Elastic Constants and Related Properties of Compressed Rocksalt CuX (X = Cl, Br): Ab Initio Study

Abstract: First-principles calculations are performed to study the structural and elastic properties, sound velocities, and Debye temperature of rocksalt-structured copper monochloride (CuCl) and copper monobromide (CuBr). The structural parameters, elastic constants, longitudinal, transverse, and average elastic wave velocities, and the Debye temperature in the pressure range 10–20 GPa are successfully predicted and analysed. The variation of the elastic constants and bulk modulus as a function of pressure is found to be non-linear for CuCl and almost linear for CuBr. Based on the obtained values of the elastic constants, the bulk modulus, the isotropic shear modulus, Young’s modulus, Poisson’s ratio, and Pugh’s ratio of the aggregate materials are also investigated. The analysis of Poisson’s and Pugh’s ratios shows that these materials become ductile for pressures in the range 10–20 GPa. The evolution of the longitudinal sound velocity under pressure indicates the hardening of the corresponding phonons in both materials.

Keywords: Copper Halide Materials; Debye Temperature; Elastic Properties; High Pressure; Sound Velocity.

1 Introduction

The copper halides CuX (X = Cl, Br and I) have attracted much research interest in the last few years because of their some unusual properties compared to other II–VI, III–V, and IV–IV binary materials [1]. Their ionicity values approach 0.7 according to the Phillips ionicity scale [2]. Under normal conditions, these compounds crystallise in the zinc blende structure and form the end of the class of tetrahedrally coordinated materials [3–5]. They are characterised by large bandgaps [6, 7] and small values of the phase-transition pressure [8–11]. Blacha et al. [12] studied the electronic structure of the high-pressure modifications of copper halide CuX (X = Cl, Br, I) semiconductors, where the absorption spectra of edge excitons in thin films were measured as a function of hydrostatic pressure using a diamond anvil. Their results showed that the rhombohedral and tetragonal valence bands of the copper halides are significantly affected by the hybridisation of copper 3d and halogen p than those of the zinc blende.

Using some experimental elastic constants and structural parameters, Takeuchi and Yamashita [13] predicted the surface acoustic wave (SAW) characteristics of the monochloride (CuCl). They suggest that CuCl is a potential SAW material for low-frequency filter and delay line applications.

To gain more information on the effect of high pressure on some other physical properties of copper halides compounds, Bioud et al. [14] investigated the phase transition, elastic constants, and the thermodynamic properties of copper iodide (CuI). According to the generalised elastic stability criteria, they found that the high-pressure rocksalt phase will be mechanically stable up to 57 GPa.

To obtain more information on the bandgaps of copper halides, recently Lv et al. [15] used large transparent tetrahedral CuX (X = Cl, Br) single crystals that were grown by the temperature reduction method in the range 40–50 °C. The crystals were characterised by X-ray powder diffraction and other techniques. They found that the CuX single crystals have cubic structures with a nearly standard ratio of Cu/X and wide direct bandgaps (3.21 eV for CuCl and 2.95 eV for CuBr).
On the theoretical side, some complementary data to those of experiments have been reported on the fundamental properties of both compounds and their ternary alloys \( \text{CuCl}_{x-\text{Br}} \) [1, 16]. Nevertheless, most of these theoretical results deal with the materials in question in the zinc blende structure, whereas data regarding their properties in the rocksalt phase are scarce. In order to have a more comprehensive understanding of copper halide semiconductors in the rocksalt structure, structural and elastic properties, sound velocities, and the Debye temperature for rocksalt \( \text{CuCl} \) and \( \text{CuBr} \) in the pressure range 10–20 GPa have been calculated, which are reported here. Note that the phase transition pressure from the zinc blende to rocksalt structure has been reported to be \( \sim 7.8 \) and 6.95 GPa for semiconducting \( \text{CuCl} \) and \( \text{CuBr} \), respectively [10].

The elastic constants and sound velocities along the major crystallographic directions under pressure were obtained. In addition, the longitudinal, transverse, and average elastic wave velocities, the Debye temperature, and some other mechanical moduli of the aggregate polycrystalline materials were predicted and analysed. On the basis of the elastic constants, the mechanical behaviour of the aggregate polycrystalline materials was also investigated.

The rest of the paper is organised as follows. In Section 2, the computational methodology used in this work is described. In Section 3 we provide a brief review of the theoretical formalism, accompanied by the presentation and discussion of the results. Finally, Section 4 gives the conclusion.

## 2 Computational Methodology

In the present work, the calculations were performed using the CASTEP code [17], which is based on the density functional theory and the pseudopotential method. The Vanderbilt ultrasoft pseudopotential [18] within the generalised gradient approximation (GGA) as revised in the Perdew-Burke-Ernzerhof (PBESOL) [19] approach is adopted. The \( 3d^{10\text{ }4s^{1}, \text{ }3s^{2}\text{ }3p^{5}}, \text{ and } 4s^{2}\text{ }4p^{5} \) valence electrons were chosen for \( \text{Cu}, \text{Cl}, \text{and } \text{Br} \) atoms, respectively. As a matter of fact, the functional PBESOL is a revised PBE functional for a GGA. In the present work, this functional is used in order to improve the equilibrium properties of the materials of interest. The plane wave cut-off energy is taken to be 600 eV. The Monkhorst and Pack \( k \)-point meshes [20] with a \( 12 \times 12 \times 12 \) special \( k \)-point mesh are used so as to sample the Brillouin zone. The error bars of the total energy are less than \( 5 \times 10^{-7} \text{ eV/atom} \).

Besides, in the subsequent geometry optimisation, the atoms are allowed to fully relax when the force and stress tensor on each atom is less than \( 10^{-2} \text{ eV/Å} \) and 0.02 GPa, respectively. The maximum displacement is obtained as \( 5 \times 10^{-4} \text{ Å} \). The total energy of the materials under investigation for one formula unit is minimised by changing the lattice constant under the restriction of the given symmetry. The elastic constants are obtained by computing the stress generated by applying a small strain to an optimised unit cell [14, 21], where the amplitude of the maximum strain is set as 0.003, within which six distorted structures are generated (more details can be found in [14, 21]).

## 3 Results and Discussion

### 3.1 Elastic Properties

#### 3.1.1 Elastic Stiffness Constants

The elastic properties of semiconductor materials play a very important role in the physics of solid state matter because they are linked directly with other physical quantities such as the Debye temperature, heat capacity, thermal expansion, and Grüneisen parameter [22]. In the case of cubic crystals, there are only three independent elastic constants (\( C_{11}, C_{12}, \text{and } C_{44} \)). The elastic constant \( C_{11} \) is a measure of resistance in a solid to a deformation by a stress applied on (100) crystallographic plane with polarisation in the \( <100> \) direction, whereas the elastic constant \( C_{44} \) refers to the measurement of resistance in a solid to a deformation to a shear stress applied across the (100) crystallographic plane with polarisation in the direction \( <010> \) [22]. For cubic crystals, the bulk modulus \( B \) (which is the inverse of the compressibility) and the elastic constants are related by the expression \( B = (C_{11} + 2C_{12})/3 \).

Figure 1 shows the variation of the elastic constants \( C_{ij} \) and their aggregate bulk modulus \( B \) with hydrostatic pressure for \( \text{CuCl} \) and \( \text{CuBr} \) in the pressure range 10–20 GPa. Note that all parameters of interest increase (except for the elastic constant \( C_{44} \), which decreases very slowly) monotonically with increasing pressure. The best fit of our data regarding the pressure dependence of the elastic constants \( C_{ij} \) and the bulk modulus \( B \) of \( \text{CuCl} \) and \( \text{CuBr} \) showed a linear behaviour according to the following expressions:

For \( \text{CuCl} \)

\[
C_{11} = 96.10 + 8.19p, \quad (1a)
\]

\[
C_{12} = 70.98 + 2.46p, \quad (1b)
\]

\[
C_{44} = 10.33 - 0.30p, \quad (1c)
\]

\[
B = 79.35 + 4.37p. \quad (1d)
\]
Elastic constants $C_{ij}$, $B$ (GPa)

\begin{align*}
C_{11} &= 96.30 + 8.20 p, \\
C_{12} &= 56.97 + 2.49 p, \\
C_{44} &= 14.87 - 0.13 p, \\
B &= 70.08 + 4.40 p.
\end{align*}

For CuBr, we notice that the elastic constants $C_{ij}$ of high-pressure rocksalt copper halides CuX ($X = \text{Cl, Br}$) are relatively high. This is due to the fact that the elastic properties of materials are directly related to the atomic arrangements and the nature of the bonding between their constituents. For CuX ($X = \text{Cl, Br}$), the bonding is dominated by the ionic bond caused by the Coulomb attraction between the ions in these compounds (the ionic factor $f_l \approx 0.7$ according to the Phillips ionicity scale [2]).

From the above equations, one can see that the first pressure derivatives of $C_{ij}$ and $B$, namely $\partial C_{11}/\partial P$, $\partial C_{12}/\partial P$, $\partial C_{44}/\partial P$, and $\partial B/\partial P$ of CuCl are 8.19, 2.46, $-0.30$, and 4.37 respectively, whereas those of CuBr are 8.20, 2.49, $-0.13$, and 4.40, respectively. Accordingly, we notice that the elastic constant $C_{11}$ is very sensitive to the hydrostatic pressure compared to $C_{12}$ and $C_{44}$. On the contrary, the elastic constant $C_{44}$ is less sensitive to the pressure than the other stiffness constants. In fact, $C_{12}$ and $C_{44}$ are related to the elasticity in shape [23]. A transverse strain causes a change in shape without a change in volume and hence $C_{12}$ and $C_{44}$ are less sensitive to pressure compared to $C_{11}$ [23]. The increase of the bulk modulus with increasing pressure indicates that the stiffness of the materials of interest becomes larger under pressure. To the best of our knowledge, there are no data available in the literature on the pressure derivatives of $C_{ij}$ and $B$ for both compounds and hence our results are only for reference.

Our findings regarding the elastic constants $C_{ij}$ of cubic rocksalt copper halides CuX ($X = \text{Cl, Br}$) perhaps can be used to explain most of the physical properties of these compounds under high pressure. This is due to the fact that most of the physical properties of materials are related to the bonding of atoms, which can be characterized with a good analysis of the elastic constants and the mechanical strength.

3.1.2 Young’s Modulus, Poisson’s Ratio, and Anisotropy Factor

Young’s modulus ($E$) is a measure of the stiffness of a solid material. It is a mechanical property that shows the relationship between the stress and strain in a material. On the other hand, Poisson’s ratio ($\sigma$) is an important mechanical parameter that is associated with the volume change during a uniaxial deformation. Thus, there is no volume change during the elastic deformation when $\sigma = 0.5$ [24]. However, a large volume change is expected to be associated with the solid deformation when the value of $\sigma$ is low. Furthermore, $\sigma$ provides more information regarding the characteristics of the bonding forces than any of the other elastic parameters [24]. For an isotropic material (aggregate polycrystalline materials), $E$ and $\sigma$ are calculated using the equations $E = 9BG/(3B + G)$ and $\sigma = (3B - 2G)/(6B + 2G)$, where $G = (G_V + G_R)/2$ is the isotropic shear modulus [24]. $G_V$ is the Voigt modulus and $G_R$ is the Reuss modulus, which are given by the following [25]:

\begin{align*}
G_V &= (C_{11} - C_{12} + 3C_{44})/5, \\
G_R &= 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})].
\end{align*}
Figure 2 displays the variation of Young’s modulus and Poisson’s ratio as a function of pressure in the range 10–20 GPa. It can be observed that the calculated values of $\sigma$ are higher than 0.25, which indicates that a small volume change is associated with the deformation of these materials. In fact, it appears that the calculated values of $\sigma$ for both materials under load lie between 0.4 and 0.5, suggesting that the interatomic forces of these materials are central in the pressure range 10–20 GPa. Note that both $E$ and $\sigma$ increase gradually with increasing pressure. The increase of $\sigma$ with increasing pressure suggests that the material becomes more resistant to changes in its bond length.

The elastic anisotropy in semiconductor materials is of geophysical interest. It is known that the anisotropic parameter $A$ is unity for materials that have isotropic elasticity. However, cubic crystals that are isotropic have elastic anisotropy different from unity. This is due to the fourth-rank tensor property of elasticity [26]. Hence, the magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy of the crystal. The elastic anisotropy parameter (called also the Zener anisotropy factor) of cubic crystals is given usually by the formula $A = 2C_{44}/(C_{11} - C_{12})$. If $A < 1$, the crystal is stiffest along the $<100>$ cube axes, and when $A > 1$ it is stiffest along the $<111>$ body diagonals [27]. On the other hand, the shear modulus $C_s$, which is defined by the relation $C_s = (C_{11} - C_{12})/2$, has also been calculated as a function of pressure for both CuCl and CuBr rocksalt materials. Our results regarding $A$ and $C_s$ versus pressure are shown in Figure 3. Note that our values of $A$ are less than 1, indicating that both CuCl and CuBr rocksalt materials have the highest stiffness along the $<100>$ crystallographic directions. The stiffest directions are generally aligned with near-neighbour bonds [27]. From Figure 3, one can see that $A$ decreases non-monotonically with increasing pressure. The situation seems to be different for $C_s$, which increases monotonically when the materials under investigation are compressed. The increase of the shear modulus with increasing pressure is crucial for high lattice stability.

3.1.3 Pugh’s Ratio

Ductility and brittleness of a material are two mechanical properties of substantial importance, which can be obtained directly from the elastic constants [22]. Pugh proposed that the ratio of the bulk to the shear modulus ($B/G$) of polycrystalline phases [28] is an indication of ductile versus brittle character. Indeed, one may argue that $G$ represents the resistance to plastic deformation, while $B$ represents the resistance to fracture [24]. A high $B/G$ value indicates the tendency for ductility, while a low value indicates a tendency for brittleness. The critical value that separates ductile and brittle materials has been evaluated to be 1.75 [24]. Here, the ratio $B/G$ appears to be much larger than 1.75. These results suggest that both CuCl and CuBr in the rocksalt phase are prone to ductility. In Figure 4, Pugh’s ratio is plotted against pressure. As shown in Figure 4, Pugh’s ratio increases slowly and almost linearly with increasing pressure. The behaviour is monotonic, indicating that the materials of interest are prone to ductility in the pressure range 10–20 GPa.

3.2 Elastic Wave Velocities and Debye Temperature

The acoustic velocities are generally used to obtain the second-order elastic stiffness constants $C_{ij}$ of materials
and, vice versa, if the second-order elastic stiffness constants \( C_{ij} \) and the density of the crystal are known, it is possible to predict the acoustic sound velocities. As was mentioned previously, for a cubic crystal the three independent elastic constants \( C_{11}, C_{12}, \) and \( C_{44} \) can be determined from the sound velocities propagating in the \([100], [110],\) and \([111]\) directions, respectively \([21, 29, 30]\). (More details on the expressions used to predict the directional dependence of the sound velocities in cubic crystals can be found in \([21]\).) The values of the sound velocities for the main directions in CuCl and CuBr in the rocksalt phase predicted in this work are reported in Tables 1 and 2, respectively. To the best of our knowledge, there are no data available in the literature on the sound velocities in the main directions in both materials. Hence, our findings are only for reference.

The Debye temperature \( (\theta_D) \) is one of the fundamental quantities for the characterisation of materials and the micro-hardness of semiconductors \([30]\). Usually, two methods are used to determine the Debye temperature of semiconductors. The first one is deduced from the sound velocity, and the second one is obtained from the specific heat measurement. The Debye temperature \( \theta_D \) of a crystal can be obtained from the average sound velocity \( v_m \) using the following formula \([30]\):

\[
\theta_D = \frac{h}{k} \left( \frac{3 n N \rho}{4 \pi M} \right)^{1/3} v_m.
\]

Here \( h = h/2\pi \), where \( h \) is the Planck constant, \( k \) is the Boltzmann constant, \( N \) is the Avogadro number, \( \rho \) the crystal density, \( M \) the molecular weight, \( n \) the number of atoms in a molecule, and \( v_m \) is the average sound velocity.

For aggregate polycrystalline materials, the average sound velocity \( v_m \) is given by the following expression \([25]\):

\[
v_m = \sqrt{(3B + 4G)/3p} \quad \text{and} \quad v_l = \sqrt{G/p}.
\]

In Figure 5, the transverse, longitudinal, and average sound velocities are plotted against the applied hydrostatic pressure in the range 10–20 GPa. As can be seen from Figure 5, all sound velocities increase monotonically with increasing hydrostatic pressure. The best fits of our data regarding \( v_l, v_t, \) and \( v_m \) (in km/s) for CuCl and CuBr semiconductors obey the following expressions:

For CuCl:

\[
\begin{align*}
    v_l &= 4.27 + 7.40 \times 10^{-2}p - 5.93 \times 10^{-6}p^2, \\
    v_t &= 1.52 + 1.47 \times 10^{-2}p - 2.25 \times 10^{-6}p^2, \\
    v_m &= 1.72 + 1.69 \times 10^{-2}p - 2.58 \times 10^{-6}p^2.
\end{align*}
\] (8)

For CuBr:

\[
\begin{align*}
    v_l &= 3.76 + 7.74 \times 10^{-2}p - 8.04 \times 10^{-6}p^2, \\
    v_t &= 1.62 + 1.90 \times 10^{-2}p - 2.53 \times 10^{-6}p^2, \\
    v_m &= 1.83 + 2.20 \times 10^{-2}p - 2.92 \times 10^{-6}p^2.
\end{align*}
\] (9)

### Table 1: Pressure dependence of the longitudinal \((v_p)\) and two shear wave velocities \((v_{s1} \quad \text{and} \quad v_{s2})\) (km/s) in the three directions \([100], [110], \) and \([111]\) for semiconducting CuCl with the rocksalt structure.

<table>
<thead>
<tr>
<th>CuCl</th>
<th>([100])</th>
<th>([110])</th>
<th>([111])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P) (GPa)</td>
<td>(v_p) (km/s)</td>
<td>(v_{s1,s2}) (km/s)</td>
<td>(v_p) (km/s)</td>
</tr>
<tr>
<td>14</td>
<td>8.117</td>
<td>2.437</td>
<td>6.911</td>
</tr>
<tr>
<td>16</td>
<td>8.287</td>
<td>2.481</td>
<td>7.068</td>
</tr>
<tr>
<td>18</td>
<td>8.449</td>
<td>2.511</td>
<td>7.211</td>
</tr>
<tr>
<td>20</td>
<td>8.601</td>
<td>2.543</td>
<td>7.348</td>
</tr>
</tbody>
</table>
Table 2: Pressure dependence of the longitudinal ($V_p$) and two shear wave velocities ($V_{s1}$ and $V_{s2}$) (km/s) in the three directions [100], [110], and [111] for CuBr semiconductor material in the rocksalt structure.

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$V_p$ (km/s)</th>
<th>$V_{s1,s2}$ (km/s)</th>
<th>$V_p$ (km/s)</th>
<th>$V_{s1}$ (km/s)</th>
<th>$V_{s2}$ (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>4.435</td>
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<td>1.342</td>
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</tr>
<tr>
<td>14</td>
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<td>2.815</td>
<td>1.320</td>
</tr>
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<td>1.297</td>
</tr>
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<td>1.275</td>
<td>4.892</td>
<td>3.028</td>
<td>1.275</td>
</tr>
<tr>
<td>20</td>
<td>5.753</td>
<td>1.252</td>
<td>4.989</td>
<td>3.126</td>
<td>1.252</td>
</tr>
</tbody>
</table>

Figure 5: Longitudinal, transverse, and average sound velocity versus hydrostatic pressure for semiconducting CuCl and CuBr.

The sound velocity in materials is directly related to their corresponding phonons. Thus, the increase of the acoustic velocities of both CuCl and CuBr reflects the hardening of their corresponding phonons.

The variation of the Debye temperature as a function of the applied hydrostatic pressure in the range 10–20 GPa is plotted in Figure 6 for both compounds. As shown in Figure 6, the Debye temperature increases gradually with increasing hydrostatic pressure and reaches values of $\sim 248$ and $259$ K at pressure of 20 GPa for CuCl and CuBr, respectively. This behaviour has also been observed in TlP with the zinc blende structure [25]. The increase of the Debye temperature with applied pressure is due to the increase of the elastic constants, which reflects the shortening of the inter-atomic bond of the material under pressure. Our data regarding $\theta_D$ have been fitted by a least-squares procedure giving the following analytical relations:

For CuCl

$$\theta_D = 206.63 + 2.81p - 3.70 \times 10^{-2}p^2.$$  \hspace{1cm} (10a)

For CuBr

$$\theta_D = 207.56 + 3.37p - 3.97 \times 10^{-2}p^2.$$  \hspace{1cm} (10b)

Our finding concerning the Debye temperature $\theta_D$ of high-pressure rocksalt copper halides CuX (X = Cl, Br) can be useful, for example, in the prediction of the thermophysical quantities (lattice thermal conductivity, Lindemann melting criterion, Grüneisen parameters, etc.) of these compounds. This is because most of the
thermophysical properties of materials are directly related to the value \((T/\theta_D)\).

## 4 Conclusion

Using first-principles calculations, the elastic constants, longitudinal, transverse, and average elastic wave velocities, Debye temperature, Young’s modulus, Poisson’s ratio, Pugh’s ratio, and the anisotropy factor and their pressure dependence for the semiconducting materials CuCl and CuBr with rocksalt structure were predicted and analysed.

Our results show that the elastic constants \(C_{11}\) and \(C_{12}\) and their aggregate bulk modulus \(B\) increase with increasing hydrostatic pressure, whereas \(C_{44}\) decreases very slowly with increasing pressure. Based on Pugh’s ratio, it is found that both materials are prone to becoming ductile in the pressure range 10–20 GPa.

The interatomic bonding in a material determines a number of its physical properties (such as mechanical strength and thermal properties), so our findings on the elastic constants and the Debye temperature \(\theta_D\) can be helpful in the prediction and explanation of several other physical properties of these compounds.

As far as we know, there is no data available in the literature on the effect of pressure on the elastic constants and their related properties for both CuCl and CuBr in the rocksalt phase. Thus, our findings are predictions which may serve as a reference for future investigations.

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## References


