

The marokite Pbcm - CaMn_2O_4 crystallises in an orthorhombic structure. It is characterised by the edge-sharing chains of MnO_6 octahedra forming double-rutile chains that are connected by edge-sharing and corner-sharing oxygens, which causes tunnels in the framework, providing 8-coordinated sites for large calcium atoms to occupy [52]. The schematic representation of atomic coordination is in **Figure 2.1**. Moreover, thermal-expansion measurements suggest that CaMn_2O_4 may be considered layered from a crystallographic perspective as it exhibits the same anisotropy observed in layered compounds, providing a quasi-2D nature to the phonons while magnetic super exchange interactions remain relatively isotropic and 3D in nature [56]. Under high pressure, the marokite changes to a CaFe_2O_4 or CaTi_2O_4 type and can be viewed as a low-symmetry variant of these two structures [52, 57].

The postspinel (CaFe_2O_4 type, S.G. Pnma) CaMn_2O_4 is a transformation of the marokite under high pressure treatment which is built up from edge-sharing chains of MnO_6 octahedra,

forming double rutile chains (see **Figure 2.1**). The double-rutile chains are interconnected only through vertex sharing oxygen. Tunnels appear in the framework where Ca ions can reside. The post-spinal structure the CaFe_2O_4 type still has an unusual feature which is the strong distortion of the MnO_6 octahedra with a strong Jahn-Teller effect on Mn^{3+} cations [52, 57]. At 30 GPa to 35 GPa, CaMn_2O_4 (S.G. Pmab) transforms to the CaTi_2O_4 (S.G. Bbmm) structure type. This is a first-order transition by atomic displacement from Pmab to Bbmm. The transition causes a slight unit-cell volume reduction of 3.8%, and the Jahn-Teller distortion in the MnO_6 octahedra disappears at high pressure [57].

The spinel- CaMn_2O_4 to the best of our knowledge is a virtual structure that belongs to a family of compounds which are isostructural with mineral hausmannite (MnO_4) characterized by a full replacement of the Mn^{2+} ions on the tetrahedral sites by M^{2+} ions ($\text{M} = \text{Ni, Co, Zn, Mg, or Cd}$) accompanied by large tetragonal distortions [58]. We are costumed to the marokite transforming into different structures under high pressure conditions, but Arroyo-de Dompablo et al. [35] proposed that the transformation of the marokite to the spinel might occur under high temperature and not pressure, which they estimated the temperature to be $T > 3000\text{K}$ which is very large for a fully ordered spinel but could be substantially low for spinel structures presenting Ca^{2+} ions both in tetrahedral and octahedral interstices. These disordered spinels will have Mn ions most likely occupying tetrahedral sites preventing Ca diffusion which will prevent the use of solid-state preparation routes to synthesis the spinel or Mn oxides with Ca in tetrahedral sites. Arroyo-de Dompablo et al. [35] suggested an alternative by removing lithium from LiMn_2O_4 using acidic media treatment leaving a $[\text{Mn}_2]\text{O}_4$ spinel framework where Ca ions can be electrochemically intercalated in the tetrahedral sites resulting in $[\text{Ca}_x]_{\text{T},\text{O}}[\text{Mn}_2]_{\text{T},\text{O}}\text{O}_4$ ($0 < x \leq 1$) compounds due to the possibility that the driving force of Ca ions to occupy octahedral sites could induce the migration of Mn^{3+} ions to the tetrahedral sites [59]. Kim et al. [60] carried out a similar strategy for Mg. S.G given in the literature for a postspinel structure is different, depending on the axis settings used. In early literature, the marokite was defined to have Pmab as the S.G but recent literature uses Pbcm. Similar with the CaFe_2O_4 type the S.G is either Pnam or Pnma [57].

Riboud and Muan synthesized marokite CaMn_2O_4 in 1963 successfully but there are few available experimental physical properties [61]. CaMn_2O_4 is a potential candidate to initiate the quest for a cathode material for CIBs.

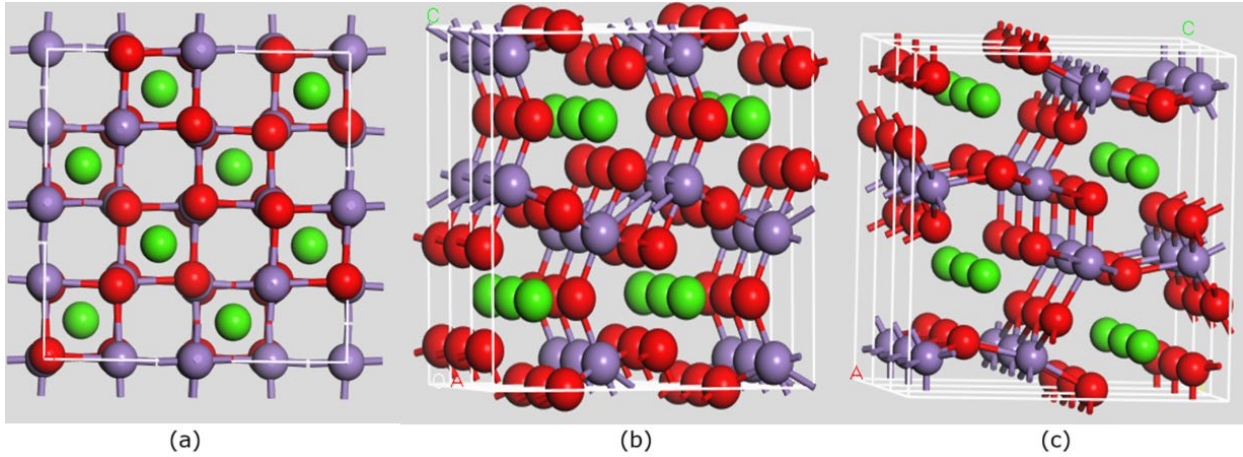


Figure 2.1 Schematic representation of atomic arrangement for (a) $Fd3m$ - CaMn_2O_4 , (b) $Pbcm$ - CaMn_2O_4 and (c) $Pnma$ - CaMn_2O_4 .

2.2. Theoretical Background of the Calculated Properties

2.2.1. Lattice Parameters

Solid materials possess crystalline structures. This crystalline phenomenon occurs when the charges with the same sign are apart, electrons are close to ions, and electron kinetic energy is low by the quantum mechanical spreading of electrons. Lattice can be obtained by repetition of a basis [62]. In 3-D, we assume three non-coplanar vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ (called primitive vectors) that leave all the properties of the crystal unchanged after a shift by any of those vectors. Any lattice point R' can be obtained from another point R as $R' = R + m_1\vec{a} + m_2\vec{b} + m_3\vec{c}$ (most textbooks use a_1, a_2, a_3 instead of a, b, c). These lattices are called Bravais lattices [63]. Structural lattice parameters are a key concept in materials science and solid-state physics [64]. Lattice parameters refer to the physical dimensions of a crystalline structure, typically represented by the lengths of the unit cell vectors that define the crystal lattice. These parameters play a crucial role in determining various properties of materials, such as mechanical strength, thermal conductivity, and electrical conductivity. Understanding and controlling the lattice parameters of a material is essential for designing and engineering advanced materials with specific desired properties.

One of the key aspects of structural lattice parameters is the relationship between the lattice parameters and the atomic arrangements within a crystal lattice. The lattice parameters are directly influenced by the positions of atoms within the crystal structure, as well as the bonding interactions between atoms. By manipulating the lattice parameters through techniques such as doping, alloying, substitution, and strain engineering, researchers can tailor the properties of materials for specific applications. This ability to finely tune the

structural lattice parameters allows for the development of novel materials with enhanced performance characteristics, leading to advancements in various technological fields such as electronics, energy storage, and catalysis. Moreover, in computational simulation studies, such as first-principles calculations utilized in this study, understanding the lattice parameters of a material is essential for comparing with experimental results [65]. Inaccurate calculations of lattice parameters can lead to discrepancies between theoretical models and experimental data, hindering the ability to accurately predict and understand the material's properties. By calculating lattice parameters with precision and accuracy, one can validate and refine their theoretical models, leading to a deeper understanding of the material's behaviour and properties.

2.2.2. Heats of Formation

In thermodynamics, the standard enthalpy of formation or standard heat of formation (H_f) of a compound is the change of enthalpy during the formation of one mole of a substance from its constituent elements in their reference state with all substances in their standard states (298K, 1 atm) [66]. The reference state of an element is referred to as the most stable state. The sign of heats of formation of a compound gives the relative stability of a compound. Negative heats of formation indicates that the energy it takes to break bonds is less than the energy released during bonding. Thus, the reaction is exothermic. Endothermic reactions have positive heats of formation. This occurs when the energy it takes to break the bonds is greater than the energy released when making the bonds [67]. The following formula estimates the heats of formation:

Equation 2.1

$$\Delta H_f = E_c - \sum_i x_i E_i$$

where E_c is the calculated total energy of the compound E_i is the estimated total energy of the element i in the compound. The heats of formation for the polymorphs studied will be calculated using the following expression [68]:

Equation 2.2 heats of formation

$$\Delta H_f = [E_{CaMn_2O_4} - E_{Ca} - 2E_{Mn} - 4E_O]$$

where $E_{CaMn_2O_4}$ is the total energy of the $CaMn_2O_4$ compound, while E_{Ca} , E_{Mn} and E_O

are the elemental energies of Calcium (Ca), Manganese (Mn) and Oxygen (O) respectively. The stoichiometric coefficients determine how the heats of formation are applied. For example, if two moles of a product are formed, the heat of formation for that product must be multiplied by two. The correct application of stoichiometry ensures that the total enthalpy change for the reaction is accurately calculated.

2.2.3. Density of States (DOS)

One can find the energies and wavefunctions of a particle of interest by solving its Schrödinger equation (SE). Knowing all the possible energies and wavefunctions will give us complete (almost) information about a system (particle) of interest. However, calculating every possible carrier wavefunction with its corresponding energy is impractical since many valid energies with associated wavefunctions exist in some cases where some states possess the same energy. This problem can be solved using the density of states (DOS). The density of states is a function that, when multiplied by an interval of energy, provides the total concentration of available states of a system in that energy range [69, 70]. This can be derived from basic quantum mechanics.

Equation 2.3

$$N_{interval} = \rho_{energy}(E)dE$$

$N_{interval}$ – represents carrier density present in the energy range dE

$\rho_{energy}(E)$ – represents our desired density of states function.

To represent the total concentration of available states in a system between E_1 and E_2 , one can integrate the DOS over the range of E_1 to E_2 which yields:

Equation 2.4 Density of States

$$N(E) = \int_{E_1}^{E_2} \rho_{energy}(E) dE$$

2.2.4. Elasticity

When an outside force is applied to a solid, its original shape and form change depending on the nature of the force [71]. We call this process deformation. During deformation, the atoms are displaced from their equilibrium positions. This results in the change in separation distance between the atoms. When the distance increases, strong, attractive forces develop, and strong repulsive forces develop when it decreases. These attractive and repulsive forces

try to restore the atoms to their lattice sites. We call these forces restoring forces. This phenomenon is called elasticity (the ability of matter to regain its original shape and size after deformation). There are two groups of internal restoring force, namely stress and strain. Stress is defined as the internal restoring force acting per unit area of the cross-section of a deformed body, and Strain is defined as the change in dimension per unit dimension of the material [72]. The stress-strain relationship helps us understand the elasticity properties. Thankfully, Robert Hooke [73] established a law of elasticity named after him in 1678. This law states that within the elastic limit, stress is directly proportional to the corresponding strain, mathematically written as $stress \propto strain$

Or

Equation 2.5 Stress-strain Relationship

$$\frac{stress}{strain} = constant(E)$$

where E is the proportionality constant. The constant measures a solid's elasticity, which we call this constant modulus of elasticity. There are three kinds of stress: longitudinal, normal, and shear. Each relationship has its unique constant modulus. For the longitudinal stress-strain relationship, we have Young's modulus (E); the normal stress-volume strain relationship has the bulk modulus (B or K), and the shear stress-strain relationship has the shear modulus (G) or modulus of rigidity. The elastic constant C relates the stress and strain linearly as follows:

Equation 2.6 Stress components in terms of elastic and strain components

$$\sigma_{ij} = \sum_{kl} C_{ijkl} \epsilon_{kl}$$

with σ stress components, C elastic component and ϵ is the strain components. This summation gives us a system of linear equations which can be represented in a matrix form.

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ \epsilon_{yz} \\ \epsilon_{zx} \\ \epsilon_{xy} \end{pmatrix}$$

Notice that the matrix C has 36 components instead of the 81, these components became 36 components due to the symmetrical form of σ_{ij} and ε_{ij} each of them having 6 independent components. The constants are denoted by C_{mn} where indices m and n are defined as 1 = xx, 2 = yy, 3 = zz for compression components, 4 = yz, 5 = zx, and 6 = xy for shear components. Some of the components turn to zero due to the structural symmetry of the crystal. The following matrix shows the resulting elastic constants for orthorhombic crystal systems.

$$\begin{vmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{vmatrix}$$

Others are the same particularly in cubic crystals $C_{11} = C_{22} = C_{33}$, $C_{44} = C_{55} = C_{66}$, $C_{12} = C_{21} = C_{23} = C_{32} = C_{13} = C_{31}$ resulting in 3 independent constants. (We only showed the matrix for a cubic and orthorhombic crystal systems since the structures we are investigation are a cubic structure and two orthorhombic structures.)

$$\begin{vmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{vmatrix}$$

For a cubic system the following criteria should be satisfied for the system to be determined as elastically stable [74]:

Equation 2.7 Elastic stability criteria for cubic system

$$C_{44} > 0 ; C_{11} > |C_{12}| ; C_{11} + 2C_{12} > 0$$

The elastic module for such crystal system can be determined using the following expressions:

Equation 2.8 Elastic moduli for cubic crystal

$$B = \frac{C_{11} + 2C_{12}}{3}$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, G_R = \frac{C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}, \quad G = G_H = \frac{G_V + G_R}{2}$$

$$E_{\mathcal{X}} = \frac{9B_{\mathcal{X}}G_{\mathcal{X}}}{3B_{\mathcal{X}} + G_{\mathcal{X}}}, \mathcal{X} = V, R, H$$

The orthorhombic crystals elastic constants are reduced to 9 (C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} , C_{66}) due to crystal symmetry [75, 76, 77].

For an orthorhombic system to be considered elastically stable the following Born necessary elastic stability conditions must be satisfied.

Equation 2.9 Mechanical stability conditions for orthorhombic crystals

$$C_{ij} > 0 \text{ where } ij = 123456$$

$$C_{11} + C_{33} - C_{12} > 0$$

$$C_{11} + C_{22} - 2C_{12} > 0$$

$$C_{22} + C_{33} - 2C_{23} > 0$$

$$C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0$$

We can determine the elastic moduli using the following expressions for an orthorhombic system:

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Equation 2.10 Bulk modulus (B) for orthorhombic system

$$B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23})$$

$$\frac{1}{B_R} = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})$$

$$B_H = \frac{1}{2}(B_V + B_R)$$

for the Bulk moduli (B)

Equation 2.11 Shear modulus (G) for orthorhombic system

$$G_V = \frac{1}{15}[C_{11} + C_{22} + C_{33} - (C_{12} + C_{13} + C_{23})] + \frac{3}{15}(C_{44} + C_{55} + C_{66})$$

$$\frac{1}{G_R} = \frac{1}{15}[4(S_{11} + S_{22} + S_{33}) + 3(S_{44} + S_{55} + S_{66}) - 4(S_{12} + S_{13} + S_{23})]$$

$$G_H = \frac{1}{2}(G_V + G_R)$$

for the Shear moduli (G)

Equation 2.12 *Young's modulus (E)*

$$E_{\mathcal{X}} = \frac{9B_{\mathcal{X}}G_{\mathcal{X}}}{3B_{\mathcal{X}} + G_{\mathcal{X}}}, \mathcal{X} = V, R, H$$

For Young's modules (E).

The bulk modulus (B) represents the strain response of a body to stress involving a change in volume without a change of shape. Strain response occurs when the body is under external stress. The bulk modulus helps us determine a material's resistance to fracture. The Shear modulus (G) represents the strain response of the body to shear stress. This involves the change of shape without change of volume, and Young's modulus (E) measures the stiffness of an isotropic elastic. The plastic deformation resistance of a material can be represented by its shear modulus. Notice that B and G have three expressions, each with V, R and H subscripts. These are approximations that were described by Voigt (V), Reuss (R) and Hill (H), which are now known as the Voigt-Reuss-Hill (VRH) approximation. The Voigt (V) and Reuss (R) approximations represent the theoretical maximum and minimum values of isotropic elastic moduli, respectively, while the Hill (H) approximation is the average [65].

The S_{ij} coefficients are entries in the inverse matrix S of the elastic constant's matrix C . These S_{ij} coefficients can be determined using the following [78]:

Equation 2.13 *Coefficients for inverse matrix S for orthorhombic system*

$$\begin{aligned} S_{11} &= \frac{C_{22}C_{33} - C_{23}^2}{C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2} \\ S_{12} &= \frac{C_{13}C_{23} - C_{12}C_{33}}{C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2} \\ S_{13} &= \frac{C_{12}C_{23} - C_{22}C_{13}}{C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2} \\ S_{22} &= \frac{C_{11}C_{33} - C_{13}^2}{C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2} \\ S_{23} &= \frac{C_{12}C_{13} - C_{11}C_{23}}{C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2} \\ S_{33} &= \frac{C_{11}C_{22} - C_{12}^2}{C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2} \\ S_{44} &= \frac{1}{C_{44}}; \quad S_{55} = \frac{1}{C_{55}}; \quad S_{66} = \frac{1}{C_{66}} \end{aligned}$$

Chapter 3

Method

3.1. Density Functional Theory (DFT)

This study used a computational approach based on the Density Functional Theory (DFT) method. DFT is widely used to solve the ground-state many-electron problems, in particular atoms, molecules, and the condensed phases in quantum chemistry, computational material science, biochemistry, and nano-electrons to determine the properties of materials. This theory utilizes functionals, which are functions of another function, specifically the spatially dependent electron density as opposed to the wavefunction in quantum mechanics [79]. Hence, the name "density functional theory" stems from the fact that it relies on the functionals of electron density. The theory stems from the work of Thomas [80] and Fermi [81] expressing electronic structure and was subsequently developed by Hohenberg and Kohn [82] and later Kohn and Sham [83], hence is normally referred to as the Kohn-Sham density functional theory (KS-DFT). This theory imagines a reference system of simplicity with non-interacting electrons in a common one-body potential V_{ks} yielding the same density as the "real" fully interacting system, meaning that DFT requires approximations for the exchange-correlation (XC) energy as a functional of the density [84]. There are different ways to numerically carry out the DFT formalism, with the most used method being the plane wave pseudopotential (PWP) method involving the expansion of the wave function in plane-waves and a pseudopotential replacing the nucleus and core electrons, which gives a computationally very efficient approach allowing the study of supercells with hundreds of atoms on modest sized parallel computers [85, 86]. There are several approximations required to implement the theory. These are the choice of basis set, XC functional, mesh size for Brillouin zone (BZ) integration, and plane-wave cut-off for plane-wave basis [87]. DFT is based on the Hohenberg-Kohn and Kohn-Sham theorems. DFT practical implementation require an explicit construction of the Hohenberg-Kohn free energy functional $F_{HK}[\rho(r)]$ which is given as

Equation 3.1 Hohenberg-Kohn free energy functional

$$F_{HK}[\rho(r)] = F_{ni}[\rho(r)] + E_{es}[\rho(r)] + E_{xc}[\rho(r)]$$

where $F_{ni}[\rho(r)]$ is the sum of the noninteracting kinetic energy, $E_{es}[\rho(r)]$ is the electrostatic energy and $E_{xc}[\rho(r)]$ the XC energy which is defined as the remainder that contains

everything that is not included in $F_{ni}[\rho(r)]$ and $E_{es}[\rho(r)]$. $E_{es}[\rho(r)]$ can be easily expressed as

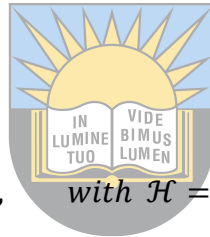
Equation 3.2 *Electrostatic energy*

$$E_{es}[\rho(r)] = \frac{e^2}{2} \int \frac{dr dr'}{|r - r'|} \rho(r) \rho(r')$$

$F_{ni}[\rho(r)]$ and $E_{xc}[\rho(r)]$ are complicated to express explicitly because $F_{ni}[\rho(r)]$ requires full understanding of the quantum-mechanical noninteracting problem and $E_{xc}[\rho(r)]$ contains all the many-body physics. There are two alternative methods for tackling this and the orbital method developed by Kohn and Sham is one of them. Kohn and Sham in their quest to do quantitative modelling of the electronic structure introduced the orbital method in which F_{IN} (sum of the noninteracting kinetic energy) can be evaluated exactly [83]. To evaluate the kinetic energy of N noninteracting particles given only the density distribution $\rho(r)$, Kohn and Sham found the corresponding potential $V_{eff}(r)$ and used the noninteracting Schrodinger equation,

Equation 3.3 *KS equation from SE*

$$\mathcal{H}\Psi_i(r) = \varepsilon_i \Psi_i(r), \quad \text{with } \mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r)$$



such that $\rho(r) = \sum_{i=1}^N |\Psi_i(r)|^2$. ε_i are nondecreasing thanks to the ordering of the states Ψ_i . If ε_N is degenerate with ε_{N+1} then fractional occupations f_i are used with $\rho(r) = \sum_{i=1}^{\infty} f_i |\Psi_i(r)|^2$. But if only spin degeneracy is involved, then the density is not affected. The kinetic energy is expressed as

Equation 3.4 *KS equation for Kinetic energy*

$$F_{ni}[\rho(r)] = \sum_{i=1}^N \langle \Psi_i | \hat{t}_i | \Psi_i \rangle = \sum_{i=1}^N \varepsilon_i - \int dr \rho(r) V_{eff}(r)$$

where $\hat{t}_i$ is the kinetic energy operator for the i th electron ($\hat{T} = \sum_i \hat{t}_i$). The density distribution or the effective potential are unknown in practice only the external potential of the system is known. Taking the functional derivative of $F_{HK}[\rho(r)]$ and rearrange the terms we can get the effective potential.

Equation 3.5 *KS equation for effective potential*

$$V_{eff}(r) = V(r) - e\phi(r) + V_{xc}(r)$$

$$\frac{\delta F(r)}{\delta \rho(r)} = -V(r) \text{ both interacting and noninteracting systems}$$

The electrostatic potential is given as

Equation 3.6 KS equation for electrostatic potential

$$\phi(r) = -e \int dr' \frac{\rho(r')}{|r - r'|}$$

and the XC potential is expressed as

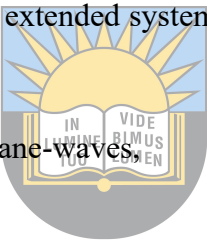
Equation 3.7 KS equation for XC potential

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}.$$

The practical approximation of E_{xc} can be determined using XC functional. V_{eff} can be found from $\rho(r)$ for a given $V(r)$. These are called the Kohn-Sham (KS) equation of DFT that we can use to treat both finite and extended systems and must be solved self-consistently [88].

The wave functions are expanded in plane-waves.

Equation 3.8 wave function



$$\Psi(r) = \sum_g a(g) e^{ig \cdot r}$$

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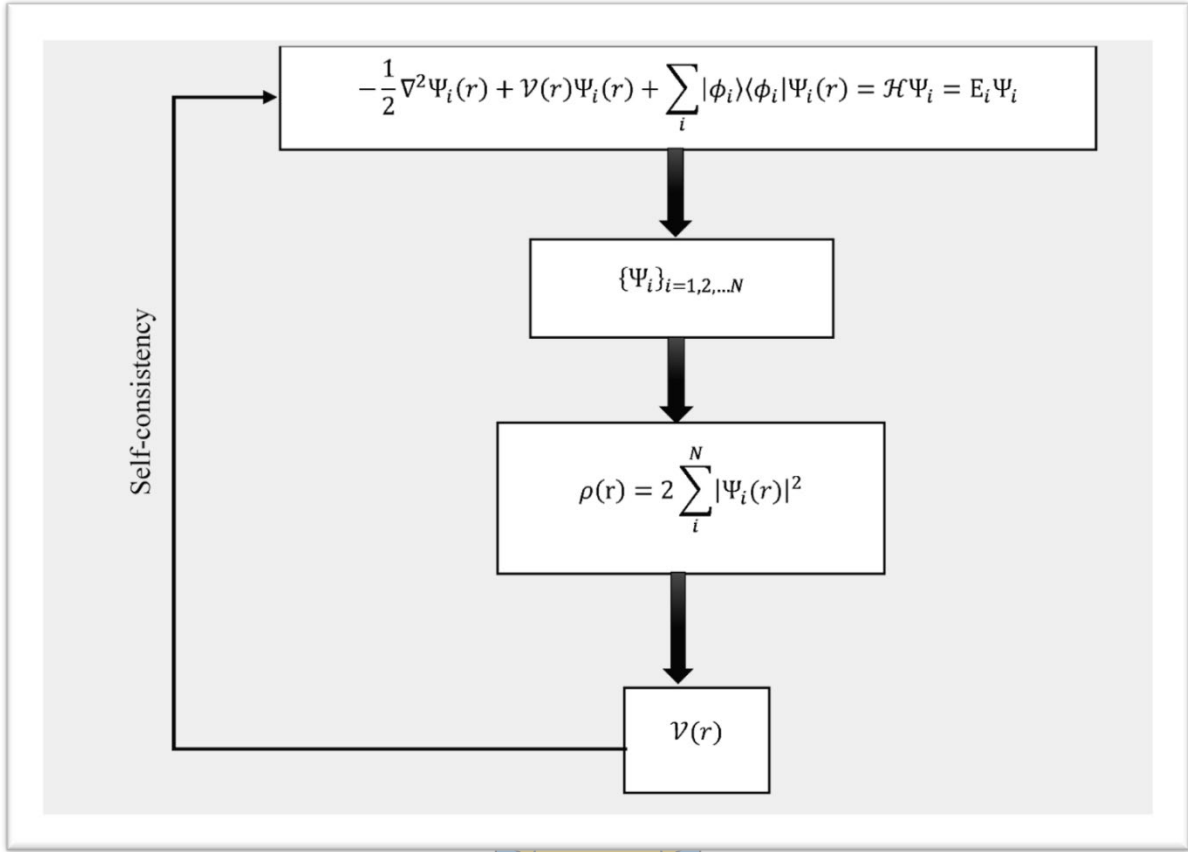
The selection of the number of plane-waves is determined by a cut-off E_{cut} in the plane-wave kinetic energy $\frac{1}{2} |g|^2$ where $\{g\}$ are the reciprocal lattice vectors [86].

Equation 3.9 cut-off energy

$$E_{cut} = \frac{\hbar^2}{2m} |G_{cut}|^2 \quad \text{with } |G + k| < G_{cut}$$

The cut-off used to generate the pseudopotentials and volume per axis is highly correlated to the plane wave parameters. Cut-off and k-points should be independent of the functional but mainly dependent on the type of materials [87].

Figure 3.1 Basic chart of a DFT calculation:



3.2. Exchange-Correlation (XC) Functional

The XC energy is generally defined as the sum of the remaining interactions from the noninteracting kinetic energy, and the electrostatic energy excluded (continuous transition between the interacting and noninteracting systems). The XC energy alone carries the entire burden of the true n -electron effects. This is the result of using a fictitious model instead of the true n -electron model. Orbitals require electrons with the same spin to occupy distinct orthogonal orbitals which results in a special separation between those electrons. This will lead to less repulsion, which lowers the system energy and reduces electron density. This is referred to as the exchange hole, which is responsible for the exchange energy. The self-interaction in the Hartree energy will be removed due to electrons moving away from each other. Two electrons with different spin can occupy the same orbital but will repel each other due to their similar charge. This phenomenon also reduces the electron density and is called the correlation hole. The XC energy is due to the exchange energy and correlation energy. The XC energy can be assumed to be semilocal or local functional of the electron density [89]. The local XC energy per electron is the electrostatic interaction energy of an electron at r with XC hole density at r' :

Equation 3.10 XC energy

$$\epsilon_{xc}[\rho(r)] = \frac{1}{2} \int \frac{\rho_{xc}^{hole}(r, r')}{|r - r'|} dr'$$

Integrating over the whole space of the density multiplied by the local XC energy per electron gives us the XC energy functional.

Equation 3.11 XC energy Functional

$$E_{xc}[\rho(r)] = \int \rho(r) \epsilon_{xc}(r, \rho) dr$$
$$E_{xc}[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r) \rho_{xc}^{hole}(r, r')}{|r - r'|} dr dr'$$

ρ_{xc}^{hole} represents the region in r' -space from which an electron is ‘missing’ if it is known at point r . Hence the total amount of the XC hole is subject to the sum rule which equals exactly one electron.

Equation 3.12 Unity


$$\int \rho_{xc}^{hole}(r, r') dr' = -1$$

Two simple methods are used to determine the approximation of the XC functional. These are the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA).

3.2.1. Local Density Approximation (LDA)

Kohn and Sham suggested the local density approximation (LDA) as a practical approximation expression for XC functional. As the term local suggests, we simply take the electron density local to each electron which transforms the electron density into many pieces of uniform electron density with different values. The XC energy can be determined by finding the energies associated with each local uniform electron density and sum them up (it's almost similar to what mathematicians do when finding the area under a curve). Simply put the LDA specifies the specific functional by finding the electronic density at each point in space. This is the primary principle behind LDA [83]. Since these local uniform electron densities around each electron are homogenous, we can determine the exchange energies per electron with electron density, $\rho(r)$.

Equation 3.13 Exchange energy for homogeneous electron gas

$$\mathcal{E}_x^{hom}(\rho) = -C\rho^{\frac{1}{3}}(r)$$

Using Hartree-Fock (HF) methods, one can determine the exact exchange energy, but it's more computationally expensive than Hartree or kinetic energy calculations. Thus, it's better to approximate the exchange energy along with the correlation energy assuming a homogenous electron gas.

Equation 3.14 *Exchange energy Functional for LDA*

$$E_x^{LDA}[\rho(r)] = -C \int \rho^{4/3}(r) dr$$

$$V_x^{LDA}[\rho(r)] = -C\mathcal{E}_x^{hom}[\rho(r)] = -C\rho^{\frac{1}{3}}(r)$$

The correlation energy is difficult to express in an analytic form, only its lower and upper bounds can be analytically expressed. The upper bound (high-density limit) correlation energy is given as [90, 91]

Equation 3.15 *Upper bound Correlation energy Functional for LDA*

$$E_C^{LDA} = C_1 + C_2 \ln r_s + r_s(C_3 + C_4 \ln r_s), \text{ with } r_s < 1$$

and the lower bound (low-density limit)

Equation 3.16 *Lower bound Correlation energy Functional for LDA*

$$E_C^{LDA} = \frac{1}{2} \left(\frac{\rho_0}{r_s} + \frac{\rho_1}{r_s^{3/2}} + \dots \right)$$

C_i are constants and r_s is the Wigner-Seitz radius (roughly the mean interelectronic spacing) given as

Equation 3.17 *Wigner-Seitz radius*

$$r_s = \sqrt[3]{\frac{3}{4\pi\rho(r)}}$$

The sum of two functions is a function on itself, thus we expect the XC energy to be a functional since both the exchange and correlation energies are functionals of the electron density.

Equation 3.18 *XC energy Functional for LDA*

$$E_{XC}^{LDA}[\rho(r)] = E_X^{LDA}[\rho(r)] + E_C^{LDA}[\rho(r)]$$

By multiplying $\mathcal{E}_x^{hom}[\rho(r)]$ with the local electron density and integrating it over space, we get the XC energy of the LDA.

Equation 3.19 XC Functional for LDA

$$E_{XC}^{LDA}[\rho(r)] = \int \rho(r) \mathcal{E}_{xc}^{hom}[\rho(r)] dr$$

$$E_{XC}^{LDA}[\rho(r)] = \int \rho(r) [\mathcal{E}_x^{hom}[\rho(r)] + \mathcal{E}_c^{hom}[\rho(r)]] dr$$

By taking the derivative of the energy functional, the corresponding XC potential of the LDA is

Equation 3.20 XC potential for LDA

$$V_{XC}^{LDA}[\rho(r)] = \frac{\delta E_{XC}^{LDA}[\rho(r)]}{\delta \rho(r)}$$

The LDA works well with covalent systems and simple metals. The LDA doesn't work well with transition metals or strongly correlated systems such as transition metal oxides (the compound we are working on hence we used GGA). There have been some improvements done to improve the accuracy of LDA and such improvement is the implementation of local spin-density approximation (LSDA). The XC hole is very different for electrons with parallel and antiparallel spin, resulting in separate densities for spin-up and spin-down electrons. These separate densities are used as functional variables $\rho_\uparrow(r)$ and $\rho_\downarrow(r)$ [$\rho_\uparrow(r) + \rho_\downarrow(r) = \rho(r)$] and the Hamiltonian contains separate potentials for spin-up and spin-down electrons [91, 92]. The LSDA functional for the XC energy is mathematically expressed as:

Equation 3.21 XC Functional for LSDA

$$E_{XC}^{LSDA}[\rho_\uparrow(r), \rho_\downarrow(r)] = \int d^3r \rho(r) \mathcal{E}_{xc}^{hom}[\rho_\uparrow(r), \rho_\downarrow(r)]$$

The use of the LDA/LSDA have decreased thanks to the introduction of the GGA which generally describes the XC energy functional more accurately.

3.2.2. Generalised Gradient Approximation (GGA)

After being suggested by Kohn and Sham, the LDA worked surprisingly well exceeding Kohn and Sham's expectations. It worked well with systems with homogeneous electron gas

or electron density that varies slightly, but not all systems are like this. The majority of majority of real systems have inhomogeneous and varying electron densities resulting in some errors and problems when calculating the XC energy using LDA or LSDA. Thus, improvements in LDA and LSDA were needed. Therefore, GGA was developed. [93]. There was an idea to include the gradient of the density to the LDA considering how inhomogeneous and varying the electron density is. With this it meant the XC functional will have the electron density and its gradient at a given point. In theory this should generate better results with the general formula with density gradient as an additional variable. However, introducing the gradient corrections in a straightforward and systematic manner by expanding around the uniform electron gas violates the sum rule resulting in less accurate results (LDA is accurate because it obeys the sum rule) [94]. Thus, various generalised gradient approximations (GGAs) were developed which succeeded in reducing errors of the LDA by factor 4.

Equation 3.22 XC Functional for GGA

$$E_{XC}^{GGA} = \int \rho(r) \mathcal{E}_{xc}^{GGA}(\rho, \nabla \rho) dr$$

The functional form of GGA in practice is expressed based on the LDA and an additional factor $f(s)$ with s depending on both the electron density and its gradient.

Equation 3.23 XC energy Functional for GGA

$$E_{XC}^{GGA}[\rho(r), s] = \int \rho(r) \mathcal{E}_{xc}^{LDA}[\rho(r)] f(s) dr$$

$$s = c \frac{|\nabla \rho(r)|}{\rho^{4/3}(r)}$$

There have been many different forms of GGA that have been proposed with the PW91 proposed by Perdew and Wang in 1992 [95] and the PBE introduced by Perdew, Berke, and Ernzerhof in 1996 [96] being the popular choices.

3.3. Density Functional Theory with Hubbard Correction (DFT+U)

Despite the robustness of density functional theory in predicting various properties in different materials, it is limited in accurately determining properties such as the electronic structure in mott insulators (semiconductors) along with transition metals with filled d and f

orbitals [97, 98, 99]. This is primarily due to the tendency of exchange functionals to overly spread out (delocalise) valence electrons and excessively stabilize metallic ground states [100, 101]. With filled d and f orbitals, the electrons are subjected to strong Coulomb interactions, and to address this, researchers looked for alternative corrective approaches which can be computationally expensive [102, 103]. One option is to utilize larger basis sets or hybrid functionals that incorporate the exact solution of the Hartree-Fock (HF) equations, which offer the potential to enhance higher accuracy levels [104]. Nevertheless, in certain instances, solving exact Hartree-Fock equations may prove inadequate in accurately predicting the bandgap for a specific group of semiconductors characterized by strong electron correlations, such as Mott insulators [100, 101].

Another alternative approach to compensate the limitations in the normal DFT, is to add a Hubbard U [100, 105] parameter to DFT calculations to treat the on-site Coulomb interaction of strongly correlated localised electrons. The Hubbard model incorporates the "on-site repulsion," which arises from the Coulomb repulsion between electrons occupying the same atomic orbitals. This feature enables the model to elucidate the transition from conducting to insulating behaviour in these systems. The DFT+ U approach has advantages over the hybrid functionals and the post-Hartree-Fock methods since it remains within the DFT formalism, and thus does not require significant alteration to the existing DFT codes leading to it being computationally less demanding, i.e. cost effective. Moreover, DFT+ U successfully corrects the electronic structure, thus further enabling further accurate calculations of other physical and chemical properties such as formation energies, densities of states, magnetic properties, and mechanical properties. Thus, a new Hamiltonian derived from the Hubbard Model (Hubbard-like term) was added to the DFT Hamiltonian, which resulted in the Density Functional Theory with the Hubbard Correction (DFT+ U) method. The newly formulated Hamiltonian can be written as follow:

Equation 3.24 *Hubbard Hamiltonian*

$$\hat{\mathcal{H}}_0 = U \sum_i \hat{n}_i \uparrow \hat{n}_i \downarrow - t \sum_{\langle ij \rangle} a_{i\sigma}^\dagger a_{j\sigma}$$

$\langle ij \rangle$ denotes nearest-neighbour atomic sites, $a_i^\dagger, a_j$ and n_i denotes electronic creation, annihilation, and number operators for electrons of spin on site i respectively. Thus, the Hubbard Hamiltonian is influenced by two key factors: the hopping amplitude, denoted as t , and the on-site Coulomb repulsion term, denoted as U . The hopping amplitude t is directly

related to the bandwidth of the valence electrons, while the on-site Coulomb repulsion term U is determined by the product of the occupation numbers of atomic states on the same site. These parameters play a crucial role in determining the behaviour of the system and are essential for understanding the electronic properties of materials.

Equation 3.25 DFT+U functional

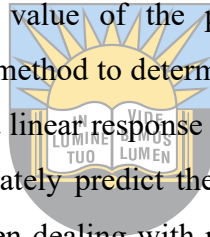
$$E^{DFT+U}[\rho(r)] = E^{DFT}[\rho(r)] + E_U^o[n_i] - E_U^{dc}[n_i]$$

$$\text{with } \rho(r) = \sum_i |\psi_i(r)|^2$$

ρ is the electron density

E_U^o is the energy contribution due to Hubbard model description, which models the localised electronic states, n_i is the orbital occupation, i is the lattice site and E_U^{dc} is the “double counting term”.

Tuning/changing the U -parameter's value of the properties of materials with existing experimental results is the most used method to determine the most suitable U -parameter [99, 103]. First-principles calculations or a linear response approach can be used to find a suitable U -parameter [106, 107]. It can accurately predict the electronic structure of some strongly correlated systems but falls short when dealing with more delocalised electrons (metals and alloys) [99].



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3.4. Plane-wave Pseudopotential Method (PWP)

3.3.1. Pseudopotentials

When one is studying condensed matter physics or material science, one is firmly interested in the valence electrons of atoms and what they do. This is simply because, during chemical bonding, the valence electrons participate while the core electrons don't. This is one of the reasons the properties of materials are determined by how the valence electrons are shared among atoms because bonds are crucial in determining most material properties. This means that whether an atom is in a chemical bond or not, the core electrons and the nucleus distribution won't change. Since the influence of the core electrons is negligible on the surrounding atoms, one can replace the core electrons and nucleus with a pseudopotential, reducing the number of electrons in the calculations. A pseudopotential replaces the atomic nucleus and the core electrons with a fixed effective potential that, in a unique sense, reproduces the effect of the nuclear potential and the orthogonality requirement [86, 79].

Modern pseudopotentials are constructed from first principles. The needed characteristics of pseudopotentials are as follows: it must be such that the valence orbital eigenvalues are the same as those in an all-electron calculation, and the atom must preserve the continuity of the wave functions and their first derivatives across the core boundary. It must be norm-conserving, meaning integrating the charge in the core region should give the same answer for the pseudo-atom and the all-electron one [79, 108]. The general form of the pseudopotential is,

Equation 3.26

$$V_{NL} = \sum_{lm} |lm\rangle V_l \langle lm| ,$$

where $|lm\rangle$ are spherical harmonics, and V_l is the pseudopotential for angular momentum (l) [109].

3.3.2. Ultrasoft Pseudopotentials

When using the plane wave pseudopotential (PWP) method on first-row elements, transitional metals, and rare-earth elements, higher computational power is required to use standard norm-conserving pseudopotentials. Vanderbilt introduced the ultrasoft pseudopotentials (US-PP) after various attempts were made to generate soft pseudopotentials in 1990. Blochl further developed the concept by combining ideas from pseudopotential and linearised augmented-plane wave (LAPW) methods in an elegant concept framework [108]. Hamann, Schluter, and Chiang were the first ones to use and introduce norm-conserving pseudopotentials. In their approach, they have a soft nodeless pseudo-(PS) wave function inside some core radius instead of an all-electron (AE) wave function [110, 111]. This has a significant restriction: the PS wave function must have the same norm as the AE wave function within the chosen core radius; outside the core radius, the PS and AE wave functions are identical. Good transferability requires a core radius around the outer-most maximum of the AE wave function. When this occurs, the AE wave functions' charge distribution and moments are well reproduced by the PS wave functions. The resulting pseudopotentials will require a sizeable plane-wave basis for elements with strongly localised orbitals. Increasing the core radius significantly beyond the outermost maximum in the AE wave function, the ultrasoft pseudopotential can reduce the plane-wave basis set [108].

3.5. Cambridge Serial Total Energy Package (CASTEP) Code

The CASTEP code is a widely used computational tool in the field of materials science and chemistry which uses quantum mechanical calculations to determine the electronic structure of solid-state materials. Developed by the Theory of Condensed Matter group at the University of Cambridge, CASTEP is a software package that allows researchers to perform first-principles calculations on the electronic structure of materials. By solving the quantum mechanical equations governing the behaviour of electrons within a material, CASTEP can provide valuable insights into its properties and behaviour. One of the key features of the CASTEP code is its ability to handle a wide range of materials, from simple elements to complex crystals and nanomaterials. This versatility allows researchers to investigate a diverse range of materials and systems, making it a valuable tool for interdisciplinary research. Additionally, CASTEP incorporates state-of-the-art algorithms and models that enable researchers to perform high-quality calculations with great efficiency. This makes it an invaluable resource for exploring new materials, designing novel compounds, and understanding the fundamental principles governing their behaviour. Payne and co-workers originally developed the CASTEP program in the late 1980s and early 1990s, which uses the combination of pseudopotentials and plane wave basis sets, enabling extremely efficient geometry optimisations of molecules, solids, surfaces, and interfaces. The CASTEP program replaces core electrons with effective potentials acting only on the system's valence electrons, which helps reduce the number of electrons in the computational calculations [79]. The first line of code was written using FORTRAN77 and 'functional programming' to produce a fully functioning program. This old version of CASTEP had no modular structure to the code and no written specifications making it difficult to further enhance or improve the code. Thus from 1999 CASTEP was redesigned, and a new modular FORTRAN 90 code was written. This new design made it easy to add new methods and technology to CASTEP. From first principles, CASTEP can calculate several physical properties of a system. CASTEP meets this goal by first calculating the total energy of the system and then determine other quantities from the total energy. Since CASTEP uses quantum mechanical calculations to determine the electronic structure, it does that by first solving the Kohn-Sham equations using plane-wave pseudopotential approach. After determining the wavefunctions, it expands them using a plane wave basis set defined using periodic boundary conditions along with Bloch's Theorem. The electron-ion potential is described by means of ab initio pseudopotentials within both norm-

conserving and ultrasoft formulations. The self-consistent, electronic wavefunctions, and corresponding charge density are obtained by using the direct energy minimisation schemes.

3.6. Methodology

All the calculations in this work were performed using the CAMbridge Serial Total Energy Package (CASTEP) simulation code embedded in the Materials Studio program [112]. CASTEP is a quantum mechanics-based code that uses the density functional theory (DFT) plane-wave pseudopotential technique to perform first-principles calculations to investigate various properties of solid-state materials. The generalised gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) with Hubbard correction (U) was chosen as the exchange–correlation functional during the calculations since it provides an adequate description of the electronic system over the local density approximation (LDA). Moreover, the on-the-fly generated (OTFG) ultrasoft pseudopotentials, known for their high accuracy in describing ground state electronic structures were preferred for all calculations. We also imposed collinear spin polarization as recommended for transition metal oxides and for the relativistic treatment, the Koelling-Harmon scheme was employed [113]. To determine the appropriate cut-off energy for the plane-wave basis and k-mesh points for the integration of the Brillouin zone (BZ), the convergence test was performed. Cut-off energies of 500eV, 750eV and 650eV and default Monkhorst-Pack k-point grid mesh of $2 \times 2 \times 2$, $2 \times 6 \times 2$ and $6 \times 6 \times 6$ were chosen for $Fd3m\text{-CaMn}_2\text{O}_4$, $Pbcm\text{-CaMn}_2\text{O}_4$, and $Pnma\text{-CaMn}_2\text{O}_4$, respectively. During geometry optimisation, the Hubbard U -correction had to be considered to deal with the strongly correlated d -orbitals in the transition manganese (Mn) atoms. A Hubbard U parameter value of 6.50eV (where $U_{eff} = U - J$, with $J = 1\text{eV}$) was determined to accurately reproduce the ground state lattice parameters that are similar to the experimental data, hence chosen in all the calculations of this study [114, 115]. Since we were dealing with systems with a large number of atoms, the LBFGS (low-memory Broyden–Fletcher–Goldfarb–Shanno) algorithm was used for the geometry optimization of the crystal structures. The LBFGS algorithm incorporates a universal sparse preconditioner that significantly speeds up geometry optimization. This acceleration is particularly noticeable for small systems, where it can cut optimization time in half, and for very large systems, where it can reduce optimization time by a factor of ten. From the geometry optimization calculation, properties such as structural lattice parameters and heats of formation were obtained. After performing full geometry optimization, subsequent calculations of the electronic density of states (DOS) and band structure; elastic constants and moduli were performed on the optimized crystal

systems. The elastic constants and moduli were computed using the MT-Elastic Properties module as integrated into the CASTEP interface. This module computes elastic constants and other mechanical and thermodynamic properties using the stress-strain relation. The maximum strain amplitude was set at 0.004 for Pbcm-CaMn₂O₄, 0.003 for Fd3m-CaMn₂O₄ and 0.001 for Pnma-CaMn₂O₄. Lastly, the densities of states and band structures were computed using the properties module also integrated in Materials Studio.



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Chapter 4

Results and Discussions

4.1. Convergence Test

The first step before proceeding with calculations of any properties is to perform the convergence test to determine the suitable cut-off energies for the plane wave basis and the k-points for the Brillouin zone sampling. Accurate calculations rely on well-converged geometry in the input structure, as optimization to a true ground state requires well-converged forces. Convergence of k-points with respect to energy assures that material properties will remain unaffected by the number of k-points used. Additionally, it ensures that we are not using an excessive number of k-points, which could lead to costly computations. **Table 4.1** and **Figure 4.1** present the total energy versus the customized cut-off energy of the CaMn_2O_4 systems. Cut-off energies of 500 eV, 750 eV and 650 eV were chosen.

Table 4.1 Cut-off and total energies for $\text{Fd3m-CaMn}_2\text{O}_4$, $\text{Pbcm-CaMn}_2\text{O}_4$, and $\text{Pnma-CaMn}_2\text{O}_4$.

Cut-off (eV)	Total Energy (eV)		
	$\text{Fd3m-CaMn}_2\text{O}_4$	$\text{Pbcm-CaMn}_2\text{O}_4$	$\text{Pnma-CaMn}_2\text{O}_4$
100	-15101.0262	-30 148.60314	-29937.0858
150	-16256.5134	-32 524.20591	-32574.3989
200	-16702.6293	-33 477.47552	-33439.2781
250	-16843.0612	-33 729.24076	-33726.6994
300	-16911.5129	-33 859.62435	-33849.6010
350	-16942.3778	-33 914.31101	-33908.4815
400	-16959.5317	-33 942.95502	-33935.1816
450	-16966.3098	-33 957.41091	-33946.7883
500	-16969.3428	-33 963.22805	-33952.6666
550	-16970.8612	-33 965.80541	-33954.0868
600	-16971.3976	-33 966.87721	-33955.1445
650	-16971.8463	-33 967.25815	-33955.2058
700	-16971.8949	-33 967.32266	-33955.1445
750	-16971.9016	-33 967.34773	-33955.0754
800	-16971.9245	-33 967.33844	-33955.0782
850	-16971.9302	-33 967.32564	-33955.0892
900	-16971.9395	-33 967.33151	-33955.0874

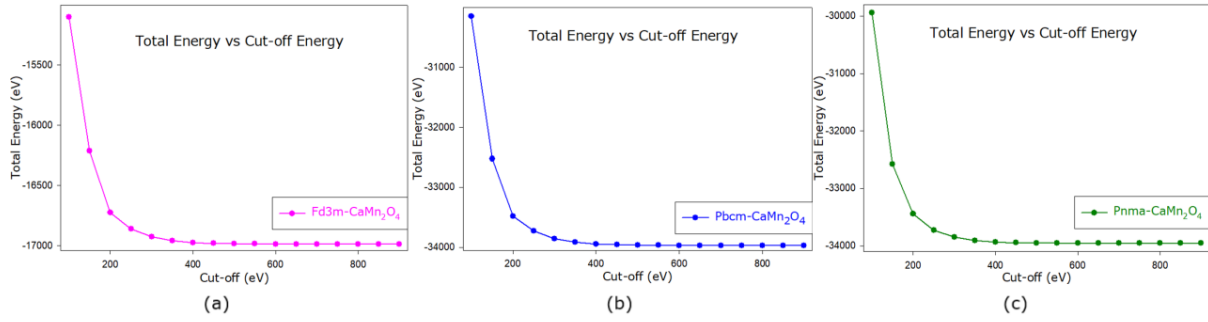


Figure 4.1 Total energy vs Cut-Off energy for (a) Fd3m-CaMn₂O₄, (b) Pbcm-CaMn₂O₄, and (c) Pnma-CaMn₂O₄.

4.2. Determination of Hubbard U Correction

The Calcium manganese oxides (CaMn₂O₄) compounds investigated in this work are a strongly correlated transition oxide which contain a manganese (Mn) element with localised open shell d orbitals. CaMn₂O₄ is a complex many-electron system composed of electrons occupying the localised orbitals. These electrons are subjected to strong correlations among each other and have a weak coupling with the extended states. The idea in applying the Hubbard correction is to isolate few degrees of freedom relevant to the correlation, thus pushing the localised d states in the band gap away from the Fermi energy [105].

Table 4.2 U_{eff} values vs lattice parameters for Pbcm-CaMn₂O₄

$U_{eff}(eV)$	Band gap (eV)
1.0	1.462
1.5	1.353
2.0	1.286
2.5	1.261
3.0	1.222
3.5	1.168
4.0	1.164
4.5	1.093
5.0	0.926
5.5	0.824
6.0	0.710
6.5	0.599
7.0	0.473
7.5	0.356
8.0	0.236
8.5	0.087

Thus, applying the Hubbard correction is crucial in predicting different properties of the transition metal oxides. One of the methods to find a suitable numerical value of the effective potential U_{eff} is to calculate the material's properties such as lattice parameters and band

gaps, compare with existing experimental results, and choose the U value that gives the least percentage difference. We used the predetermined cut-off energy of 750eV and, k-points mesh of $6 \times 6 \times 6$, PBE-GGA functional, varied the U value and optimized the structure to find its band gap. The results are recorded in **Table 4.2**. We chose $U = 6.50\text{eV}$ ($U = U_{eff} - J$, $J = 1\text{eV}$) due to the band gap found to be in good agreement with the reported experimental value [35].

It is important to note that utilizing excessively large values of U can result in the over-localization of states and lead to an unphysical flattening of the relevant bands. This can negatively impact the fitting process, unlike many other properties. Additionally, an increase in the U value may lead to an overestimation of lattice constants and an inaccurate estimation of ground state energy due to electronic interaction errors. It is crucial to carefully consider and optimize the value of U to ensure accurate and reliable results in computational simulations.

4.3. Structural Properties

Table 4.3 lists the calculated structural cell parameters and enthalpies of formation for the three considered CaMn_2O_4 polymorphs. The following primitive Bravais lattice configurations were used: face-centred cubic $\text{Fd}3\text{m}-\text{CaMn}_2\text{O}_4$ with $\alpha = \beta = \gamma = 60^\circ$; body-centred orthorhombic $\text{Pnma}-\text{CaMn}_2\text{O}_4$ with $\alpha = \beta = \gamma = 90^\circ$ and orthorhombic $\text{Pbcm}-\text{CaMn}_2\text{O}_4$ with $\alpha = \beta = \gamma = 90^\circ$. Upon comparing the computed lattice parameters with the available experimental results, we observed a percentage difference of less than 5%, validating the computational approach employed to determine the properties of these polymorphs. Moreover, they are in good agreement with the previous computational work [35]. We also note that our DFT+ U results overestimate the experimental data.

Table 4.3 Calculated equilibrium lattice parameters, unit cell volume and enthalpy of formation for $\text{Fd}3\text{m}-\text{CaMn}_2\text{O}_4$, $\text{Pbcm}-\text{CaMn}_2\text{O}_4$ and $\text{Pnma}-\text{CaMn}_2\text{O}_4$. Experimental data is also given where available.

	Fd3m-CaMn_2O_4	Pbcm-CaMn_2O_4 [116]	Pnma-CaMn_2O_4
a (Å)	6.065	3.258 (3.15)	9.441
b (Å)		10.371 (9.95)	3.220
c (Å)		9.840 (9.67)	11.006
V (Å³)	157.760	332.488	334.539
ΔH (eV)	-1.697	-3.396	-3.396

We note that the orthorhombic Pbcm-CaMn₂O₄ (332.448 Å³) and Pnma-CaMn₂O₄ (334.539 Å³) have relatively large cell volumes as compared to cubic Fd3m-CaMn₂O₄ (157.760 Å³) system. The large volumes suggest that the Pbcm-CaMn₂O₄ and Pnma-CaMn₂O₄ polymorphs offer large volumetric capacity and adequate diffusion channels for Ca-ion insertion and removal. According to a study done by Xuefeng Wei et al. [117], cathodes with a high volumetric capacity exhibit superior rate capability. This indicates that Pbcm-CaMn₂O₄ and Pnma-CaMn₂O₄ polymorphs are likely to exhibit better Ca reversible rate capability than Fd3m-CaMn₂O₄ during the insertion and removal of Ca ions from the host structure.

4.4. Thermodynamic Properties

In order to determine the thermodynamic stability of our systems, we computed the enthalpy of formation. Enthalpies of formation give an insight into the type of reaction during the formation of a compound. Compounds with negative enthalpies of formation are exothermic and positive enthalpies of formation indicate endothermic reaction. The enthalpies of formation as listed in **Table 4.3** were calculated using **Equation 2.2**. We note that the computed enthalpies of formation for Fd3m-CaMn₂O₄, Pbcm-CaMn₂O₄ and Pnma-CaMn₂O₄ structures are negative suggesting that during the formation of these structures, energy will be excreted (energy will be a product) and thus thermodynamic stability. The negative heats of formation suggests that the three considered polymorphs can be synthesized experimentally without the need to inject additional energy into the reaction. Moreover, they assure safety during the cycling performance of the battery chemistry. The orthorhombic Pbcm-CaMn₂O₄ and Pnma-CaMn₂O₄ polymorphs, which are volumetrically large, exhibit lower enthalpies of formation (-3.396 eV) compared to the cubic Fd3m-CaMn₂O₄ (-1.697 eV). This suggests that they are more thermodynamically stable than Fd3m-CaMn₂O₄. Therefore, Pbcm-CaMn₂O₄ and Pnma-CaMn₂O₄ are more easily formed than Fd3m-CaMn₂O₄ under ambient conditions [35].

4.5. Electronic Properties

In this subsection, we present the total electronic density of states (DOS) for CaMn₂O₄ and partial density of states (PDOS) for Ca, Mn, and O for the three polymorphs. The total DOS for the three polymorphs and PDOS for the atoms Ca, Mn and O are shown in **Figure 4.3**. Our DFT+*U* calculated densities of states reveal that the cubic Fd3m-CaMn₂O₄ has a wide energy band gap of 1.966 eV around the Fermi level, suggesting semiconductor behaviour characteristic. On the other hand, the total density of states for Pbcm-CaMn₂O₄, and Pnma-

CaMn_2O_4 polymorphs reveals metallic conductivity in the spin-up energy bands, as indicated by the electronic overlap between the valence and conduction bands near the Fermi level. The Fermi level is the highest occupied energy level at absolute zero temperature (0 K). It serves as a crucial reference point for the energy distribution of electrons within a material, aiding in the understanding of how electrons fill the available energy states [118]. Moreover, their density of states near the Fermi level are high due to the presence of delocalized electrons, leading to high electrical conductivities.

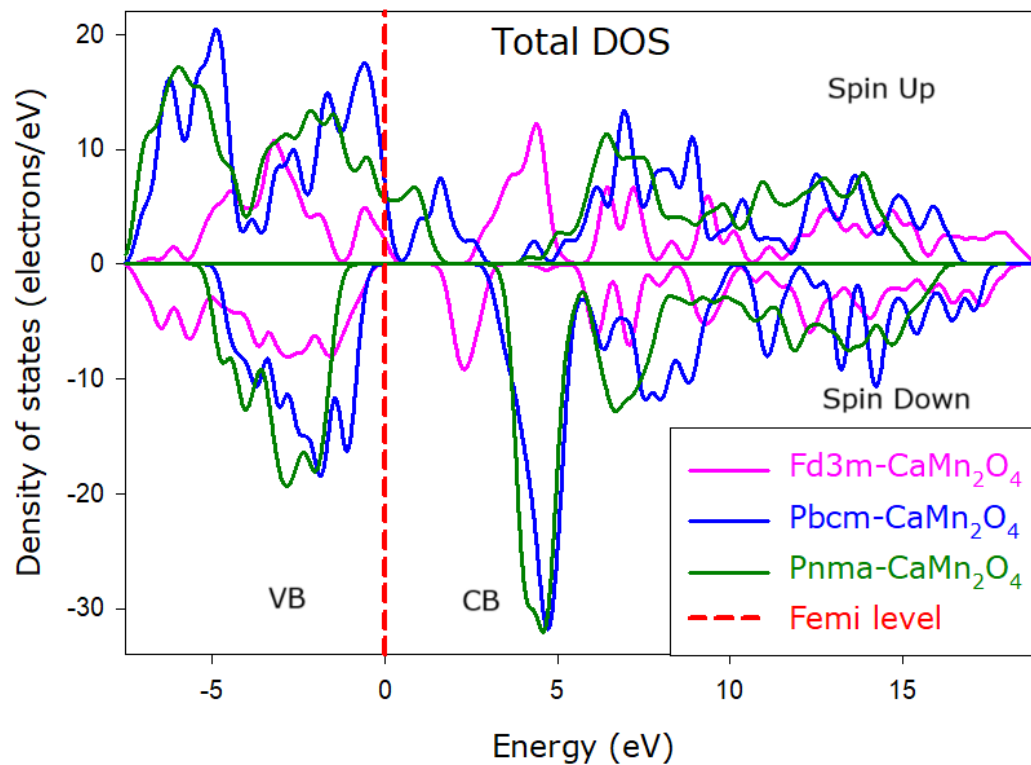


Figure 4.2 Total density of states for $\text{Fd3m-CaMn}_2\text{O}_4$, $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Pnma-CaMn}_2\text{O}_4$. Fermi level is used as zero on the energy level

This also suggests that electrons are permitted to overlap from the valence band (VB) to conduction band (CB) in $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Pnma-CaMn}_2\text{O}_4$ polymorphs, while not permitted in $\text{Fd3m-CaMn}_2\text{O}_4$. Thus $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Pnma-CaMn}_2\text{O}_4$ polymorphs exhibit good electronic conductivity. Moreover, we observe that the $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Pnma-CaMn}_2\text{O}_4$ plots (**Figure 4.2**) are characterised by pronounced and shallow pseudo gaps (region of suppressed spectral weight) around the Fermi level, respectively, suggesting strong electronic correlations. Since the presence of a pseudo gap is associated with a suppression of certain electronic states, it can lead to a more stable electronic configuration overall, resulting in improved thermal and mechanical stability of the material and enhanced resistance to external perturbations [119]. Further analysis of the TDOS for $\text{Fd3m-CaMn}_2\text{O}_4$ reveals a high

concentration of energy states near the Fermi level within the valence band (VB), while the conduction band (CB) states are located further from the Fermi level. This configuration indicates p-type behaviour, suggesting that electrons in the valence band require less energy to move to the Fermi level, thereby creating holes. In p-type materials, electrical conduction occurs primarily through the movement of holes, which are the absence of electrons in the valence band. The presence of states close to the Fermi level implies that doping these materials could enhance their electrical conductivity, as more states would be available for thermal excitation near the Fermi level [120]. For Pbcm- CaMn_2O_4 and Pnma- CaMn_2O_4 , the valence states are close to the Fermi level, while in the CB, only spin-up states are near the Fermi level, with spin-down states positioned further away. This spin-split behaviour suggests that Pbcm- CaMn_2O_4 and Pnma- CaMn_2O_4 might exhibit spintronic properties, where both the spin and charge of the electrons influence the material's conductive behaviour [121].

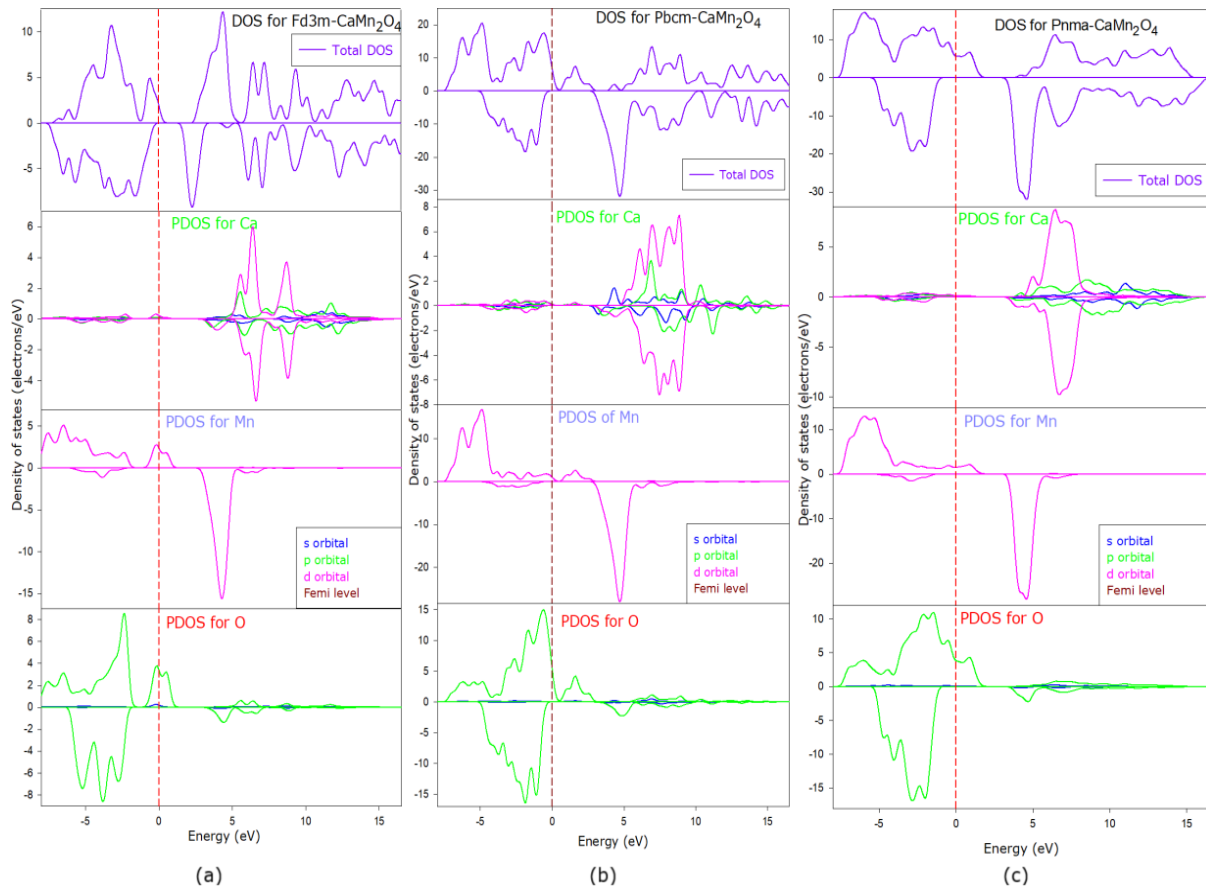


Figure 4.3 (a) Fd3m- CaMn_2O_4 , (b) Pbcm- CaMn_2O_4 and (c) Pnma- CaMn_2O_4 . The Fermi energy is used as zero on the energy scale.

The partial densities of states (PDOS) reveal the presence of localized or delocalized states and the contribution of specific orbitals to the overall electronic structure and orbital hybridization. By breaking down the total density of states into partial contributions from

different atomic orbitals or regions within the material, we can better understand the bonding and electronic behaviour of our systems. Our DFT+*U* calculated PDOS show that the states around the Fermi level predominantly emanate from the hybridization of oxygen (O) 2*p* states and manganese (Mn) 3*d* states, with minimal contribution from calcium states. Thus, the electronic behaviour of these polymorphs is significantly influenced by Mn and O states, which are the constituents of the host structure. Further analysis of the PDOS is summarised as follows. The spin-down peak in the range 4.5 – 7 eV emanates from the Mn 3*d* states. The VB is characterised by the hybridisation of O 2*p* states and Mn 3*d* state, while the CB is predominated by *d* states of Ca.

4.6. Mechanical Properties

Understanding the elastic properties of a material is essential to understanding the mechanical properties and predicting the material's response to various loading conditions such as external pressure. They quantify the relationship between stress and strain in a material. By knowing the elastic constants of a material, engineers can predict how a structure will deform and respond to external forces, allowing to design materials that are resistant to failure and deformation. The three polymorphs have different Bravais lattice crystal systems; Fd3m-CaMn₂O₄ is a cubic crystal system, Pbcm-CaMn₂O₄ and Pnma-CaMn₂O₄ are orthorhombic crystal systems. The two crystal systems also have different mechanical stability criteria. The elastic constants must satisfy the mechanical stability criteria postulated by Born to consider the three polymorphs mechanically stable. Mechanically stable crystals must have positive strain energy. Normally there are 81 elastic components but due to symmetry (see [subsection 2.2.4.](#)) they reduced to 3 independent elastic constants C_{11} , C_{12} , C_{44} for cubic systems and 9 independent elastic constants C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} , C_{23} for an orthorhombic system [74, 76]. The monocrystalline elastic constants are determined by applying the Debye model and Taylor expansion on the total energy. The energy of a strained system is expressed by the following **Equation 4.1** [122, 123]:

Equation 4.1 *Energy of strained system*

$$U(V, \varepsilon) = U(V_0, 0) + V_0 \left[\sum_i \tau_i \varepsilon_i \xi_i + \frac{1}{2} \sum_{ij} C_{ij} \varepsilon_i \xi_i \varepsilon_j \xi_j \right]$$

where $U(V_0, 0)$ is the energy of the unstrained system with equilibrium volume V_0 , τ_i is an element in the stress tensor and ξ_i is a factor to take care of the Voigt index. The computed

elastic constants for the three polymorphs are listed in **Table 4.4**. For a cubic crystal system to be considered mechanically stable the conditions in **Equation 2.7** must be fulfilled and **Equation 2.9** for orthorhombic crystal systems.

Table 4.4 The computed elastic constants, Moduli, Pugh ratio, Poisson ratio, Hardness, Universal Anisotropy Index and Debye temperature for Fd3m-CaMn₂O₄, Pbcm-CaMn₂O₄ and Pnma-CaMn₂O₄.

ELASTIC CONSTANTS			
C_{ij} (GPa)	Fd3m-CaMn ₂ O ₄	Pbcm-CaMn ₂ O ₄	Pnma-CaMn ₂ O ₄
C_{11}	371.04	141.85	152.37
C_{12}	305.72	18.76	30.30
C_{13}	-	40.76	36.54
C_{22}	-	171.65	187.16
C_{23}	-	71.39	31.51
C_{33}	-	239.05	152.73
C_{44}	191.08	76.19	-66.56
C_{55}	-	43.41	43.62
C_{66}	-	44.99	-38.24
ELASTIC MODULI			
B_V	329.82	90.49	76.55
B_R	329.82	82.00	76.13
B_H	329.82	86.24	76.34
G_V	129.11	61.03	14.02
G_R	70.42	56.58	393.30
G_H	99.76	58.80	203.66
E_V	342.62	149.48	39.65
E_R	197.21	138.00	433.45
E_H	271.88	143.74	323.40
B_V/G_V	2.55	1.43	5.46
B_R/G_R	4.68	1.45	0.19
B_H/G_H	3.31	1.47	0.37
ν_V	0.33	0.22	0.41
ν_R	0.40	0.22	-0.45
ν_H	0.36	0.22	-0.21
H_V	9.89	10.80	0.87
H_R	3.23	10.51	409.01
H_H	6.15	10.65	121.07
A^U	4.17	0.50	-4.82
θ_D (K)	674.96	529.54	

We observed that the elastic constants for Fd3m-CaMn₂O₄ and Pbcm-CaMn₂O₄ polymorphs obey the Born mechanical stability conditions outlined in **Equation 2.7** and **Equation 2.9**, respectively. This is an indication that Fd3m-CaMn₂O₄ and Pbcm-CaMn₂O₄ are mechanically stable. In the contrary, some calculated elastic constants for the Pnma-CaMn₂O₄ polymorph do not satisfy the mechanical stability conditions, in particular C_{44} and C_{66} , which is an

indication of mechanical instability. From the monocrystalline elastic constants, the macroscopic elastic coefficient such as bulk (B), shear (G) and Young's (E) moduli according to the Voigt [124] and Reuss [125] postulations were extrapolated using **Equation 2.8** for $Fd3m\text{-CaMn}_2\text{O}_4$ and **Equation 2.10**, **Equation 2.11** and **Equation 2.12** for $Pbcm\text{-CaMn}_2\text{O}_4$ and $Pnma\text{-CaMn}_2\text{O}_4$, respectively.

The bulk modulus is a measure of a material's resistance to fracture. The shear modulus, denoted as G, indicates a material's ability to withstand plastic deformation. Lastly, the coefficient E represents Young's modulus, also known as the tensile modulus, which is defined as the ratio of uniaxial stress to uniaxial strain. Each modulus has 3 approximations known as the Voigt-Reuss-Hill approximations that were suggested by Voigt (V) [124], Reuss (R) [125] and Hill (H) [126]. The Voigt upper bound assumes perfect bonding between the constituent materials and calculates the maximum possible stiffness of the composite. On the other hand, the Reuss lower bound assumes no bonding between the materials and calculates the minimum stiffness. In addition, Hill proposed an average value which takes a more realistic approach by considering a mixture of perfect bonding and no bonding between the materials, providing a more accurate prediction of the overall mechanical properties. Generally superhard material possesses a high bulk modulus (B), a high shear modulus (G) and a high shear strength [127]. Our analysis reveals that the $Fd3m\text{-CaMn}_2\text{O}_4$ polymorph exhibits the highest bulk modulus at 329.82 GPa, surpassing the values of 82.0 GPa for $Pbcm\text{-CaMn}_2\text{O}_4$ and 76.0 GPa for $Pnma\text{-CaMn}_2\text{O}_4$. This indicates that $Fd3m\text{-CaMn}_2\text{O}_4$ is less compressible compared to $Pbcm\text{-CaMn}_2\text{O}_4$ and $Pnma\text{-CaMn}_2\text{O}_4$, respectively. Additionally, the $Fd3m\text{-CaMn}_2\text{O}_4$ polymorph demonstrates a higher shear modulus (G) than $Pbcm\text{-CaMn}_2\text{O}_4$, suggesting greater resistance to deformation.

The shear modulus estimations for $Pnma\text{-CaMn}_2\text{O}_4$ present anomalies, with G_V at 14.02 GPa being the lowest and G_R at 393.30 GPa being the highest. However, in accordance with the Voigt-Reuss-Hill approach, G_V serves as the upper bound and G_R as the lower bound. The presence of negative values for C_{44} and C_{66} may have influenced these results, as they play a role in determining G_V and G_R (see **Equation 2.11**). The Young's modulus exhibits a similar pattern to the bulk and shear moduli in the materials studied; specifically, $E(Fd3m - CaMn_2O_4) > E(Pbcm - CaMn_2O_4)$. Young's modulus is also anomalous as the shear modulus for $Pnma\text{-CaMn}_2\text{O}_4$. With this we can see that $Fd3m\text{-CaMn}_2\text{O}_4$ is expected to elastically resist linear compression more than $Pbcm\text{-CaMn}_2\text{O}_4$. To determine the ductility and brittleness of the considered polymorphs, we have computed the Pugh and Poisson ratios.

According to the Pugh criterion, a material is ductile if the ration of bulk to shear (B/G) is greater than the critical value of 1.75 and brittle if less than the value [128]. From our calculations, we observed that the Fd3m-CaMn₂O₄ polymorph is ductile while Pbcm-CaMn₂O₄ is brittle. The Pugh ratios for Pnma-CaMn₂O₄ still show anomalous behaviour, B_V/G_V is greater than 1.75 while B_R/G_R and B_H/B_R are less than 1.75. The Poisson's ratio, which measures the volume changes in directions perpendicular to the applied tension during deformation, typically falls within the range of -1 to 0.5. A material is considered ductile if its Poisson's ratio exceeds 0.26; otherwise, it is deemed brittle. We expect Poisson ratio for Fd3m-CaMn₂O₄ to be greater than that of Pbcm-CaMn₂O₄ since most brittle materials tend to have small Poisson ratios. Poisson ratios ν_x measures the stability of a crystal against shear. Small Poisson ratios suggest stability against shear. Materials generally appear to become more flexible as the Poisson ratio increases [129]. Poisson ratios were calculated using the following expression [76]:

Equation 4.2 Poisson ratio

$$\nu_x = \frac{3B_x - 2G_x}{2(3B_x + G_x)}, \text{ where } x = V, R, H$$

The Poisson ratios calculated were relatively small indicating stability against shear with Pbcm-CaMn₂O₄ having the smallest values. Moreover, Fd3m-CaMn₂O₄ and Pbcm-CaMn₂O₄ were predicted to be ductile, while Pnma-CaMn₂O₄ is brittle. In order to determine anisotropy, we made use of the universal anisotropy index [130].

Equation 4.3 Universal Anisotropy Index

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6$$

Local isotropic single crystals have $A^U = 0$ and any deviation from zero indicates the extent of single-crystal anisotropy including both shear and bulk contributions. Our results in **Table 4.4** show that Fd3m-CaMn₂O₄ is more anisotropic ($A^U = 4.168$) and Pbcm-CaMn₂O₄ is intermediately isotropic ($A^U = 0.496$). A^U is negative for Pnma-CaMn₂O₄ (-4.816) suggesting that Pnma-CaMn₂O₄ does not exist under low pressure only under high pressure since Pnma-CaMn₂O₄ is a transformation of Pbcm-CaMn₂O₄ under high pressure conditions. Knowing the specific heat capacity and melting temperature will help in knowing in which temperature ranges will the material deform under additional thermal energy. Debye's

temperature is very important in determining some thermal properties of a material. The standard method in determining Debye's temperature from elastic moduli is as follows [131]:

Equation 4.4 Debye's temperature

$$\theta_D = \frac{h}{k_B} \left(\sqrt[3]{\frac{3nN_A\rho}{4\pi M}} \right) v_m$$

where h is Plank's constant, k_B Boltzmann's constant, n is the number of atoms in the unit cell, N_A Avogadro's number, ρ density, M molecular mass and v_m average sound velocity which can be calculated using the expression [131] in **Equation 4.5**.

Equation 4.5 velocity

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_p^3} \right) \right]^{-1/3}$$

$$v_s = \sqrt{\frac{G_X}{\rho}}, \quad v_p = \sqrt{\frac{1}{\rho} \left(B_X + 4 \frac{G_X}{3} \right)} \quad \text{where } X = V, R \text{ or } H$$

v_s and v_p are the shear wave and compressional wave velocities respectively. The Fd3m- CaMn_2O_4 polymorph has a larger Debye temperature compared to Pbcm- CaMn_2O_4 , indicating stronger bonding and higher thermal conductivity.

Chapter 5

Conclusion

To summarise, we performed first-principles computations employing the density functional theory within the CASTEP code to determine the structural, energetic, electronic and mechanical properties of CaMn_2O_4 polymorphs at ambient conditions. We have particularly computed the equilibrium cell parameters, enthalpies of formation, density of states and elastic constants. The obtained DFT+U structural cell parameters were found to be more than 95% in agreement with available experimental results, which validates the computational approach employed. The orthorhombic $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Pnma-CaMn}_2\text{O}_4$ have twice the volume compared to $\text{Fd3m-CaMn}_2\text{O}_4$ suggesting that the two polymorphs may offer a larger volumetric capacity, better reversible rate capability and more favourable diffusion channels for the insertion and removal of Ca ions from the host structure (Mn_2O_4) during battery operation. The calculated enthalpies of formation are negative indicating that the polymorphs will form under ambient conditions with $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Pnma-CaMn}_2\text{O}_4$ having the least values. Furthermore, the analysis of the electronic densities of states indicated that the orthorhombic $\text{Pbcm-CaMn}_2\text{O}_4$ and $\text{Pnma-CaMn}_2\text{O}_4$ polymorphs are metallic suggesting good electronic conductivity as compared to the semiconductor behaviour of the $\text{Fd3m-CaMn}_2\text{O}_4$ characterised by the energy band gap of 1.966 eV. Finally, the mechanical elastic constants have shown that the $\text{Fd3m-CaMn}_2\text{O}_4$ and $\text{Pbcm-CaMn}_2\text{O}_4$ are mechanically stable, while the $\text{Pnma-CaMn}_2\text{O}_4$ possesses an anomalous mechanical instability. The negative anisotropy index on $\text{Pnma-CaMn}_2\text{O}_4$ hinted that the structure may not exist under low pressure, but under high pressure since $\text{Pnma-CaMn}_2\text{O}_4$ is a transformation of $\text{Pbcm-CaMn}_2\text{O}_4$ under high-pressure conditions. Overall, the current study showed that the $\text{Pbcm-CaMn}_2\text{O}_4$ is the most favourable polymorph due to larger volume, lower negative enthalpy of formation, absence of energy band gap and deep pseudo gap around the Fermi, positive elastic constants and lower anisotropy index value.

The next phase of the project will be to achieve the following objectives:

1. Construct a convex hull diagram for the $\text{Ca}_x\text{Mn}_2\text{O}_4$ to determine the most stable composition.
2. Calculate the elastic constants and moduli of $\text{Ca}_x\text{Mn}_2\text{O}_4$ to determine the mechanical stability.

3. Calculate the electronic densities of states and band structure of $\text{Ca}_x\text{Mn}_2\text{O}_4$ to determine the electronic structure and conductivity.
4. Compute the phonon dispersion curves to determine the vibrational properties of the $\text{Ca}_x\text{Mn}_2\text{O}_4$ internal lattice structure.
5. Calculate the Ca intercalation potentials on Mn_2O_4 to determine the operating voltages.

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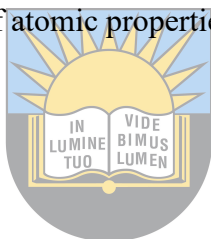
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Appendices
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Conference attendance

1. O. Roberts and N.L. Lethole “Structural, Thermodynamic, Electronic and Mechanical Properties of CaMn₂O₄ Polymorphs” CHPC National Conference, Kruger National Park (SA), 4-8 December 2023
2. O. Roberts and N.L. Lethole “Stabilities of calcium manganese oxide (CaMn₂O₄) polymorphs for application as cathode materials in calcium ion batteries” South African Institute of Physics Conference, University of Zululand, (SA), 3-7 July 2023

Publications

1. O. Roberts and N.L. Lethole “Structural, Thermodynamic and Electronic Properties of Calcium Manganese Oxide (CaMn₂O₄) Polymorphs: A First-Principles Study”, South African Institute of Physics, Proceedings of SAIP 2023; ISBN: 978-0-7961-3774-6, 105.

2. O. Roberts, N.L. Lethole and P. Mukumba “Insights into the Structural, Thermodynamic, Electronic, and Mechanical Properties of CaMn_2O_4 Polymorphs via Density Functional Theory Analysis” *Journal of Materials Research*, submitted.



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