

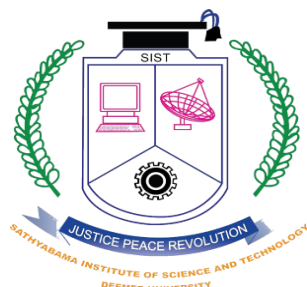
# **ABINITIO STUDIES OF $\text{ACr}_x\text{Ti}_{(1-x)}\text{O}_3$ (A=La, Nd) INTERMETALLICS FOR ENERGY STORAGE APPLICATIONS**

Submitted in partial fulfillment of the requirements for the award of  
**Master of Science degree in Physics**

By

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(41590007)



**DEPARTMENT OF PHYSICS  
SCHOOL OF SCIENCE AND HUMANITIES**

## **SATHYABAMA**

**INSTITUTE OF SCIENCE AND TECHNOLOGY  
(DEEMED TO BE UNIVERSITY)  
Accredited with "A" grade by NAAC | 12B Status by  
UGC Approved by AICTE**

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**May 2023**



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## DEPARTMENT OF PHYSICS

### BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of Jenolin Shalom S (41590007) who carried out the project entitled "**Abinitio studies of  $\text{ACr}_x\text{Ti}_{(1-x)}\text{O}_3$  (A=La, Nd) intermetallics for Energy storage applications**" under my supervision from November 2022 to May 2023.

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## DECLARATION

I Jenolin Shalom S hereby declare that the Project Report entitled “Abinitio studies of  $ACr_xTi_{(1-x)}O_3$  (A=La, Nd) intermetallics for Energy storage applications” done by me under the guidance of Dr. D S Jayalakshmi (Internal), Department of Physics, Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Physics.

DATE: 09-05-2023



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SIGNATURE OF THE CANDIDATE

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## ABSTRACT

The structural stability, electronic, optical, thermal and thermoelectric properties of the Ti-doped  $\text{LaCrO}_3$  and  $\text{NdCrO}_3$  have been studied by using the full-potential Linearized augmented plane-wave method (FP-LAPW) within density functional theory (DFT). The calculations were performed in the wien2k software for  $\text{ACr}_x\text{Ti}_{(1-x)}\text{O}_3$  ( $\text{A}=\text{La}, \text{Nd}$ ) ( $x=0,0.25,0.5,0.75,1$ ). The structure of this compound and the proposed combinations are obtained by creating supercell. The calculations are performed with 1000 k-points in the Brillouin zone. The plane wave expansion ( $R_{\text{MT}}*K_{\text{MAX}}$ ) is taken as 7. A phase transition occurs from cubic to tetragonal while doping Ti to the  $\text{LaCrO}_3$  material and  $\text{NdCrO}_3$  material. The optical conductivity, reflectivity and absorption coefficient of the compound shows a maximum in the visible, UV and IR energy region applicable in solar cell materials. The computed band structure along the high symmetry in the Brillouin zone states clearly that the material is conductor. In this study, the efficient energy storage material is observed. The Power factor of  $\text{NdCrO}_3$  compound is found to have higher value than other compounds, hence more power can be generated by it. Since it has an high power it can be useful in battery energy storage systems. The  $zT$  value of  $\text{NdCrO}_3$  is high and is suitable for the applications in thermoelectric devices. Comparing all the compounds  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  is better for the energy storage applications.

Keywords:  $\text{LaCrO}_3$ ; Doping; Phase Transition; WIEN2K code.

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## **LIST OF SYMBOLS AND ABBREVIATION**

|             |                                                   |
|-------------|---------------------------------------------------|
| DFT         | Density Functional Theory                         |
| FP-LAPW     | Full Potential-Linearized Augmented Plane<br>Wave |
| DOS         | Density Of States                                 |
| NN DISTANCE | Nearest Neighbour Distance                        |
| SCF         | Self-Consistent Cycle                             |
| $R_{MT}$    | Muffin Tin Radius Sphere                          |
| GGA         | Generalized Gradient Approximation                |
| EF          | Fermi Energy Level                                |
| KS          | Kohn Sham                                         |

## **CHAPTER 1**

### **1.INTRODUCTION**

#### **1.1 MOTIVATION**

It is very important to understand the nature of the material to the modern hypothetical compound, in order to reduce the probability of error in experiment. The complex material that contains many electrons is studied by computer simulation. To analysis and to explain the complicated levels or to plan future experiments in a rational way the complex material act as a key element in this process. We can improve a material by synthesizing, characterizing and functional analysing by using simulation method. The simulation method is more efficient compared to old trial and error method (Schwarz K Blaha P, 2002).

Advanced batteries are of crucial importance to our daily life and the economic development of the modern society. It is greatly desired for powering portable devices and electric vehicles to meet increasing energy demands (Armand, M, 2008) Furthermore, in order to solve the worldwide concerns of rising energy consumption and rising CO<sub>2</sub> emissions, it is necessary to develop effective methods for converting and storing renewable but sporadically available energy sources into reliable energy forms (Dunn, 2011) Low-cost battery systems with high energy density and long cycling life have been proposed as promising solutions for storing renewable energy sources (Dunn, 2011). Density functional theory (DFT) is a well-established method for calculating the electrical characteristics of solids. DFT is a well-known computational quantum mechanical modelling method that is utilised in the physics, chemistry, and material science of many body systems, specifically atoms, molecules, and condensed phases. It treats both exchange and correlation and is based on electron density rather than wave function (Hartree Fock). There are numerous computer codes available, and our chemicals are investigated using the WIEN2K code.

The majority of solid-state interactions are critically dependent on interatomic distance. Pressure alters the inter-atomic distance and modifies the structure and electrical characteristics while introducing no chemical complexity and

minimising physical complexity. As a result, high pressure techniques have been widely employed in recent years to investigate the physical states of solids, establish new ground states in solids, test theoretical models, and aid in the development of new theories. In the last half-century, for example, there have been more naturally non-superconducting elements converted into superconductors by applying pressure than naturally existing elemental superconductors. This opens up the high pressure system to computational investigation.

## 1.2 DENSITY FUNCTIONAL THEORY

One of the early yet fundamental challenges in theoretical physics is the description of the structures and dynamics of many-electron systems. As Dirac noted, the underlying 8 physical laws required for the mathematical theory of a substantial part of physics and the entire field of chemistry are thus totally understood, and the only difficulty is that the exact application of these rules leads to equations that are far too convoluted to be solved. Despite this, the seemingly daunting task of solving the Schrödinger wave equation for realistic (many-particle) systems has opened up a whole new domain in modern physics and chemistry, as well as the way we comprehend chemical processes. Kohn et al. proposed it in 1964. Density functional theory (DFT) is a powerful method for obtaining approximate solutions to many-particle problems. The Thomas-Fermi model of a uniform electron gas, coupled with the Slater local exchange approximation, serves as the conceptual foundation for DFT. The ground state of a system is translated to the ground-state electron density within the DFT framework in such a way that the Schrödinger wave equation,

$$H\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (1.1)$$

For many-particle systems, where  $N$  is the number of electrons at locations  $\mathbf{r}_1, \dots, \mathbf{r}_N$ , is satisfied. Although many DFT approaches are ab initio because they derive the energy eigenvalue of the Schrödinger wave equation from the wavefunction, others get the energy eigenvalue from the electronic density. If functionals have been fitted to experimental data, the latter could be a semiempirical DFT technique. For many particle systems, ab initio (first principles) theory encompasses all fundamentally non-empirical and wavefunction-based techniques of solving Eq. (1.1). The Kohn Sham (KS) equation is the Schrödinger wave equation for many-particle systems. Particles in many-particle systems constantly interact, making

analytical solutions to the KS equation nearly unattainable. As a result, the development of approximate-solution schemes has progressed, with each scheme having its unique set of assumptions. DFT has effectively researched features ranging from electronic structure, lattice vibration, superconductivity, magnetic properties, to bonding and bond characterisation (Adebayo Abayomi Adeleke, 2021). The well-established scheme for calculating solid-state electrical characteristics is based on density functional theory (DFT), for which Walter Kohn got the Nobel Prize in chemistry in 1988. An ab-initio calculation is one that begins with the basic equations of motion, either from Schrodinger or from the Dirac equation, and does not include any empirical parameters. One of the ab-initio calculation approaches that has successfully explained the ground state properties of metals, semiconductors, and insulators is DFT. DFT is used in computational solid state physics to study structural, electrical, magnetic, and optical properties of materials at rest and under pressure/temperature conditions using fundamental principles. Because computing is faster and easier than experimentation, the band structure calculation can be used to validate the experimental data as well as the theory. Density functional theory (DFT) has become a widely established many-particle approach for calculating band structure. The basic principle of DFT is to represent a many-body issue of an interacting system of electrons and nuclei by mapping it onto a one-electron reference system, which results in the same density as the original system. The whole energy is separated into three parts in DFT: kinetic energy, coulomb energy, and exchange-correlation energy, and the great simplification is that the many-body electronic wave function is not required. Consider the extremely simple scenario of a tiny system (atom or molecule) with 100 electrons to clarify this concept in the Hartree-Fock (HF) Method. Each electron must be characterised by a wave function that is determined by three spatial coordinates and its spin. As a result, the many-body wave function is determined by three spatial coordinates and the spin. As a result, the many-body wave function would be determined by 400 coordinates (Hartree D.R, 1928).

There are several computational codes available to make "ab initio" calculations of the electronic structure of solids using DFT. The following are the computational codes that are currently available: Plane wave codes include ABINIT, VASP ESPRESSO, QUANTUM ESPRESSO, SOCORRO, and others; local orbital codes include CRYSTAL, SIESTA, and others; molecular codes include

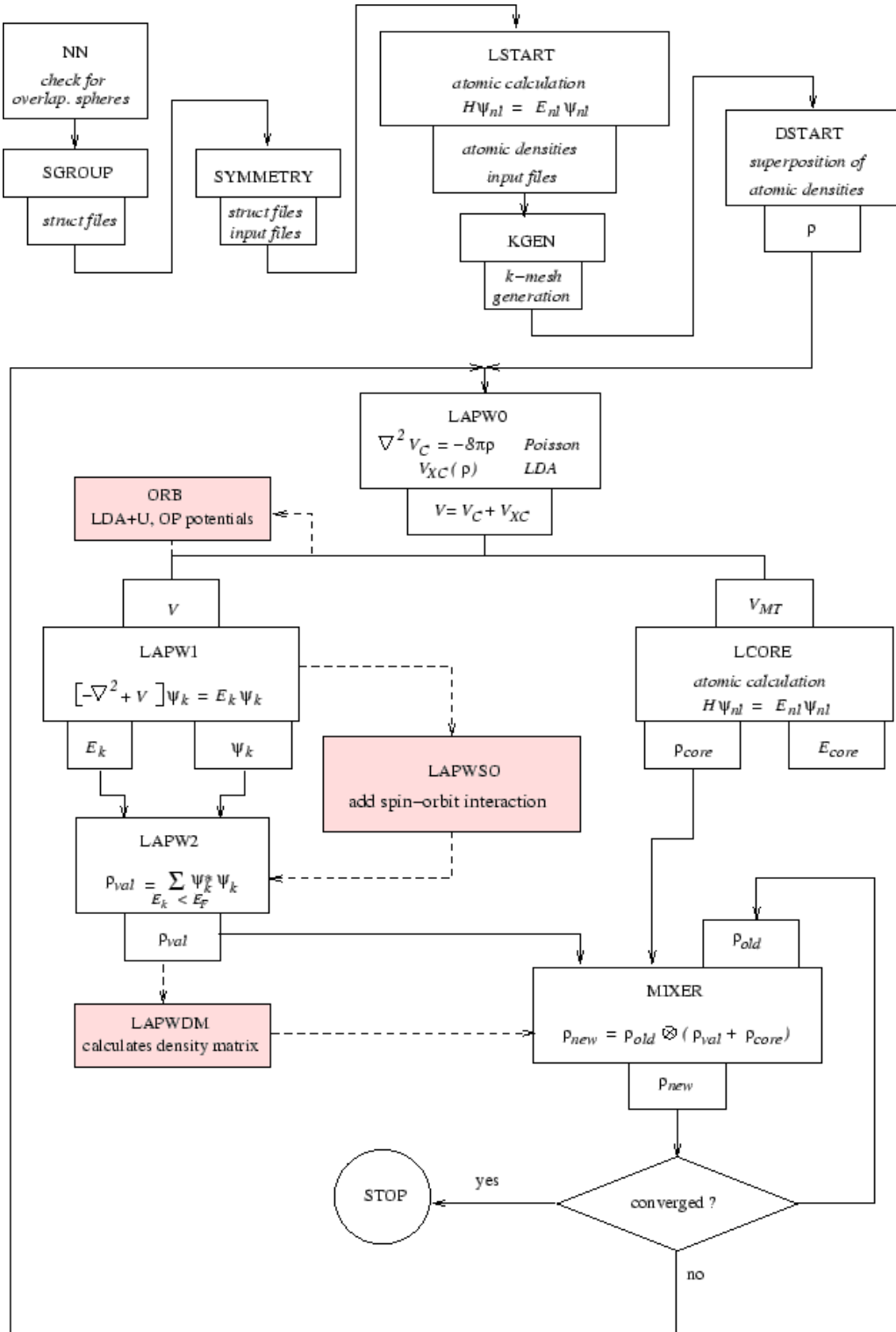
GAUSSIAN, OCTOPUS, TURBOMOLE, and others; and augmented plane wave codes include Stuttgart Linear Muffin Tin Orbital (LMTO) codes, FLEUR, and WIEN2K.

### 1.3 WIEN2K CODE

Peter Blaha and Karlheinz Schwarz created the first WIEN2k code. The programme calculates electronic structure using the density functional theory's full potential linearized augmented plane-wave (FP-LAPW) technique (O. K. Andersen, 1975). The Wien2k code is an all-electron scheme. LAPW implementation in Wien2k captures relativistic impact with the ability to implement LDA, GGA, meta-GGA, LDA+U, and hybrid-DFT. When wien2k is linked to the Phonopy programme, it can do phonon dispersion calculations (P. Blaha, 2001). The wien2k code is written in FORTRAN90 and supports fine grain parallelization for multi-core machines or clusters of computers. The wien2k also has a web user interface (W2web) that allows for seamless material modelling, input generation, and adaptation. In Wien2k, the self-consistent field (scf)-cycle can be implemented with or without simultaneous atomic position optimisation.

All calculations in this paper were performed using the WIEN2K code, an APW+LO programme proposed by Blaha (2001). It enables solid electronic structure calculations using density functional theory (DFT). The method is based on the full-potential (linearized) augmented plane-wave ((L)APW)+local orbital's (lo). The input routine begins with a structure file providing information on the system's atomic configuration, lattice parameters, atomic species, atomic locations, muffin-tin radii, and so on. Based on these inputs, the subroutines NN, SGROUP, and SYMMETRY check for overlap between the muffin tin spheres and determine the symmetry of the unit cell; in the following step, LSTART calculates the atomic densities for all atoms in the unit cell, which KGEN uses in conjunction with the other input files to determine a sustainable k-mesh; and in the final initialization step, DSTART, a starting electron density is All of the essential parameters are fixed during this initialization, including the exchange-correlation approximation,  $R_{MTK_{max}}$ , and the energy value that divides the core states from the valence states. A proper choice of

$R_{MTK_{max}}$  and the k-mesh is required for an efficient use of computation time: the calculation is more accurate and takes less time.



**Figure 1.1: Program flow in WIEN2K**

## **CHAPTER 2**

### **2. AIM AND SCOPE**

#### **2.1 AIM OF THE PROJECT**

The purpose of this work is to investigate the structural, electronic, optical, thermal, and thermoelectric properties of the La based compounds namely  $\text{LaCrO}_3$ ,  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ ,  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ,  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ ,  $\text{LaTiO}_3$  and Nd based compounds  $\text{NdCrO}_3$ ,  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ,  $\text{NdTiO}_3$  using the Full Potential-Linearized Augmented Plane Wave (FP-LAPW) method as implemented in the WIEN2K code. The major goal is to overcome the significant energy losses, a lack of acceptability and effectiveness or widely adopted standards, and challenging maintenance.

#### **2.2 SCOPE OF THE PROJECT**

Perovskite oxides are employed in hydrogen evolution reactions, photocatalysis, photovoltaic solar cells, electrocatalysis, solid oxide fuel cells, supercapacitors, and metal-air batteries for effective electrocatalysis. Human development and well-being are based on energy. Today, energy is derived from the combustion of fossil fuels (coal, natural gas, and oil). These sources not only generate major environmental problems by emitting greenhouse gases, but also are rapidly exhausted owing to their massive usage. By Using  $\text{ACr}_x\text{Ti}_{(1-x)}\text{O}_3$  ( $A=\text{La, Nd}$ ) we are going to determine the energy storage applications.

Perovskites are a type of chemical with the general formula  $\text{ABO}_3$ . These compounds have gained prominence in the scientific community because to specific features that can be attributed to highly correlated d-band electrons and strong electron-lattice couplings. Perovskites may have applications in many technological devices due to their unique properties, such as sensors, catalysts, superconductors, dielectrics, piezoelectric, semiconductors, ferromagnetic, ferroelectric, antiferromagnetic, ceramic fuel cells, massive magneto resistance, insulators, metal transitions, ionic conduction characteristics, ferroelasticity, and so on. The majority of perovskites, such as  $\text{CaTiO}_3$ ,  $\text{SrZrO}_3$ , and  $\text{LaTiO}_3$ , have a cubic structure (Nadeem, S, 2016). Lanthanum chromite,  $\text{LaCrO}_3$ , is a common perovskite with the general formula  $\text{ABO}_3$ .  $\text{ABO}_3$ , the ideal perovskite structure, has cubic symmetry

and may be represented as a three-dimensional network of corner-sharing  $\text{CrO}_3$  octahedra with Cr-O-Cr angles of  $180^\circ$ , the majority of which are distorted. It has some unusual physical properties, such as high mechanical strength, a high melting point ( $2400^\circ\text{C}$ ), good electronic conductivity, a high thermal expansion coefficient, physical and chemical stability in oxidising and reducing atmospheres, and the ability to withstand higher temperatures and electro-catalytic activity, making it useful in high temperature applications such as interconnects in solid oxide fuel cells, sensors, catalysis, and so on (V.D. Nithya, 2012)  $\text{NdTiO}_3$  are semiconductors having identical activation energies. The origin of semiconducting behaviour cannot be determined only by resistivity statistics (David A. Maclean, 1981).

Lanthanum's high production cost limits its use in commercial products. Researchers have been interested in rare earth perovskite  $\text{ABO}_3$  type oxides as potential materials for hydrogen storage throughout the last decade. These are regarded as one of the most valuable options for hydrogen solid storage. Perovskite materials have traditionally had an  $\text{ABX}_3$  structure, where A and B are cations and X is an anion. Researchers have paid special attention to magnesium-based perovskite-type hydrides because to their high hydrogen storage capacity. Indeed, Lefevre et al used ab initio calculations to investigate the hydrogen storage capacity of  $\text{MgNi}_3\text{H}_2$  and  $\text{MgCuH}_3$ . These alloys have been found to be stable and may be employed in transportation applications. Furthermore, Reshak et al investigated the structural, elastic, and electronic properties of the perovskite  $\text{KMgH}_3$ . Furthermore,  $\text{CaNiH}_3$  perovskite hydrides are being considered for hydrogen storage, and Ikeda et al reported similar desorption characteristics, with  $\text{CaNiH}_3$  having higher hydrogen desorption than  $\text{CaCoH}_3$ . This fascination stems from their abundance, thermal resistance, and lower cost when compared to traditional intermetallic alloys. Because of their high hydrogen storage capacity, magnesium-based perovskites such as  $\text{NaMgH}_3$  were of particular interest. Furthermore,  $\text{CaNiH}_3$  perovskite hydrides have been investigated for hydrogen storage (Lahlou Nabil, 2022).

## CHAPTER 3

### 3. MATERIAL AND METHODOLOGY

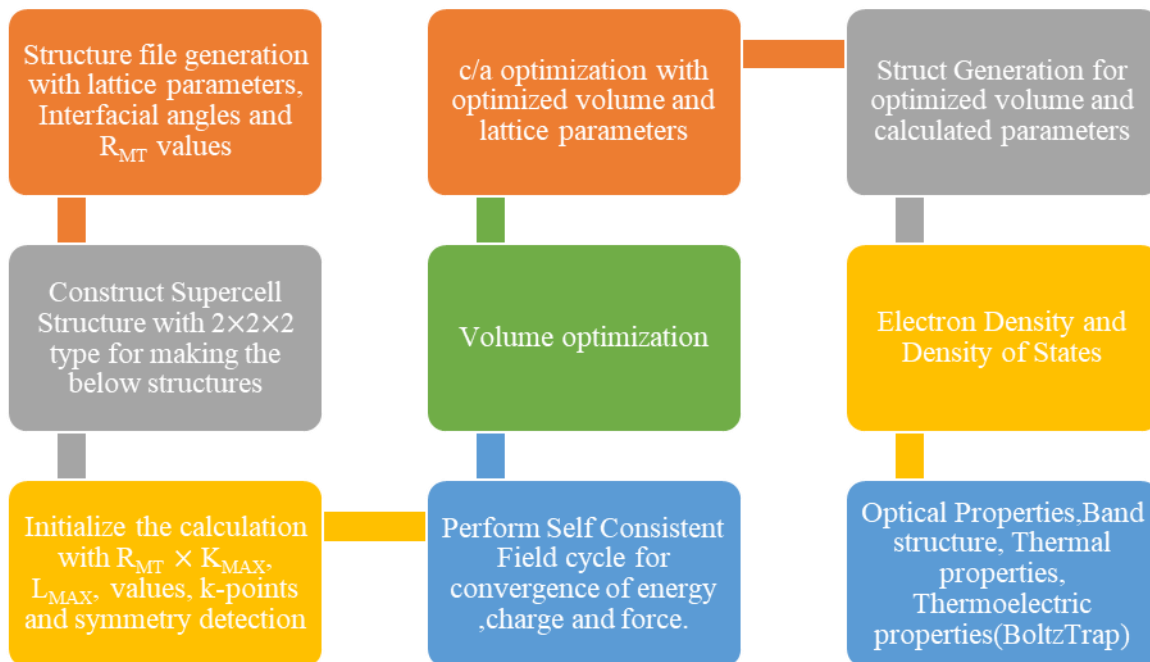
#### 3.1 MATERIALS

Obtaining new and enhanced insights into material behavior, properties and phenomena. Recently, perovskite-type oxides have attracted researchers as new materials for energy storage. Perovskite, originated from  $\text{CaTiO}_3$ , is now a general name for oxides having the structural formula  $\text{ABO}_3$  or  $\text{A}_2\text{BO}_4$ . Perovskite oxides with formula  $\text{ABO}_3$  or  $\text{A}_2\text{BO}_4$  are a very important class of functional materials that exhibit a range of stoichiometries and crystal structures. Their high thermal and hydrothermal stability enable them suitable catalytic materials either for gas or solid reactions carried out at high temperatures, or liquid reactions carried out at low temperatures. A large number of different elements can be combined together to form perovskite structures. Lanthanum chromite-based perovskite oxides ( $\text{LaCrO}_3$ ) have been widely recognized as promising interconnect materials for solid oxide fuel cells (Lahlou Nabil, 2022). And we observed that Lanthanum titanium-based perovskite oxides ( $\text{LaTiO}_3$ ) which allows for the strong coupling of the lattice, orbital, and magnetic subsystems of this crystal (Nadeem, S, 2016). Then we have observed that chromium and titanium element (Cu-Cr-Ti) can be doped (Huang, Z., 2021). And the studies shows that we have  $\text{ACrO}_3$  ( $\text{A}=\text{La}, \text{Nd}$ ). In our present work, we will carry out research on the  $\text{ACr}_x\text{Ti}_{(1-x)}\text{O}_3$  ( $\text{A}=\text{La}, \text{Nd}$ ). The proposed combinations are  $\text{LaCr}_{0.5}\text{Ti}_{0.25}\text{O}_3$ ,  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ ,  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ ,  $\text{ACr}_x\text{Ti}_{(1-x)}\text{O}_3$  ( $\text{A}=\text{La}, \text{Nd}$ ).

#### 3.2 COMPUTATIONAL DETATILS

The calculations are carried out by means of Full Potential Linearized Augmented Plane Wave (FP-LAPW) method as implemented in the WIEN2K code. The Generalized Gradient Approximation (GGA) can be applied to calculate the exchange correlation potential. Muffin tin spheres of radius  $R_{\text{MT}}$  are chosen in such a way that there is minimal charge leakage from the core. The calculations are performed with 1000 k-points in the Brillouin zone. The plane wave expansion ( $R_{\text{MT}}*K_{\text{MAX}}$ ) is taken as 7. The atomic position of La is (0.5,0.5,0.5), Cr is (0,0,0), O

is (0.5,0,0) and Ti is (0.5,0,0). Here in the initialization the cubic structure  $\text{LaCrO}_3$  undergoes phase transition while doping Ti and the compound changes into tetragonal. When it is completely replaced by Titanium it again undergoes phase transition and changes into cubic. The atomic position for Nd is (0,0,0), Cr is (0.5,0.5,0.5), Ti is (0,0.5,0.5) and O is (0.5,0,0). In the initialization process the cubic structure  $\text{NdCrO}_3$  undergoes phase transition and changes into tetragonal  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  and  $\text{NdTiO}_3$ . We can observe that  $\text{NdCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$  and  $\text{NdCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$  is in unstable state so it is not suitable for energy storage applications. The self-consistent calculations are carried out to an accuracy of 0.0001Ry energy and 0.001e charge. The computations are performed to find the total energy of the given system and the obtained total energies are then fitted into the Birch-Murnaghan equation of state to get the energy- volume relation. The pressure is obtained by taking the volume derivative of the total energy. The computation repeated for each compression for various compression and expansion of volume. Initially the volume of the compound is optimized then from the optimized volume lattice parameters further c/a optimization has been done. Finally by using the optimized lattice parameters, position of the compound has been optimized. The Thermo electric properties have been found by using BoltzTraP.



**Figure 3.1: Methodology**

## CHAPTER 4

### 4. RESULT AND DISCUSSIONS

#### 4.1 STRUCTURAL PROPERTIES OF $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$

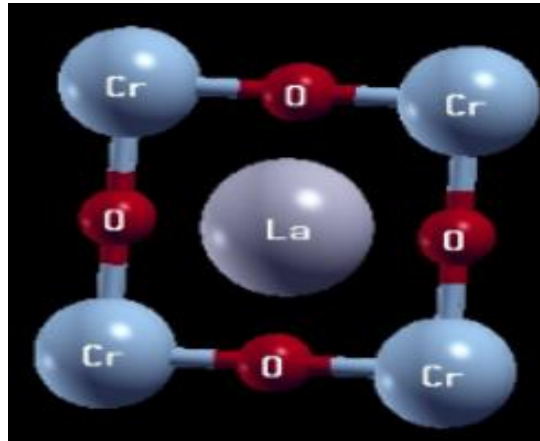
The generalised gradient approximation (GGA), which is included in the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave technique wien2k were used for all computations presented here. The calculations are performed with 1000 k-points in the Brillouin zone. The plane wave expansion ( $R_{\text{MT}} \cdot K_{\text{MAX}}$ ) is taken as 7.

**TABLE 4.1: CRYSTALLOGRAPHIC PARAMETERS AND POSITIONS USED IN OUR CALCULATIONS OF  $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$ .**

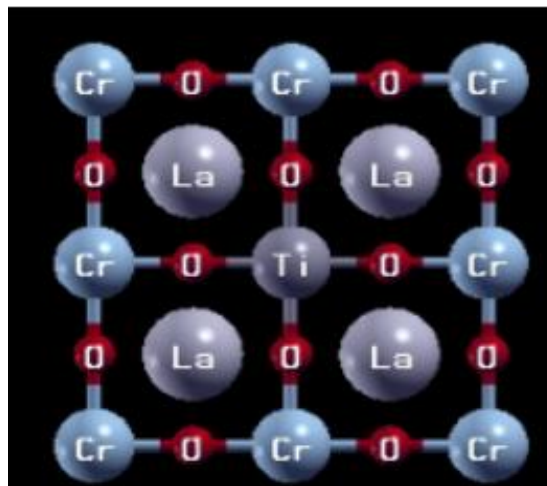
| COMPOUND AND SPACE GROUP                                                   | POSITIONS                                                             | LATTICE PARAMETERS                                               |
|----------------------------------------------------------------------------|-----------------------------------------------------------------------|------------------------------------------------------------------|
| $\text{LaCrO}_3$ , $\text{Pm}\bar{3}\text{m}$                              | Cr (0, 0, 0)<br>La (0.5, 0.5, 0.5)<br>O (0.5, 0, 0)                   | $a=b=c=3.93 \text{ \AA}^\circ$<br>$\alpha=\beta=\gamma=90^\circ$ |
| $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ ,<br>$\text{P4}/\text{mmm}$ | La (0.5, 0.5, 0.5)<br>Cr (0, 0, 0)<br>Ti (0.5, 0, 0)<br>O (0.5, 0, 0) | $a=b=c=3.93 \text{ \AA}^\circ$<br>$\alpha=\beta=\gamma=90^\circ$ |
| $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ , $\text{P4}/\text{mmm}$      | La (0.5, 0.5, 0.5)<br>Cr (0, 0, 0)<br>Ti (0.5, 0, 0)<br>O (0.5, 0, 0) | $a=b=c=3.93 \text{ \AA}^\circ$<br>$\alpha=\beta=\gamma=90^\circ$ |
| $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ ,<br>$\text{P4}/\text{mmm}$ | La (0.5, 0.5, 0.5)<br>Cr (0, 0, 0)<br>Ti (0.5, 0, 0)<br>O (0.5, 0, 0) | $a=b=c=3.93 \text{ \AA}^\circ$<br>$\alpha=\beta=\gamma=90^\circ$ |
| $\text{LaTiO}_3$ , $\text{Pm}\bar{3}\text{m}$                              | La (0.5, 0.5, 0.5)<br>Ti (0, 0, 0.5)<br>O (0.5, 0, 0)                 | $a=b=c=3.93 \text{ \AA}^\circ$<br>$\alpha=\beta=\gamma=90^\circ$ |

#### 4.1.1 STRUCTURE VIEW OF $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$

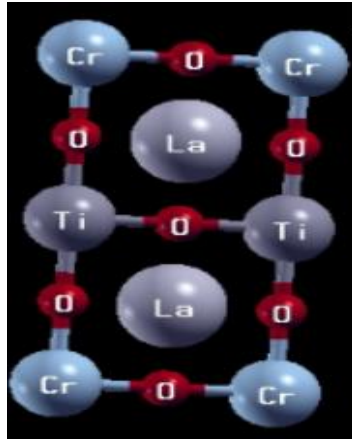
The structure of  $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$  can be derived using WIEN2k, as shown in figure (4.1 - 4.5) for ..... Respectively.



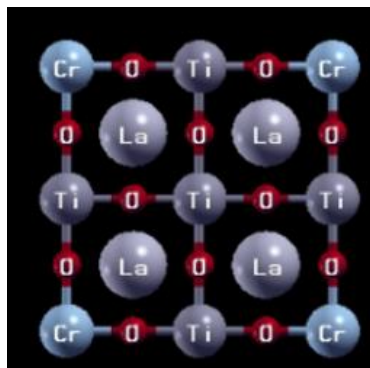
**Figure:4.1:** The crystal structure of cubic perovskite oxide  $\text{LaCrO}_3$



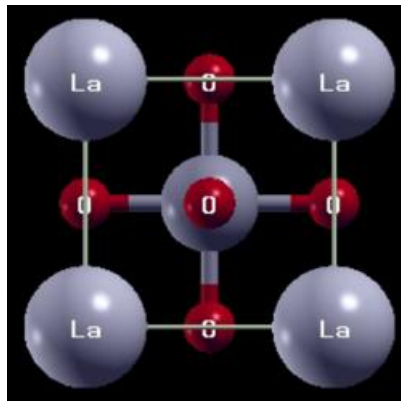
**Figure:4.2:** The crystal structure of tetragonal perovskite oxide  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$



***Figure:4.3: The crystal structure of tetragonal perovskite oxide  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$***



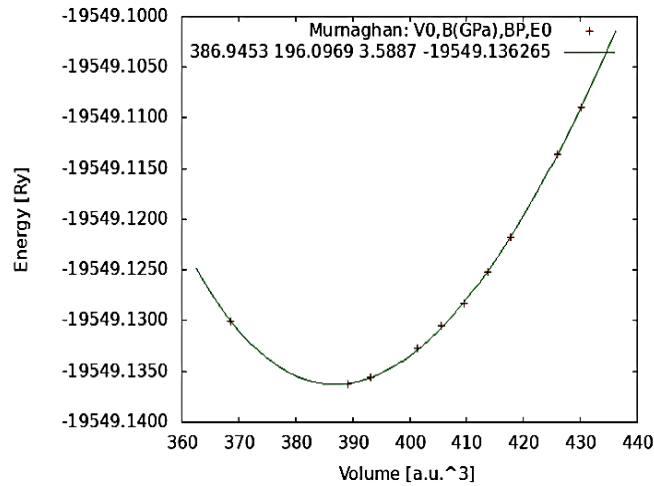
***Figure:4.4: The crystal structure of tetragonal perovskite oxide  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$***



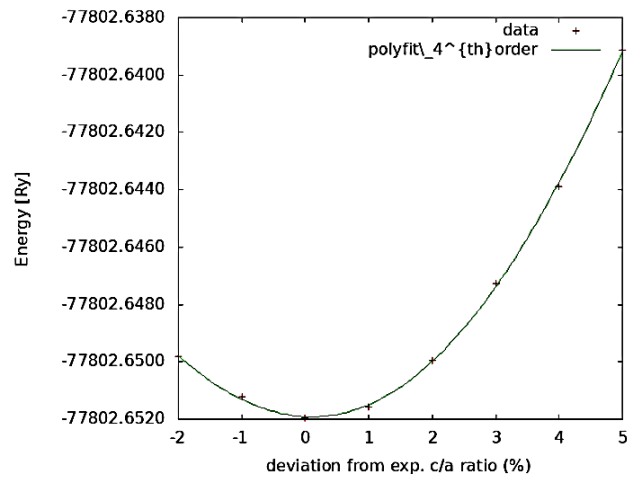
***Figure:4.5: The crystal structure of cubic perovskite oxide  $\text{LaCrO}_3$***

#### 4.1.2 VOLUME OPTIMIZATION OF $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$

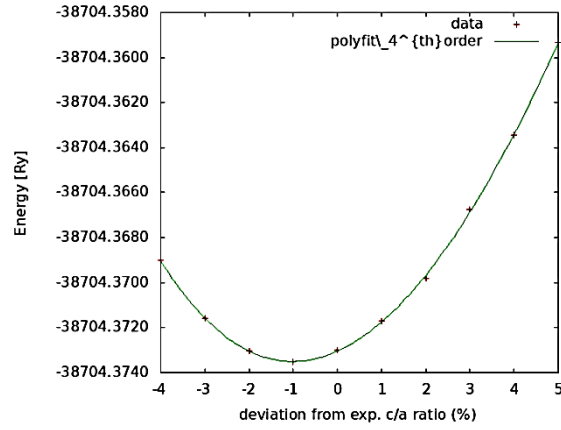
To determine the ground state properties, the total energies at different volumes are calculated around the equilibrium. It is then fitted to Murnaghan's state equation. Because the system is in equilibrium, at a certain value the energy becomes minimum and then increases. This minimized energy is called optimised equilibrium energy. The Energy-Volume curve for this compound is shown in these figures.



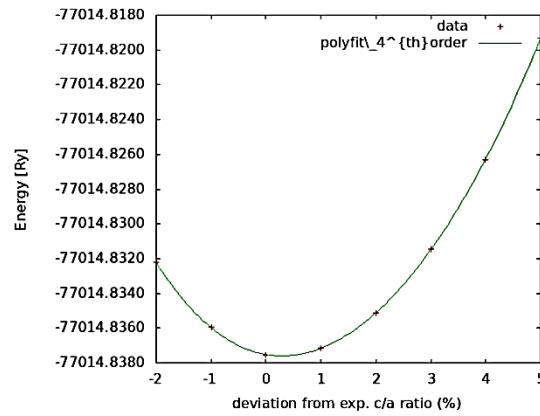
**Figure:4.6: Total energy (Ry) vs. unit cell volume for  $\text{LaCrO}_3$ .**



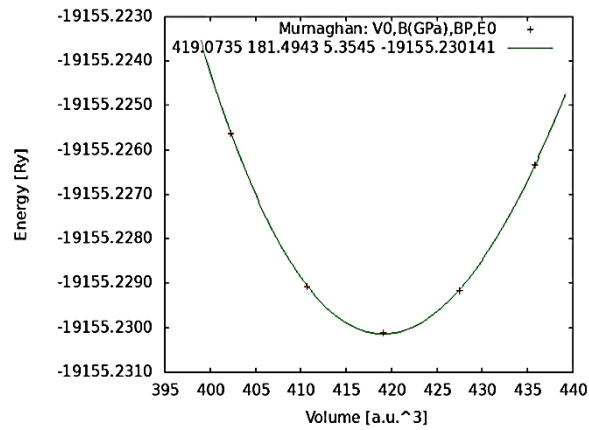
**Figure:4.7: Energy (Ry) vs. deviation graph (c/a ratio) for  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$**



**Figure:4.8: Energy (Ry) vs. deviation graph (c/a ratio) for  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$**



**Figure:4.9: Energy (Ry) vs. deviation graph (c/a ratio) for  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$**



**Figure:4.10: Total energy (Ry) vs. unit cell volume for  $\text{LaTiO}_3$**

**TABLE 4.2: VOLUME OPTIMIZATION PARAMETERS OF  $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$** 

| COMPOUND                                       | a, b, c (Å)                   | SPACE GROUP                     | STRUCTURE  | MINIMUM ENERGY(Ry) |
|------------------------------------------------|-------------------------------|---------------------------------|------------|--------------------|
| $\text{LaCrO}_3$                               | $a=b=c=3.856$                 | $221 \text{ Pm}\bar{3}\text{m}$ | Cubic      | -19549.1362        |
| $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ | $a=b=7.85015$<br>$c=3.9398$   | $123 \text{ P4/mmm}$            | Tetragonal | -77082.6519        |
| $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$   | $a=b=3.94332$<br>$c=7.80701$  | $123 \text{ P4/mmm}$            | Tetragonal | -38704.3743        |
| $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ | $a=b=7.85226,$<br>$c=3.93776$ | $123 \text{ P4/mmm}$            | Tetragonal | -77014.83759       |
| $\text{LaTiO}_3$                               | $a=b=c=3.856$                 | $221 \text{ Pm}\bar{3}\text{m}$ | Cubic      | -19155.23014       |

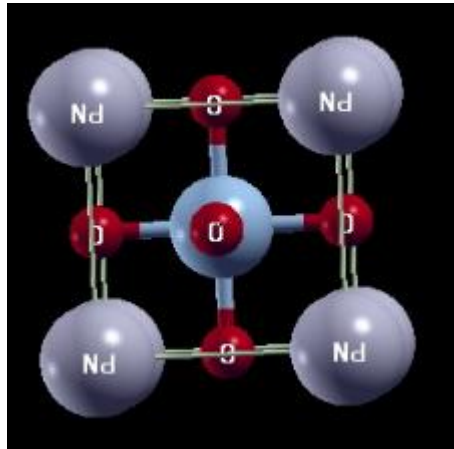
## 4.2 STRUCTURAL PARAMETERS OF $\text{NdCr}_x\text{Ti}_{1-x}\text{O}_3$

The generalised gradient approximation (GGA), which is included in the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave technique wien2k were used for all computations presented here. The cubic structures in these compounds belong to the space group (221  $\text{Pm}\bar{3}\text{m}$ ). The tetragonal structures in these compounds belong to the space group 123  $\text{P4}/\text{mmm}$ . The calculations are performed with 1000 k-points in the Brillouin zone. The plane wave expansion ( $R_{\text{MT}}*K_{\text{MAX}}$ ) is taken as 7.

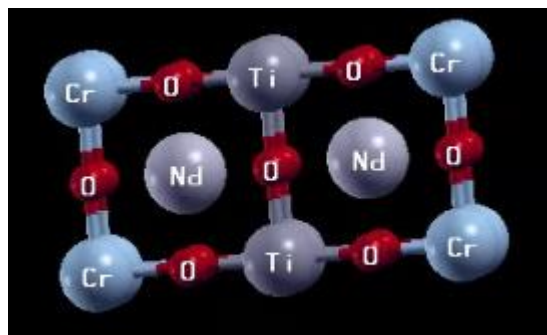
**TABLE 4.3: CRYSTALLOGRAPHIC PARAMETERS AND POSITIONS USED IN OUR CALCULATIONS OF  $\text{NdCr}_x\text{Ti}_{1-x}\text{O}_3$**

| COMPOUND AND SPACE GROUP                                              | POSITIONS                                                             | LATTICE PARAMETERS                                         |
|-----------------------------------------------------------------------|-----------------------------------------------------------------------|------------------------------------------------------------|
| $\text{NdCrO}_3$ , $\text{Pm}\bar{3}\text{m}$                         | Nd (0, 0, 0)<br>Cr (0.5, 0.5, 0.5)<br>O (0, 0.5, 0.5)                 | $a=b=c=3.90 \text{ \AA}$<br>$\alpha=\beta=\gamma=90^\circ$ |
| $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ , $\text{P4}/\text{mmm}$ | Nd (0, 0, 0)<br>Cr (0.5, 0.5, 0.5)<br>Ti (0, 0, 0.5)<br>O (0.5, 0, 0) | $a=b=c=3.90 \text{ \AA}$<br>$\alpha=\beta=\gamma=90^\circ$ |
| $\text{NdTiO}_3$ , $\text{P4}/\text{mmm}$                             | Nd (0.5, 0.5, 0.5)<br>Ti (0, 0, 0)<br>O (0.5, 0, 0)                   | $a=b=c=3.90 \text{ \AA}$<br>$\alpha=\beta=\gamma=90^\circ$ |

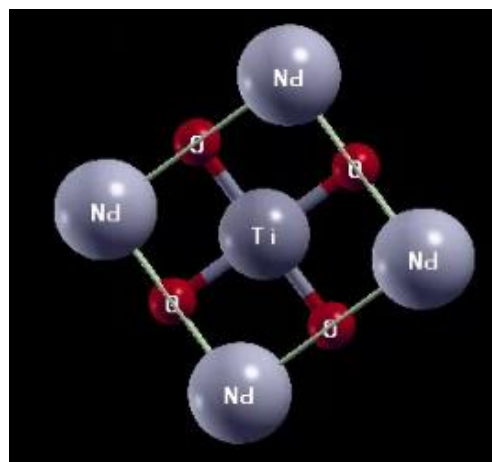
#### 4.2.1 STRUCTURE VIEW OF $\text{NdCr}_x\text{Ti}_{1-x}\text{O}_3$



*Figure 4.11: The crystal structure of cubic perovskite oxide  $\text{NdCrO}_3$*



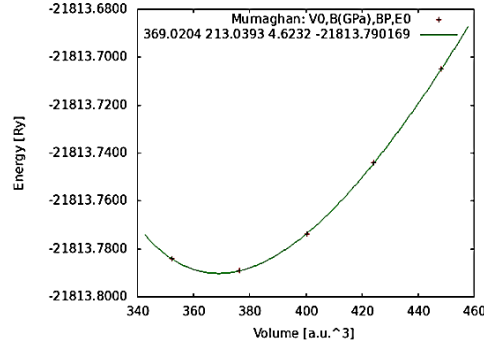
*Figure 4.12: The crystal structure of tetragonal perovskite oxide  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$*



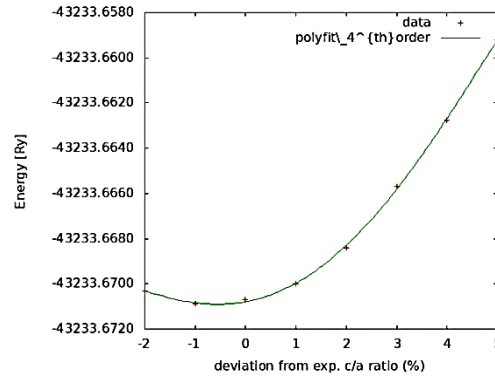
**Figure 4.13: The crystal structure of tetragonal perovskite oxide  $\text{NdTiO}_3$**

#### 4.2.2 VOLUME OPTIMIZATION OF $\text{NdCr}_x\text{Ti}_{1-x}\text{O}_3$

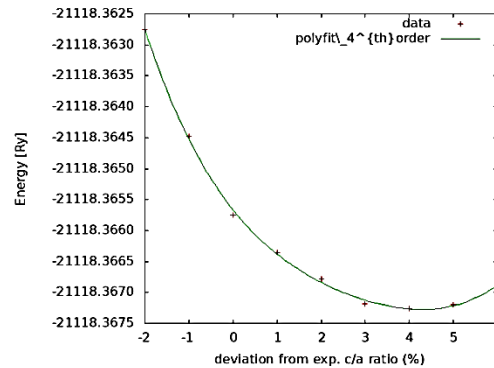
To determine the ground state properties, the total energies at different volumes are calculated around the equilibrium. It is then fitted to Murnaghan's state equation. Because the system is in equilibrium, at a certain value the energy becomes minimum and then increases. This minimized energy is called optimised equilibrium energy. The Energy-Volume curve for this compound is shown in these figures.



**Figure:4.14: Total energy (Ry) vs. unit cell volume for  $\text{NdCrO}_3$**



**Figure:4.15: Energy (Ry) vs. deviation graph (c/a ratio) for  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$**



**Figure:4.16: Energy (Ry) vs. deviation graph (c/a ratio) for NdTiO<sub>3</sub>**

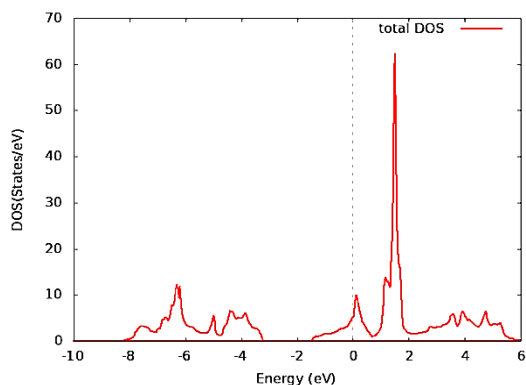
**TABLE 4.4 VOLUME OPTIMIZATION PARAMETERS OF NdCr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>**

| COMPOUND                                             | a, b, c (Å)          | SPACE GROUP           | STRUCTURE  | MINIMUM ENERGY(Ry) |
|------------------------------------------------------|----------------------|-----------------------|------------|--------------------|
| NdCrO <sub>3</sub>                                   | a=b=c=3.797          | 221<br>Pm $\bar{3}$ m | Cubic      | -21813.7901        |
| NdCr <sub>0.5</sub> Ti <sub>0.5</sub> O <sub>3</sub> | a=b=3.90,<br>c=7.77  | 123<br>P4/mmm         | Tetragonal | -43233.6708        |
| NdTiO <sub>3</sub>                                   | a=b=3.90,<br>c=4.073 | 123<br>P4/mmm         | Tetragonal | -21118.3672        |

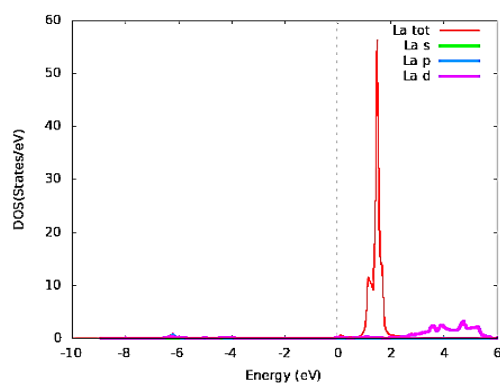
## 4.3 BAND STRUCTURE AND DENSITY OF STATES

### 4.3.1 DENSITY OF STATES

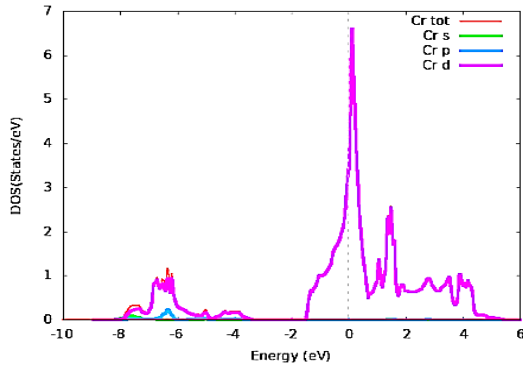
One of the most essential aspects that tells us about the behaviour and electrical character of this system is its density of state. It also allows one to learn about the chemical bonds that exist between atoms.



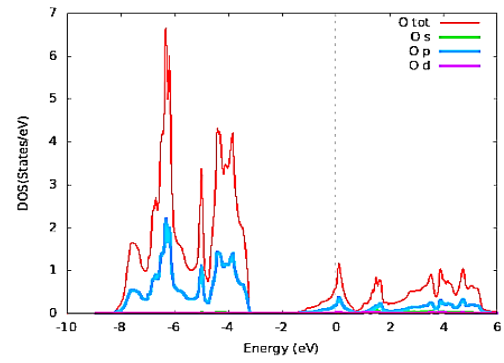
**(a)**



**(b)**



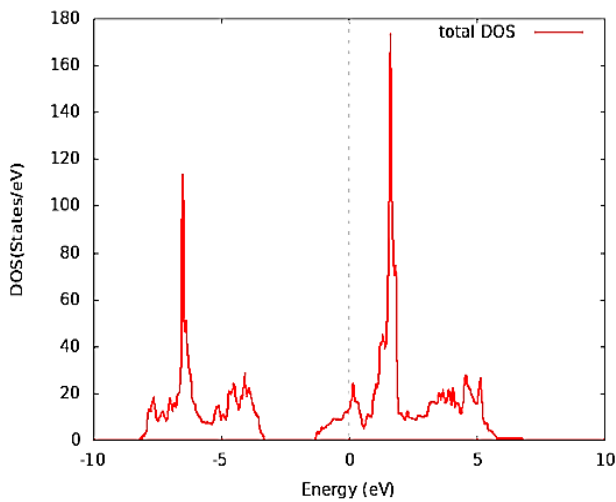
(c)



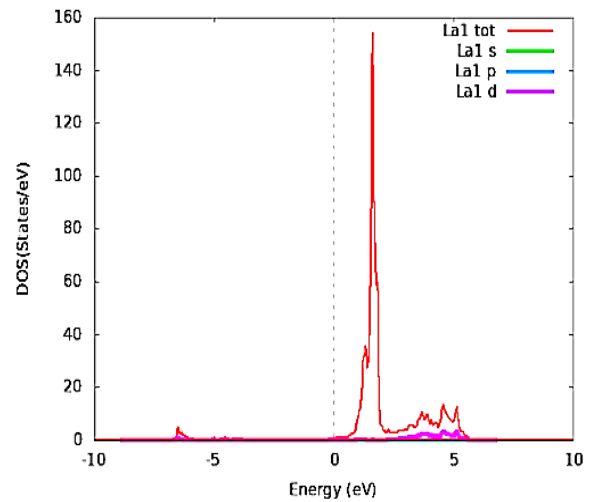
(d)

**Figure:4.17: (a), (b), (c), (d) shows the Total density of states of  $\text{LaCrO}_3$**

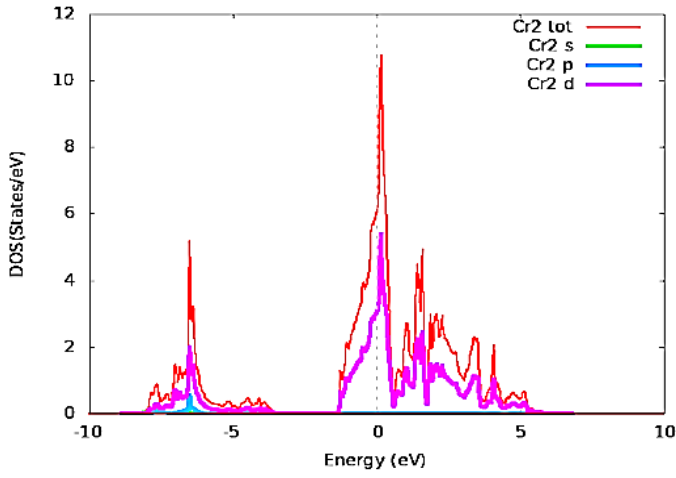
Fig:4.17: This graph is plotted between energy and DOS. The unit used for the energy is eV and for the DoS is (states/eV), the energy is taken along the x-axis and DoS is on the y-axis. In downstream (Valence band) of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms. In upstream (Conduction band) of the Fermi level, the greatest contribution is that of Cr-d and La-d, which determine the total DOS shape.



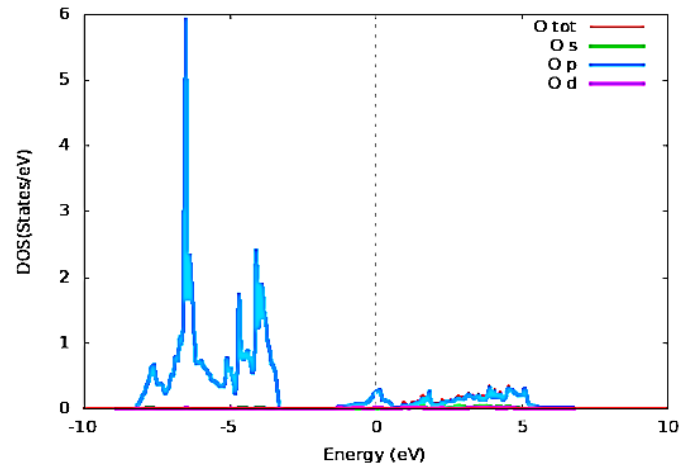
(a)



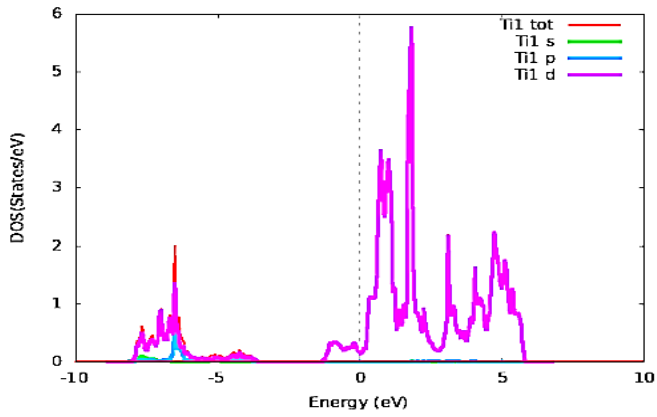
(b)



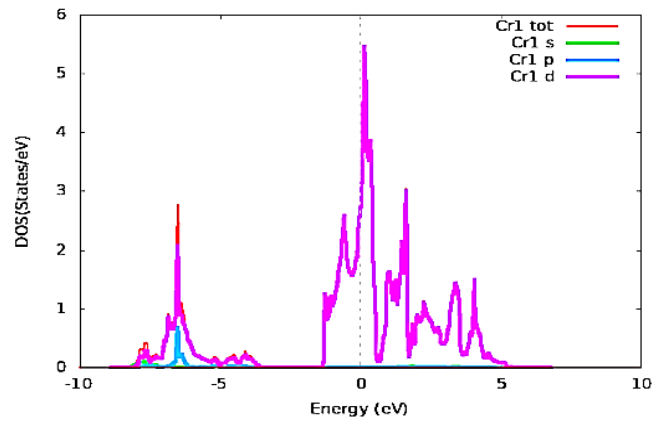
(c)



(d)



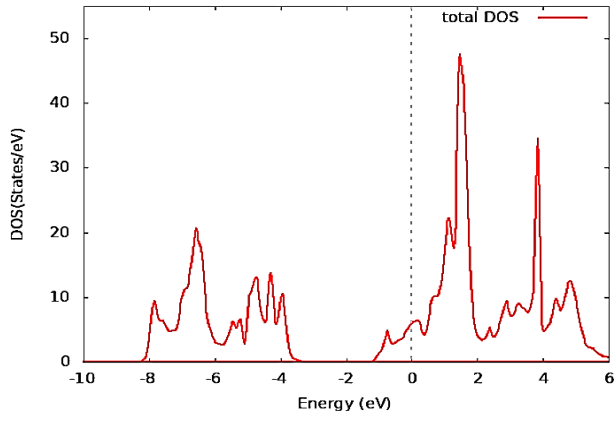
(e)



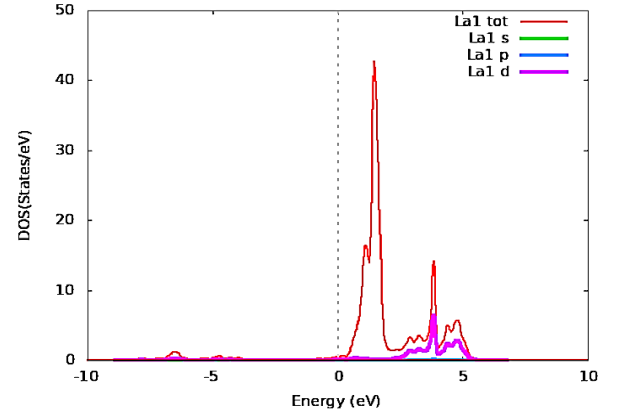
(f)

**Figure:4.18: (a), (b), (c), (d) and (e) shows the Total density of states of  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ .**

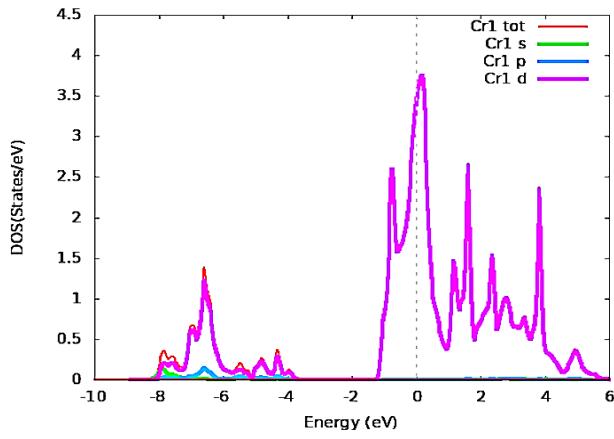
Fig:4.18: The graph shows that in downstream of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms. In upstream of the Fermi level, the greatest contribution is that of Cr1-d, Cr2-d, Ti1-d and La1-d, which determine the total DOS shape.



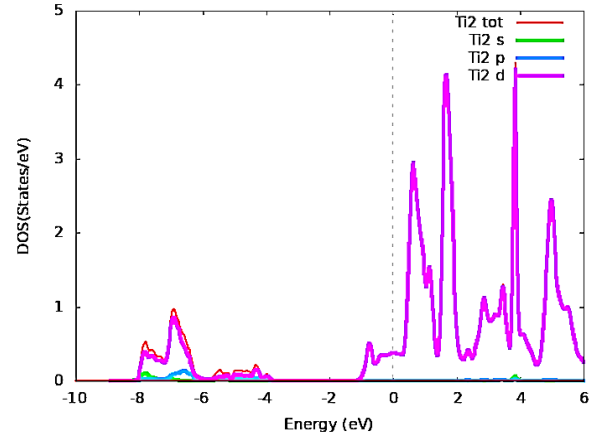
(a)



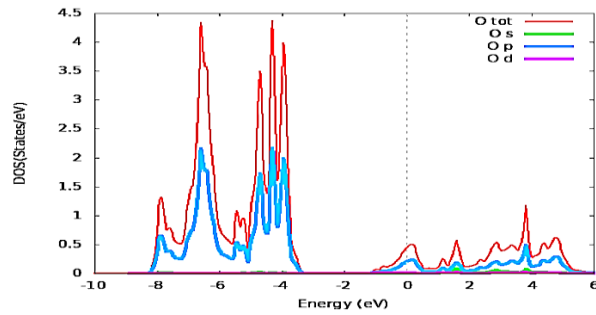
(b)



(c)



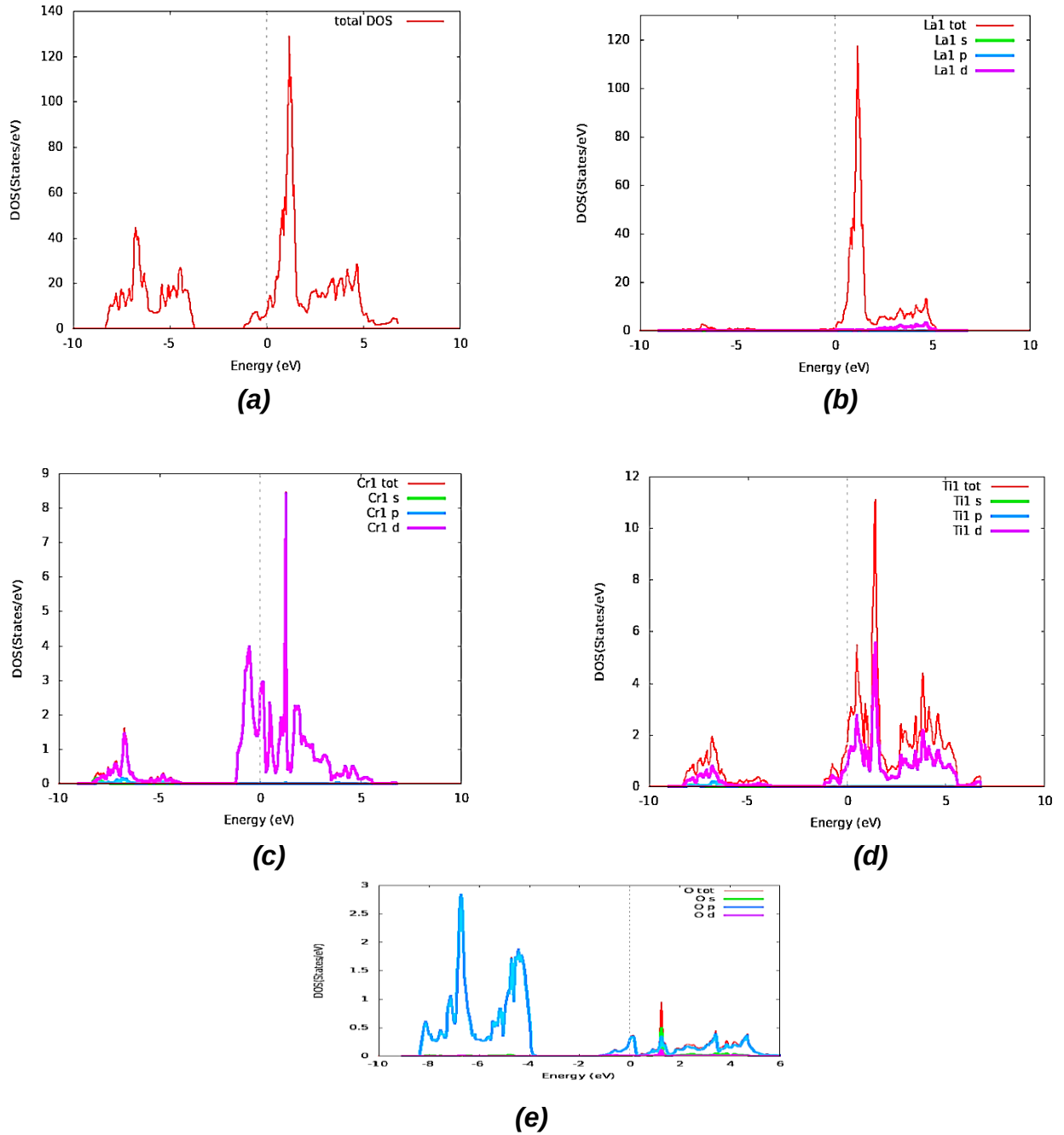
(d)



(e)

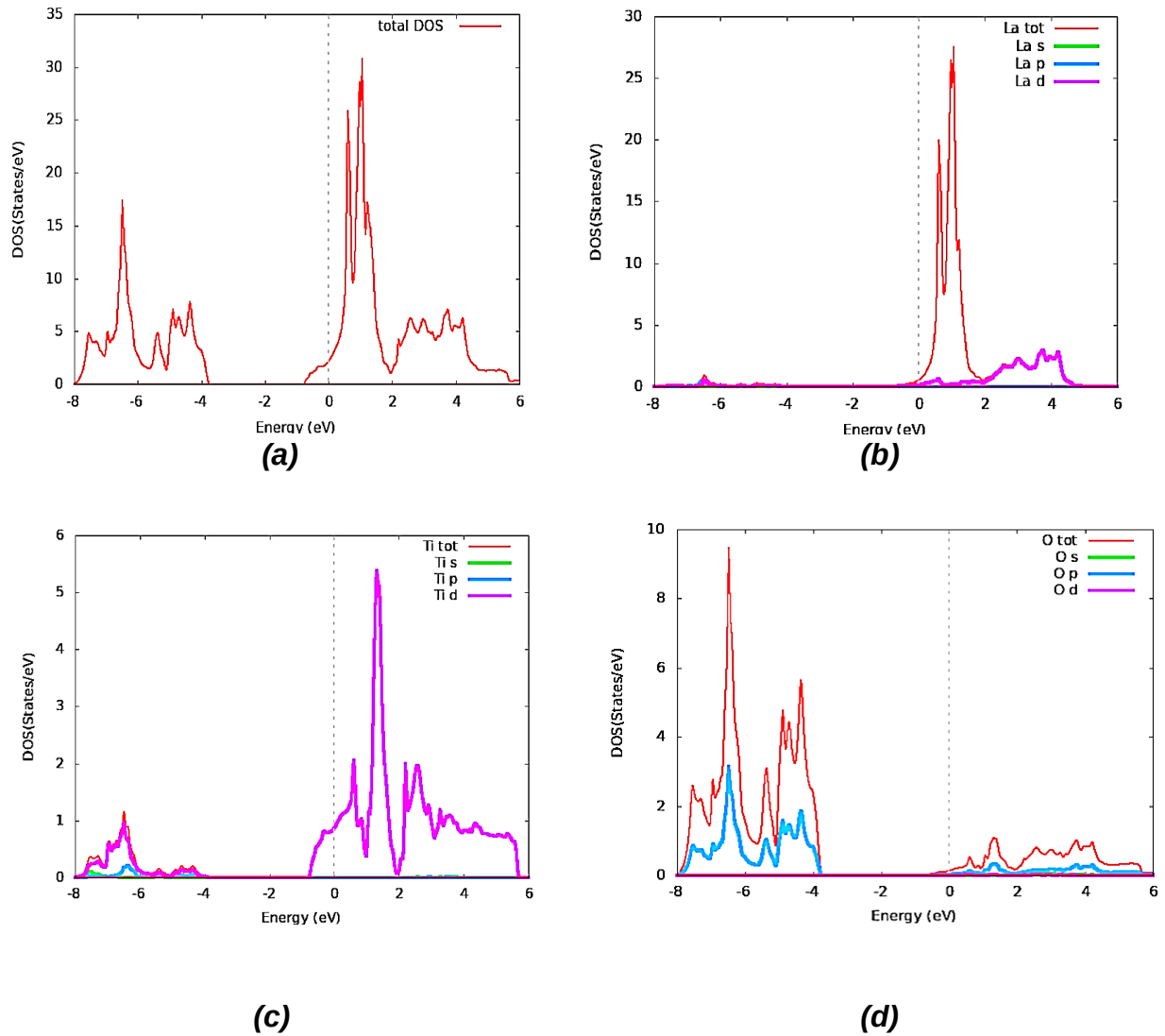
**Figure:4.19: (a), (b), (c), (d) and (e) shows the Total density of states of  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ .**

Fig:4.19: The graph shows that in downstream of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms. In upstream of the Fermi level, the greatest contribution is that of Cr1-d, Ti2-d and La1-Tot, which determine the total DOS shape.



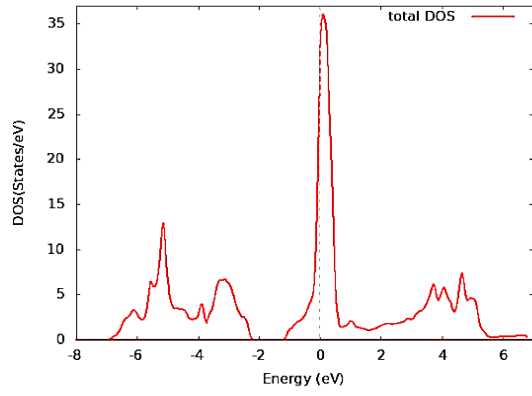
**Figure:4.20: (a), (b), (c), (d) and (e) shows the Total density of states of  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ .**

Fig:4.20: The graph shows that in downstream of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms. In upstream of the Fermi level, the greatest contribution is that of Cr1-d, Ti1-Tot and La1-Tot, which determine the total DOS shape.

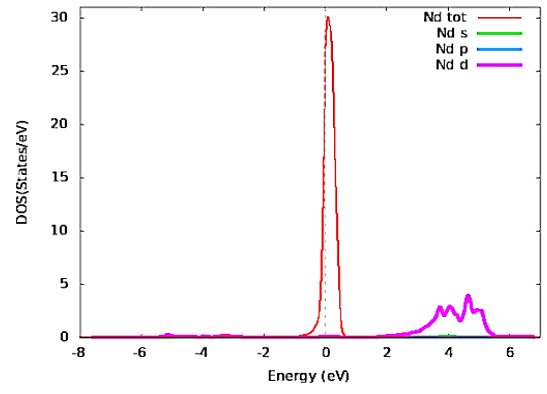


**Figure:4.21: (a), (b), (c), (d) shows the Total density of states of  $\text{LaTiO}_3$ .**

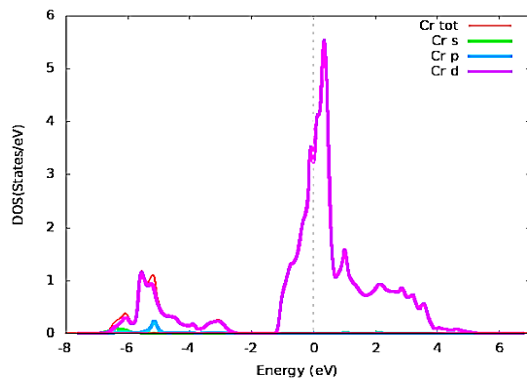
Fig:4.21: The graph shows that in downstream of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms. In upstream of the Fermi level, the greatest contribution is that of Ti-d and La-d, which determine the total DOS shape.



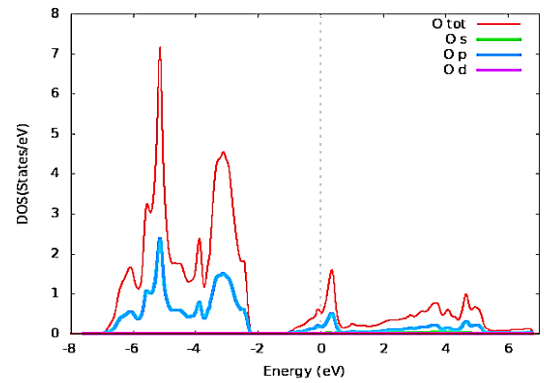
(a)



(b)



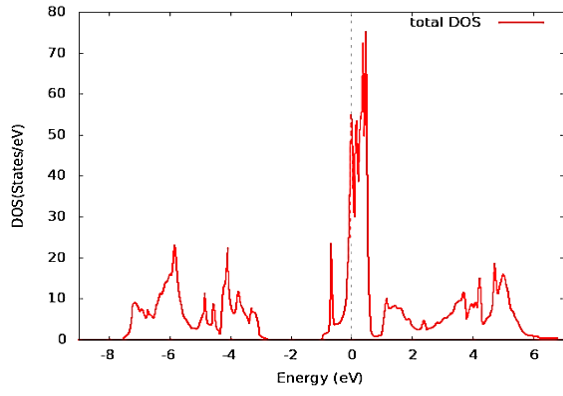
(c)



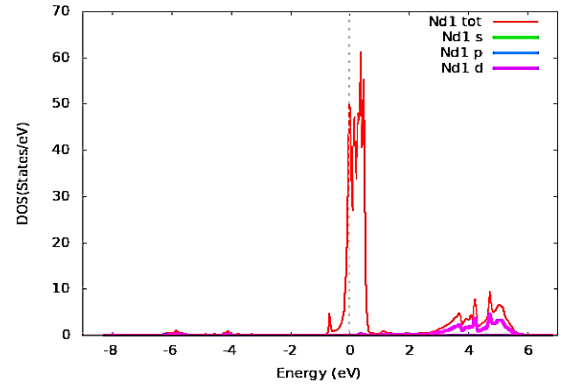
(d)

**Figure:4.22: (a), (b), (c), (d) shows the Total density of states of  $\text{NdCrO}_3$ .**

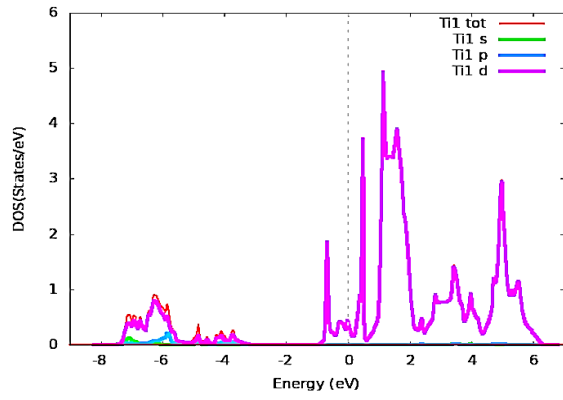
Fig:4.22: The graph shows that in upstream of the Fermi level, the greatest contribution is that of Cr-d and Nd-Tot, which determine the total DOS shape. In downstream of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms.



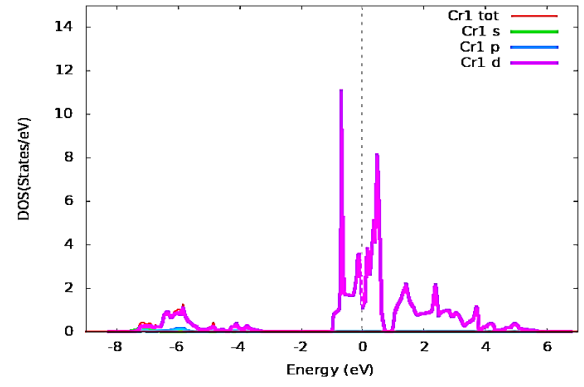
(a)



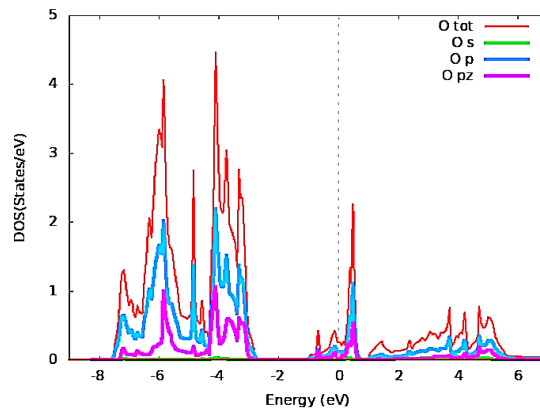
(b)



(d)



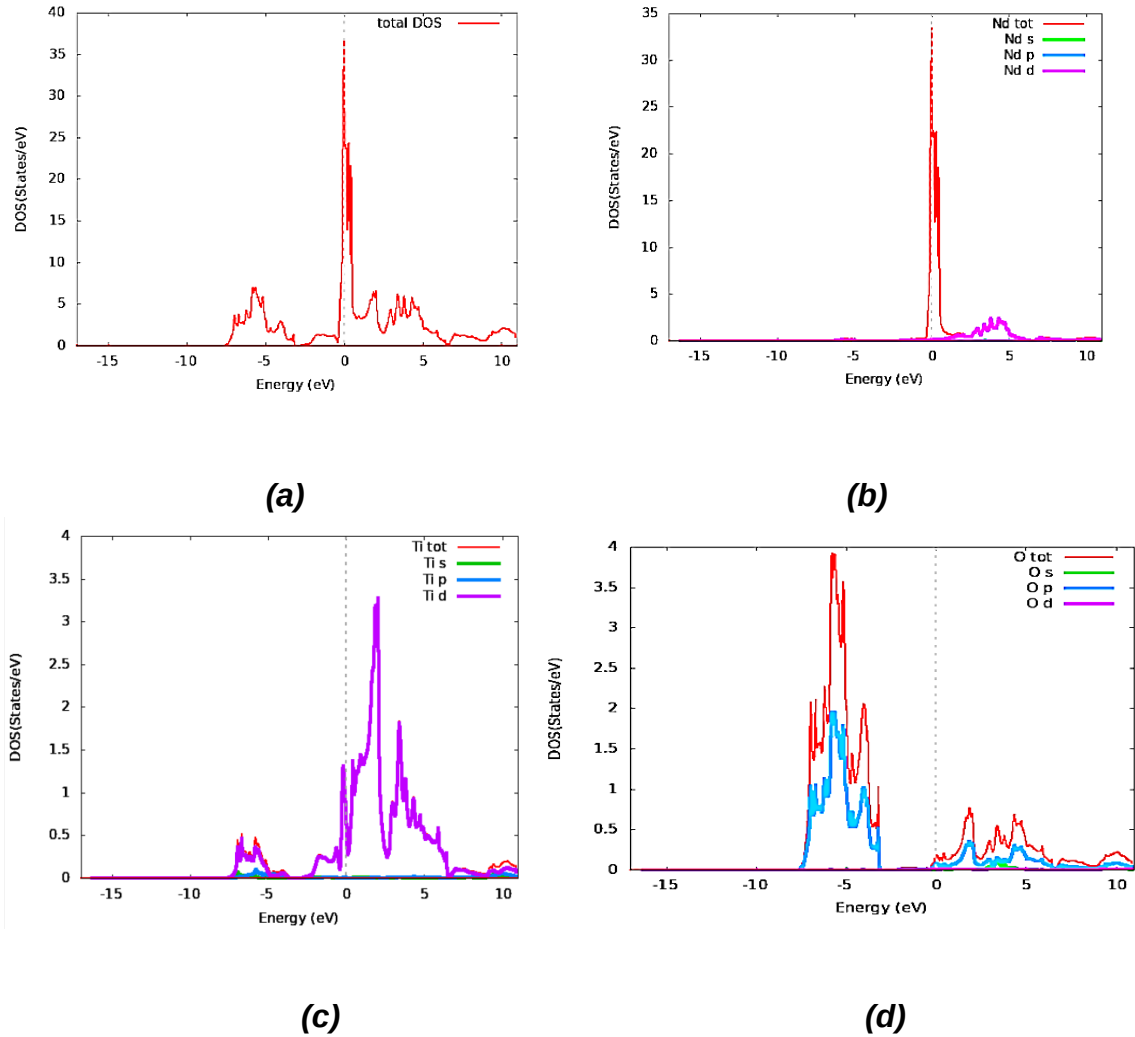
(c)



(e)

**Figure:4.23: (a), (b), (c), (d) and (e) shows the Total density of states of  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ .**

Fig:4.23: The graph shows that in upstream of the Fermi level, the greatest contribution is that of Ti-d and Nd-Tot, which determine the total DOS shape. In downstream of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms and Cr-d atoms.

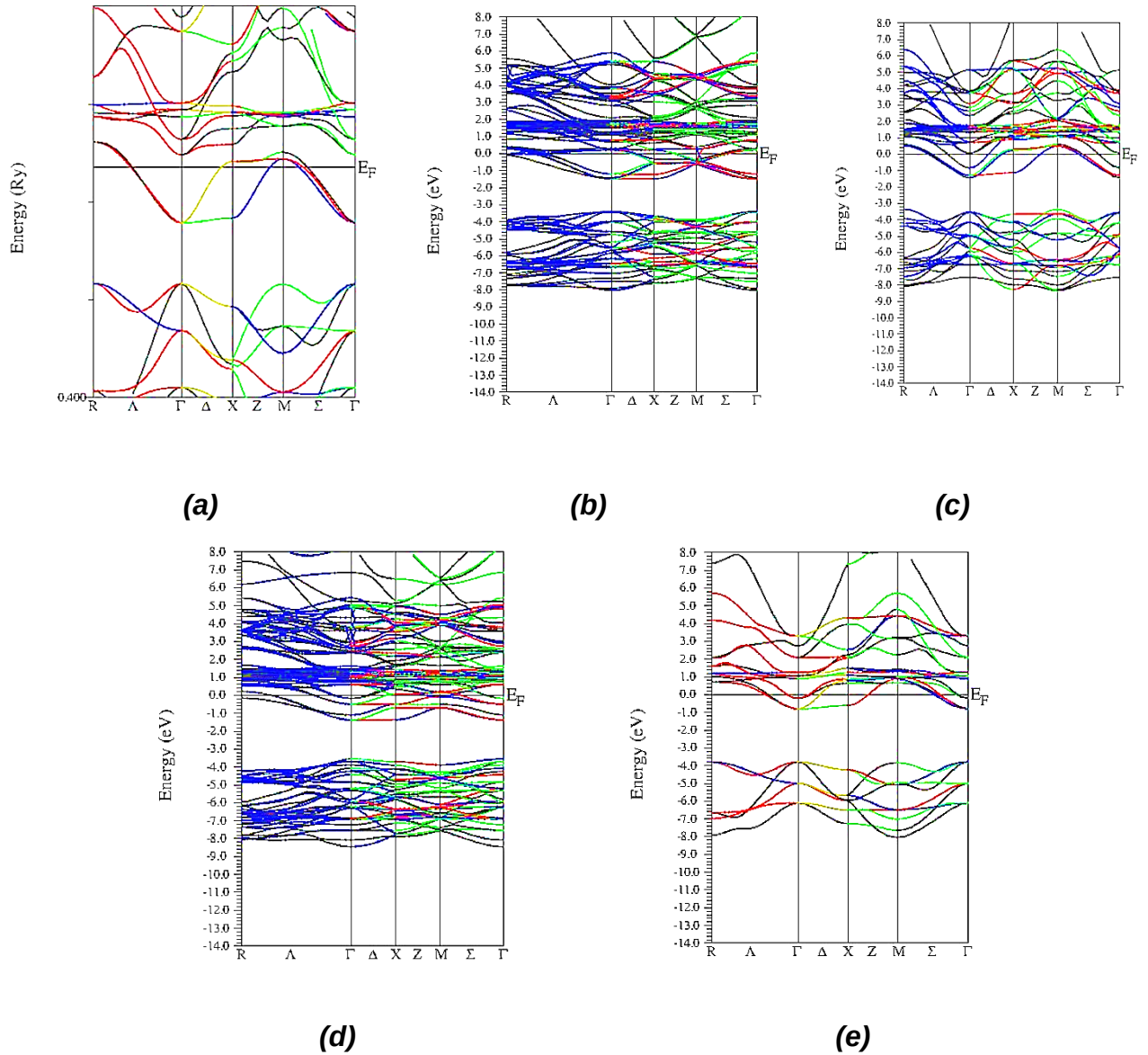


**Figure:4.24: (a), (b), (c), (d) shows the Total density of states of NdTiO<sub>3</sub>**

Fig:4.24: The graph shows that in upstream of the Fermi level, the greatest contribution is that of Ti-d and Nd-Tot, which determine the total DOS shape. In downstream of the Fermi level, it can be seen that the main contributions are those of O oxygen atoms.

### 4.3.2 BAND GAP

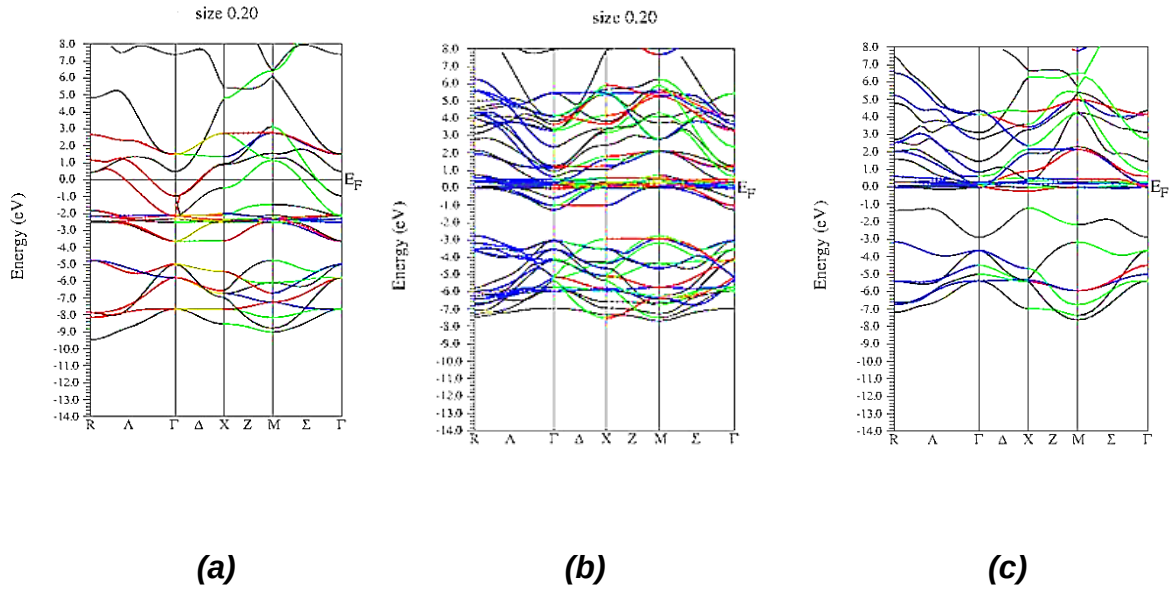
To investigate the role the metal Ti plays in the band structure, and the effect of La and Nd on it, we calculated the band structure, the total density of states. Following the band structure and the densities of that intercalation of Titanium in the parent materials leads to phase transitions from cubic to tetragonal structure, and pushing the conduction and valence bands towards lower and higher energies with respect to Fermi energy ( $E_F$ ).



**Figure:4.25: Band structure of (a)  $\text{LaCrO}_3$ ,**

**(b)  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ , (c)  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ , (d)  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ , (e)  $\text{LaTiO}_3$ .**

Fig:4.25-(a), (b), (c), (d) and (e) : The band structure determines the electronic energy levels of solid material and are used to better inform their electrical properties. we can find the hybridization of conduction band minima (CBM) and valence band maxima (VBM) of compounds. Hence there is no band gap. Hence these materials are conductor.

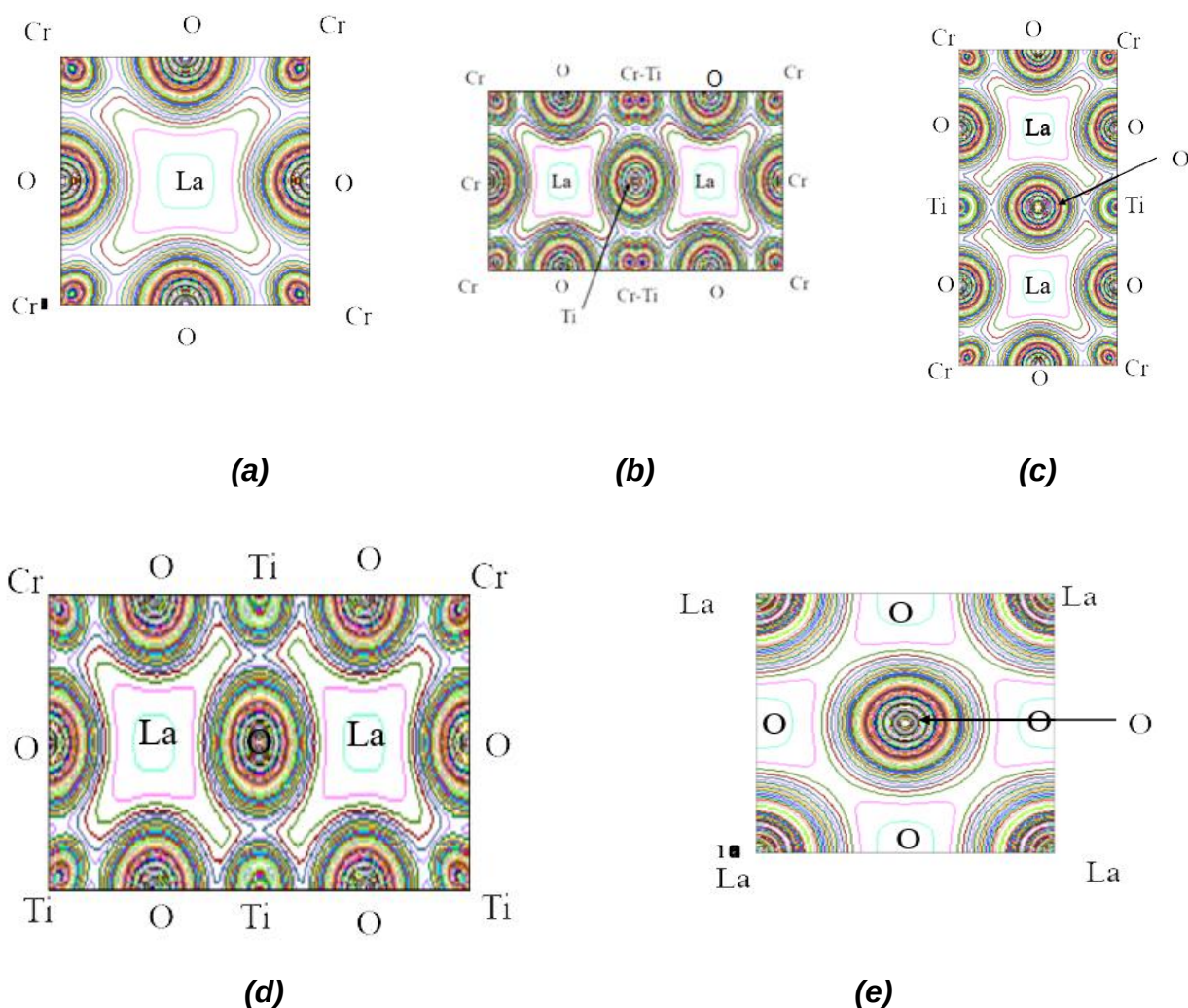


**Figure:4.26: Band structure of (a)  $\text{NdCrO}_3$ , (b)  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ , (c)  $\text{NdTiO}_3$ .**

Fig:4.26-(a), (b) and (c): The band structure determines the electronic energy levels of solid material and are used to better inform their electrical properties. we can find the hybridization of conduction band minima (CBM) and valence band maxima (VBM) of compounds. Hence there is no band gap. Hence these materials are conductor.

## 4.4 ELECTRON DENSITY

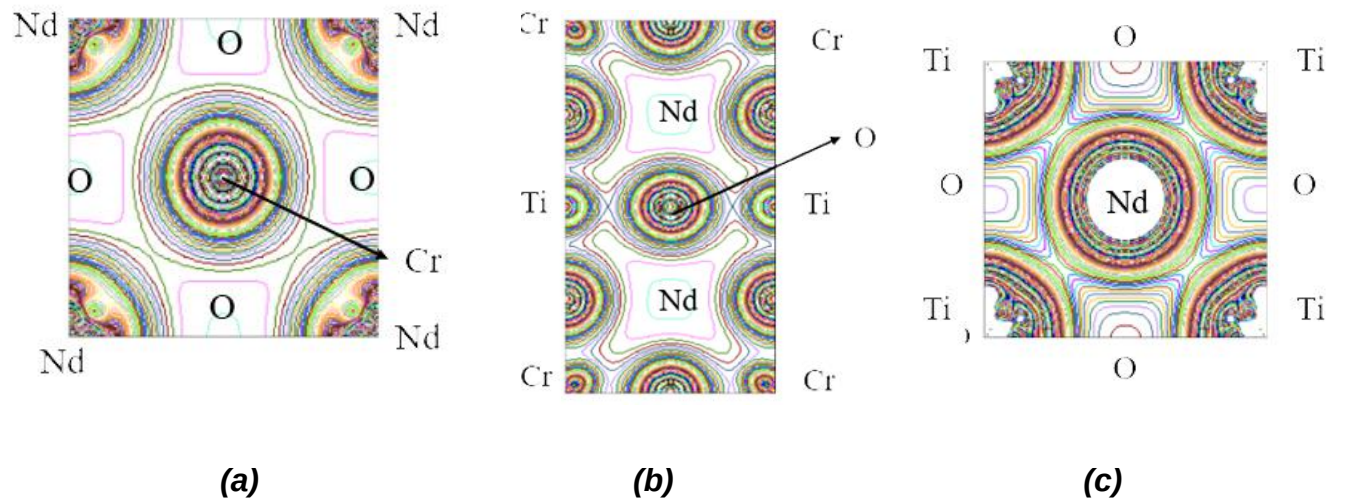
The electron density, which gives the bonding between atoms, is a measure of the likelihood of electrons around the atom. Electron density is related to electron wavefunction. Electron density reveals information on the type of bonds and atom interactions. In this study 2-D plots are used to determine the electron density of the proposed compounds.



**Figure:4.27: Shows Electron density of (a)  $\text{LaCrO}_3$ , (b)  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ , (c)  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ , (d)  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ , (e)  $\text{LaTiO}_3$ .**

**TABLE 4.5: CHARGE DENSITY PARAMETERS FOR  $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$**

| MATERIAL           | $\text{LaCrO}_3$ | $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ | $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ | $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ | $\text{LaTiO}_3$ |
|--------------------|------------------|------------------------------------------------|----------------------------------------------|------------------------------------------------|------------------|
| Fermi energy level | 0.86741Ry        | 0.87931Ry                                      | 0.90304Ry                                    | 0.92509Ry                                      | 0.86134Ry        |
| CV/T               | 11.50 J/K        | 30.90 J/K                                      | 14.44 J/K                                    | 18.72 J/K                                      | 5.08 J/K         |
| No of DOS          | 66.38Ry          | 178.36Ry                                       | 83.32Ry                                      | 108.06Ry                                       | 29.33Ry          |



**Figure:4.28: Shows (a) Electron density of (a)  $\text{NdCrO}_3$ , (b)  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  (c)  $\text{NdTiO}_3$ .**

**TABLE 4.6: CHARGE DENSITY PARAMETERS FOR  $\text{NdCr}_x\text{Ti}_{1-x}\text{O}_3$**

| MATERIAL           | $\text{NdCrO}_3$ | $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ | $\text{NdTiO}_3$ |
|--------------------|------------------|----------------------------------------------|------------------|
| Fermi energy level | 0.83795Ry        | 0.76205Ry                                    | 0.69573Ry        |
| CV/T               | 53.60 J/K        | 150.3 J/K                                    | 98.46 J/K        |
| No of DOS          | 309.37Ry         | 865.99Ry                                     | 568.33Ry         |

## 4.5 OPTICAL PROPERTIES

The study of solid optical properties proved to be a powerful tool for understanding material electrical properties.

The complex dielectric function can describe the optical characteristics of any material (A.G. El Hachimi, 2019)

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

(4.1)

The real and imaginary components of the dielectric function are denoted by  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$ , respectively. The electrical band structure is intimately related to  $\varepsilon_2(\omega)$ . It is computed by adding all transitions from occupied to unoccupied states using the well-known relation (A.G. El Hachimi, 2019).

$$\text{Im } \varepsilon(\omega) = \varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{i,j} \int |\langle i|M|j \rangle|^2 - (f_i(1-f_j)) \delta(E_f - E_i - \hbar\omega) d^3k \quad (4.2)$$

where M is the dipole matrix and i and j are the starting and end states.  $f_i$  is the Fermi distribution as a function of the i–th state, and  $E_i$  is the energy of the electron in the i–th state.

The Kramers-Kronig relation can be used to calculate the real part of the dielectric function (A.G. El Hachimi, 2019).

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\varepsilon_2(\alpha) \alpha d\alpha}{\alpha^2 - \omega^2} \quad (4.3)$$

where the main value of the integral is represented by P.

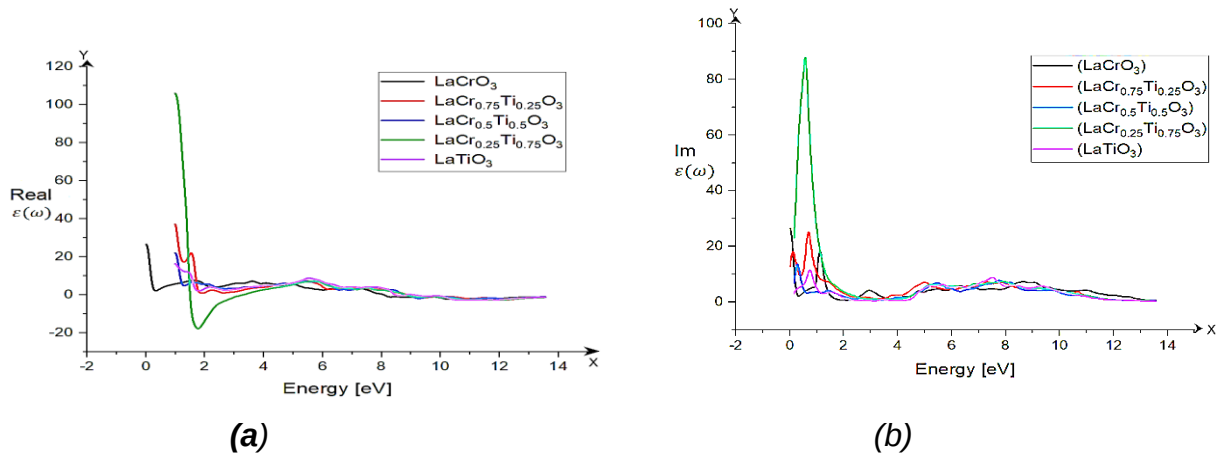
The following relationship yields the absorption coefficient (M. Houmad, 2015)

$$\alpha(\omega) = \frac{\sqrt{2}}{c} \omega \sqrt{-\varepsilon_1(\omega) + \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}} \quad (4.4)$$

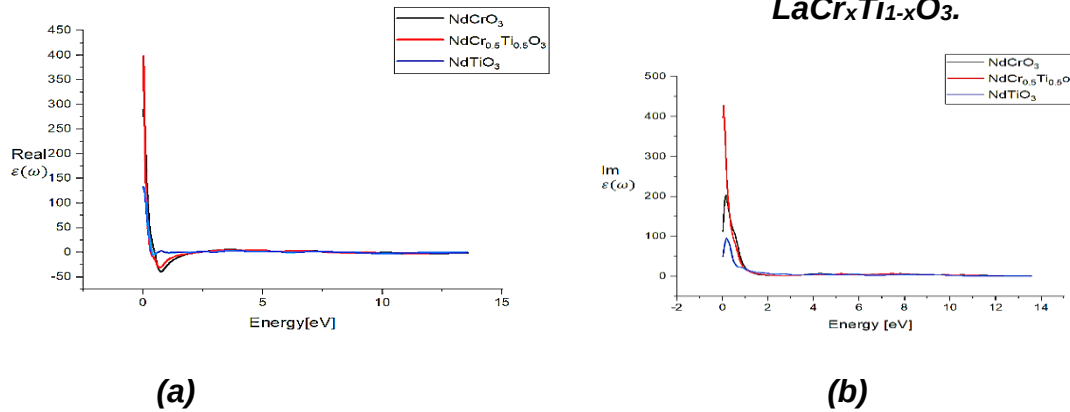
The optical conductivity is (M. Houmad, 2015)

$$R_s \sigma_{\alpha\beta}(\omega) = \frac{\omega}{4\pi} \text{Im} \varepsilon_{\alpha\beta}(\omega) \quad (4.5)$$

#### 4.5.1 DIELECTRIC FUNCTION



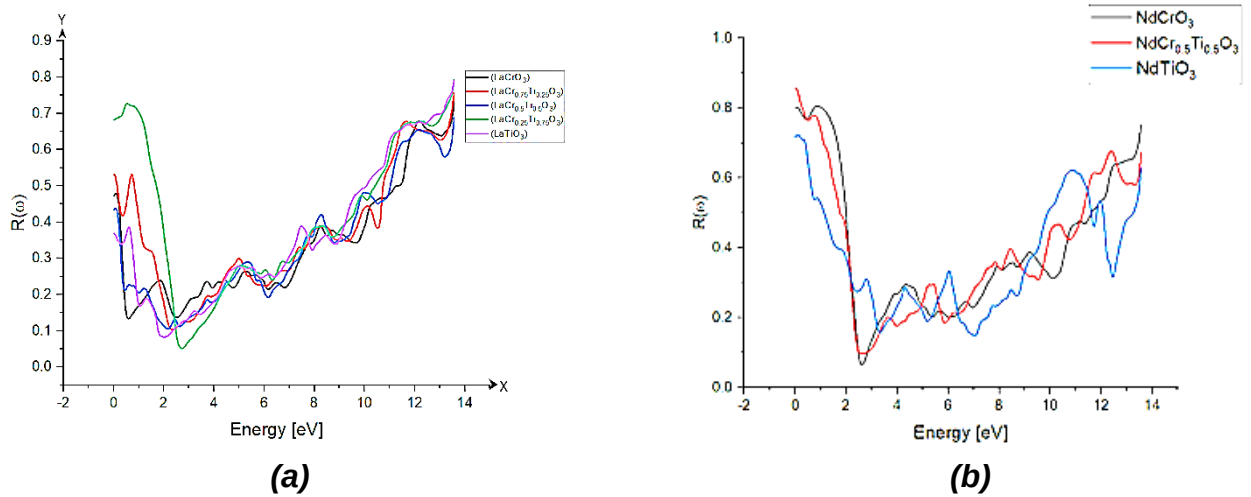
**Figure:4.29: Shows (a), (b) Real and imaginary part of dielectric constant of  $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$ .**



**Figure:4.30: Shows (a), (b) Real and imaginary part of dielectric constant of  $\text{NdCr}_x\text{Ti}_{1-x}\text{O}_3$ .**

The imaginary component of the dielectric function is widely known to be intimately related to the electronic band structure and exhibits light absorption in the material. Whereas the real part of the dielectric function is concerned with the dispersion of incident photons by crystals (H. Absike, 2019). To showcase the material's potential in optoelectronic applications, a thorough study of its optical characteristics is required. The frequency optical spectra are used to provide a full explanation of optical properties. The real component of the dielectric tensor provides information about the compound's internal structure. The optical conductivity, reflectivity and absorption coefficient of the compound shows a maximum in the visible, UV and IR energy region applicable in solar cell materials ref.. (H. Absike, 2019)

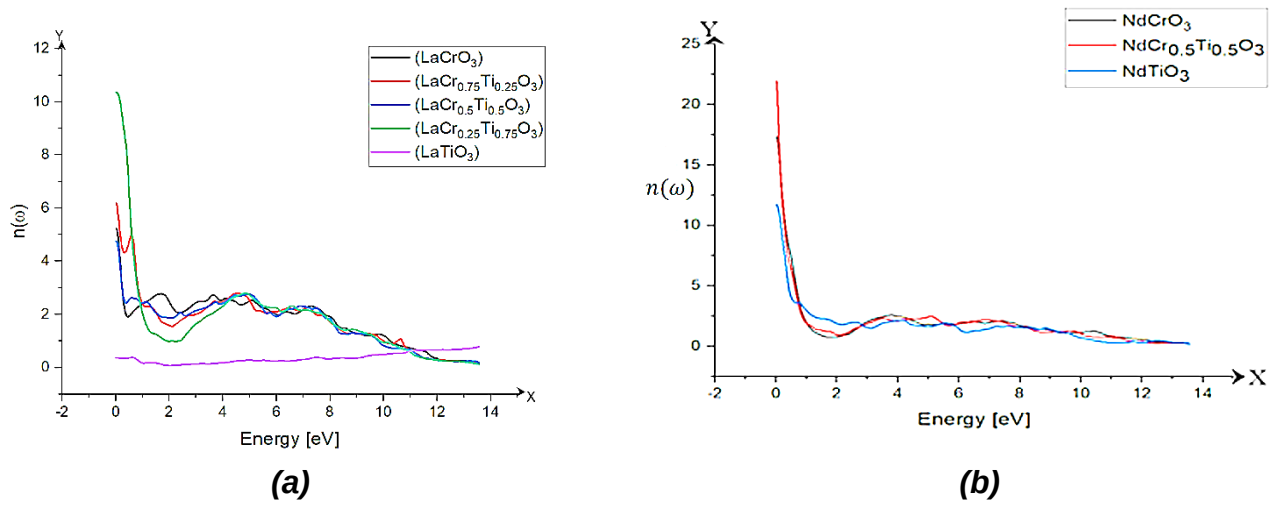
#### 4.5.2 REFLECTIVITY SPECTRA OF $ACr_xTi_{1-x}O_3$ [A=La, Nd]



**Figure:4.31: Shows (a), (b) Reflectivity of  $ACr_xTi_{1-x}O_3$  [A=La, Nd].**

The amount of energy reflected in relation to the incident energy is represented by the reflection coefficient. The static value of reflection coefficient for  $LaCrO_3$ ,  $LaCr_{0.75}Ti_{0.25}O_3$ ,  $LaCr_{0.5}Ti_{0.5}O_3$ ,  $LaCr_{0.25}Ti_{0.75}O_3$ ,  $LaTiO_3$  is 0.479, 0.54, 0.44, 0.68, 0.36 in x-direction respectively. The static value of reflection coefficient of  $NdCrO_3$ ,  $NdCr_{0.5}Ti_{0.5}O_3$ ,  $NdTiO_3$  is 0.8, 0.88, 0.66 respectively. The reflection coefficient begins to increase for  $ACr_xTi_{1-x}O_3$  [A=La, Nd] until reaching maximum values.

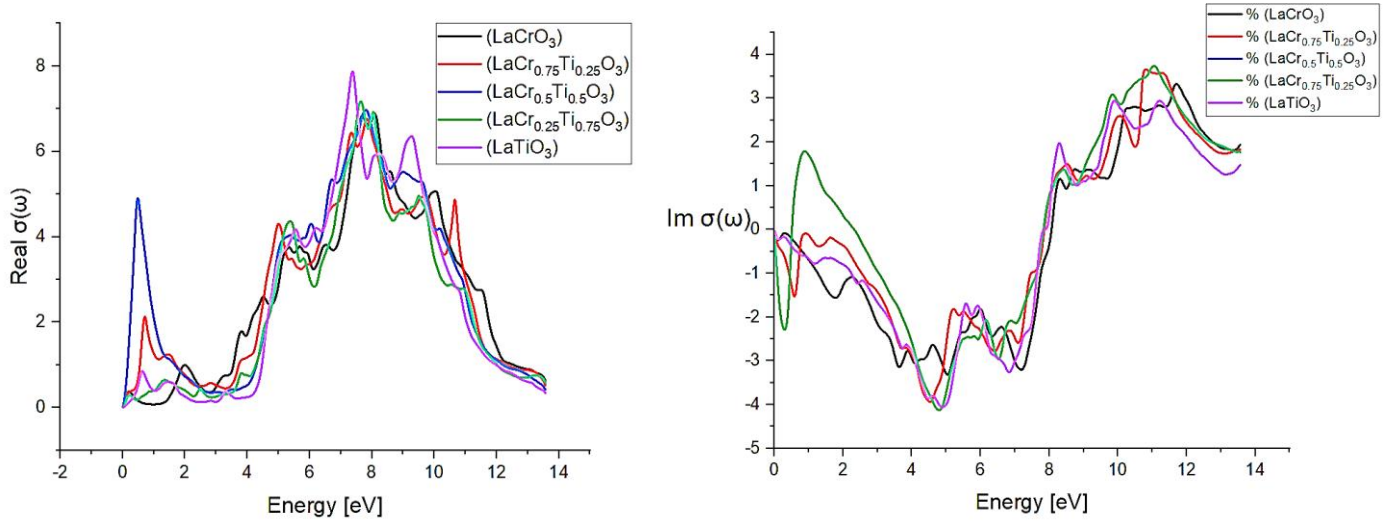
#### 4.5.3 REFRACTIVITY SPECTRA OF $ACr_xTi_{1-x}O_3$ [A=La, Nd]



**Figure:4.32: Shows (a), (b) Refractivity of  $ACr_xTi_{1-x}O_3$  [A=La, Nd].**

The refractive index for  $LaCrO_3$ ,  $LaCr_{0.75}Ti_{0.25}O_3$ ,  $LaCr_{0.5}Ti_{0.5}O_3$ ,  $LaCr_{0.25}Ti_{0.75}O_3$ ,  $LaTiO_3$  is obtained as 4.6, 6.2, 4.4, 10.3, 0.19 respectively. The refractive index for  $NdCrO_3$ ,  $NdCr_{0.5}Ti_{0.5}O_3$ ,  $NdTiO_3$  is obtained as 15.5, 20.4, 10.4. At this point, the refraction phenomena disappears because the refractive index approaches "1" and the material behaves like empty space. The fluctuation in the refractive index from this minimum is tiny, and so the dispersion is very low. The dispersion phenomena is highly prominent in the visible spectrum region, as we can see.

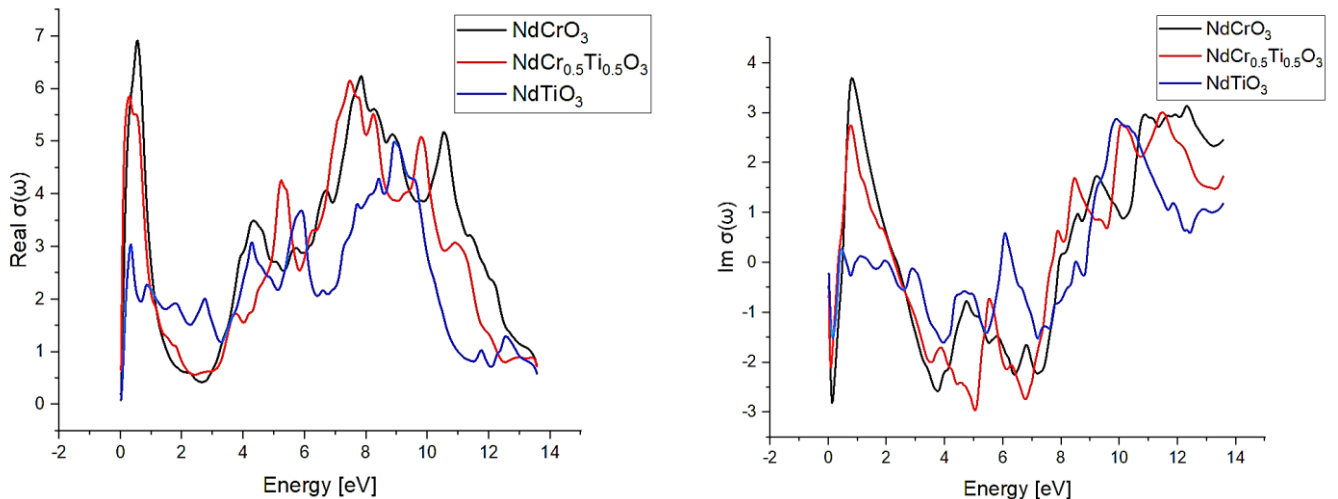
#### 4.5.4 CONDUCTIVITY SPECTRA OF $ACr_xTi_{1-x}O_3$ [A=La, Nd]



**Figure:4.33: Shows (a), (b) Conductivity of  $LaCr_xTi_{1-x}O_3$ .**

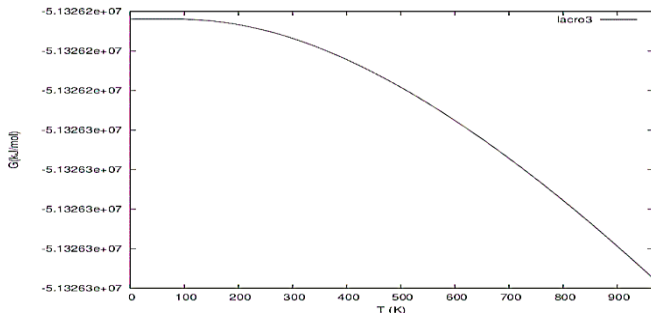
**Figure:4.34: Shows (a), (b) Conductivity of  $NdCr_xTi_{1-x}O_3$ .**

The static value of real conductivity for  $LaCrO_3$ ,  $LaCr_{0.75}Ti_{0.25}O_3$ ,  $LaCr_{0.5}Ti_{0.5}O_3$ ,  $LaCr_{0.25}Ti_{0.75}O_3$ ,  $LaTiO_3$  is obtained as 0.39, 0.495, 0.35, 0.789, 0.367 respectively. The static value of imaginary conductivity for  $LaCrO_3$ ,  $LaCr_{0.75}Ti_{0.25}O_3$ ,  $LaCr_{0.5}Ti_{0.5}O_3$ ,  $LaCr_{0.25}Ti_{0.75}O_3$ ,  $LaTiO_3$  is obtained as 0.367, 0.911, 0.2857, 0.884, 0.258 respectively. The static value of real conductivity for  $NdCrO_3$ ,  $NdCr_{0.5}Ti_{0.5}O_3$ ,  $NdTiO_3$  is obtained as 0.495, 0.351, 0.293. The static value of imaginary conductivity for  $NdCrO_3$ ,  $NdCr_{0.5}Ti_{0.5}O_3$ ,  $NdTiO_3$  is obtained as 0.802, 0.748, 0.421.

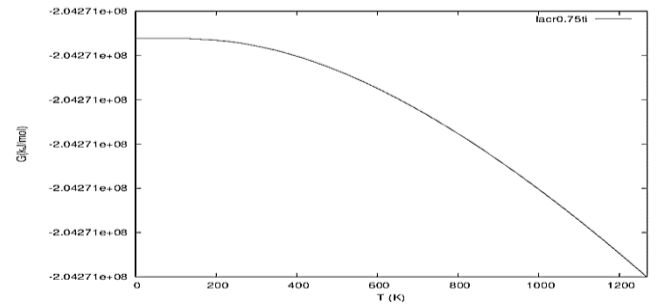


## 4.6 THERMAL PROPERTIES

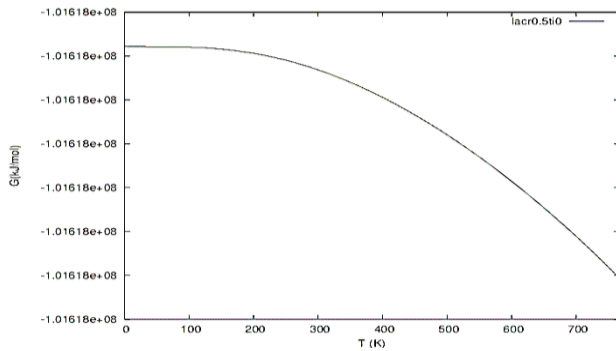
To investigate the elastic wave property and stiffness of the composite, phonon modes of vibration were determined using elastic wave velocities. The mean velocity parameter was used to calculate the Debye temperature factor  $\Theta$ , which is the fundamental physical feature utilized to differentiate between low and high temperature vibrational zones in a solid.  $T > \Theta$  and  $T < \Theta$  provided high-frequency modes of vibration and frozen phonons, respectively.



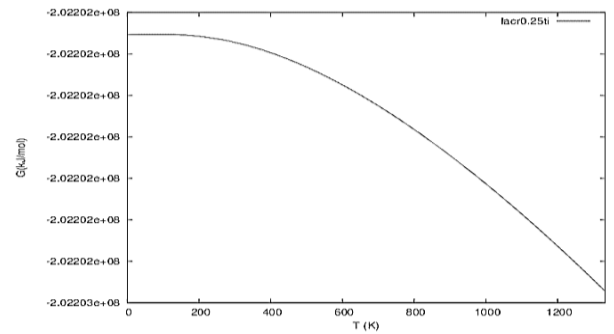
(a)



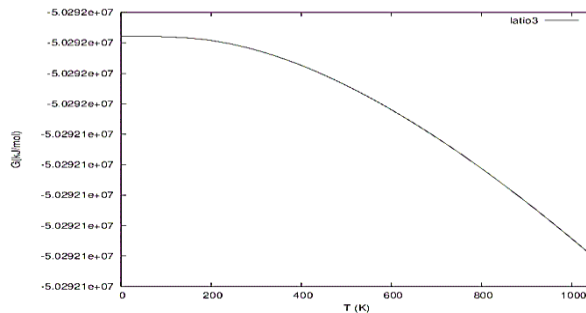
(b)



(c)

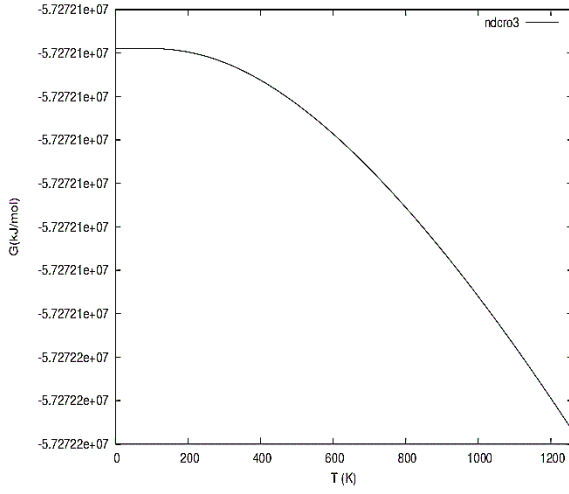


(d)

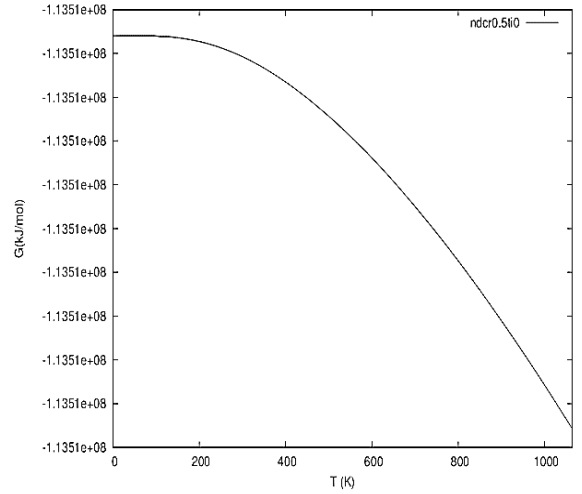


(e)

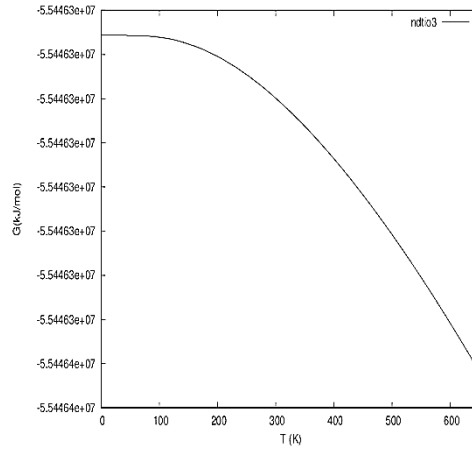
Figure:4.35: (a), (b), (c), (d), (e) shows the thermal graph of  $\text{LaCr}_x\text{Ti}_{1-x}\text{O}_3$ .



(a)



(b)



(c)

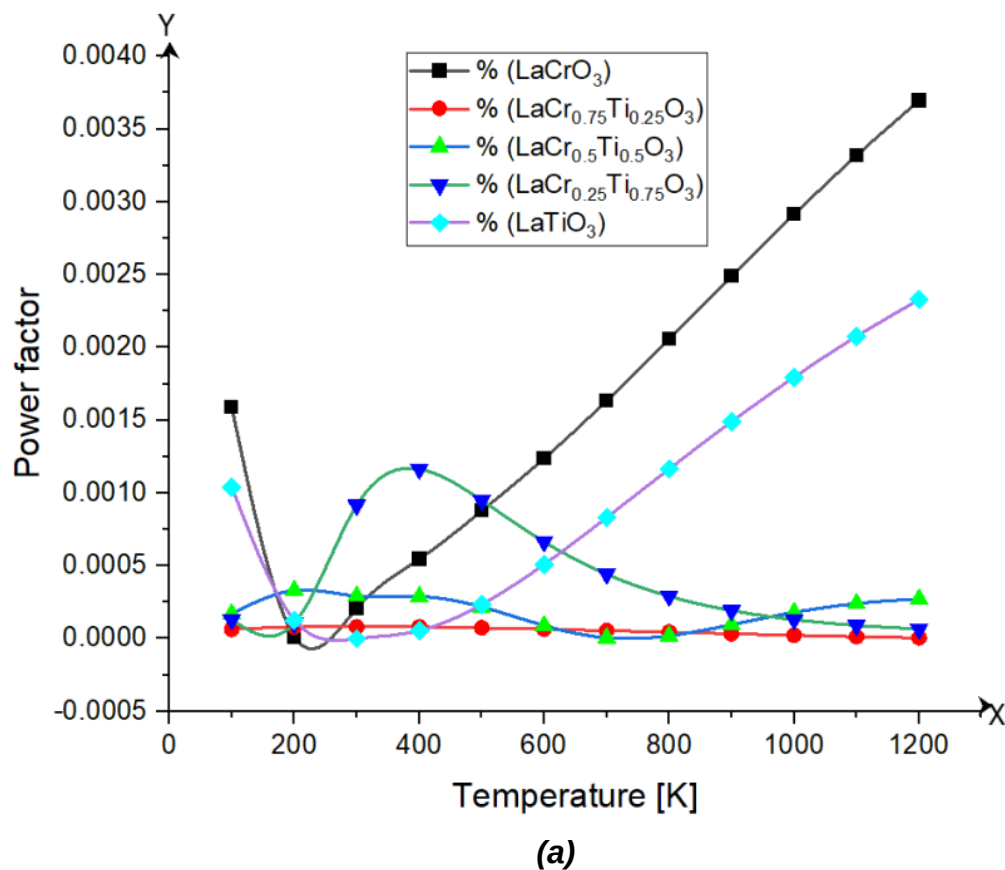
**Figure:4.36: (a), (b), (c), (d), (e) shows the thermal graph of  $\text{NdCr}_x\text{Ti}_{1-x}\text{O}_3$**

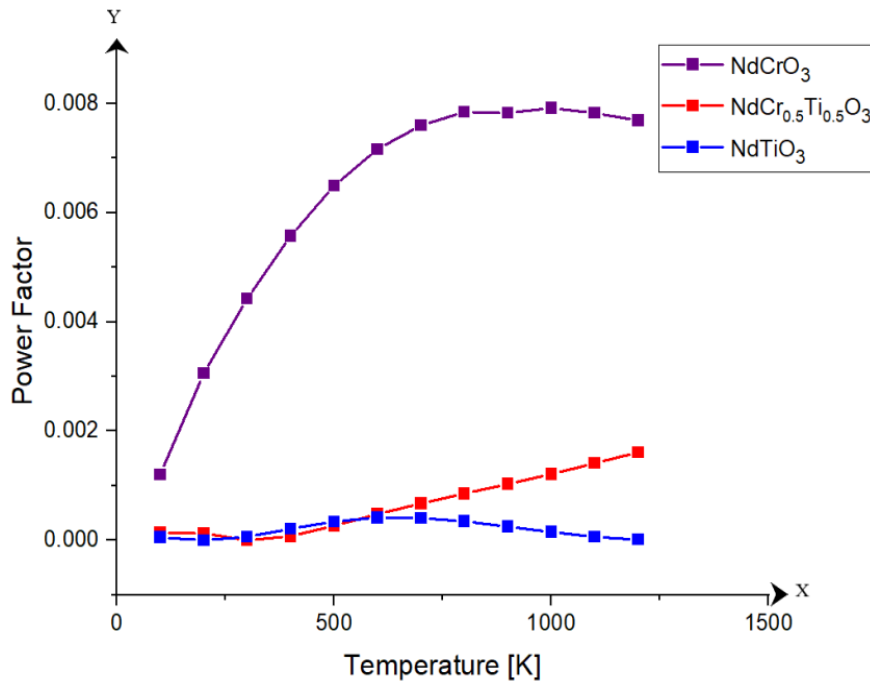
The thermal properties of the composed materials are shown here. On increasing the temperature the gibbs free energy is decreasing. Gibbs free energy combines enthalpy and entropy in a single value. As quantitatively established for many metal combinations, electrochemical processes in batteries occur in conjunction with a spontaneous drop in Gibbs free energy due to variations in lattice cohesive energies and ionisation free energies (in water) of reactants and products. When there are no dissolved ions as reactants or products in a battery, the highest cohesive (free) energy per atom frequently identifies the high-energy species that contains the chemical energy. According to the analysis, atom transfer from the

metallic bulk into solution or an oxide is at least as essential as electron transfer.  
Implement urs

## 4.7 THERMOELECTRIC PROPERTIES

To gain an understanding of a compound's thermoelectric behaviour, transport coefficients near to the Fermi levels are computed as a function of temperature, such as the Seebeck coefficient ( $S$ ), electrical conductivities relative to relaxation time ( $\sigma/\tau$ ), and the figure of merit ( $zT$ ). Using the Boltzmann transport theory implemented in the BoltzTrap code, the thermoelectric (TE) properties of materials can be determined close to the Fermi level (Georg K.H. Madsen, 2006).  $zT$  is defined as  $zT = \sigma S^2 T / \kappa$  where  $S^2$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity, and  $\kappa$  is the thermal conductivity.



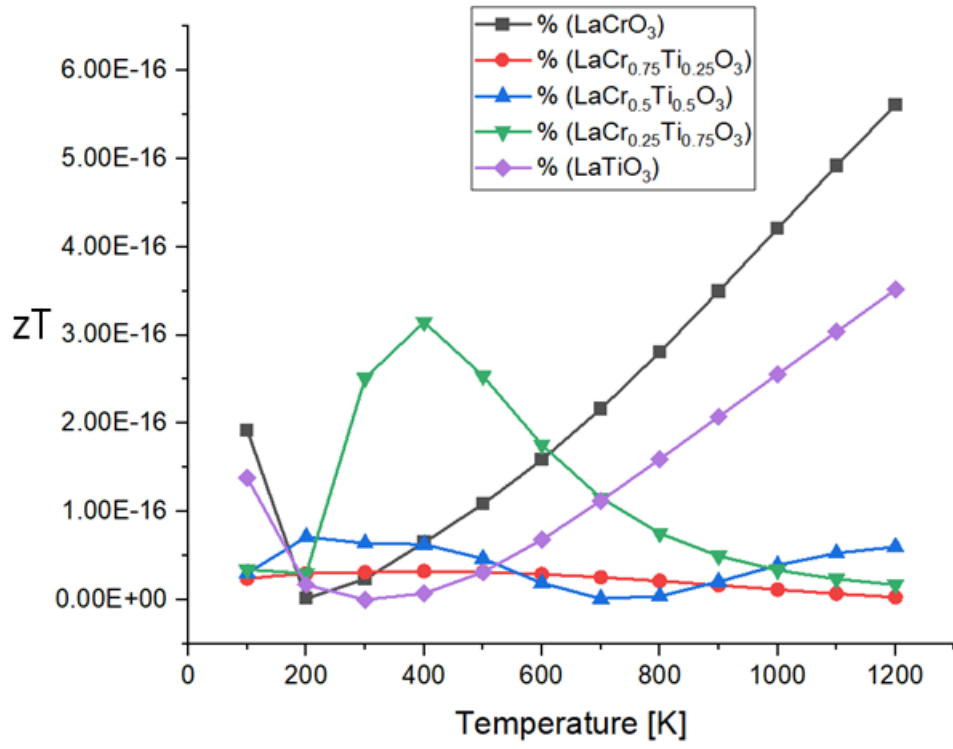


(b)

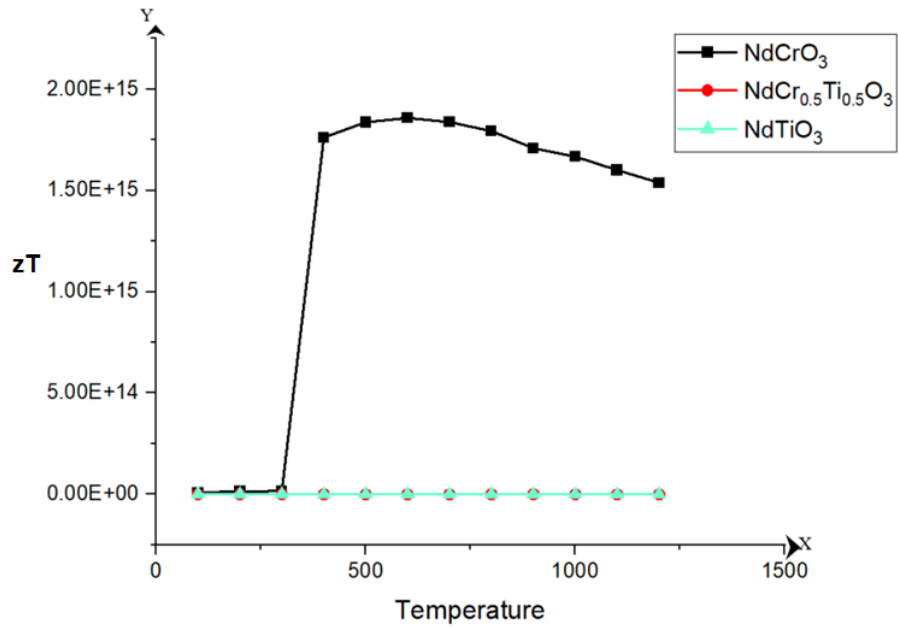
**Figure:4.37: (a), (b) shows the Temperature vs Power Factor of  $ACr_xTi_{1-x}O_3$  [A=La, Nd]**

Figure:4.23:(a) The comparison of power factor for  $LaCrO_3$ ,  $LaCr_{0.75}Ti_{0.25}O_3$ ,  $LaCr_{0.5}Ti_{0.5}O_3$ ,  $LaCr_{0.25}Ti_{0.75}O_3$  and  $LaTiO_3$  compounds are shown here. The Power Factor is found to be decreasing from 0K-200K and increasing from 200K-1200K for  $LaCrO_3$ .  $LaCrO_3$  is showing more power factor than other compounds at 1000K to 1200K as 0.0036, hence more power can be generated by using  $LaCrO_3$ . From this we can say that  $LaCrO_3$  shows better thermoelectric property.

Figure:4.23:(b) The comparison of power factor for  $NdCrO_3$ ,  $NdCr_{0.5}Ti_{0.5}O_3$  and  $NdTiO_3$  compounds are shown here. The Power Factor is found to be increasing from 0K-900K and decreasing from 900K-1200K for  $NdCrO_3$ . whereas even though all the compounds show an increase in power factor  $NdCrO_3$  is showing more power factor than other compounds at 900K, hence more power can be generated by using  $NdCrO_3$ . From this we can say that  $NdCrO_3$  shows better thermoelectric property.



(a)



(b)

Figure:4.38: (a), (b) shows the Temperature vs  $zT$  of  $\text{ACr}_x\text{Ti}_{1-x}\text{O}_3$  [ $A=\text{La}, \text{Nd}$ ]

Figure:4.24:(a) The comparison of ZT for  $\text{LaCrO}_3$ ,  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ ,  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ,  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$  and  $\text{LaTiO}_3$  compounds are shown here. The compounds show an increase in ZT.  $\text{LaCrO}_3$  is showing more ZT than other compounds at 1200K. From this we can say that  $\text{LaCrO}_3$  shows better thermoelectric property.

Figure:4.24:(b) The comparison of ZT for  $\text{NdCrO}_3$ ,  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  and  $\text{NdTiO}_3$  compounds are shown here. The compounds show an increase in ZT.  $\text{NdCrO}_3$  is showing more ZT than other compounds at 500K. From this we can say that  $\text{NdCrO}_3$  shows better thermoelectric property.

## CHAPTER 5

### 5.1 SUMMARY

In this study, the structural, mechanical, electronic, optical, thermal and thermoelectric properties of  $\text{ACr}_x\text{Ti}_{1-x}\text{O}_3$  [ $\text{A}=\text{La}, \text{Nd}$ ] are studied. The calculations are carried out by means of Full Potential Linearized Augmented Plane Wave (FP-LAPW) method as implemented in the WIEN2K code. The Generalized Gradient Approximation (GGA) can be applied to calculate the exchange correlation potential. Muffin tin spheres of radius  $R_{\text{MT}}$  are chosen in such a way that there is minimal charge leakage from the core. The calculations are performed with 1000 k-points in the Brillouin zone. The plane wave expansion ( $R_{\text{MT}}*K_{\text{MAX}}$ ) is taken as 7. The atomic position of La is (0.5,0.5,0.5), Cr is (0,0,0), O is (0.5,0,0) and Ti is (0.5,0,0). Here in the initialization the cubic structure  $\text{LaCrO}_3$  undergoes phase transition while doping Ti and the compound changes into tetragonal. When it is completely replaced by Titanium it again undergoes phase transition and changes into cubic. The atomic position for Nd is (0,0,0), Cr is (0.5,0.5,0.5), Ti is (0,0.5,0.5) and O is (0.5,0,0). In the initialization process the cubic structure  $\text{NdCrO}_3$  undergoes phase transition and changes into tetragonal  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  and  $\text{NdTiO}_3$ . We can observe that  $\text{NdCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$  and  $\text{NdCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$  is in unstable state so it is not suitable for energy storage applications. The self-consistent calculations are carried out to an accuracy of 0.0001Ry energy and 0.001e charge. The band structure, electron density plot, density of states plot and other existing parameters are analyzed.

### 5.2 CONCLUSION

- ❖ This study gives the structural, electronic, optical, thermal and thermoelectric properties of  $\text{ACr}_x\text{Ti}_{1-x}\text{O}_3$  [ $\text{A}=\text{La}, \text{Nd}$ ]. Phase transition occurs while doping Ti to  $\text{LaCrO}_3$  and  $\text{NdCrO}_3$  by changing the cubic structure into tetragonal structure.
- ❖ The compounds  $\text{LaCrO}_3$ ,  $\text{LaCr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ ,  $\text{LaCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ,  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ ,  $\text{LaTiO}_3$  and  $\text{NdCrO}_3$ ,  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  and  $\text{NdTiO}_3$  compounds show no band gap hence it is the conductor.

- ❖ From the optical properties  $\text{LaCr}_{0.25}\text{Ti}_{0.75}\text{O}_3$  and  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  have high refractive index, high reflectivity, and high dielectric function.  $\text{LaTiO}_3$  and  $\text{NdTiO}_3$  have high conductivity. By comparing all the output we got  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  is very suitable for energy storage applications like solar cell device etc.
- ❖ For thermal all the materials show good thermal stability. Comparatively  $\text{NdCrO}_3$  have a good thermal stability.
- ❖ The Power factor of  $\text{NdCrO}_3$  compound is found to have higher value than other compounds, hence more power can be generated by it. Since it has an high power it can be useful in battery energy storage systems. The  $zT$  value of  $\text{NdCrO}_3$  is high and is suitable for the applications in thermoelectric devices.
- ❖ Comparing all the compounds  $\text{NdCr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  is better for the energy storage applications.

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