Structural, elastic, electronic, chemical bonding and optical properties of Cu-based oxides ACuO (A = Li, Na, K and Rb): An ab initio study

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ABSTRACT

Ab initio total energy calculations were performed to study in details the structural, elastic, electronic, chemical bonding and optical properties of Cu-based ternary oxides ACuO (A = Li, Na, K and Rb). Optimized atomic coordinates and lattice constants agree well with the existing experimental and theoretical data. Numerical estimations of the six independent elastic constants $C_{ij}$ and their related properties for monocristalline ACuO were obtained. A set of elastic moduli for polycristalline ACuO, namely bulk modulus $B$, shear modulus $G$, Young’s modulus $E$, Poisson’s ratio $\nu$, Lamé coefficients $\lambda$ and $\mu$, and Debye temperature $\Theta_D$ were evaluated. Band structure, total and site-projected density-decomposed densities of states, charge-carrier effective masses, charge transfers and charge density distribution maps were obtained; analyzed and compared with the available theoretical data. Complex dielectric function, refractive index, extinction coefficient, reflectivity and loss function spectra were calculated with an incident radiation polarized parallel to both [100] and [001] crystalline directions.

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1. Introduction

Noncentrosymmetric (NCS) oxide materials are the basis for numerous applications due to their symmetry dependent properties such as pyroelectricity, piezoelectricity, ferroelectricity and second-order non linear optical (NLO) behavior [1; and references therein]. ACuO compounds, where A = Li, Na, K and Rb, belong to the NCS non-polar crystals. At ambient conditions ACuO compounds crystallize in the tetragonal KAgO-type structure [1–4].

Theoretical and experimental information on the ACuO compounds, where A is an alkaline metal (Li, Na, K and Rb), are rather scarce. On the experimental side, Klassen and Hope [2], Losert and Hope [3] and Fischer et al. [4] have reported some information on the elaboration and structural properties of these compounds. The X-ray diffraction analysis of elaborated single crystals [2–4] revealed the tetragonal crystalline structure of the ACuO materials. Theoretically, Umamaheswari and co-workers [1] have reported some results on the structural and electronic properties of the ACuO crystals using the tight-binding linear muffin-tin orbital (TB-LMTO) method within the local density approximation (LDA).

From the energy–volume relations, they found that these materials are stable in the tetragonal KAgO-type structure (symmetry group I4/mmm) at ambient conditions and undergo structural phase transition to hypothetical cubic structure in the high pressure region. The results of their electronic band structure calculations revealed the semiconducting nature of these materials. To the best of the authors’ knowledge, some fundamental physical properties of the ACuO materials, such as the elastic constants and their related properties, chemical bonding, charge-carrier effective mass and optical properties, are still lacking.

It is well known that knowledge of the elastic properties of materials is important because of their closely relations with various fundamental physical properties. In particular, they provide information on the stability and stiffness of the materials against externally applied stresses. Knowledge of the pressure dependence of elastic constants and lattice parameters are the most significant in many modern technologies [5]. For example, semiconductor layers are commonly subjected to a large built-in strain since they are often grown on different substrates having considerable lattice mismatch [6,7]. Measurements of elastic moduli and lattice constants under pressure are generally very difficult, so the lack of experimental data can be compensated by theoretical simulation based on accurate ab initio theories. Thus, the first objective of...
the present work is to study the variations of the structural and elastic properties as a function of pressure. The band gap value, charge-carrier effective mass, chemical bonding and optical constants are the most required data for an eventual application of these materials in the optoelectronic technology. Thus, the prediction of these physical parameters for the ACuO compounds constitutes the second objective of the present work.

Computer modeling of materials based on accurate *ab initio* methods has been a driving issue in the prediction of physical properties and provides an important tool to explore some properties which are not yet (or are difficult to be) experimentally investigated. Thus, we have performed *ab initio* calculations of a wide range of physical properties of LiCuO, NaCuO, KCuO and RbCuO materials. The herein reported results include the optimized crystalline parameters and their pressure dependences, monocristalline and polycristalline elastic moduli and their related properties, band structure, density of states, charge-carrier effective masses, charge density distributions, charge transfers and optical constants.

The rest of this paper is organized as follows. After this introduction, a brief description of the computational methods and details are given in Section 2. The results of our total energy *ab initio* calculations are presented and discussed in Section 3. We then summarize and conclude in Section 4.

### 2. Computational details

All herein performed *ab initio* calculations were carried out using pseudopotential plane-wave (PP-PW) method within the density functional theory (DFT), as is implemented in the CASTEP packages [8]. Exchange–correlation effects were taken into account using the generalized gradient approximation in the Perdew–Burke–Ernerzhof form [9]; the so-called GGA-PBE. In all electronic total energy calculations, Vanderbilt-type ultra-soft pseudopotential [10] was used to treat the potential seen by the valence electrons because of the nucleus and the frozen core electrons. The Li $1s^22s^1$, O $2s^22p^4$, Cu $3d^{10}4s^1$, K $3s^23p^64s^1$, Na $2s^22p^63s^1$ and Rb $4s^24p^55s^1$ electrons were treated as valence states. Valence electronic wave functions were expanded in a plane-wave basis set truncated at maximum plane-wave energy (the cut-off energy) of 400 eV. The Brillouin zone (BZ) was sampled on a $6\times6\times3$ Monkhorst–Pack special $k$-mesh [11]. The self-consistent calculations were considered to be converged when the difference in the total energy was within $5\times10^{-7}$ eV/atom. Very careful step analysis is done to ensure convergence of the total energy, lattice parameters, elastic constants and optical properties in terms of the variational cut-off energy and number of $k$-points in the Brillouin zone. We have verified that further increase in the energy cut-off and $k$-point number did not lead to any noticeable changes in the total energy. We have also experimented with the basis set cut-off and number of $k$-points that at the equilibrium volume the cut-off energy of 400 eV and $6\times6\times3$ Monkhorst–Pack special $k$-mesh were sufficient in the sense that the predicted lattice parameters and elastic constants did not change noticeably when we increased the number of basis functions and $k$-point number. For optical properties, since the imaginary part of the dielectric function is usually calculated first, we choose it as a reference for the assessment of convergence. In optical calculations, a $16\times16\times9$ Monkhorst–Pack $k$-points sampling is found to be enough to get convergence value. The geometry optimization of all free lattice parameters and internal coordinates was determined using the Broyden–Fletcher–Goldfarb–Shanno minimization technique [BFGS] [12], which is known to provide a fast way to find the lowest energy structure. The optimization was performed until the forces on the atoms were less than 0.01 eV/Å, all the stress components were less than 0.02 GPa and the tolerance in the self-consistent field (SCF) calculations was $5.0\times10^{-7}$ eV/atom.

The elastic constants $C_{ij}$ are the fundamental physical parameters which establish the stress–strain relation in the elastic regime based on the Hook’s law. Therefore, the elastic constants were determined from *ab initio* calculations by applying a set of given homogeneous deformations with a finite value $\varepsilon$ and calculating the resulting stress by optimizing the internal atomic freedoms [13]. Two strain patterns, one with non-zero $e_{11}$ and $e_{22}$ components and the second one with non-zero $e_{33}$ and $e_{12}$, brought out stresses related to all six independent elastic constants ($C_{11}$, $C_{33}$, $C_{44}$, $C_{66}$, $C_{12}$ and $C_{13}$) for the tetragonal unit cell. Three positive and three negative amplitudes were used for each strain component with a maximum strain value of 0.5%. Then the elastic constants were determined from a linear fit of the calculated stress as a function of strain.

### 3. Results and discussion

#### 3.1. Structural properties

The ACuO compounds, $A = Li, Na, K$ and $Rb$, have a tetragonal structure and belong to the $I4/mmm$ space group (No. 139 in the International X-ray tables) [4]. There are four chemical formula units in one primitive cell and eight formula units in one conventional cell. The atomic positions for the alkaline metal $A$ ($A = Li, Na, K$ and $Rb$), $Cu$ and $O$ atoms are respectively $8j$ (0.5,$y_A$,$0$), $8h$ ($x_{Cu}$,$0$,$0$) and $8i$ ($x_O$,$0$,$0$), where $y_A$, $x_{Cu}$ and $x_O$ are the so-called internal coordinates for the indicated atoms. So, the crystalline structure of the ACuO compounds is characterized by five structural parameters (not fixed by the symmetry): two lattice constants, $a$ and $c$, and three internal coordinates, $y_A$, $x_{Cu}$ and $x_O$. Before performing calculations of the elastic, electronic and optical properties of the compounds, we have optimized their structural parameters, including lattice constants and internal coordinates, using the BFGS method. The ground-state structure parameters of the tetragonal ACuO materials are determined from the zero pressure geometry optimization. These parameters are displayed in Table 1 along with the experimental findings [4] and available *ab initio* calculations [1] for the sake of comparison. The obtained optimized lattice parameters, including the lattice constants, $a_0$ and $c_0$, and the internal parameters, $y_A$, $x_{Cu}$ and $x_O$, for the four considered compounds are in good agreement with the existing experimental data [4]. Both lattice constants $a$ and $c$ are obtained within less than 2% deviation, in the worst case, from experimental values. This illustrates the level of accuracy that can be achieved in the modern DFT calculations. The error in the internal coordinates $y_A$, $x_{Cu}$ and $x_O$ is also small. As can be seen from Table 1, the $a_0$ and $c_0$ values of the ACuO compounds increase in the following sequence: ($a_0$ and $c_0$)(LiCuO) < ($a_0$ and $c_0$)(CuO) < ($a_0$ and $c_0$)(NaCuO) < ($a_0$ and $c_0$)(KCuO) < ($a_0$ and $c_0$)(RbCuO). Since Cu and $O$ atoms are the same in the four compounds, this result can be easily explained by considering the atomic radii of $Ri$, Na, $K$ and $Rb$, which belong to the same column of the periodic table: $Ri(Li) = 2.05$ Å, $R(Na) = 2.23$ Å, $R(K) = 2.77$ Å and $R(Rb) = 2.98$ Å; the larger size of $A$ atom forces the system to have larger lattice constants.

To investigate the response of the ACuO ($A = Li, Na, K, Rb$) materials to an external pressure, a hydrostatic compression was applied to the unit cell in a $0–20$ GPa pressure range with steps of 5 GPa. At each pressure a complete optimization of the structural parameters was performed. In Fig. 1, we plot the relative changes of the lattice constants, $a/a_0$ and $c/c_0$, versus applied hydrostatic pressure $P$. The symbols indicate the *ab initio* results for the given pressures. These data can be fitted by the following quadratic least-squares fits ($X/A_0 = 1 + sp + p^2$):
From Fig. 1, one can note that the shrinkage degree along the c axis is practically the same for the four studied materials; this means that all these materials have practically the same stiffness against stress applied along the c axis. However, the compressibility along the a axis increases from LiCuO to NaCuO to KCuO to RbCuO. The compressibility along the c axis is greater than that along the a axis in LiCuO and NaCuO. In KCuO, the compressibility along the c axis is greater than that along the a axis up to a certain pressure, then the compressibility along the c axis becomes smaller than that along the a axis. The compressibility along the c axis is smaller than that along the a axis in the RbCuO compound. These results indicate that LiCuO and NaCuO are stiffer for stresses applied along the a axis than those applied along the c axis for all considered pressure range. Similar observation can be made.
for KCuO, but for pressures up to approximately 10 GPa. The RbCuO crystal is stiffer for strains along the c axis than those along the a axis. One can state that these four compounds have practically the same average bonding strength along the c axis, whereas the average bonding strength along the a axis decreases with the increase of the atomic number Z of the A (A = Li, Na, K, Rb) atom.

In Fig. 2 we show the relative variations of the Cu–O and A–O bond-lengths for the ACuO compounds with pressure. The symbols indicate the ab initio results for the given pressures. The Cu–O chemical bond appears to be the stiffest, whereas the A–O is the weakest one in the four considered compounds. One can also note that the degree of weakness of the A–O chemical bond increases when Li is substituted by Na, then Na by K and K by Rb. This could explain the shrinkage behaviour of these compounds along the a axis. The relative variations of Cu–O and A–O bond-lengths with the pressure P could be approximated by the following quadratic least-squares fits \( (d/d_0)_P = 1 + \alpha P + \beta P^2 \):

\[
\text{LiCuO:} \begin{cases} 
\text{Cu – O:} & (d/d_0)_P = 1 - 0.001839 P + 1.87665 \times 10^{-5} P^2 \\
\text{Li – O:} & (d/d_0)_P = 1 - 0.06777 P + 1.19678 \times 10^{-4} P^2 
\end{cases}
\]

\[
\text{NaCuO:} \begin{cases} 
\text{Cu – O:} & (d/d_0)_P = 1 - 0.001999 P + 2.22004 \times 10^{-5} P^2 \\
\text{Na – O:} & (d/d_0)_P = 1 - 0.00718 P + 1.1535 \times 10^{-4} P^2 
\end{cases}
\]

\[
\text{KCuO:} \begin{cases} 
\text{Cu – O:} & (d/d_0)_P = 1 - 0.00234 P + 4.2573 \times 10^{-5} P^2 \\
\text{K – O:} & (d/d_0)_P = 1 - 0.00969 P + 2.07724 \times 10^{-4} P^2 
\end{cases}
\]

\[
\text{RbCuO:} \begin{cases} 
\text{Cu – O:} & (d/d_0)_P = 1 - 0.0032 P + 4.8169 \times 10^{-5} P^2 \\
\text{Rb – O:} & (d/d_0)_P = 1 - 0.01098 P + 2.4844 \times 10^{-4} P^2 
\end{cases}
\]

These relations can readily be used to estimate the Cu–O and A–O bond-lengths for any arbitrary pressure up to 20 GPa.

The calculated pressure dependence primitive-cell volumes were used to construct the equation of state (EOS) \( P(V) \) as shown in Fig. 3. From the Pressure–Volume data, fitted to the third-order Birch equation of state [14] (solid lines in Fig. 3), we obtain the bulk modulus at zero pressure \( B_0 \) and its pressure derivative \( B \). These are listed in Table 1. Our obtained bulk modulus values, using the GGA-PBE, are slightly smaller than the ones reported in Ref. [1]; this slight deviation could be attributed to the use of the LDA approach in Ref. [1], which is known to overestimate the bulk modulus value compared to the one obtained using the GGA approach. We did not find experimental results for \( B_0 \) and \( B \) in the literature to confirm these theoretical results. The ACuO bulk modulus values decrease in the following sequence: \( B_0 \) (LiCuO) > \( B_0 \) (NaCuO) > \( B_0 \) (KCuO) > \( B_0 \) (RbCuO), i.e. in the reverse order compared to the \( a_0 \) and \( c_0 \) case; this is in agreement with the well-known relationship between \( B_0 \) and the lattice constants: \( B_0 \propto V_0^{\frac{1}{3}} \), where \( V_0 \) is the primitive-cell volume.

### 3.2. Elastic constants and their related properties

The six independent lattice constants \( C_{ij} \) values of the tetragonal crystals ACuO, namely \( C_{11}, C_{33}, C_{44}, C_{66}, C_{12} \) and \( C_{13} \), with no external pressure and at the optimized lattice parameters are presented in Table 2. To the best of our knowledge, there are no experimental or theoretical data for the elastic constants of these materials mentioned in the literature. So, our results can provide reference data for future investigations.

First of all, all calculated elastic constants \( C_{ij} \) for the considered materials are positive and satisfy Born’s mechanical stability criteria [15]: \( C_{11} > 0 \), \( C_{33} > 0 \), \( C_{44} > 0 \), \( C_{66} > 0 \), \( (C_{11} - C_{12}) > 0 \), \( (C_{11} + C_{33} - 2C_{12}) > 0 \) and \( 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0 \).

From Table 2, it can be seen that all calculated elastic constants become smaller from LiCuO to NaCuO to KCuO to RbCuO, indicating the decrease of the stiffness of these materials against external stress in the following sequence: LiCuO → NaCuO → KCuO → RbCuO. A key point is that these materials are anisotropic from an elastic point of view, indeed \( C_{11} \) is larger than \( C_{33} \), \( C_{66} \) is larger than \( C_{44} \), and \( C_{12} \) is larger than \( C_{13} \). One can note that \( C_{33} \) is smaller than \( C_{11} \), but the difference between them decreases from LiCuO to NaCuO to KCuO to RbCuO; they become practically equal in RbCuO. Since \( C_{11} \) and \( C_{33} \) reflect the stiffness-to-uniaxial strains along the a \(([100]) \) and c \(([001]) \) directions, this result is in accordance with the response of a and c under hydrostatic pressure as shown in Fig. 1 and discussed previously in Section 2.1. This means also that the compressional elastic anisotropy decreases from LiCuO to NaCuO to KCuO to RbCuO.
Fig. 3. Computed pressure versus primitive-cell volume data for the LiCuO, NaCuO, KCuO and RbCuO materials. The symbols are the calculated results and the continuous lines are Birch EOS fits.

Table 2
Calculated elastic constants \( (C_{ij}, \text{ in GPa}) \), Bulk modulus \( (B, \text{ in GPa}) \), shear modulus \( (G, \text{ in GPa}) \), Pugh’s indicator \( (B/G) \), Young’s modulus \( (E, \text{ in GPa}) \), Poisson’s ratio \( (\sigma) \), Lamé’s coefficient \( (\lambda, \text{ in GPa}) \), longitudinal, transverse and average sound velocities \( (V_L, V_T \text{ and } V_V, \text{ in m/s}) \), and Debye temperature \( (\theta_D, \text{ in K}) \) for the LiCuO, NaCuO, KCuO and RbCuO materials. \( B \) was obtained from the elastic constants \( C_{ij} \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LiCuO</th>
<th>NaCuO</th>
<th>KCuO</th>
<th>RbCuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{11} )</td>
<td>125.48</td>
<td>86.38</td>
<td>58.46</td>
<td>48.27</td>
</tr>
<tr>
<td>( C_{22} )</td>
<td>94.28</td>
<td>73.81</td>
<td>53.67</td>
<td>47.64</td>
</tr>
<tr>
<td>( C_{44} )</td>
<td>25.08</td>
<td>15.40</td>
<td>9.45</td>
<td>7.00</td>
</tr>
<tr>
<td>( C_{66} )</td>
<td>58.68</td>
<td>34.65</td>
<td>23.47</td>
<td>19.31</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>72.68</td>
<td>41.82</td>
<td>25.36</td>
<td>21.25</td>
</tr>
<tr>
<td>( B )</td>
<td>39.97</td>
<td>21.33</td>
<td>14.37</td>
<td>13.89</td>
</tr>
<tr>
<td>( G )</td>
<td>70.32</td>
<td>45.55</td>
<td>30.89</td>
<td>26.92</td>
</tr>
<tr>
<td>( B/G )</td>
<td>32.80</td>
<td>22.19</td>
<td>14.94</td>
<td>12.00</td>
</tr>
<tr>
<td>( E )</td>
<td>2.14</td>
<td>2.05</td>
<td>2.07</td>
<td>2.24</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>85.09</td>
<td>57.24</td>
<td>38.50</td>
<td>31.22</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>0.2972</td>
<td>0.2897</td>
<td>0.2883</td>
<td>0.3012</td>
</tr>
<tr>
<td>( \theta_D )</td>
<td>40.5</td>
<td>38.7</td>
<td>30.79</td>
<td>24.01</td>
</tr>
</tbody>
</table>

The calculated sound velocities at zero pressure (from the elastic constants at zero pressure) for the LiCuO, NaCuO, KCuO and RbCuO materials are given in Table 3 for wave vector along the \([100], [110] \text{ and } [001] \) crystalline directions. From Table 3 data, it can be seen that the fastest and slowest longitudinal waves propagate along the \([110] \text{ and } [001] \) directions, respectively; whereas the fastest and slowest transverse waves propagate along the \([110] \text{ and } [100] \) directions, respectively. Moreover, both longitudinal and transverse wave velocities decrease in the same trend as the elastic constants \( C_{ij} \), i.e., from LiCuO to NaCuO to KCuO to RbCuO, since the sound velocities are proportional to the square root of the corresponding elastic constants as given by Eq. (2).

Table 3
Sound velocities (in m/s) at zero pressure for the LiCuO, NaCuO, KCuO and RbCuO materials calculated from the elastic constants, \( V^{(\lambda,n)\|\parallel\parallel\parallel\}_{V} \) is the velocity of an elastic wave propagating along the \( \vec{n} \) direction and polarized along the \( \vec{\lambda} \) direction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LiCuO</th>
<th>NaCuO</th>
<th>KCuO</th>
<th>RbCuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V^{(100)}_{[100]} )</td>
<td>5555.6</td>
<td>4868.8</td>
<td>4194.24</td>
<td>3429.4</td>
</tr>
<tr>
<td>( V^{(100)}_{[110]} )</td>
<td>3786.2</td>
<td>3065.4</td>
<td>2648.5</td>
<td>2162.8</td>
</tr>
<tr>
<td>( V^{(100)}_{[110]} )</td>
<td>2513.3</td>
<td>2043.5</td>
<td>1714.3</td>
<td>1364.5</td>
</tr>
<tr>
<td>( V^{(110)}_{[110]} )</td>
<td>6219.3</td>
<td>5194.5</td>
<td>4423.1</td>
<td>3617.4</td>
</tr>
<tr>
<td>( V^{(110)}_{[110]} )</td>
<td>2559.7</td>
<td>2473.7</td>
<td>2245.5</td>
<td>1831.0</td>
</tr>
<tr>
<td>( V^{(001)}_{[001]} )</td>
<td>2513.3</td>
<td>2043.4</td>
<td>1714.3</td>
<td>1364.5</td>
</tr>
</tbody>
</table>

To further extend the elastic characteristics study of the ACuO compounds, we have estimated the elastic wave velocities in the \([100], [110] \text{ and } [001] \) directions from the calculated monocry stalline elastic constants \( C_{ij} \). The acoustic vibrational modes of a solid in the long-wavelength limit can be obtained by solving the Christoffell equation [16]:

\[
(C_{ijkl} n_i n_j - \rho V^2 \delta_{ij}) u_l = 0. \tag{1}
\]

Here \( C_{ijkl} \) is the single-crystal elastic constant tensor, \( \vec{n} \) is the wave propagation direction, \( \rho \) is the mass density, \( \vec{\lambda} \) is the wave polarization direction and \( V \) is the wave velocity. The solutions of this equation are of two types: a longitudinal wave with polarization parallel to the direction of propagation \( (V_L) \) and two shear waves \( (V_T1 \text{ and } V_T2) \) with polarization perpendicular to \( \vec{n} \). The elastic wave velocities for tetragonal crystals are [17]:

\[
\begin{align*}
V_{L}^{[100]} & = \sqrt{C_{11} / \rho}, \\
V_{T1}^{[110]} & = \sqrt{(C_{11} + C_{12} + 2C_{66}) / 2\rho}, \\
V_{T2}^{[110]} & = \sqrt{(C_{11} - C_{12}) / 2\rho}, \\
V_{V}^{[001]} & = \sqrt{C_{44} / 2\rho}.
\end{align*}
\]
Generally, large single-crystals are currently unavailable and consequently measurements of the individual elastic constants are impossible. The bulk modulus \( B \) and shear modulus \( G \) may be experimentally determined for polycrystalline samples to characterize their mechanical properties. Theoretically, the calculated elastic constants of a single-crystal allow us to obtain macroscopic mechanical properties in bulk polycrystalline form, namely the bulk modulus \( B \) and shear modulus \( G \) via the Voigt–Reuss–Hill approximations [18–20]. Here, Voigt and Reuss approximations represent extreme values. Hill recommended that the arithmetic mean of these two limits be used, in practice, as effective moduli for polycrystalline samples. Their definitions for tetragonal systems can be found in Ref. [21]. The calculated values for the four studied materials are shown in Table 2. Using the calculated values of the bulk and shear moduli, we have evaluated the Young’s modulus \( E \) and the Poisson’s coefficient \( \sigma \) using the known relations [21]. The results are summarized in Table 2. We can make the following conclusions:

(i) From Tables 1 and 2, one can see that the bulk modulus value evaluated for each compound from the single-crystal elastic constants is in good agreement with its value derived from the Birch equation of state \( V(P) \) depicted in Fig. 1. This might be an estimate of the reliability and accuracy of our calculated elastic constants for the LiCuO, NaCuO, KCuO and RbCuO compounds.

(ii) The bulk moduli of the studied materials decrease in the following sequence: \( B_b(\text{LiCuO}) > B_b(\text{NaCuO}) > B_b(\text{KCuO}) > B_b(\text{RbCuO}) \). As the bulk modulus represents the resistance to volume change under hydrostatic pressures, this indicates that the average bond strength decreases from LiCuO to NaCuO to KCuO to RbCuO; this is consistent with the response of the Cu–O and A(Li, Na, K, Rb)–O bond-lengths under hydrostatic pressure as shown in Fig. 3 and discussed in Section 2.1. The bulk moduli of the four considered materials are quite small (lower than 100 GPa) and so these materials should be classified as relatively soft materials with high compressibility (higher than 0.01). In addition, the Young’s modulus, defined as the ratio of linear stress and linear strain, can give information about the stiffness of a material. The Young’s moduli of LiCuO, NaCuO, KCuO and RbCuO were found to be 85, 57, 39 and 31 GPa, respectively; thus, these compounds show a rather small stiffness.

(iii) Pugh’s \( B/G \) ratio empirical criterion [22] is one of the widely used to provide information about brittle (ductile) nature of materials. If \( B/G > 1.75 \), ductile behavior is predicted; otherwise, the material behaves in a brittle manner. According to the calculation results in Table 2, the \( B/G \) ratios of all ACuO compounds are higher than 1.75, i.e., indicating a ductile nature of these materials and thus they will be resistant to thermal shocks; their mechanic properties decrease slowly with increasing temperature.

(iv) To visualize the mechanical anisotropy of the ACuO phases, we have plotted a three-dimensional representation of a directional dependence of the Young’s modulus \( E \) using the equation given in Ref. [23] for a tetragonal structure. In Fig. 4, we have presented the visualization of the Young’s moduli surfaces and their cross-sections in the \((100), (010) \) and \((001) \) planes for the LiCuO, NaCuO, KCuO and RbCuO compounds. In all considered cases the lowest value, \( E_{\text{min}} \), is about 50% of the highest value of the Young’s modulus, \( E_{\text{max}} \), indicating a strong anisotropic elastic behavior.

Debye temperature, which determines the thermal characteristics of a material, can be estimated from the average sound velocity in an isotropic material [24]. The obtained values of the longitudinal, transverse and average sound velocities \( (V_L, V_T \) and \( V_n \), respectively), and the Debye temperature \( \theta_D \) for polycrystalline LiCuO, NaCuO, KCuO and RbCuO are gathered in Table 2. The value of \( \theta_D \) decreases from LiCuO to NaCuO to KCuO to RbCuO; this result is expected due to the fact that the stiffness decreases in the same sequence.

Finally, we turn to the pressure dependence of the elastic constants and bulk modulus. In Fig. 5, we show the pressure dependence of the elastic constants and bulk modulus. The dots show the \( \text{ab initio} \) results for the given pressures and the full lines are obtained by a simultaneous least squares fit of each of the six independent elastic constants \( (C_{11}, C_{33}, C_{44}, C_{66}, C_{12} \) and \( C_{13} ) \) and the bulk modulus \( (B) \) to a second-order polynomial expression \( C_{ij}(P) = q + rP + tP^2 \). The second-order polynomials describe the pressure dependence of the elastic constants and bulk modulus for the LiCuO, NaCuO, KCuO and RbCuO materials summarized in Table 4. The elastic constants \( C_{11} \) and \( C_{33} \) represent the elasticity in length; they change with the longitudinal strain. The elastic constants \( C_{12}, C_{13}, C_{44} \) and \( C_{66} \) are related to the elasticity in shape. We can see quite different behaviours depending on the considered elastic constants. The elastic constant \( C_{11}, C_{33}, C_{66}, C_{12} \) and \( C_{13} \) increase with increasing pressure. The exception is \( C_{44} \), which decreases with the pressure, predicting a mechanical instability of these materials at high pressure; this is in agreement with the reported result of Umamaheswari et al. [1].

3.3. Electronic properties

For better understanding of the electronic and optical properties of these compounds, the investigation of the electronic eigen energies \( E \) as a function of the wave vector \( k (E(k)) \), in the first Brillouin zone (BZ), would be useful. We have calculated the energy band structure \( E(k) \) on a discrete \( k \)-mesh following high-symmetry directions in the \( k \)-space at the equilibrium lattice parameters within the GGA-PBE for the LiCuO, NaCuO, KCuO and RbCuO compounds. The obtained results are depicted in Fig. 6. The energy values were gauged to ensure that the highest energy for a valence electron is exactly equal to 0 eV. The obtained fundamental energy band gaps for the ACuO (\( A = \text{Li, Na, K, Rb} \) ) compounds are summarized in Table 5, along with the available theoretical results [1] for the sake of comparison. We are not aware of any optical spectroscopic measurements of the gaps for the studied materials. It is a well-known problem that both LDA and GGA approximations usually underestimate the band gap when using self-consistent band structure calculations within DFT [25,26]. Typically, in the DFT calculation the underestimation of the band gap when compared with experimental data is about 30–100% [27]. This is mainly due to the fact that they have simple forms that are not sufficiently flexible for accurately reproducing both exchange–correlation energy and its charge derivative. So, the herein studied materials would have gap higher values than those obtained using DFT within GGA and LDA approximations. As seen from Fig. 6, the four considered materials have an indirect band gap \( (Z–I) \) and the value of the fundamental band gap decreases when the atomic number \( Z \) of the \( A \) atom increases. Our calculated energy band gap values are somewhat larger than those reported in Ref. [1]. This is probably due to the use of a different \( \text{ab initio} \) method (TB-LMTO within the LDA) by Umamaheswari and co-workers [1]; their method is known to underestimate the energy band gap value compared to the GGA used in the present work. Our predicted indirect band gap character \( (Z–I) \) for LiCuO and NaCuO is in agreement with the prediction of Ref. [1]. However, there is a discrepancy concerning the nature of the fundamental band gap for the KCuO and RbCuO compounds; Ref. [1] predicted a direct band gap \( (Γ–I) \) for KCuO and RbCuO. Our calculations have predicted an indirect band gap \( (Z–I) \) for the four studied compounds; however, there are some differences on how this “indirect character” of the band
gap is formed in these four materials. The enlarged view of the band gaps of these materials (Fig. 7) clearly illustrates these differences. For example, the top of the valence band of RbCuO is very flat near the Z point and this flatness decreases going from
The second-order polynomials describing the pressure dependence of the elastic constants, $C_{ij}$, are in GPa.

For LiCuO:
- $C_{11} = 125.48 + 5.787P - 0.0387P^2$
- $C_{12} = 94.28 + 7.539P - 0.0419P^2$
- $C_{44} = 25.38 - 0.192P - 0.0039P^2$
- $C_{66} = 58.68 + 3.303P - 0.0347P^2$
- $C_{13} = 72.68 + 5.579P - 0.0359P^2$
- $B = 70.32 + 4.62P - 0.022P^2$

For NaCuO:
- $C_{11} = 86.38 + 5.183P - 0.0611P^2$
- $C_{12} = 73.81 + 8.603P - 0.0292P^2$
- $C_{44} = 15.40 - 0.002P + 0.0024P^2$
- $C_{66} = 34.65 + 1.599P - 0.0307P^2$
- $C_{13} = 41.82 + 4.597P - 0.0555P^2$
- $C_{10} = 21.33 + 2.667P - 0.0095P^2$
- $B = 45.55 + 4.410P - 0.0372P^2$

For KCuO:
- $C_{11} = 58.46 + 4.039P - 0.0377P^2$
- $C_{12} = 53.68 + 9.328P - 0.0553P^2$
- $C_{44} = 9.45 + 9.013P - 0.0126P^2$
- $C_{66} = 23.47 + 1.048P - 0.0148P^2$
- $C_{13} = 25.368 + 3.338P - 0.0306P^2$
- $C_{10} = 14.37 + 1.715P - 0.0585P^2$
- $B = 30.89 + 3.88P - 0.049P^2$

For RbCuO:
- $C_{11} = 48.27 + 3.134P - 0.0643P^2$
- $C_{12} = 47.64 + 10.039P - 0.0809P^2$
- $C_{44} = 7.00 + 0.291P - 0.0404P^2$
- $C_{66} = 19.31 + 0.607P - 0.0859P^2$
- $C_{13} = 215.25 + 2.307P + 0.0926P^2$
- $C_{10} = 13.89 + 2.283P - 0.0557P^2$
- $B = 26.92 + 3.276P + 0.0041P^2$

The difference between these two bands gaps decreases; this is clearly shown in Fig. 7. It can be seen that the energy of the $\Gamma$ point in the valence bands becomes progressively closer to the Fermi level in the following sequence: LiCuO → NaCuO → KCuO → RbCuO.
The calculated effective masses for electrons and holes, derived from the electronic band energy dispersions at points of interest in the Brillouin zone, are summarized in Table 5 for the ACuO compounds (all in units of electron mass). The effective electron mass is indicated by the under script “e” ($m_e$) and the hole mass by “h” ($m_h$). Our calculations show that the charge-carrier effective masses increase in the following sequence: LiCuO → NaCuO → KCuO → RbCuO. This predicts an increase of the mobility of the charge-carrier in the following sequence: RbCuO → KCuO → NaCuO → LiCuO. One can note that the electron effective mass values along the $\Gamma - X$ and $\Gamma - Z$ directions in the BZ are equal, indicating an isotropy of the electron effective mass in these compounds. The effective masses of holes are larger than those of the electrons. The low effective masses of electrons indicate that the electrons are the main sources of charge-carriers since the holes have heavier masses. The hole effective mass in RbCuO is higher than that of the other studied materials, which reflects the VBM flatness of RbCuO.

In order to understand the origin of the important band structure features of the herein studied materials, we must consider the relative contributions of each atom species to the density of electronic states. Partial density of states (PDOS) and total density of states (TDOS) diagrams for the ACuO compounds are depicted in Fig. 8. These diagrams allow us to conclude that the lowest conduction band is formed by the hybridization of the A-p and O-2p states. The upper valence bands consist of one manifold in the LiCuO, while they split into three sub-bands in NaCuO, and four distinct narrow bands in KCuO and RbCuO. This can be clearly seen in the band structures shown in Fig. 6. The upper one arises from the hybridization of Cu-3d states and O-2p states, suggesting the presence of a covalent bonding character between O and Cu atoms.

The valence electron charge distribution in a crystal is an important aspect of the electronic structure since it reveals the bonding pattern of the crystal. Thus, we have calculated the effective charge $Q_e$ on each atom of the studied crystals using two different calculation methods: The Mulliken (MPA) [28,29] and the Hirshfeld (HPA) [30] population analysis. The obtained results are summarized in Table 6. It is well known that the absolute values of the atomic charges, yielded by the population analysis, have little physical meaning, since they display a high degree of sensibility to the atomic basis set [31]. However, we can still find some useful information by considering the relative values of bond populations. MPA is less reliable, as it arbitrarily divides the overlap electron population [32]. For small charge transfers, Fukui function indices estimated using MAP is eventually unpredictable [33]. HPA, in contrast, is more accurate, leading to improved Fukui function indices which are able to predict reactivity trends within a molecule better than MPA [34]. Due to the higher electronegativity of the oxygen (O) compared to the metals A (A = Li, Na, K and Rb) and copper (Cu), we observe charge transfers from A and Cu atoms to the O atom. The negatively charged O atom is bounded to two positive metal atoms: A (A = Li, Na, K and Rb) and Cu. This reveals
the presence of ionic bonding character in these materials. The effective ionic valences are defined as the difference between the formal ionic and the calculated charges on the ion species in the crystal and can be used as a measure of ionicity; a vanishing value implies an ideal ionic bond, while a value greater than zero indicates the presence of covalent bonding character. We can also exploit the ratio of the net charge of an atom in a material to the charge of its nominal oxidation state to evaluate the ionic bonding character percentage. The nominal oxidation states of the atoms of our considered materials are $A^{+1}$ ($A = \text{Li, Na, K, Rb}$), Cu$^{+1}$ and O$^{-2}$. Thus, from Hirshfeld charge values given in Table 6, we have estimated that the ionic bonding characters are about 18% in LiCuO, 20% in NaCuO, 21% in KCuO, and 25% in RbCuO. From Table 6, one can see that when the A atom goes downward the alkaline metal column of the periodic table, the oxygen and the A atom Hirshfeld charge values increase, while the Cu atom one decreases. This means that the degree of ionic bonding character (degree of covalent bonding character) of the A–O bond increases (decreases), while that of the Cu–O bond decreases (increases) in the following sequence: LiCuO → NaCuO → KCuO → RbCuO, indicating a decrease of the strength of the A–O bond; this is in good agreement with the pressure dependence of this bond, discussed above in Section 2.1. It is known that the elastic constants monotonically decrease as the ionic bonding character of a material increases, so the decrease of the elastic constants values when going from LiCuO to NaCuO to KCuO to RbCuO may be a consequence of the increase of the ionic bonding character following that sequence. For further understanding of the bonding nature between atoms in the ACuO ($A = \text{Li, Na, K, Rb}$) compounds, we have plotted, in Fig. 9, the contour maps of the charge density distributions along...
the (001) plane for LiCuO and RbCuO as prototype since there is no noticeable difference between the contour maps of the four materials. The presence of charge in bond region between Cu and O indicates the existence of a degree of covalent bonding character between them, which coincides with the hybridization between Cu-3d and O-2p electrons shown in the DOS spectra (Fig. 8). There is less charge in bond region between A and O atoms, this indicates a more ionic bonding character between A and O atoms. Ionic bonding character between A and O atoms slightly increases from LiCuO to RbCuO, which is consistent with the Hirshfeld population analysis discussed above.

3.4. Optical properties

One of the main optical parameter of a material is its dielectric function, \( \epsilon(\omega) = \epsilon_1(\omega) + j\epsilon_2(\omega) \), because it is the fundamental feature of the linear response to an electromagnetic wave. The imaginary part \( \epsilon_2(\omega) \) of the dielectric function can be computed from the electronic band structure by calculating the momentum matrix elements between the occupied and unoccupied wave functions respecting the selection rules [35]:

\[
\text{Im}\epsilon_{\text{el}}(\omega) = \frac{\epsilon_2(\omega)}{\epsilon_0} = \frac{4\pi\epsilon^2}{m^2}\omega^2 \sum_{ij} \left| \langle f|p^i|j\rangle \langle j|p^j|f\rangle \right|^2 W_{ij}(1 - W_{ij})\delta(E_f - E_i - \hbar\omega)d^3k.
\]

(4)

In this expression, \( \langle f|p^i|j\rangle \) and \( \langle j|p^j|f\rangle \) are the dipole matrix elements corresponding to the \( x \) and \( \vec{\beta} \) directions of the crystal (x, y or z), and \( f, i \) are the final and initial states, respectively. \( W_{ij} \) is the Fermi distribution function for the \( n \)th state and \( E_n \) is the electron energy in the nth state. The real part of the frequency-dependent dielectric function expression \( \epsilon_{\text{re}}(\omega) \) can be numerically calculated from \( \epsilon_2(\omega) \) using the Kramers–Kronig transform:

\[
\epsilon_{\text{re}}(\omega) = \frac{2}{\pi} P \int_{0}^{\infty} \frac{\epsilon_2(\omega')\omega'^2}{(\omega'^2 - \omega^2)} d\omega',
\]

(5)

where \( P \) is the Cauchy principal value of the integral. The other optical constants, such as the refractive index \( n(\omega) \), the extinction coefficient \( k(\omega) \), the reflectivity \( R(\omega) \) and the loss function \( L(\omega) \), can be calculated from the dielectric function \( \epsilon(\omega) = \epsilon_1(\omega) + j\epsilon_2(\omega) \) using the following relations:

\[
n(\omega) = \frac{\epsilon_1(\omega)}{\epsilon_0} + \sqrt{\frac{\epsilon_1(\omega) + \epsilon_2(\omega)}{2}}
\]

(6)

\[
k(\omega) = \sqrt{\frac{[\epsilon(\omega)] - \epsilon_1(\omega)}{2}}
\]

(7)

\[
R(\omega) = \frac{\sqrt{\epsilon(\omega) - 1}}{\sqrt{\epsilon(\omega) + 1}}
\]

(8)

\[
L(\omega) = \epsilon_2(\omega)/[\epsilon_1(\omega) + \epsilon_2(\omega)].
\]

(9)

It is worth to note here that the approach implemented in CA-STEP code to calculate \( \epsilon_2(\omega) \) has some limitations. First of all, the local field effects (related to the fact that the electric field experienced at a particular site of a crystal is screened by the polarizability of the atom at this site) are neglected. Second, phonon contributions to the optical spectra, which are especially important for the crystals with indirect gap, are not taken into account. However, even with these limitations, it has been reported in the literature [36–39] that the calculated spectra for different materials are generally in a reasonable agreement with the experimental ones (see for example, calculations of absorption spectra for PbWO4 [37,38], TiO2 [39], etc.).

The computed absorptive \( (\epsilon_2(\omega)) \) and dispersive parts \( (\epsilon_1(\omega)) \) of the complex dielectric functions \( \epsilon(\omega) \) are displayed in Fig. 10, as a function of the photon energy for the four studied compounds. Due to the tetragonal structure of the studied materials, optical spectra were calculated for incident light polarized along the [100] and [001] crystalline directions. The instrumental smearing of 0.1 eV was used to model the broadening effects. In spite of the anisotropy in the structural and elastic properties, we find that both the real \( \epsilon_1(\omega) \) and the imaginary \( \epsilon_2(\omega) \) parts of the dielectric function do not demonstrate any optical anisotropy. The behavior of \( \epsilon_2(\omega) \) is rather similar for all the studied compounds with some small differences. This is attributed to the fact that the band structures of these materials are similar with minor differences causing insignificant changes in the structures of \( \epsilon_2(\omega) \). The prominent structures in \( \epsilon_2(\omega) \) spectrum are mainly ascribed to the transitions from O-2p and Cu-2d states in the valence bands to A-p and Cu-3p states in the conduction bands.

The real parts \( \epsilon_1(\omega) \), in the limit of zero energy values (the infinite wavelengths) i.e. the so-called static dielectric constant \( \epsilon_1(0) \),
are 7.232, 5.798, 4.879 and 4.439 for the LiCuO, NaCuO, KCuO and RbCuO materials, respectively.

The refractive index \( n(\omega) \) and extinction coefficient \( k(\omega) \) of the ACuO \( (A = \text{Li, Na, K, Rb}) \) compounds are displayed in Fig. 11. The calculated zero energy \( (\lambda = \infty) \) \( n(0) \) values for the LiCuO, NaCuO, KCuO and RbCuO compounds are equal to 2.689, 2.408, 2.209 and 2.107, respectively. The energies for which the dispersion is null, \( E(n = 1) \), are equal to 12.948, 12.687, 12.769, 12.736 eV for LiCuO, NaCuO, KCuO and RbCuO respectively.

In Fig. 12, we show the reflectivity spectra \( R(\omega) \) for the herein studied materials. The \( R(\omega) \) values of these compounds do not approach the unity when the light frequency \( \omega \) tends to zero, which means that these compounds behave like semiconductors.

MLahk in Fig. 13, we present the electron energy loss functions \( L(\omega) \). The \( L(\omega) \) function is an important factor describing the energy loss of a fast electron traversing a material. The peaks in \( L(\omega) \) spectra is associated with the plasma resonance and the corresponding frequency is the so-called plasma frequency \( \omega_p \). The peaks of \( L(\omega) \) correspond to the trailing edges in the reflection spectra. We do not find optical data in the literature for the ACuO \( (A = \text{Li, Na, K and Rb}) \) compounds, and we hope that our calculations will lead to further experimental efforts on these materials. By combining
the measured data with the calculation results, a near total understanding of the electronic and optical properties of the herein studied materials is possible.

4. Conclusions

In this work, we have performed \textit{ab initio} calculations of the structural, elastic, electronic, chemical bonding and optical properties for the tetragonal ACuO ($A = \text{Li, Na, K and Rb}$) compounds. Our optimized lattice parameters are in good agreement with the existing experimental data. We have found an anisotropic behavior of the pressure dependence of the lattice constants. The predicted single-crystal elastic constants show that these materials are mechanically stable at zero pressure and that they become smaller in the following sequence: LiCuO $\rightarrow$ NaCuO $\rightarrow$ KCuO $\rightarrow$ RbCuO. Sound wave velocities along some crystalline symmetric directions have been derived from the calculated elastic constants. The obtained polycrystalline elastic moduli using the Voigt–Reuss–Hill approximations demonstrate that when we go down the alkali metals column from Li to Rb, the bulk modulus $B$, shear modulus, Young’s modulus $E$ and Lamé coefficient $\lambda$ become smaller, indicating a decrease in the stiffness in that sequence. According to the Pugh’s criterion, all these compounds behave in a brittle manner. We have found a nonlinear behaviour of the pressure dependence of the elastic constants. The decrease of $C_{44}$ with the increasing pressure predicts probable instabilities of these materials at high pressure. We have found that these materials are indirect band gap semiconductors. The fundamental band gap value decreases with the increase of the atomic number $Z$ of the alkaline metal $A$. Analysis of the chemical bonding in these materials, via the calculation of the density of states, charge transfers and charge density distributions, shows that the Cu–O bond is more covalent than the A–O one. The behaviour of the lattice constants and elastic constants versus pressure is explained on the light of the stiffness of these bonds. We have showed that the elastic constants are lower in materials with higher ionicity. The ACuO compounds are found to be optically isotropic though they are structurally and elastically anisotropic. Some macroscopic optical constants have been predicted in the 0–20 eV energy range. As far as the ACuO ($A = \text{Li, Na, K and Rb}$) compounds are concerned, our results for the elastic and optical properties are predictions, and we welcome experiments to prove them.

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References
