

COMPARATIVE DFT ANALYSIS OF ELECTRONIC CORRELATIONS IN CACU₃FE₄O₁₂ AND SRCU₃FE₄O₁₂ PEROVSKITES: A QUANTUM MECHANICAL STUDY

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ABSTRACT

Quadruple perovskite oxides have attracted considerable attention owing to their intriguing electronic, magnetic, and catalytic properties. They are the focus of much interest due to their interesting electronic, magnetic and catalytic properties. The structural, chemical bonding and electronic structures of CaCu₃Fe₄O₁₂ (CCFO) and SrCu₃Fe₄O₁₂ (SCFO) have been investigated by using the density functional theory (DFT) method in the full-potential linearized augmented plane wave (FP-LAPW) approach using WIEN2k package. The generalized gradient approximation (GGA-PBEsol) was used for structural optimization in this work, and the modified Becke–Johnson (mBJ) potential was used to calculate the electronic properties. The optimized lattice parameters were known to be good agreement to the available experimental data, which proved the reliability of the computational approach. Using the electron charge density analysis, it was found that Fe–3d, Cu–3d and O–2p orbitals exhibit mixed ionic–covalent bonding nature due to strong hybridization. The calculated density of states in both compounds had shown significant electronic states crossing the Fermi level, implying metallic behavior in both compounds. In addition, spin-polarized calculations indicated significant contributions from Fe–3d and Cu–3d orbitals around the Fermi energy, indicating strong magnetic interactions. The results give useful insight into the structural stability and into the electronic properties of these quadruple perovskites of the iron-based type, and show their potential as

spintronic and catalytic technologies.

Keywords: Density Functional Theory, Quadruple Perovskites, $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, Electronic Structure, WIEN2k, Chemical Bonding

INTRODUCTION

The general chemical formula $\text{AA}'_3\text{B}_4\text{O}_{12}$ of quadruple perovskite oxides has been the subject of intense interest due to their remarkable structural flexibility and catalytic, magnetic and electronic properties. The compounds are part of a significant class of transition-metal oxides displaying phenomena like ferromagnetism, anti ferromagnetism, superconductivity, colossal magneto resistance and ferro electricity. Their crystal structure has an unusual arrangement of the cations which results in strong electron correlation effects and complex magnetic interactions, making them interesting for fundamental studies and for technological applications (Caetano et al., 2016; Yamada, 2017). The crystal structure of the perovskites $\text{AA}'_3\text{B}_4\text{O}_{12}$ can be considered as a derivative of the classical ABO_3 perovskite structure where one-fourth of the A-sites is a classic alkaline-earth or rare-earth element (A), and the other three-quarters is the transition metal ion (A'). This ordered structure leads to an extremely distorted perovskite structure with tilted BO_6 octahedra and interactions between the A'-site and B-site cations. The materials therefore have a variety of physical characteristics which do not apply to the simple perovskites (Shimakawa & Takano, 2009).

In particular, the charge-transfer behavior and magnetic properties of the quadruple perovskites $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (CCFO) and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (SCFO) have been of special interest. The electronic structures and magnetic interactions are complicated, with the presence of mixed-valence Fe ions and the strong Cu–O–Fe hybridization.

Experimental studies have shown that charge disproportionation of Fe ions occurs in CCFO and in SCFO, the intersite charge-transfer transition of Cu and Fe ions occurs during the heat-treatment process, which results in NTE behavior (Yamada et al., 2011, 2014). Cu 3d, Fe 3d and O 2p orbitals play a strong role in the electronic structure of these compounds. This hybridization has a profound influence on their magnetic ordering, electrical conductivity and catalytic activity.

Recent work has shown that Fe^{4+} -based quadruple perovskites have superior oxygen evolution reaction (OER) catalytic activity, rivaling state of the art catalyst materials. Their high catalytic activity and stability have been attributed to the enhanced metal–oxygen covalency (Yagi et al., 2015). $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ has been reported to exhibit a ferromagnetic metallic ground state and an inverse charge-transfer transition which is related to the changes in Fe and Cu valence states. Likewise, a charge transfer between Cu and Fe ions is responsible for the giant negative thermal expansion of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, which is also antiferromagnetically ordered. Both compounds are interesting for use in spintronic devices, magnetic sensors and technologies for energy conversion because of these unique properties (Shimakawa & Takano, 2009; Yamada et al., 2014).

Although a comprehensive experimental study has been conducted, the theoretical research on the structural stability, chemical bonding and electronic properties of CCFO and SCFO is quite limited. The properties of complex oxides, which are notable for their wide range of applications, have been the subject of study using computational methods, particularly the power of Density Functional Theory (DFT). Atomic-scale electronic structures, interactions, and bonding mechanisms which are often hard to measure experimentally can be easily obtained through DFT calculations (Hohenberg & Kohn, 1964; Perdew et al., 1996). For this reason, the present study uses first-principles calculations from DFT methodology to study the structural, chemical bonding and electronic characteristics of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$. The Generalized Gradient Approximation (GGA) is used for the structural optimization, and the modified Becke–Johnson (mBJ) potential is used for the electronic properties analysis. The results give a complete picture on the bonding characteristics, electronic behavior, and structural stability of these technologically important quadruple perovskite oxides.

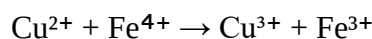
LITERATURE REVIEW

The $\text{AA}'\text{B}_4\text{O}_{12}$ quadruple perovskite oxides are a significant class of oxide materials with a wide range of structural, magnetic and electronic properties. The crystal structure can be regarded as a variant of the usual ABO_3 perovskite lattice in which the A and A' sites are ordered, and this causes noticeable distortions and strong electronic interactions between the TMs. The materials have been a matter of scientific interest due to their unusual physical phenomena such as charge transfer, charge disproportionation, giant negative thermal expansion, magnetoresistance and metal–insulator transitions (Shimakawa & Takano, 2009).

The iron based compounds have attracted special interest among the different types of quadruple perovskites on account of the presence of multiple oxidation state of Fe, Cu and hybridization between Fe 3d, Cu 3d, and O 2p orbitals. These interactions have a substantial effect on their structural stability, magnetic order and electronic transport. The experimental investigations have revealed that the presence of transition metal ions at the A' and B sites generates complex magnetic interactions which may lead to either ferromagnetic or antiferromagnetic ground state depending on the composition and external conditions (Yamada et al., 2017).

Moreover, the structural and electronic properties of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ are explored. The structure and electronic properties of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ are investigated. The crystal structure of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (SCFO) is cubic quadruple perovskite with the space group $\text{Im}\bar{3}$. The crystal structure is a framework of CuO_4 square-planar units and FeO_6 octahedra connected by oxygen ions in three dimensions. As a consequence, this arrangement ensures high electronic coupling between the Cu and Fe ions and greatly affects the electronic and magnetic properties of the compound (Yamada et al., 2014). Similarly, a remarkable property of SCFO is its giant negative thermal expansion (NTE) in the temperature range of around 170-270K, which is in contrast to the normal expansion of thermal materials. The detailed investigations with synchrotron

X-ray diffraction and Mössbauer spectroscopy have shown that the NTE phenomenon is due to an intersite charge-transfer process between the Cu and Fe ions that can be written as:



This charge transfer causes the Fe–O bond length to be changed and lattice contraction, which results in the negative thermal expansion (Yamada et al., 2011). In addition, the Fe ions are in a mixed-valence state which makes significant contribution to its magnetic properties, and SCFO has antiferromagnetic ordering below its Néel temperature of ~180 K. The structure of SCFO has been shown to be stable over a wide temperature range by first-principles calculations. The electronic structure studies suggest that the electronic density near the Fermi level is dominated by Fe 3d states, and strong hybridization between Fe 3d and Cu 3d and O 2p states help to induce the metallic conductivity. These results indicate that the structural and magnetic properties of SCFO are highly dependent on the electronic interactions (Li et al., 2015).

STRUCTURAL AND ELECTRONIC PROPERTIES OF $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$

Another interesting member of the quadruple perovskite family is $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (CCFO). As in the case of SCFO, CCFO crystallizes in the cubic $\text{Im}\bar{3}$ structure and exhibits very different electronic properties because of the smaller ionic radius of Ca^{2+} than Sr^{2+} . This difference changes the Fe–O–Cu bond angles, and affects the electronic bandwidth and magnetic exchange interactions (Yamada et al., 2016). Experimental research has revealed that a charge disproportionation transition of Fe ions takes place in CCFO as follows:



Along the way, there are large changes in electrical conductivity and magnetic ordering. In the high pressure states, the charge disproportionation can be inhibited, producing more uniform valence state of Fe and changed magnetic properties (Kawakami et al., 2016). Based on first-principles investigations, CCFO is predicted to have a ferrimagnetic metallic ground state. The calculated magnetic moments suggest that the Fe–Cu and Cu–Cu interactions are ferromagnetic, while Fe–Fe interactions are antiferromagnetic. The hybridization between Fe 3d and O 2p states is strong, which should be responsible for the metallic character and magnetic stability of the compound (Xiang et al., 2007). The focus of this class is the electronic structure of engineered materials. This class is focused on the electronic properties of engineered materials and calculations.

The Density Functional Theory (DFT) is one of the most powerful computational tools to investigate the electronic and structural properties of condensed matter systems. The origin of the theory of DFT is the Hohenberg–Kohn theorems which say that the properties of the ground state of a many-electron system are completely defined by its electron density, and not its many-body wave function (Hohenberg and Kohn, 1964). The practical application of DFT was made possible by the Kohn–Sham formalism, which reduced the problem of interacting many electrons to an equivalent set of non-interacting electrons that move in an effective potential.

There are several approximations for the exchange-correlation effects in the DFT, and the quality of the DFT calculations will critically depend on which one is used. The Generalized Gradient Approximation (GGA) (Perdew et al., 1996) is one of the most popular approximations, and it is quite accurate for predicting structural properties for a large number of materials. Traditional GGA, however, tends to underestimate electronic band gaps and is not necessarily accurate for strongly-correlated transition metal systems. To address these constraints a modified Becke–Johnson (mBJ) exchange potential was developed. The mBJ potential markedly enhances the description of electronic structures and it has been well tested with predicting the density-of-states features and band gaps of transition-metal oxides and related compounds (Tran & Blaha, 2009).

SYNTHESIS OF THE PEROVSKITE SrCu₃Fe₄O₁₂

A polycrystalline perovskite SrCu₃Fe₄O₁₂ was prepared under high pressure 20GPa and high temperature 1473K conditions. X-ray diffraction (XRD) was conducted at temperature between 100 and 450 K using Rigaku Ultima IV X-ray diffraction. SXRD measurement were performed at temperature between 100 and 450 K at the BL02B2 beam line of Spring-8. The powder samples were put into Lindeman glass capillary tubes of 0.2 mm of inner diameter. The wavelength used in SXRD measurements for SrCu₃Fe₄O₁₂ is 0.42085 Å. Electron diffraction (ED) patterns were collected at 108 and 296K using a JEOL JEM-2100F transmission electron microscope. At a temperature range between 8 and 300K at the BLO1B1 beam line of Spring-8, Cu K-edge XANES data for SrCu₃Fe₄O₁₂ was collected. At a temperature range between 12 and 300 K XAS measurement of the Cu L₃-edge were conducted using a total electron yield method at the BL27SU beam line of Spring-8. At a temperature between 4 and 400 K, Fe Mossbauer spectra of perovskite were collected in transmission geometry mode using Co/Rh as a radiation source. Using the Lorentzian function the Mossbauer spectra collected were fitted. At a temperature between 20 and 300K, hard X-ray photoemission spectroscopy (HAXPES) data of the SrCu₃Fe₄ were collected at a beam line using a high resolution hemispherical electron analyzer (VGSCIENTA R4000). The incident photon energy was set to 5.95 keV. The energy resolution was 235 meV.

RESEARCH GAP

Despite extensive experimental research on CCFO and SCFO, theoretical research, which is directed at comparative analysis of the structural stability, chemical bonding properties and electronic properties of these compounds, is limited. Specifically, the role of Fe–O–Cu hybridization in the metallic behavior and magnetic interactions need to be further clarified. Furthermore, DFT studies are not systematic and make use of advanced exchange correlation functionals like mBJ are rarely used. Thus, a thorough first-principles investigation is required to shed light on the electronic structure and bonding properties behind the physical properties of these technologically significant quadruple perovskites.

COMPUTATIONAL METHODOLOGY

First-principles calculations based on DFT were used to examine the structural, electronic, and chemical bonding properties of quadruple perovskites, $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (CCFO) and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (SCFO). All calculations were carried out with the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method, with the WIEN2k simulation package (Blaha et al., 1990).

DENSITY FUNCTIONAL THEORY

The Density Functional Theory is one of the most reliable computational methods to study electronic structure of solids. The theoretical underpinning of DFT is provided by the Hohenberg–Kohn theorems that state that the ground state properties of a many-electron system are determined by the ground-state electron density of the system and are unique to that density (Hohenberg & Kohn, 1964). In practice, DFT is implemented via the Kohn–Sham formalism, which consists of a non-interacting electron system that is equivalent to the interacting many electron system in the sense that it operates in an effective potential (Kohn & Sham, 1965).

Hohenberg-Kohn Theorem

1st Theorem: It is stated that “The external potential and ground state density of many particle system there is one-to-one correspondence in between them”.

2nd Theorem: It is stated that “The total energy that minimizes by density which is the exact ground state density”.

Kohn sham Equations

In density functional theory, the Kohn Sham equation is the one electron Schrodinger equation of the Kohn Sham system of non-interacting particles. The Kohn Sham equation is defined by a local effective external potential in which the non-interacting particles move, denoted as $V_{\text{eff}}(\mathbf{r})$ called the Kohn Sham potential. To find the ground state density we use Kohn Sham equations. Kohn Sham equations.

$$[-\hbar^2/2m \nabla^2 + V_{\text{eff}}(\mathbf{r})] \Psi_i(\mathbf{r}) = E_i \Psi_i(\mathbf{r}) \dots\dots\dots (3.1)$$

$$V_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d\mathbf{r} + v_{\text{xc}}[\mathbf{r}] \dots\dots\dots (3.2)$$

Where $v_{\text{xc}}(\mathbf{r})$ is the exchange co-relation potential given by importance in the accuracy of DFT calculations. The third term in the effective potential is the exchange co-relation potential. This is of central importance in the accuracy of DFT calculations.

GENERALIZED GRADIENT APPROXIMATION

Perdew and Schmidt were organized, that what had been the historical development and some of the issues confronting any attempt at systematic increase of the accuracy of exchange correlation functional, through what they called jacob’s ladder. On it local spin density approximation (LDA) in which the functional is determined only in terms of the local values of spin up and down electronics densities also the expansion for the homogeneous electron gas, is placed on the first rung.

The second rung consists of functionals that depend, additionally, on the magnitude of the gradients of the spin up and spin down densities, to account for inhomogeneities. Because the form of that dependence is not simply that of the gradient expansion, such functionals are usually referred as generalized gradient approximation (GGA). Since the birth of kohen-sham density function theory (DFT), the local spin density approximation (LDA) and generalized gradient approximation (GGA) have been widely applied in solid state physics. With the most popular GGA being that of Perdew, Burke and Ernzerhof (PBE). Hybrid functional and meta GGAs have been popularly and successfully applied in molecular quantum chemistry. In the present work, we focus on the development of GGA for solids. The physical properties of the compounds will be calculated by solving kohen-sham equations. The FP-LAPW method used with GGA PBE-sol exchange correlation functional which is given by

$$E^{GGA}_{xc}[\rho(r)] = \int \rho_{xc}[\rho(r)] d^3r \dots\dots\dots (3.3)$$

Where E^{GGA}_{xc} are the total exchange correlation energy and individual particle exchange ϵ_{xc} and correlation energy respectively. In comparison with LSD, GGAs to improve total energies, atomization energies, energy barriers and structural energy difference. The derivations and 12 formal properties of the various GGA's can guide a rotational choice among them. Semi empirical GGA's remarkably successful for small molecules but fail for delocalized electrons in the uniform gas and thus in simple metals.

MODIFIED BECKE JOHNSON POTENTIAL

By calculating the ground state properties like lattice constant and ground state energies etc. GGA depend on DFT LDA or GGA gives unacceptable results by calculating the electronic and optical properties. The determined and experimental data of bands gaps and position of distinct orbitals are different from each other. To solve the difficulty, we used various approximations like GW and hybrid functionals.

In our work, the major use is to correctly represent the band gaps and optical properties m-BJ [19] which combines to GGA and m-BJ correlation potential and to get larger band gap results match with the experimental results. To treat d-state more precisely m-BJ exchange potential along with GGA will be used. The equation of m-BJ potential is given by

$$V^{B,J}_{x,\delta} = V^{B,J}_{x,\delta(r)} + \frac{1}{\pi\sqrt{6}} \sqrt{\frac{t_{\delta}(r)}{\rho\delta(r)}} \dots\dots\dots (3.4)$$

Where $V_{x\delta}$ is the Becke-Roussel potential, t_{δ} is the electron $\delta\rho$ is the kinetic energy density and density. The modified Becke Johnson exchange potential is used in different types of solids which are difficult to describe theoretically, nonmagnetic semiconductor transition metal oxides, sulfides metals (Fe, Cu, Ni, and Co) and anti-ferromagnetic insulators. The Becke-Johnson exchange potential has been widely used for the calculation of electronic structure with in density functional theory. However, in its original form the potential fail may dramatically in system with non-coulombic external potentials, or in the presence of external electric and magnetic

field.

3WIEN 2K PACKAGE

The WIEN code evolved for the first time by Blaha and Schwarz in 1990 [26] and then different modification are received for the development of the code [27].

Currently WIEN 2k is a main technique to investigate the physical properties of compounds and play important rule for the explanation of band structure.

RESULTS AND DISCUSSION

In this research we studied the structure, chemical bonding and electronic properties of the perovskites CCFO and SCFO by using different methods GGA, GGA+mBJ in the hold of DFT.

STRUCTURAL PROPERTIES

Using Density Functional Theory (DFT) within the Generalized Gradient Approximation (GGA), properties of the structures of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (CCFO) and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (SCFO) have been studied. The equilibrium lattice parameters were calculated using structure optimization and fitting the energy–volume data with the Birch–Murnaghan equation of state. The calculated lattice constant for CCFO was obtained as 7.25 Å and the experimental value is 7.28 Å, which is very good agreement. Likewise, the optimized value of the lattice constant for SCFO was found to be 7.32 Å whereas the experimental value was 7.34 Å. The small deviations of the structural properties are less than 1%, which confirms the reliability of the computational methodology adopted and the suitability of the GGA functional for describing the structural properties of these quadruple perovskites.

The bulk moduli calculated for CCFO and SCFO were 265.26 GPa and 243.52 GPa, respectively. The bulk modulus of CCFO is larger than that of CCF, which means that CCFO is more resistant to compression and implies stronger interatomic interactions in CCFO's crystal lattice. This is because the ionic radius of Ca^{2+} is smaller than Sr^{2+} , leading to a decrease in bond lengths and increase in lattice rigidity. The optimized volumes of the unit-cells corroborate this interpretation further. The equilibrium volume of CCFO is smaller than SCFO, 381.07 Å³ and 392.22 Å³ respectively, which means that the crystal structure of CCFO is more compact. Usually, the more compact the structure the better the orbital overlap between neighbouring atoms, and the greater the effect on the electronic and magnetic properties of the material. In general, the theoretical parameters are in good agreement with the experimental ones; this validates the accuracy of the theoretical method and offers a solid basis for further studies on the bonding and electronic properties of such compounds.

Table 4.1 Calculated and experimental lattice constants of the quaternary perovskites

$\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$

Compound/Parameters	DFT	LR Method	V.E Method	Experimental
$\text{CaCu}_3\text{Fe}_4\text{O}_{12}$				
a_o (Å)	7.25	7.458	7.5	7.28 ^a
V (Å) ³	381.07	414.82	343	385.82 ^a
B (GPa)	265.256			
B'	4.723			
E_a (Ry)	-45451.53			
E_{coh} (Ry)	-22227.8902			
$\text{SrCu}_3\text{Fe}_4\text{O}_{12}$				
a_o (Å)	7.32	7.5	7.9	7.34 ^b
Volume (Å) ³	392.22	421.875	493.039	395.44 ^b
B (GPa)	243.521			
B'	5.00			
Energy (Ry)	-51321.41			
E_{coh} (Ry)	-17233.2149			

In the Table 4.1 the lattice constant of CCFO DFT by I.R method is 7.458 so from above formula, 2.335% less than the experimental value so it is underestimate and by V.E Method is 7.5, hence -3.846% less than the experimental value and thus it is underestimate while the experimental value is 7.28. For perovskites SCFO by I.R method is 7.5 so from formula 2.1798 % less than the experimental value. Similarly by V. E method is 7.9 hence 7.629% which is greater than the experimental value so it is overestimate while the experimental value is 7.34. Generally V.E method overestimate the lattice constants of perovskites, and I.R method is closed to experiments. DFT is the most reliable quantum mechanical approach hence the DFT results are much consistent to experiments.

TOLERANCE FACTOR AND STRUCTURAL STABILITY

The Goldschmidt tolerance factor is well known to assess the structural stability and distortion of perovskite materials. Ideal cubic perovskites have values of the tolerance factor near to unity, while values away from unity signify structural distortion and octahedral tilting. The tolerance factors found in the quadruple perovskites examined in this work are nearing the range of stability of perovskites with cubic crystal structure. The optimized lattices and calculated lattice parameters suggest that the

structures are stable with minimal lattice distortions in both compounds. Cubic symmetry is preserved as in CCFO and SCFO experiments. The stability of these structures can be attributed to the favourable ionic size matching between the A-site, A'-site and the B-site cations. In addition, Cu–O and Fe–O bonding interactions play an important role in stabilizing the crystal structure.

The first description of tolerance factor for perovskites was made by Victor Meritz Goldschmidt in 1926. Tolerance factor are useful in the structure of perovskites symmetry. Goldschmidt's concept of ionic tolerance factor was recently showing to be a valuable guideline for the preparations of new compounds within the of field of organic-inorganic perovskites. Here we extend this approach and calculate the tolerance factors for over 2500 amine-metal-anion permutations of the periodic table. Goldschmidt's tolerance factor concept, which has been a central mantra in the development of solid state perovskite. Tolerance factor has been successfully used as a guide in the synthesis of complex hybrid perovskites-type materials including the system $[\text{CH}_3\text{NH}_3]\text{Ca}(\text{BH}_4)_3$. With the help of tolerance factor we can also explain the existence of low dimensional materials with perovskite like building motifs. [30]. Goldschmidt develop the tolerance factor for cubic perovskites which is found in different color i.e. brown black orange gray and yellow [31]. Goldschmidt tolerance factor is an indicator for the stability and distortion of crystal structures, but the new tolerance factor also used for ilmenite. Alternatively, tolerance factor can be used to calculate the compatibility of ions with a crystal structure. The Goldschmidt tolerance factor is dimensionless number. For cubic perovskite the tolerance factor can be calculated from the ratio of ionic radii. Where r_A is the radius of the A cation, r_B is the radius of B-cation and r_O is the radius of anion (usually oxygen). In ideal cubic perovskite structure the axis of the unit cell (a) can be described with the following equation.

$$a_0 = (2)^{1/2}(r^A + r^O) = 2(r_B + r_O) \dots\dots\dots (4.1)$$

In generally the compounds having tolerance factor 1 are considered to be simple cubic while $t < 1$ indicates octahedral and $t > 1$ shows hexagonal perovskite structures

COHESIVE ENERGY AND THERMODYNAMIC STABILITY

The cohesive energy gives useful information about the thermodynamic stability of a material. The more negative the cohesive energy the more bound the molecule is and more stable the structure. In both CCFO and SCFO, the calculated cohesive energies are very negative, which is indicative of the fact that both the CCFO and the SCFO compounds form energetically favourably. The magnitude of the cohesive energies is large, indicating that the Cu, Fe, and O atoms in the quadruple perovskite framework have strong bonding interactions. This improved stability is due to an important degree of hybridization between the d-orbitals of the transition metals and the p-orbitals of the oxygen. Such hybridization increases chemical bonding and decreases the overall energy of the system. Both of these compounds are therefore likely to be structurally stable under ambient conditions as observed in the experiment.

The high bond strength of these compounds also indicates their potential in thermally and chemically stable applications, such as catalytic and spintronic devices. The charge-density distributions have been studied to understand the nature of chemical bonding. The calculated charge-density maps show that there is a significant amount of charge density around the oxygen atoms, which have a higher electronegativity than Ca, Sr, Cu and Fe. The contours of the charge density show that the number of electrons around each atom is not strictly an integer, but a fractional one. From this behavior, one would infer that these two compounds contain both ionic and covalent bonding. The charge overlap between Fe–O and Cu–O bonds is a significant one, suggesting strong covalent character due to the orbital hybridization between Fe-3d, Cu-3d and O-2p states. Concurrently, the Ca-Sr interaction is mainly ionic due to the tendency of Ca and Sr to donate valence electrons to surrounding oxygen network. The mixed ionic–covalent bonding nature plays a crucial role in determining the electronic and magnetic properties of these materials. Covalent interactions are strong and allow for charge transfer and electronic conduction, and ionic contributions increase the structural stability.

The amount of energy evolved when a crystalline solid is formed infinitely separated atoms or the amount of energy required to separate atoms in a crystalline solid to infinite distance is known as cohesive or binding energy of the crystal. The interaction forces which hold the atoms together in a solid are responsible for crystal formation. So, the energy of the crystal is lower than that of the free atoms by an amount equal to the energy required to pull the atoms to an infinite distance. This energy is called the binding energy of the crystal. The cohesive energy of the both compounds is calculated by the following well known Equation.

$$E_{\text{Coh}} = E_{\text{Total}} - (E_{\text{Ca/Sr}} + 3E_{\text{Cu}} + 4E_{\text{Fe}} + 12E_{\text{O}}) \dots\dots\dots (4.2)$$

In above equation E_{Total} is the ground state energy of a compound, $E_{\text{Ca/Sr}}$ is the ground state energy of Ca/Sr, E_{Cu} of Cu, E_{Fe} of Fe and E_{O} is the ground state energy of O.

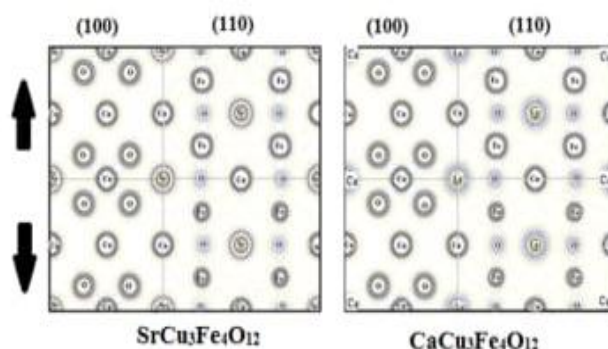


Fig4.1. Electron charge density of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$

TOTAL DENSITY OF STATES (TDOS)

The total density of states (TDOS) gives an idea of the electronic behavior of the studied compounds. Electronic density of states calculated for both CCFO and SCFO reveal too high density of states near the Fermi level. The lack of a gap at the Fermi level is definitely a sign of metallic character in both materials. The high electrical conductivity is due to the fact that the electrons are free to traverse the Fermi level.

This has a metallic character, which is consistent with all previous theoretical and experimental investigations of iron-based quadruple perovskites.

What is remarkable about the TDOS spectra is that it is asymmetric for the spin-up and spin-down channels. This spin polarization suggests that the compounds are magnetically ordered materials. This behavior is mainly due to the half filled d orbital of Fe and Cu ions.

The metallic nature of both compounds points to potential applications in electronic and spintronic technologies demanding a high mobility of charge carriers, in addition to magnetic functionality. The partial density of states (PDOS) is shown as a function of the solid's energy band gap in 4.6. Partial density-of-states calculations were done to find out what orbital contributions were responsible for the electronic behaviour observed.

Fe-3d states are found to be strongly dominant in the electronic structure around the Fermi level from the PDOS analysis. The metallic conductivity and magnetic properties of both compounds are significant contributions from these states. The presence of Fe-3d orbitals at the Fermi energy is particularly significant, suggesting that Fe ions are key players in determining the electronic properties. Additionally, Cu-3d states make significant contributions in the vicinity of the Fermi level. The overlap of Cu-3d and Fe-3d states gives rise to strong electronic interactions, which lead to improved charge transport and affect magnetic exchange mechanisms.

The electronic nature of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ by using exchange correlations such as GGA-mBJ shown in the Fig. The calculated density of these compounds is almost the same by all potential with small difference in detail expand. The Fermi level is covered by conduction band for both compounds which shows the metallic behavior of these materials. It can also be seen from the figure that polarization is exited at the Fermi level. The spin down states explains that the Cu-3d and Fe-3d states are responsible for this polarization which causes magnetic effect in the compound. To further study the origin of the electronic and magnetic properties partial density of states of both compounds are plotted as shown in Fig4.2.

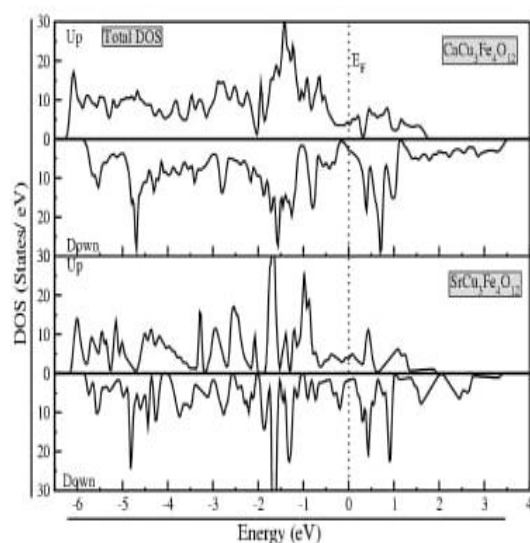


Fig4.2. Total density of states of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$

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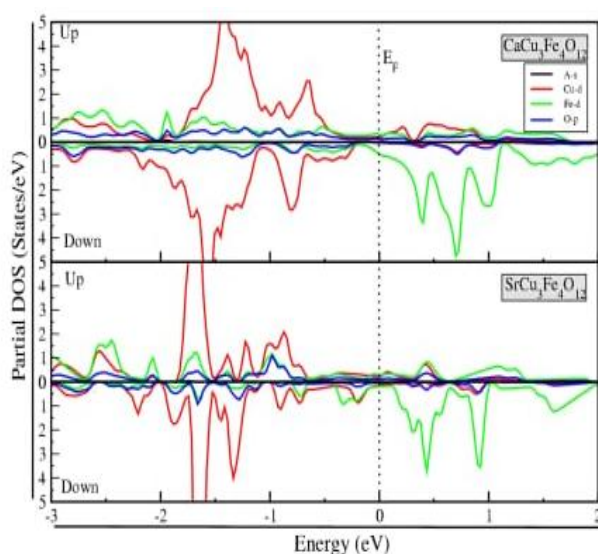


Fig4.3. Total density of states of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$

In the valence-band region, the contribution of the 2p orbitals of oxygen is the main factor. However, strong p–d hybridization is seen, as there is a significant overlap between the O-2p and transition metal d-orbitals. This hybridization leads to an increased covalent bonding and an increase in the electronic delocalization throughout the crystal lattice. The contribution to the electronic part of the PDOS is relatively small at the Fermi level for the Ca and Sr elements. They function mainly as structural stabilizers, not directly in the electronic conduction.

RECOMMENDATIONS

In conclusion the PDOS analysis indicates that the metallic character of CCFO and SCFO is primarily associated with the Fe-3d and Cu-3d states, whereas the O-2p states play a role via strong hybridization effects. The results of this study were compared with findings from previous studies. The present results are in good agreement with the previous theoretical and experimental studies. The lattice parameters calculated are very close to those reported by Yamada et al. for both CCFO and SCFO. Moreover, the predicted metallic nature is in good agreement with the first-principles calculations of Xiang et al., who predicted a metallic ferrimagnetic ground state for CCFO. The hybridization between Fe and O and Cu and O, which was found in this work, is also in accordance with the electronic structure analysis presented by Li et al. and Yamada et al., who highlighted the role of transition-metal–oxygen interactions in the physical properties of these compounds. Hence, the present study validates and complements the previous studies and provides complete insights into bonding nature, electronic properties, and stability of structural properties of these technologically fascinating quadruple perovskites.

TECHNOLOGICAL IMPLICATIONS

The structural stability, metallic conductivity and the strong magnetic interactions

make the CCFO and SCFO good candidates in technology fields of advanced applications. They are metallic and thus facilitate the transport of charge, and their spin polarized electronic states can be utilized in spintronic devices. In addition, significant transitions-metal–oxygen covalency and electronic delocalization indicate possible applications in electrocatalysis, such as oxygen-evolution reactions and energy-conversion systems. The excellent crystal structure and electronic properties suggest that these materials have potential applications as multifunctional materials in future electronic, magnetic, and energy applications.

CONCLUSIONS

The properties of structural, chemical bonding and electronic of quadruple perovskites, $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, were systematically studied by first-principles calculations based on the Density Functional Theory (DFT). The optimized lattice parameters yielded from the Generalized Gradient Approximation showed good agreement with available experimental measurement and hence the reliability of the computational methodology. The cohesive energies calculated show that both compounds are energetically and structurally stable. Based on electron charge-density analysis, ionic and covalent bonding characteristics were found to coexist in the crystal structures. The strong covalent interactions are suggested by significant charge accumulation around oxygen atoms and by the presence of strong Fe–O and Cu–O bonds. Such interactions are very significant in determining the stability of the crystal lattice and the electronic nature of the compound. The electronic density-of-states calculations showed both CCFO and SCFO are metallic with electronic states crossing the Fermi level. Near the Fermi energy, the dominant contributions are from Fe-3d and Cu-3d orbitals, with the O-2p contributions coming from strong hybridization. The magnetic interactions and the electronic conductivity observed are from this hybridization. In addition, spin-polarized electronic states indicate magnetic ordering resulting from the d-orbitals of transition metals. The results indicate that Fe–O–Cu interactions and charge-transfer mechanisms have a significant influence on the electronic and magnetic properties of these quadruple perovskites. In general, the present investigation is a theoretical study about the structural stability, bonding characteristic and electronic property of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$. These materials are characterized by their metallic properties, structural strength, and electronic structure, suggesting their potential use in spintronic devices, magnetic sensors, and energy-related technologies. These iron-based quadruple perovskites have much more technological interest when magnetic exchange interactions, transport properties and pressure dependent electronic behaviour are explored in the future.

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