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RESEARCH ARTICLE

First Principles Computation of Electronic Structure and Dynamical Properties of Perovskite $LaBa_2Cu_3O_7$

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ABSTRACT

Perovskite materials have attracted research because of their ability to transition from normal metals to superconductors. This study reports electronic structure and dynamical properties of $LaBa_2Cu_3O_7$ perovskite carried out in the framework of density functional theory (DFT) using the Quantum espresso code. This is based on plane wave self-consistent field (PWscf) and ultrasoft pseudopotential (USPP) method as treated in the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and local density approximations as implemented in Quantum Espresso Code. The electronic structure uncovers essential aspects such as bandgaps, Fermi surfaces, and density of states, offering valuable insights into the material's behaviour. Under structural properties, optimization of the material's cell dimensions, lattice parameters, k-points, and the kinetic energy cut-off values were properly checked through graphing and accurate values were obtained at the convergence of the ground state energy at minimum convergence threshold. Band structures of $LaBa_2Cu_3O_7$ are similar to that of superconducting perovskites. The results show that $LaBa_2Cu_3O_7$ is orthorhombic structure with lattice parameter calculated to be 3.925 Å which compares well with other works and a band gap of 2.043eV. The valence band is typically dominated by O 2p states, while the conduction band involves Cu 3d states. Phonon calculations shows that the compound is dynamically stable as there are no negative frequencies observed.

Keywords: *Dynamical; Electronic; Perovskite Structure*

INTRODUCTION

Perovskites superconductors are among the materials that have attracted more attention in research because of the projected benefits they can deliver if better and efficient ones are discovered (Foltyn *et al.,* 2010*;* Gutfleisch *et al.*, 2011). They are attractive for a wide range of applications due to their unique characteristics and properties applicable in areas such as light-emitting diodes, power transition cables, photovoltaics and pressure induced emission. This has motivated researchers and industrial users to improve the electronic structure and dynamical properties to achieve the conditions for better performance. Both theoretical and experimental methods have been embraced to achieve new discoveries in these efforts. Despite the efforts to elucidate the pairing mechanism and to understand the many-body properties influencing the electron dynamics in cuprate superconductors, there is no consensus on the strength of the electron correlations and the nature of the phonon coupling modes. The dynamical properties, involves investigating phonon spectra and lattice dynamics to analyse vibrational modes and their impacts on material stability and functionality (Wang *et al*., 2002).

The chemical composition of cuprates is well characterized by a layered crystal structure with one or more CuO_2 planes per unit cell, which are responsible for the low-lying electronic structure, and presumably the key to understanding the quasi-particle properties involved in the mechanism of superconductivity, for example the origin of the coupling mode which binds two electrons (holes) in the formation of Cooper pairs (Ruiz *et al.*, 2010).

The strength of a material can be explained based on phonons in a crystal lattice. These vibration modes decrease the forces acting on the displaced atoms from the equilibrium position symmetry. As a result, the frequency of their oscillation is also decreased. The effect leads to lattice distortions which are periodic in nature and as a result, the energy of the crystal is lowered and makes the distribution of energy to the soft phonons to be negative (Gonze *et al.*, 2005). In this case, the criterion for the crystal stability will be associated with the phonon frequencies; and depending on its magnitude, instability can occur. The formation of pairs gives rise to an excitation energy gap Δ in the electron density of states across the Fermi level (E_F) and its magnitude reflects the strength of the pairing interaction. In this study the electronic structure, structural properties and dynamical properties are obtained by DFT using quantum espresso code. This paper therefore reports the electronic structure and the dynamical properties where the coupling mode and strength determines the value of T_c. The next section discusses methodology used followed by results and conclusions.

METHODOLOGY

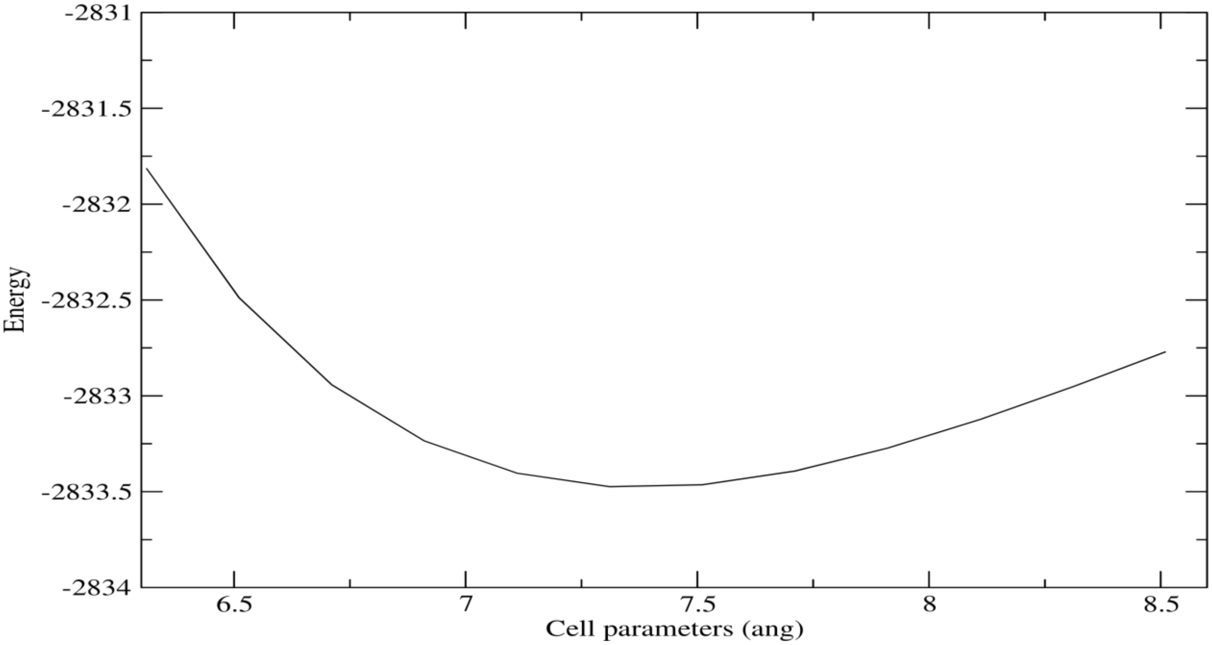
The first principles calculations study of the electronic and dynamical properties of $LaBa_2Cu_3O_7$ was undertaken in the framework of density functional theory (DFT) based on plane wave self-consistent field (PWscf) and ultrasoft pseudopotential (USPP) method as treated in the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and local density approximations as implemented in Quantum Espresso Code. The Brillouin sampling was based on the Monkhost scheme (James & Pack, 1977). The convergence test for k-point grid and energy cut off was conducted at certain lattice constants. And atomic positions relaxed at a temperature of 0 K. Volume was also adjusted while relaxing the atomic coordinates in every self-consistent field calculation. A plane wave energy cut off of 300 eV was employed throughout the calculations so as to obtain convergence.

Optimized cell dimensions, the k-points, and the kinetic energy cut-off values were properly checked through graphing and accurate values were obtained at the convergence of the ground state energy at minimum convergence threshold in the calculation using the proper basis sets (Poschmann *et al.,* 2017).

The K-point mesh in the irreducible high symmetry points in the Brillouin zone used was 8x8x4 to evaluate integrals in the reciprocal space. This Monkhorst pack grid gives a well converged electronic structure due to the flatness of the $LaBa_2Cu_3O_7$ valence bands. This Monkhorst pack approach involves integrating the irreducible portion of the Brilloun Zone. The lattice parameters and atomic positions were optimized by seeking a total energy minimum for the $LaBa_2Cu_3O_7$ unit cell, which is depicted in Figure 1 below:

Figure 1:

Graph of Cell Parameters Versus Energy.



Some of the DFT equations include finding the solutions to Schrödinger equations and also solving the Kohn–Sham equations. Solving these Kohn-Sham equations self-consistently provides the electron density and, subsequently, the electronic structure of the system. The Kohn-Sham method makes DFT computationally feasible for a broad spectrum of materials and systems (Pitts, 2021).

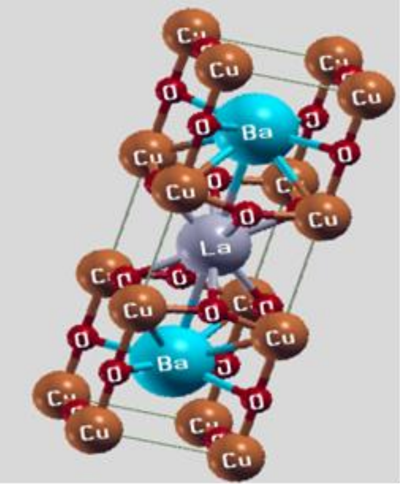
RESULTS

Structural Properties

$LaBa_2Cu_3O_7$ structure belongs to the space group of Pmmm (#47) that consists of thirteen atoms per primitive unit cell. Structural optimization was performed by minimizing the total energy of $LaBa_2Cu_3O_7$ with respect to varying unit cell volume so as to obtain lattice parameters and ground state energy. These structural parameters are key to understanding the material's geometry and its influence on electronic properties. The optimized parameters include the cell dimensions, kinetic cut-off energy, and K-points. These optimizations confirmed that $LaBa_2Cu_3O_7$ is a simple orthorhombic crystal in a stable state. The optimized primitive unit cell is given in Fig 2.

Figure 2:

The Optimized Orthorhombic of Structure of $LaBa_2Cu_3O_7$ with the Atomic Positions



Structural properties consist of lattice parameters and bond length length (Fjellvåg, 1987 & Abou *et al.*, 2024). The calculated lattice parameters compared to other works are presented in the Table 1 below:

Table 1:

Comparison of the Lattice Parameters, Volume, Methodology, Reference with Other Works

Lattice Parameter Å	Volume Å^3	Methodology	Reference
3.917	186.6	QE	This work
4.016	198.8	VASP	Aflow
3.987	181.4	Exp	Beno *et al*

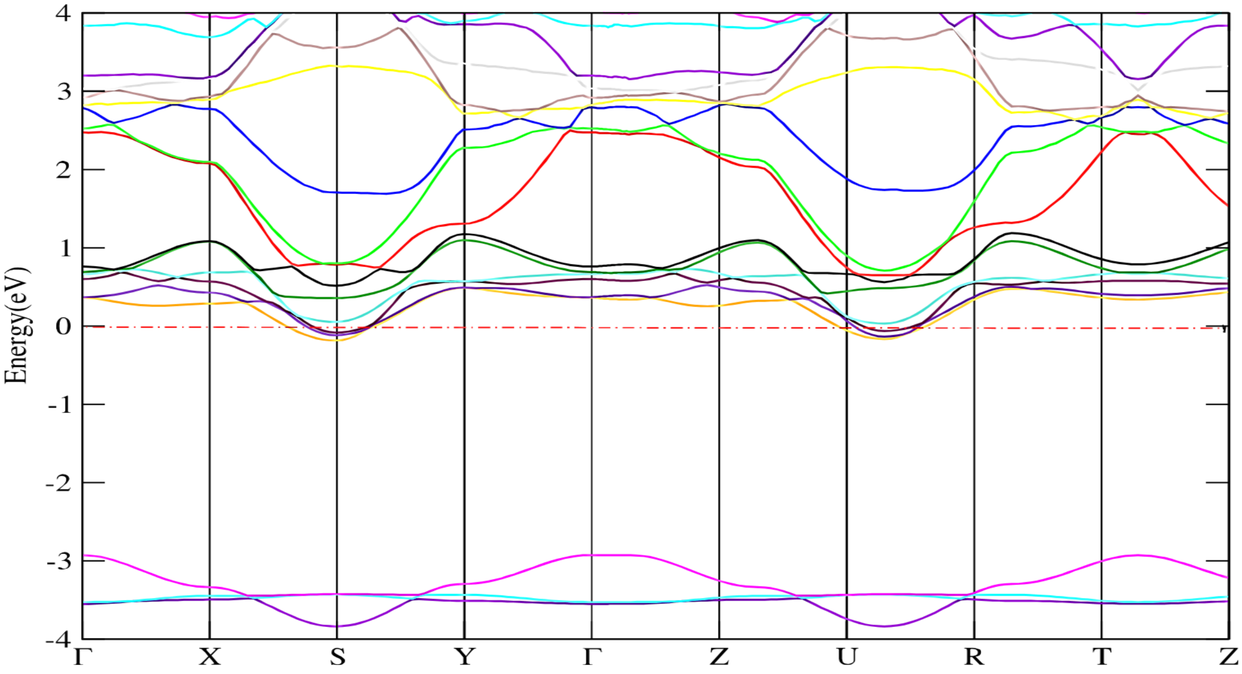
The difference between our present work results and experimental work results is less than 1.5% thus showing that the computational methodology employed in this work is reliable.

Electronic Structure Properties

Understanding the electronic structure behaviour of materials hinges significantly on their electronic properties like band gap and density of states. The electronic band structure has been plotted in high symmetry directions in the first Brillouin zone (Khan *et al.*, 2024). The electronic structure of $LaBa_2Cu_3O_7$ perovskite is characterized by interactions between Cu 3d and O 2p states with strong electron correlations. The Cu 3d and O 2p orbitals hybridize, forming bands near the Fermi level. The valence band is typically dominated by O 2p states, while the conduction band involves Cu 3d states (Ghijsen *et al.*, 1988). A higher E_F indicates more available states for Cooper pair formation. The band structures and total density of states for $LaBa_2Cu_3O_7$ are shown in Fig 3 and Fig 4. As seen in the Fig 3, the Fermi level (E_F) is set at zero energy and specified by horizontal dashed red line. The band gap is observed between the highest valence band and the lowest conduction band resulting in a band gap value of 2.043 eV.

Figure 3:

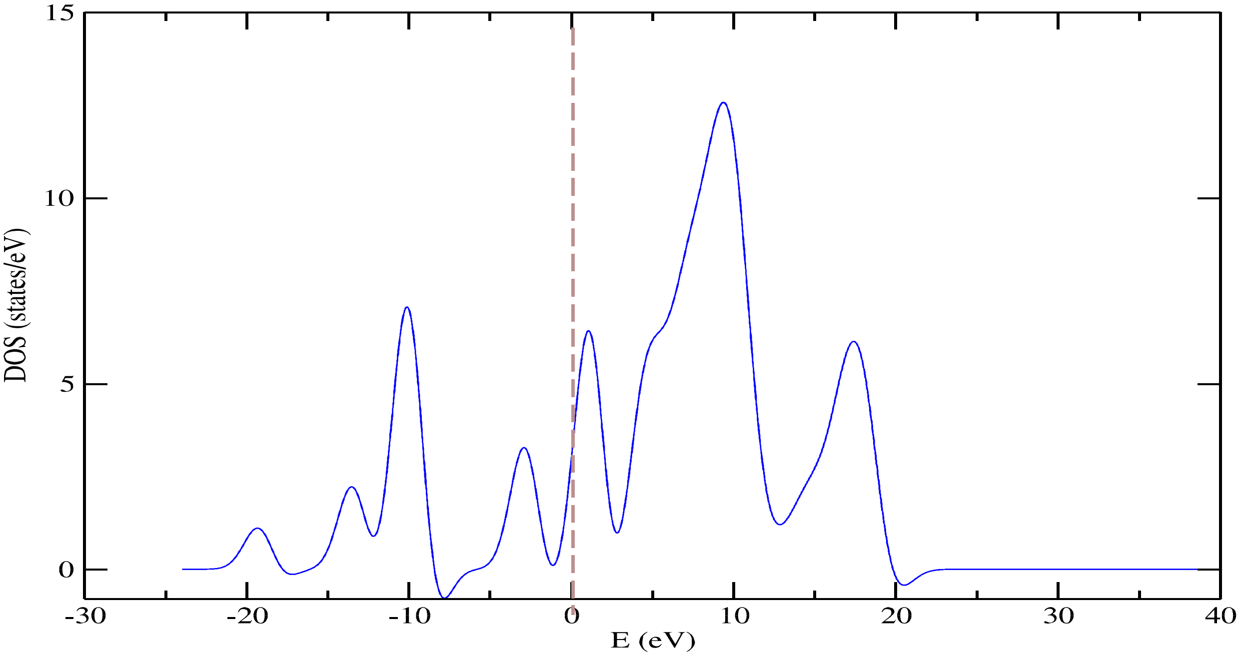
Band Structure of $LaBa_2Cu_3O_7$



The total DOS provides the number of states at each energy level, thus the density of states at the Fermi level is crucial for superconductivity (Varlamov, 1999).

Figure 4:

Density of States of $LaBa_2Cu_3O_7$



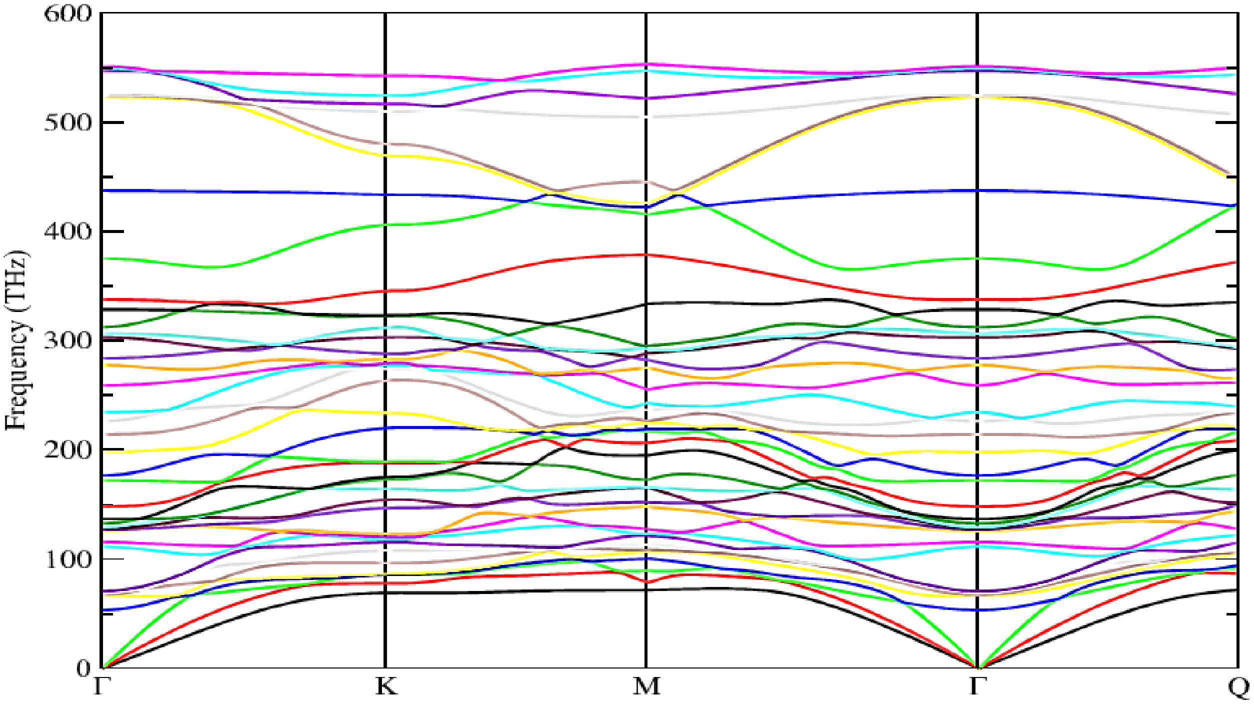
Dynamical properties

This involves investigating phonon spectra and lattice dynamics to analyse vibrational modes and their impacts on material stability and functionality. In phonon dispersion relation, there are two branches: the lower branch is the acoustic mode, characterized by in – phase vibrations and the upper branch is the optical mode, associated with out of phase vibrations. Acoustic modes vibrate at lower frequencies and are always in phase with the unit cell, while the optical modes have higher frequencies. In optical modes, adjacent atoms vibrate in opposite directions whereas in acoustic modes, adjacent atoms vibrate in the same direction. (Smith *et al.,* 1977).

The phonon dispersions were calculated using the Density functional perturbation theory as implemented in the plane wave self-consistent field. The primitive unit cell of $LaBa_2Cu_3O_7$ contain 13 atoms, thus 39 modes of vibration. The optical modes are 36 and acoustic modes are three. The acoustic modes converge at the gamma high symmetry point as shown in the phonon dispersion curve Fig 5.

Figure 5:

Phonon Dispersion Curve



The graph shows the optical mode clearly differentiated with the acoustic mode. This phonon calculation shows that the compound is dynamically stable as there are no negative frequencies observed.

Phonons should have non-negative and real frequencies for stability, which means that a system is considered dynamically stable at equilibrium if the potential energy continuously increases with any displacement of atoms. Phonon frequencies emerge from the displacement of atoms in a crystal from their equilibrium positions, causing an increase in forces. Negative frequencies indicate that the potential energy decreases, leading to an unstable system (Cohen & Louie, 2016).

DISCUSSION

This study aimed at determining the electronic structure and dynamical properties of lanthanum barium cuprate. These properties are key in understanding behaviour of the material in relation to its stability for superconductivity. Phonon dispersion curve showed dynamical stability of the compound. Quantum espresso code which is an open source was used to obtain the calculations based on plane wave pseudopotentials. Phonon calculations shows that the compound is dynamically stable as there are no negative frequencies observed.

Conclusion

In this work, we have obtained the dynamical and electronic structure properties of $LaBa_2Cu_3O_7$ perovskite using first principles computation by DFT using Quantum espresso code. It was found that CuO chains across the fermi level exhibit metallic character and band gap of 2.043eV obtained caused by CuO2 planes thus accounting for the insulating character of the CuO2 planes. The bands between the conduction and valence band doesn’t overlap and thus bandgap obtained. The calculated results obtained of electronic structure are in good agreement with the experimental structural parameters and atomic sites of orthorhombic LaBa2Cu3O7. The structural parameters show a good agreement with the experimental data.

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