Original Article

Mechanical, electronic, optical, and thermodynamic properties of orthorhombic LiCuBiO$_4$ crystal: a first-principles study

Md. Mijanur Rahaman$^{a,b,*}$, Mirza H.K. Rubel$^{a,*}$, Md. Abdur Rashid$^{c}$, M. Ashraful Alam$^{d}$, Khandaker Monower Hossain$^{a}$, Md. Imran Hossain$^{a}$, Anjuman Ara Khatun$^{e}$, Md. Mukter Hossain$^{e}$, A.K.M. Azharul Islam$^{c}$, Seiji Kojima$^{f}$, Nobuhiro Kumada$^{g}$

$^{a}$ Department of Materials Science and Engineering, University of Rajshahi, Rajshahi 6205, Bangladesh
$^{b}$ Geophysical Laboratory, Carnegie Institution for Science, Washington, DC 20015, USA
$^{c}$ Department of Physics, University of Rajshahi, Rajshahi 6205, Bangladesh
$^{d}$ Department of Physics, Maulana Bhashani Science and Technology University, Santosh, Tangail 1902, Bangladesh
$^{e}$ Department of Physics, Chittagong University of Engineering and Technology, Chittagong 4349, Bangladesh
$^{f}$ Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
$^{g}$ Center for Crystal Science and Technology, University of Yamanashi, 7-32 Miyamae, Kofu 400-011, Japan

**ABSTRACT**

Density functional theory (DFT) based first-principles calculations using GGA+U method have been performed for the first time to investigate elastic, electronic, optical, thermodynamic properties including charge density, Fermi surface, Mulliken population analysis, and theoretical Vickers hardness of the newly synthesized LiCuBiO$_4$ (LCBO) compound. The calculated structural parameters are in good agreement with available experimental results, which assessed the reliability of our calculations. The analysis of elastic constants indicates mechanical stability of the LCBO. The values of Poisson’s and Pugh’s ratios confirm the ductile nature of the LCBO. The mechanically anisotropy is found by the different anisotropy factors. The overlapping of valence and conduction bands near the Fermi level ($E_F$) and the several bands crossing the $E_F$ reveal the metallic behaviour of the LCBO. The electronic charge density mapping and Mulliken population analysis exhibits a combination of covalent, ionic, and metallic bonding of the LCBO. The calculated Fermi surface comprised of two-dimensional topology due to the low-dispersion of O-2p and Cu-3d states, which implies the possible multi-band nature of LCBO. The analysis of thermodynamic and various optical properties suggest that LCBO can be a potential candidate for optoelectronic devices in the visible and ultraviolet energy regions and as a thermal barrier coating (TBC) material.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

$^*$ Corresponding authors.
E-mails: mijan_mse@ru.ac.bd (M.M. Rahaman), mhk_mse@ru.ac.bd (M.H. Rubel).
https://doi.org/10.1016/j.jmrt.2019.06.035
2238-7854 © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

In the midst of the mixed-metal oxides, Bi-based perovskite materials are very prominent owing to their accommodation of numerous metal elements in their composition and structure. This enriched diversity reveals the varieties of intriguing chemical and physical properties such as photo catalytic activity, ferromagnetism, multiferroic behaviour, ferroelectricity, and superconductivity. Moreover, perovskite structure oxides also show antiferromagnetic property with magnetization and Neel temperatures for device applications [1–3]. However, over last few years, various novel pentavalent sodium bismuthates, NaBiO3·nH2O, have been explored via low temperature hydrothermal route [4–23]. Importantly, these bismuthates that can only be obtained by hydrothermal method, for example, ABi5+2O6-type (A: Mg, Ca, Sr, Ba, Cd, Pb) compounds are found in crystalline form by this method [12,14,22–24]. Further, there are some other methods, for instance, solution methods, induced aqueous methods, and precursor-induced methods that have been successfully employed to yield additional bismuth oxides as well [25–27]. Among these Bi5+ compounds, there have been extensive studies on a new series and novel compositional Bi-based superconductors with simple and double perovskite structures by optimizing hydrothermal conditions [28,29]. Their first principles calculations are also reported to predict various interesting physical properties such as electronic, mechanical and thermodynamic properties [30,31]. However, in recent years layered materials have attracted significance attention. Layers with different components and properties which can be brought together are the key for the synthesis and development of new multifunctional materials.

In the course of this investigation Kumada et al. have recently pursued a novel layered LiCuBiO4 (LCBO) oxide compound using well known hydrothermal reaction at 180 °C [1]. The crystal structure of this compound is determined by Synchrotron X-ray diffraction (SXRD), shows an analogy with the previous reported non-bismuthate LiCuSbO4 and LiFeSnO4 materials [32,33]. In the reported compound LiCuBiO4 the Sb atoms were substituted for Bi atoms and both Bi and Cu metals coexist in the structural composition. The X-ray powder diffraction pattern of LiCuBiO4 is indexed with the orthorhombic crystal cell with the lattice parameters (a = 10.91, b = 5.81, and c = 5.01 Å). In addition, among all possible space groups, Pnma one is determined after the reasonable atomic positions of Cu and Bi atoms in the structure. In the structure of LiCuBiO4, all metal atoms are coordinated octahedrally by six O atoms and LiO6 and CuO6 octahedra form one-dimensional chains by edge-sharing along the b-axis. The LiO6 and CuO6 chains form the layer by face-sharing in the bc plane. The Bi atoms are placed in that interlayer and BiO6 octahedra are edge-sharing with LiO6 and CuO6 octahedra. Moreover, the magnetic properties of LiCuBiO4 have been discussed by Kumada et al. [3] and the antiferromagnetic ordering of Cu2+ spin of LiCuBiO4 was observed at 6 K. But theoretical information is not available yet as on elastic, electronic, optical, thermodynamic properties and population analysis of this compound. Notably, first principle calculation is a well-known method to predict these interesting phenomena including mechanical, electronic, optical and thermodynamic properties to precisely understand a new material system.

Therefore, for the first time we attempt to calculate and investigate several microscopic and macroscopic attributes of this new magnetic material based on density functional theory (DFT) calculations. In this research, we represent the LCBO structural, mechanical (elastic constants, bulk, shear and Young’s modulus, Pugh’s and Poisson’s ratio, Vickers hardness, and Cauchy pressure), electronic (band structure, DOS, charge density map, and Fermi surface), optical (dielectric function, refractive index, photoconductivity, absorbance and reflectance) and thermodynamic properties (Debye temperature, melting temperature, and Gruneisen parameter). These LCBO properties are computed and evaluated employing CASTEP-Code software package.

2. Computational method

The calculations presented in this paper were carried out using the Cambridge Serial Total Energy Package (CASTEP) code [34]. The CASTEP employs the plane wave pseudopotential approach based on DFT [35,36]. In the first principles calculations, the choice of exchange-correlation potential is important. In this study, the exchange-correlation potential has been treated by utilizing the PBEsol [37] with generalized gradient approximation (GGA) parameterization scheme. Under this scheme, relatively high level computation method GGA+U has been implemented via spin polarized, using formal spin as initial conditions with oxidation state of each element for charge neutralization. We checked these options to carry out the calculations using different wave functions for different spins and for the number of unpaired electrons for each atom, respectively. The interactions between ions and electrons are represented with Vanderbilt-type ultrasoft pseudopotential for all atoms [38]. All calculations including electronic structures (band structure and DOS) with ferromagnetic configuration are performed with a plane-wave cut off energy of 550 eV. For the sampling of the Brillouin zone, 4 × 6 × 7 k—point grids are generated according to the Monkhorst-Pack scheme [39]. The geometry optimization of the crystal is achieved through minimizing the total energy and internal forces by applying the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [40], where the self-consistence convergence tolerance for the total energy is 5 × 10−6 eV/atom, the maximum force of the atom is 0.01 eV/Å, the maximum stress is 0.02 GPa and the maximum ionic displacement is 5 × 10−4 Å. These parameters are found to be sufficient to lead good convergence of total energy and internal forces. However, a spin–orbit coupling effect may arise on the physical properties of LCBO compound as it exhibits antiferromagnetic ordering of Cu2+ moment at 6 K. But in this investigation, we were not able to include such contribution in DFT Hamiltonian due to the limitation of our resource.

3. Results and discussion

3.1. Structural properties

The crystal structure of LCBO is first drawn using the available refinement data [1] for the geometry optimization and is
shown in Fig. 1. The LCBO belongs to the orthorhombic system with space group Pnma (No. 62), and its equilibrium lattice parameters are \( a = 10.9096 \text{ Å}, b = 5.8113 \text{ Å}, \) and \( c = 5.0073 \text{ Å} \). The atomic position of Li, Cu, Bi, and O in the unit cell of LiCuBiO\(_4\) are Li (0, 0.5, 0.5), Cu (0.5, 0, 0.5), Bi (0.7663, 0.25, 0.5569), O\(_1\) (0.963, 0.25, 0.772), O\(_2\) (0.588, 0.25, 0.359), and O\(_3\) (0.177, 0.489, 0.693) [1]. In the structure Li, Cu, and Bi atoms form three types of alternating LiO\(_6\), CuO\(_6\), and BiO\(_6\) octahedra with coordination of six O atoms in one-dimensional chains (Fig. 1, right side). The calculated lattice constants along with volume of this compound are listed in Table 1. From the value of calculated lattice constants, we conclude that the experimental and theoretical values are very close that reveals the reliability of this investigation.

### 3.2. Mechanical properties

For industrial applications of engineering materials, the study of mechanical properties such as elastic moduli, ductile/brittle behavior, and elastic anisotropy are of critical importance. The elastic stiffness constants are obtained from linear finite strain–stress method within the CASTEP [41]. The calculated nine independent elastic stiffness constants \( (C_{ij}) \) of the LCBO are displayed in Table 2. The obtained constants completely satisfy the generalized stability criteria for orthorhombic crystal, which can be expressed as:

\[
C_{ij} > 0, \quad (i, j = 1–6), \quad [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \\
[C_{11} + C_{22} - 2C_{12}] > 0, \quad [C_{11} + C_{33} - 2C_{13}] > 0, \quad [C_{22} + C_{33} - 2C_{23}] > 0 \]

[42–44]. Therefore, the deliberated orthorhombic phase of LCBO in this study is mechanically stable.

An elastic property is the measurement of the tendency of a solid to deform non-permanently in various directions with applied stress. In addition, the elastic stiffness tensors can provide information regarding the bonding nature of solids. The elastic stiffness constant \( C_{11} \) provides the elasticity along length and determines the elastic stiffness of solids with respect to the uniaxial strain \( e_1 \) along the [100] direction. The elastic stiffness constants \( C_{22} \) and \( C_{33} \) correspond to the uniaxial strain \( e_2 \) and \( e_3 \) along the [010] and [001] directions, respectively. It is apparent from Table 2 that \( C_{22} > C_{11} > C_{33} \), reflecting stronger bonding along the [010] direction than that in the [100] and [001] directions. This result reflects that it is easier to compress the compound along the crystallographic c-axis, than along the a- and b-axis. Moreover, the relation \( C_{22} > C_{11} > C_{33} \) reveals the anisotropic nature of the compound.

The shear modulus (\( G \)) and bulk modulus (\( B \)) are determined from the single crystal zero-pressure elastic constants using the Voigt-Reuss-Hill formula [45,46]. Moreover, the Poisson's ratio (\( \nu \)) and the Young's modulus (\( Y \)) can also be obtained using well-known relationships [47]. All these calculated elastic constants are summarized in Table 2. The bulk modulus evaluates the average bond strength of constituent atoms for a given solid [48]. Recently, Ali et al. have reported the strong bonding in (Zr\(_{1-x}\)Ti\(_x\))AlC\(_x\) solid solutions by obtaining the bulk modulus of 128 GPa [49]. Therefore, the calculated value of \( B \) (101 GPa) may reflect the moderate bonding strength of atoms involved in LCBO. The atom's bond strength also provides the required resistance to volume deformation under external pressure. On the other hand, the shear modulus (\( G \)) estimates the change of shape in a solid that shows a crucial relation with materials hardness. The greater the value of shear modulus, the more rigid the material is. Albeit, the bulk and shear modulus do not measure the material's harness directly, Vickers hardness of the LCBO has been estimated and discussed in population analysis section. The resistance of a material against longitudinal stress is determined by the Young's modulus (\( Y \)). Since the critical thermal shock coefficient (\( R \)) varies inversely to the Young's modulus, therefore the value of \( Y \) exerts influence on the thermal shock resistance of a solid.

### Table 1 - Calculated lattice parameters (\( a, b, \) and \( c \)) and unit cell volume (\( V \)) of the LCBO together with available experimental results.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( a (\text{Å}) )</th>
<th>( b (\text{Å}) )</th>
<th>( c (\text{Å}) )</th>
<th>( V (\text{Å}^3) )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCuBiO(_4)</td>
<td>10.9238</td>
<td>5.8116</td>
<td>4.9957</td>
<td>317.15</td>
<td>This</td>
</tr>
<tr>
<td></td>
<td>10.9096</td>
<td>5.8113</td>
<td>5.0073</td>
<td>317.46</td>
<td>[1]</td>
</tr>
</tbody>
</table>

An elastic property is the measurement of the tendency of a solid to deform non-permanently in various directions with applied stress. In addition, the elastic stiffness tensors can provide information regarding the bonding nature of solids. The elastic stiffness constant \( C_{11} \) provides the elasticity along length and determines the elastic stiffness of solids with respect to the uniaxial strain \( e_1 \) along the [100] direction. The elastic stiffness constants \( C_{22} \) and \( C_{33} \) correspond to the uniaxial strain \( e_2 \) and \( e_3 \) along the [010] and [001] directions, respectively. It is apparent from Table 2 that \( C_{22} > C_{11} > C_{33} \), reflecting stronger bonding along the [010] direction than that in the [100] and [001] directions. This result reflects that it is easier to compress the compound along the crystallographic c-axis, than along the a- and b-axis. Moreover, the relation \( C_{22} > C_{11} > C_{33} \) reveals the anisotropic nature of the compound.

The shear modulus (\( G \)) and bulk modulus (\( B \)) are determined from the single crystal zero-pressure elastic constants using the Voigt-Reuss-Hill formula [45,46]. Moreover, the Poisson's ratio (\( \nu \)) and the Young's modulus (\( Y \)) can also be obtained using well-known relationships [47]. All these calculated elastic constants are summarized in Table 2. The bulk modulus evaluates the average bond strength of constituent atoms for a given solid [48]. Recently, Ali et al. have reported the strong bonding in (Zr\(_{1-x}\)Ti\(_x\))AlC\(_x\) solid solutions by obtaining the bulk modulus of 128 GPa [49]. Therefore, the calculated value of \( B \) (101 GPa) may reflect the moderate bonding strength of atoms involved in LCBO. The atom's bond strength also provides the required resistance to volume deformation under external pressure. On the other hand, the shear modulus (\( G \)) estimates the change of shape in a solid that shows a crucial relation with materials hardness. The greater the value of shear modulus, the more rigid the material is. Albeit, the bulk and shear modulus do not measure the material's harness directly, Vickers hardness of the LCBO has been estimated and discussed in population analysis section. The resistance of a material against longitudinal stress is determined by the Young's modulus (\( Y \)). Since the critical thermal shock coefficient (\( R \)) varies inversely to the Young's modulus, therefore the value of \( Y \) exerts influence on the thermal shock resistance of a solid.
The higher the value of \( R \), the better the thermal shock resistance of a material. A material is selected as a thermal barrier coating (TBC) substance depending on thermal shock resistance. It is important to note that the value of the Young's modulus of the LCBO is comparatively lower and hence it might be suitable as a TBC material.

The failure mode study, that is, brittle or ductile behaviour of a material is technologically important. The material can be classified as either ductile or brittle for most practical situations. A material is said to be ductile if the value of Pugh's ratio is smaller than 0.57 [51]; otherwise, the material is brittle. As can be seen in Table 2, the value of Pugh's ratio is 0.425, indicating the LCBO is surely a ductile material. Besides the Pugh's ratio, Frantsevich's also proposed a critical Poisson's ratio value \( (\nu = 0.26) \) for separating the ductile and brittle behaviour of solids [52]. The calculated value of Poisson's ratio \( (\nu) \) is 0.313 (Table 2), again reflecting ductile behaviour of the compound under study. Moreover, another indicator of failure mode of materials is the Cauchy pressure, defined as \( (C_{12}-C_{44}) \) [53]. If it is negative, the material is expected to be brittle; otherwise (showing positive Cauchy pressure), it is a ductile one. Therefore, the LCBO material in this study is found to be ductile in accordance with the above mentioned three indicators.

Table 2 – The elastic constants, \( C_{ij} \) (GPa), bulk modulus, \( B \) (GPa), shear modulus, \( G \) (GPa), Young's modulus, \( Y \) (GPa), Pugh's ratio, \( (G/B) \), Poisson's ratio, \( \nu \), and Cauchy pressure of LCBO.

| \( C_{11} \) | \( C_{22} \) | \( C_{33} \) | \( C_{44} \) | \( C_{55} \) | \( C_{66} \) | \( C_{12} \) | \( C_{13} \) | \( C_{23} \) | \( B \) | \( G \) | \( Y \) | \( \nu \) | Pugh's ratio | Cauchy pressure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 196 | 231 | 151 | 30 | 22 | 56 | 82 | 28 | 75 | 101 | 43 | 113 | 0.313 | 0.425 | 42 |

A3 = \( 4C_{66}/(C_{11} + C_{22} - 2C_{12}) \) for the \( (001) \) shear planes between \([011]\) and \([010]\) directions.

From Table 3, the calculated \( A_1 \)'s exhibit that the LCBO is anisotropic (for isotropy \( A_1 = 1 \)) in three share planes. The different values of \( A_1, A_2, \) and \( A_3 \) also demonstrate the strong directional dependence of shear modulus of the LCBO material.

The elastic anisotropy can also be ascribed in terms of the bulk modulus along the c-axis \( (B_c) \) and a-axis \( (B_a) \) by the expressions as:

\[
B_c = c \left( \frac{dP}{dc} \right) = B_a/\alpha, \quad B_a = a \left( \frac{dP}{da} \right) = V / (2 + \alpha)
\]

where, \( V = 2(C_{11} + C_{12}) + 4C_{13}a + C_{33}a^2 \) and \( \alpha = (C_{11} + C_{12} - 2C_{13}) / (C_{13} + C_{12}) \) [49].

The estimated values for \( B_a \) and \( B_c \) (Table 3) exhibit the trend \( B_c > B_a \), which indicates that the compression along c-axis is more easier than along a-axis for LCBO compound. The universal anisotropic index \( A^U \), another important measure of anisotropy, is defined as

\[
A^U = \frac{G V}{R} + \frac{B V}{R} - \frac{6}{\alpha} \geq 0
\]

where, \( A^U = 0 \) is for isotropic materials, and the deviation from zero defines the elastic anisotropy of crystals [58]. The value of \( A^U \) is found to be 1.30, implying that the orthorhombic LCBO possesses significant anisotropy.

3.3. Electronic properties

3.3.1. Band structure and density of states

At equilibrium lattice constants, the energy band diagram employing ferromagnetic configuration (FM) along the high symmetry direction in the irreducible Brillouin zone is shown in Fig. 2, where the horizontal dash line denotes as the Fermi level (EF). The electronic band structures are calculated using GGA+U method with the on-site Coulomb interaction \( U = 6 \) eV for Cu in LCBO. The blue and red solid lines represent energy bands for up spin and down spin electrons, respectively. We observe that the valance and conduction band appreciably overlap with each other of the FM state that result no band gap at the EF. Therefore, the compound in this report must exhibit metallic conductivity. In addition, we see nearly flat and broader bands along Z-T direction in the vicinity of EF, which is the sign of a large DOS value. Importantly, the overall band profiles of the calculated solid in the present research are nearly identical to those noticed in previous articles [30,31,59–61].
In 3.3.2. Fig. 2 - Spin-polarized GGA+U (Ueff = 6 eV for Cu 3d) calculated band structure of LiCuBiO4 in ferromagnetic configuration along the high symmetry directions in the Brillouin zone.

To further clarify the contributions of different orbitals/atoms and nature of chemical bonding in LCBO, total density of states (TDOS) and partial density of states (PDOS) are calculated and is depicted in Fig. 3. In these figures the sharp peak of the DOS at the EF is a sign of structural instability, whereas a deep and broad valley of DOS might be responsible for the structural stability.

In the lower energy at around -43 eV the DOS is mainly originated from Li-s states only. From -20 eV to -15 eV the DOS originates from O-s and Bi-s and p states and also has a little contribution of Cu-p and d states. Finally, from -12 eV to Fermi level the TDOS has prime contributions from O-p and Cu-d states. So, there is strong hybridization among the O-2p, Cu-3d, Bi-6s, and Bi-6p orbitals for this compound. These strong hybridizations suggest strong ternary Cu-Bi-O bond in the LCBO. Notably, the total DOS at EF in this report is around 2.5 states/eV/unit cells for this compound. The value of non-zero DOS at Fermi level also indicates the conductive nature of this compound.

3.3.2. Electronic charge density and Fermi surface
In order to investigate the distribution of the total electronic charge density maps of the LCBO, the valence electronic charge density maps (in the units of e/Å²) along (100) plane using Li-Cu and Li/Cu-O surfaces/atomic layers have been calculated and depicted in Fig. 4(a and b). The scale shown in the right of both figures represents the intensity of electron charge density. The blue color shows the light density of electron whereas the red color shows high density of electron. The Cu–Bi–O bond in the Cu-Li atomic layer for LCBO is very strong, which coincides with the strong hybridization among O-2p and Cu-3d orbitals with very small contributions of Bi-6s and Bi-6p orbitals in DOS. Since, the contributions of Bi atom in the DOS at Fermi level is very weak (Fig. 3), therefore, it is difficult to distinguish the electron charge density of Bi ion in the charge density map. We should emphasize that the charge density distribution is essentially spherical around all the atoms which shows ionic nature (Fig. 4a) employing Li-Cu surface/plane. The ionic characteristics are an effect of metallic characteristics [62] as well, which hint that the Cu–Bi–O bond behaves metallic nature. Therefore, a strong isotropic combination of chemical bonds such as ionic and metallic interactions exists from this calculation for the LCBO. On the other hand, in order to investigate the covalent bonding in LCBO, we choose the surface containing both Li/Cu and O (Fig. 4b) and observe the potential overlapping of charge between Li/Cu and O atoms is a consequence of covalent nature. Moreover, the electronic charge density distribution around these ions is not perfectly spherical (as shown in Fig. 3 - Total and partial electron energy density of states of the LCBO by GGA+U (U = 6 eV for Cu 3d) method.

Fig. 2 – Spin-polarized GGA+U (Ueff = 6 eV for Cu 3d) calculated band structure of LiCuBiO4 in ferromagnetic configuration along the high symmetry directions in the Brillouin zone.
the central sheet two distinguished close sheets are observed, one is rectangular shape (second sheet) is noticed along the Y–T direction.

The third sheet is little complicated consists of rectangular shape with a small circle along the Z–T direction. The fourth sheet (blue color) is also rectangular but middle sagged shape is connected to the central sheet along the Y–S direction. Further, this sheet is expanded along the S–X direction in the same sheet as well. Here, second, third and fourth sheets have repeated position at the opposite sides of central sheet. Finally, fourth sheet is connected with bottom edge of third sheet along the X–U direction to complete the Brillouin zone path. However, the Fermi surface of the LCBO is mainly formed due to low dispersion of O-2p and Cu-3d state, which is responsible for the electrical conductivity of the compound and can also be confirmed from DOS (Fig. 2) contributions. Herein, all these sheets are separated from each other in the Fermi surface topology.

### 3.4. Optical properties

Optical properties of a material are closely related to the material response to incident electromagnetic radiation. The response to visible light is particularly important from the view of opto-electronic applications.

The response to incident radiation is completely determined by various energy dependent (frequency) parameters, namely dielectric function, refractive index, loss function, conductivity, reflectivity and absorption coefficient. The optical properties of the LCBO were predicted by GGA+U method. The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric function of the LCBO are shown in Fig. 6. A smearing value of 0.5 eV is applied to spell out Gaussian broadening is used for calculating the optical functions of the compound. Since, the present compound shows metallic behaviour, thus the Drude plasma frequency of 3 eV and damping factor of 0.05 eV are employed to investigate dielectric properties. In this calculation, the peak position of the real part of the dielectric function is related to the electron excitation and peak is mainly arisen due to the intraband transitions. It is apparent from Fig. 6(a) that the $\varepsilon_2(\omega)$ shows a peak at around 1.0 eV, which is related to the intraband transitions.

It is well known that in metal and metal—like systems the intraband contributions from the conduction electrons mainly in the low-energy infrared are the part of the spectra.

The considered LCBO here is metallic in nature on the basis of the electronic band structure. Therefore, the intraband contributions in the LCBO come from the conduction electrons. It is significant that the $\varepsilon_2(\omega)$ reaches zero from above at around 24 eV in the ultraviolet energy region, which indicates the material LCBO is transparent and optically anisotropic as well. The anisotropic nature of the LCBO was also observed by the elastic properties. The refractive index ($n$) and the extinction coefficient ($k$) denote the phase velocity and the amount of absorption loss, respectively, when the electromagnetic wave (as light) passes through the material. The refractive index ($n$) and the extinction coefficient ($k$) are displayed in Fig. 7(a) and 7(b), respectively. The calculated value of the static refractive index $n(0)$ is found to be 3.86 and decreases in the high energy region.
The real part of the photoconductivity ($\sigma$) spectrum of the LCBO material is shown in Fig. 8(a). The photoconductivity starts with zero photon energy indicating that the LCBO phase has no band gap, which is clearly seen in the electronic band structure calculations (Fig. 2). The maximum photoconductivity for this compound is established at 4.31 at 15.24 eV. The absorption coefficient ($\alpha$) provides information about the solar energy conversion efficiency, which means the penetration of a specific light energy into the material up to absorption [63].

Fig. 8(b) illustrates the absorption spectra of LCBO. It starts at 0 eV due to their metallic nature. It is also seen that the absorption coefficient is weak in the IR region but continuously increases towards the UV region, and reaches a maximum value at around 16.07 eV. This result reflects that the LCBO is a promising material for absorbing photon in the UV region. In materials, the photon absorption is increased with the high absorption coefficient and thereby exciting the electrons
from valence band to conduction band. Hence, this interesting properties makes LCBO a promising material for the applications to optical and optoelectronic devices in the visible and UV energy regions. In general, the intraband contribution to the optical properties affects mainly in the low energy infrared part of the spectra. Therefore, the peaks in the high energy part of the absorption and conductivity spectra may arise due to the interband transition. It is apparent that the variation of the conductivity spectra is similar to the absorption spectra (Fig. 8a and b). Hence, the photoconductivity and hence the electrical conductivity of the LCBO increases as a result of absorbing photons [64,65].

The reflectivity (R) is the ratio of the energy of a wave reflected from a surface to the energy of the wave incident on it. The reflectivity spectrum of LCBO is exhibited in Fig. 8(c) from which we see that the reflectivity starts from 0.34, which is the maximum value of reflectivity that occurs with zero photon energy. So, the maximum reflectivity noted in the infrared region of this compound is 34%. The reflectivity is then sharply decreasing with increasing energy up to 4.84 eV and again increases in the edges at 19.26 eV and 23.05 eV and finally goes towards zero at higher energy. The high value of reflectivity in the low energy region reveals the characteristics of high conductance in the low energy region [66].

The photon energy loss spectrum (l) of LCBO is shown in Fig. 8(d). The energy loss function is a significant index to reveal the energy loss of a fast electron when it traversed in a material [67]. In the loss function graph, the peaks are involved with the plasma resonance and the associated frequency with it is called the plasma frequency (ωp) [68]. The highest peak is found at about 24 eV, which discloses the plasma frequency of LCBO. When the frequency of incident light is higher than the plasma frequency, the material becomes transparent. Further, the loss function peak related to ωp corresponds to the edge in the reflectivity spectrum in an abrupt reduction of the reflectivity spectrum occurs (Fig. 8c), and it correlates with the zero crossing of ε1(0) with small ε2(0) (Fig. 6).

### 3.5. Thermodynamic properties

The thermodynamic properties such as Debye temperature (θD), melting temperature (Tm), minimum thermal conductivity (κmin), and Grüneisen parameter (γ) of the LCBO have been investigated to understand the behaviour of this material under high temperatures as well as high pressures. The θD is a fundamental parameter to discuss some physical process of solids, which are related to lattice vibrations, melting point, specific heat, thermal conductivity etc. By the average sound velocity, the θD can be calculated using the following equations [69],

\[
\theta_D = \frac{\hbar}{k_B} \left[ \frac{3m}{4\pi} \left( \frac{N_A\rho}{M} \right) \right]^{1/3} v_m
\]

where, \(\hbar\) and \(k_B\) are the Planck’s and the Boltzmann constants, \(N_A\) is the Avogadro’s number, \(\rho\) is the density, \(m\) is the number of atoms within a unit cell, \(M\) is the molecular weight, and \(v_m\) is the Debye sound velocity. The \(v_m\) in the crystal is estimated by the following equation,

\[
v_m = \left( \frac{1}{3} \frac{2 + 1}{\nu'_l + \nu'_t} \right)^{-\frac{1}{2}}
\]

Here, \(\nu'_l\) and \(\nu'_t\) are the longitudinal and transverse sound velocities, respectively. The \(\nu'_l\) and \(\nu'_t\) can be determined with the help of bulk modulus (B) and shear modulus (G) using the following equations,

\[
\nu'_l = \left( \frac{-B + \frac{4}{3}G}{\rho} \right) \quad \text{and} \quad \nu'_t = \left[ \frac{G}{\rho} \right]^{1/2}
\]

We also have predicted another important parameter such as melting temperature (Tm) of the LCBO compound. The Tm can be calculated via the following empirical formula using elastic stiffness constants \(c_{ij}\) [70]:

\[
T_m = 354 + \frac{4.5(2C_{11} + C_{33})}{3}
\]

In crystalline solids, the Grüneisen parameter (γ) gives a measure of the anharmonic effect, that is, the temperature dependence of phonon frequencies and phonon dampings as well as the thermal expansion effects. The Grüneisen parameter is defined by

\[
\gamma(\omega_p) = \frac{\text{dln}(\omega_p)}{\text{dln(\varphi)}}
\]

where, \(\varphi\) and \(\omega_p\) are the packing fraction and the angular frequency of the crystals, respectively [71]. We determined the value of \(\gamma\) by a simple expression, which relates the \(\gamma\) to the Poisson ratio as [71],

\[
\gamma = \frac{3(1 + \nu)}{2(2 - 3\nu)}
\]

Thermal conductivity is a parameter to investigate the heat conduction of a material. It is well known that the minimum thermal conductivity is directly concerned to the temperature

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ρ (g/cm³)</th>
<th>νl (km/s)</th>
<th>νt (km/s)</th>
<th>v_m (km/s)</th>
<th>θD (K)</th>
<th>Tm (K)</th>
<th>γ</th>
<th>Kmin (W m⁻¹ K⁻¹)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCuSiO₄</td>
<td>7.140</td>
<td>4.707</td>
<td>2.453</td>
<td>2.745</td>
<td>363</td>
<td>1168</td>
<td>1.86</td>
<td>0.74</td>
<td>This</td>
</tr>
<tr>
<td>(K₁₋ₓ(B₃₋₁ₓNaₓ)₂O₃)</td>
<td>7.539</td>
<td>5.240</td>
<td>2.891</td>
<td>3.222</td>
<td>386</td>
<td>30</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Naₓ₋₅₋ₓKₓ₋₁₋ₓBaₓ₋₁₋ₓ)₂O₁₂</td>
<td>7.566</td>
<td>5.059</td>
<td>2.931</td>
<td>3.253</td>
<td>382</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4 - The calculated density (ρ), longitudinal, transverse, and average sound velocities (νl, νt, and v_m), Debye temperature (θD), melting temperature (Tm), minimum thermal conductivity (Kmin) and Grüneisen parameter (γ) of the LCBO.
while the temperature of a material gradually increased the conductivity of the material then gradually decreased to a certain value [72]. Although many similar equations have been derived to calculate the minimum thermal conductivity, but in this report the entity $K_{\text{min}}$ has been computed by using the Clarke expression [73] and can be denoted as,

$$K_{\text{min}} = k_B v_m (M/m_A^{1/3})$$  \hspace{1cm} (9)

where, $m$ is the number of atoms per molecule. $T_m = 354 + 4 \times (Zr_{1.8} \times Th_{1.2})$. The calculated values of $\theta_D$, $T_m$, $K_{\text{min}}$, $v_m$, $v_s$, $v_l$, and $\gamma$ from above equations are listed in Table 4. We are not able to compare our calculated values of Debye and melting temperature with experimental and other theoretical values of the LCBO. For this region we compare our results with other Bi-based compounds. The values of Debye and melting temperatures of the LCBO are relatively small in comparison to the brittle ($Zr_{1.8} Th_{1.2}$) AIC solid solutions [49]. However, the value of Debye temperature is similar to the observed in Bi-based ductile single and/or double perovskite superconductors [30,31]. Therefore, the relatively low values of $\theta_D$ and $K_{\text{min}}$ indicate the low thermal conductivity and the compound might behave as a good TBC materials [30,31].

### 3.6 Population analysis

Mulliken atomic population analysis provides more insightful information to understand the chemical bonding nature in solids [74]. Mulliken orbitals and Mulliken populations obtained in this study based on GGA+U potential are listed in Table 5 as well as the estimated overlap populations for the nearest neighbour atoms of the LCBO are listed in Table 6. In the bond overlap population, zero value indicates a perfectly ionic bond and the values greater than zero indicate the increasing levels of covalency [75]. The atomic bond population of the LCBO is positive and greater than zero, which indicates the covalent nature of this compound.

Thus, the higher values of the overlap population of all bonds imply covalent bonding of the LCBO. It is noted from Table 5 that O–Cu bond is more covalent than the other bonds. In principles, the strong covalent bond creates a significant resistance, which acts against the initialization of plastic deformation and pin the dislocation, resulting in a quite large hardness. The theoretical estimation of Vickers hardness in Gao’s model is evaluated from the well-established empirical formula [76] for the crystals using the following relations:

$$H_V = \frac{1}{\pi} \left( \sqrt{b \cdot c} \right)$$  \hspace{1cm} (10)

$$\nu^e_b = \nu_{\text{free}} \left( \frac{b^2}{\nu} \right)$$  \hspace{1cm} (11)

$$P^e = \nu^e_b \left( \sum \nu^e_b \right)$$  \hspace{1cm} (12)

Here, $P^e$ denotes the Mulliken population of the $\mu$-type bond, $P^e_{\mu}$ is the metallic population of the $\mu$-type bond, $n^e_{\mu}$ is the bond number of the $\mu$-type, and $\nu^e_{\mu}$ is the volume of $\mu$-type bond, $V$ is the cell volume, $\nu_{\text{free}}$ is the number of free electrons, $d^e_{\mu}$ is the bond length of type $\mu$, and $N^e_{\mu}$ is the bond number of type $\nu$ per unit volume.

It is well known that the diamond is the hardest material with Vickers hardness in the range of 70–150 GPa. As can be seen in Table 6, the calculated value of the Vickers hardness of the LCBO is 4.25 GPa. Therefore, it is concluded that the LCBO is an extremely soft material compare with diamond. In addition, the small value of the Vickers hardness may reflect the existence of weak covalence bond in LCBO.

### 4 Conclusions

In the present study, we have used the DFT based CASTEP code for investigating various physical properties of the LiCuBiO$_4$ (LCBO). For the first time we have calculated and discussed the elastic stiffness constants, bulk modulus, shear modulus, Young’s modulus, elastic anisotropy, band data, DOS, and optical properties of an orthorhombic laves phase intermetallic compound LCBO. The calculated lattice parameters are in good agreement with the experimental values reported in literature. The calculated elastic constants of the LCBO also satisfy the mechanical stability conditions for the orthorhombic structure. The Poisson’s and Fugh’s ratios reveal that the LCBO is

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>$n^e$</th>
<th>$d^e$ (Å)</th>
<th>$P^e$</th>
<th>$P^e_{\mu}$</th>
<th>$\nu^e_{\mu}$ (Å$^3$)</th>
<th>$H_V^e$ (GPa)</th>
<th>$H_V^e$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCuBiO$_4$</td>
<td>O-Cu (I)</td>
<td>08</td>
<td>1.90374</td>
<td>0.35</td>
<td>0.125</td>
<td>4.723</td>
<td>12.533</td>
<td>4.25</td>
</tr>
<tr>
<td></td>
<td>O-Cu (II)</td>
<td>08</td>
<td>2.04322</td>
<td>0.29</td>
<td>8.679</td>
<td>5.838</td>
<td>6.455</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-Cu (III)</td>
<td>08</td>
<td>2.33185</td>
<td>0.14</td>
<td>6.712</td>
<td>6.666</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-Bi (I)</td>
<td>08</td>
<td>2.14041</td>
<td>0.33</td>
<td>6.746</td>
<td>6.303</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-Bi (II)</td>
<td>08</td>
<td>2.14041</td>
<td>0.33</td>
<td>6.785</td>
<td>5.329</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-Bi (III)</td>
<td>08</td>
<td>2.14041</td>
<td>0.33</td>
<td>7.107</td>
<td>6.061</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-Bi (IV)</td>
<td>08</td>
<td>2.18158</td>
<td>0.34</td>
<td>7.107</td>
<td>6.061</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
a ductile material. Moreover, the universal anisotropy index shows the elastically anisotropic nature of the LCBO. The intermetallic LCBO compound shows the metallic character and the primal contributions originate from the O-2p and Cu-3d orbitals at the Fermi level in DOS. Moreover, the multiple-band nature and consequently electrical conductivity of the LCBO is evident from the existence of both electron and hole—like Fermi surfaces. The charge density and population analysis of LCBO reveal the intra-atomic bond nature of Li-Cu, Li/Cu-O, Bi-O and Li-O is a mixture of ionic, covalent, and metallic interactions. The reflectivity indicates the characteristics of the high conductance in the low energy region. The absorption quality is found well in the visible region and the maximum refractive index is observed in the infrared region. The moderate photoconductivity is obtained for the LCBO. The plasma frequency is attained at about 24 eV for the LCBO compound. The Debye temperature of the LCBO is 363 K which has been evaluated by using the calculated elastic stiffness constants data and the Vicker hardness is 4.25 GPa for the LCBO. It is expected that LCBO might be a promising candidate for optoelectronic devices in the visible and UV energy regions and as a TBC substance. Finally, we hope that the present study will motivate researchers to investigate the different properties of others laves phase materials.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This research work was partly supported by grant number 12210280 from the Faculty of Engineering, University of Rajshahi, Bangladesh.

References


[63] Li S, Ahuja R, Barsoum MW, Jena P, Johansson B. Optical properties of \(\text{Ti}_3\text{SiC}_2\) and \(\text{Ti}_3\text{AlN}_3\). Appl Phys Lett 2008;92:221907.


