ULTRASONIC STUDY OF Cu$_x$Ag$_{1-x}$InTe$_2$ BULK MATERIAL

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Longitudinal and shear ultrasonic wave velocities were measured in the quaternary compounds Cu$_x$Ag$_{1-x}$InTe$_2$ ($0 \leq x \leq 1$) using pulse echo technique. Measurements were carried out at 4 MHz frequency and at room temperature. Elastic moduli and acoustic impedance have been calculated. Results indicated that these parameters are influenced by the increased addition of copper from $x = 0$ to $1$.

Keywords: semiconductors, ultrasonic wave velocity, elastic properties.

1. Introduction

Ultrasonic tools are very important for characterizing materials because they have many applications in chemistry, physics, engineering, biology, food industry, medicine, oceanography, seismology, etc. Nearly all of these applications are based on two unique features of ultrasonic waves [1]:

1. Ultrasonic waves travel slowly, about 100,000 times slower than electromagnetic waves. This provides a way to display information in time, create variable delay, etc.

2. Ultrasonic waves can easily penetrate opaque materials, whereas many other types of radiation such as visible light cannot. Since ultrasonic wave sources are inexpensive, sensitive and reliable, this provides a highly desirable way to probe and image the interior of opaque objects.

The ternary compounds ABC$_2$ (A = Cu or Ag; B = Al, or Ga, or In; C = S, or Se, or Te), which belong to the III–VI$_2$ semiconducting materials, are the isoelectronic ana-
logue of II–VI binary compound semiconductors and they crystallize in the tetragonal chalcopyrite structure with space group I42d [2]. The broad range of optical band gaps and carrier mobilities offered by the ternary ABC$_2$ semiconductors, as well as their ability to form various solid solutions and to accommodate different dopants, has led to their emergence as technologically significant device materials, including applications in photovoltaic solar cells, light-emitting diodes, infrared detectors and in various nonlinear optical devices [2, 3].

These materials show some interesting structural anomalies [2–5] relative to their binary analogue zinc-blende lattices. First, rather than a single cation, the ternary chalcopyrites have two cations. Second, these compounds often show a tetragonal distortion where the ratio between the lattice parameters, $\eta = c/2a$ (tetragonal deformation), differs from 1 by as much as 12%. Third, the anions are displaced from the ideal tetrahedral site (zinc-blende sites) by an amount $\lambda$, in units of $a$, which relates the anion position $u$ (where $\lambda = u - 1/4$). So, in binary AC zinc-blende compounds, each cation A has four anions C as nearest neighbours (and vice-versa), whereas in a ternary chalcopyrite ABC$_2$, each cation A and B has four anions C as nearest neighbours, and each anion has two A and two B cations as nearest neighbours. As a result, the anion C usually adopts an equilibrium position closer to one pair of cations than to the other, that is, unequal bond lengths $L_{AC} \neq L_{BC}$ (bond alternation).

The atomic positions in the tetragonal unit cell of the chalcopyrite family are: four A cations in sites $4a$ at (0, 0, 0), four B cations in sites $4b$ at (0, 0, 1/2) and eight C anions in sites $8d$ at (u, 1/4, 1/8) of the space group I42d (No. 122), when the origin is at 4a [3, 6]. The structure then requires three parameters only (excluding thermal vibrations coefficients) to describe its atomic arrangement completely: the unit cell parameters $a$ and $c$, and the parameter $u$ which locates the position of the anion atoms in the unit cell. When $u = 1/4a$, the chalcopyrite-type has the ideal structure, with no tetragonal distortions. JAFFE and ZUNGER [3, 4] studied the changes in the electronic band gaps induced by structural variation. They found a simple empirical adjustment that corrected the band gaps with structural parameters (anion position parameter, $u$, tetragonal deformation, $\eta = c/2a$, and unit cell parameter, $a$), obtaining a good agreement with experimental values. The accurate determination of these parameters is of great interest in the study of electronic band structure.

An ultrasonic pulse echo measurement together with some thermoelectric properties such as the electrical resistivity, Seebeck coefficient and thermal conductivity on a polycrystalline sample TISbTe$_2$, have been performed by Kurosaki et al. [7] to evaluate the elastic modulus and Debye temperature. The Seebeck coefficient of TISbTe$_2$ was positive in the whole temperature range, showing p-type semiconductor behavior.

The elastic constant $C_{11}$ of Al$_x$Ga$_{1-x}$As was determined by Krieger [8] using near infrared Brillouin scattering. It showed a linear decrease with increasing Al concentration. This linear decrease in $C_{11}$ was proposed to be dominated by the change in ionicity or the valence bonds in Al$_x$Ga$_{1-x}$As.

Ultrasonic velocities in molten (Ga$_x$In$_{1-x}$)As pseudo-binary alloys have been measured by Tsuchiya and Hisakabe [9] in the temperature range from liquidus tem-
perature to 1280°C under the saturated vapour pressure. The isotherm of the ultrasonic velocities showed a smooth increase from InAs to GaAs. They interpreted this increase in ultrasonic velocities as the fraction of covalent bonds in liquid GaAs which is considerably larger, so that changes to a structure with more isotropic local arrangement with increasing temperature would be plausible to account for the observed increase in temperature dependence of the sound velocity.

To our knowledge, no ultrasonic study has been done before on the quaternary compounds Cu$_x$Ag$_{1-x}$InTe$_2$ ($x = 0.0, 0.25, 0.50, 0.75$ and $1.0$). Therefore, this search paper aimed to investigate the structure of these compounds using ultrasonic pulse-echo technique.

2. Experimental

2.1. Preparation of samples

Polycrystalline ingots of Cu$_x$Ag$_{1-x}$InTe$_2$ solid solutions ($x = 0.0, 0.25, 0.50, 0.75$ and $1.0$) were prepared by using the constituent elements of 99.999% pure copper, silver, indium and tellurium (obtained from the Aldrich Chemical Co.) weighed in stoichiometric ratio. The mixture of each composition was taken in a silica tube, sealed under a vacuum of $\sim 1 \times 10^{-3}$ Pa and placed into the uniform zone of an electric furnace for heating the mixture. The inner surfaces of the silica tubes were coated with carbon, by pyrolysis of paraffin oil, to avoid any reaction between tellurium and glass. The temperature of the furnace was first slowly increased at the rate of 30 K h$^{-1}$ up to 723 K (the melting temperature of tellurium) and the mixture was left at such temperature for 2 hours, then increasing the temperature at a rate of 50 K h$^{-1}$ up to 1373 K at which the entire contents were melted. The melt was then kept at this temperature for 24 hours, in order to avoid the formation of the high-temperature binary X$_2$Te (X = copper or silver) and to assure compound formation. At this high temperature, the melt was subjected to occasional shaking to ensure complete mixing and reaction of constituents. The temperature was then decreased at a rate of 100 K h$^{-1}$ to a temperature 50 degrees above the melting temperature ($\sim 1000$–$1050$ K) and left there for 12 hours. Finally, the mixture was slowly cooled in the furnace to room temperature (300 K). The resulting ingots were ground and reduced to 200–300 mesh powders. The elemental compositions of the prepared materials in powdered form on a polished surface of a graphite stub were determined by using an energy-dispersive X-ray spectrometer (EDXS) unit, interfaced to a scanning electron microscope (Philips XL) operating at an accelerating voltage of 30 kV.

2.2. Density measurements

Density ($\rho$) of all samples was measured employing the Archimedes principle at 298 K, using toluene as buoyant and applying the relation:

$$\rho = \rho_b \left( \frac{W_a}{W_a - W_b} \right)$$

(1)
where \( \rho_b \) is the density of the buoyant, \( W_a \) and \( W_b \) are the sample weights in air and the buoyant respectively. The experiment was repeated three times, and the estimated error in density measurement for all samples was found to be \( \pm 0.001 \) g/cm\(^3\).

2.3. Ultrasonic velocity measurements

The ultrasonic wave velocities were obtained applying the pulse – echo technique by measuring the time elapsed between the initiation and the receipt of the pulse appearing on the screen of a flaw detector (USIP20 – Kraütkramer) via standard electronic circuit (Hewlett-Packard 54615 B). The velocity was therefore calculated by dividing the round trip distance by the elapsed time according to the relation:

\[
U = \frac{2X}{\Delta t},
\]

(2)

where \( X \) is the sample thickness and \( \Delta t \) is the time interval.

All ultrasonic wave velocity measurements were carried out at room temperature 298 K using (Karl Deutsch transducer S12 HB4) with fundamental frequency of 4 MHz to measure longitudinal ultrasonic wave velocity, and (Kraütkramer transducer K4KY) with fundamental frequency of 4 MHz for measuring the ultrasonic shear wave velocity. The estimated error in velocity measurements was \( \pm 20 \times 10^2 \) cm/s for longitudinal wave velocity \( (U_L) \) and \( \pm 13 \times 10^2 \) cm/s for shear wave velocity \( (U_s) \).

3. Determination of elastic moduli

Elastic moduli (longitudinal \( (L) \), shear \( (G) \), bulk \( (K) \), and Young’s \( (E) \)) as well as Debye temperature \( (\theta_D) \), softening temperature \( (T_s) \), Poisson’s ratio \( (\sigma) \) and micro-hardness \( (H) \) of the quaternary compounds \( \text{Cu}_x\text{Ag}_{1-x}\text{InTe}_2 \) \((x = 0.0, 0.25, 0.50, 0.75 \text{ and } 1.0)\), have been determined from the measured ultrasonic wave velocities and density using the relations [10]:

\[
L = \rho U_L^2,
\]

\[
G = \rho U_s^2,
\]

\[
K = L - \left( \frac{4G}{3} \right),
\]

\[
E = (1 + \sigma)^2 G,
\]

\[
\sigma = \left( \frac{(L - 2G)}{2(L - G)} \right),
\]

\[
H = \frac{(1 - 2\sigma) E}{6(1 + \sigma)}.
\]

(3)
Debye temperature was obtained from the relation given as
\[
\theta_D = \left( \frac{h}{k_B} \right) \left( \frac{3\psi N_A}{4\pi V_m} \right)^{1/3} U_m,
\]
where \(h\) is Planck’s constant, \(k_B\) is Boltzmann’s constant, \(N_A\) is Avogadro’s number, \(V_m\) is the molar volume calculated from the effective molecular weight and density (i.e. \(M/\rho\)), \(\psi\) is the number of atoms in the chemical formula, and \(U_m\) is the mean ultrasonic velocity defined by the relation
\[
U_m = \left( \frac{1}{3} \left( \frac{1}{U_3^l} + \frac{2}{U_3^s} \right) \right)^{-1/3}.
\]

The transmission and reflection of sound energy in the sample was determined using the acoustic impedance \(Z_i\) given by the relation
\[
Z_i = U_m \rho.
\]

4. Results and discussions

As reported earlier [11], the composition analysis of the synthesized \(\text{Cu}_{x}\text{Ag}_{1-x}\text{InTe}_2\) compounds with indicated \(x\) confirms the presence of copper and/or silver, indium, and tellurium in the prepared samples with the average atomic percentages that are illustrated in Table 1. It is revealed that all the samples contained excess of both \(\text{Cu}+\text{Ag}\) (\(\sim 0–0.21\) at. %) and \(\text{In}\) (\(\sim 0.05–0.19\) at. %), and deficient in \(\text{Te}\) (\(\sim 0.28–0.17\) at. %). So, the deviation in stoichiometry is comparable with the experimental errors and consequently, the samples composition could be considered as very nearly stoichiometric.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(\text{Cu, at. %})</th>
<th>(\text{Ag, at. %})</th>
<th>(\text{In, at. %})</th>
<th>(\text{Te, at. %})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>25.00</td>
<td>24.95</td>
</tr>
<tr>
<td>0.25</td>
<td>6.25</td>
<td>7.42</td>
<td>18.75</td>
<td>18.41</td>
</tr>
<tr>
<td>0.50</td>
<td>12.50</td>
<td>12.87</td>
<td>12.50</td>
<td>12.40</td>
</tr>
<tr>
<td>0.75</td>
<td>18.75</td>
<td>19.16</td>
<td>6.25</td>
<td>6.41</td>
</tr>
<tr>
<td>1.00</td>
<td>25.00</td>
<td>25.71</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Cal. – Calculated, Exp. – Experimental.

The density and molar volume of solid materials depend upon many factors such as structure, coordination number, cross-link density, and dimensionality of interstitial spaces [12].

Experimental values of density and molar volume are tabulated in Table 2. The density values were found to decrease from 6.049 g/cm\(^3\) to 6.042 g/cm\(^3\). In fact, this is due to the direct substitution of \(\text{Cu}\) with atomic weight of 63.546 g/mol on the expense of \(\text{Ag}\) with atomic weight of 107.8682 g/mol. On the other hand, the values of
Table 2. Variation of density ($\rho$), molar volume ($V_m$), packing density ($V_t$), longitudinal wave velocity ($U_l$), shear wave velocity ($U_s$) with Cu mol fraction.

<table>
<thead>
<tr>
<th>Mol fraction</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$V_m \times 10^6$ (cm$^3$/mol)</th>
<th>$V_t \times 10^6$ (cm$^3$/mol)</th>
<th>$U_l \times 10^2$ (cm/s)</th>
<th>$U_s \times 10^2$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>6.049 ± 0.001</td>
<td>19.739 ± 0.003</td>
<td>0.110</td>
<td>1028 ± 20</td>
<td>647 ± 13</td>
</tr>
<tr>
<td>0.25</td>
<td>6.066 ± 0.001</td>
<td>19.119 ± 0.003</td>
<td>0.128</td>
<td>1033 ± 20</td>
<td>652 ± 13</td>
</tr>
<tr>
<td>0.50</td>
<td>6.054 ± 0.001</td>
<td>18.771 ± 0.003</td>
<td>0.143</td>
<td>1036 ± 20</td>
<td>656 ± 13</td>
</tr>
<tr>
<td>0.75</td>
<td>6.062 ± 0.001</td>
<td>18.286 ± 0.003</td>
<td>0.160</td>
<td>1046 ± 20</td>
<td>665 ± 13</td>
</tr>
<tr>
<td>1.00</td>
<td>6.042 ± 0.001</td>
<td>17.859 ± 0.003</td>
<td>0.179</td>
<td>1055 ± 20</td>
<td>675 ± 13</td>
</tr>
</tbody>
</table>

Molar volume of the studied materials are decreased from $19.739 \times 10^6$ (cm$^3$/mol) to $17.859 \times 10^6$ (cm$^3$/mol). This decrease in the molar volume of the present materials may be attributed to the direct substitution of copper with ionic radius of 0.96 Å on the expense of silver with ionic radius of 1.26 Å [13]. However, the increase in packing density ($V_t$) [14, 15] from $0.110 \times 10^6$ to $0.179 \times 10^6$ (cm$^3$/mol) correlate with the decrease in molar volume indicating the increased packing of atoms. Moreover, EL-SAYAD et al. [11] reported that addition of Cu on the expense of Ag in the quaternary compounds Cu$_x$Ag$_{1-x}$InTe$_2$ caused the decrease in the lattice parameters a and c, revealing that Cu is incorporated into the lattice onto Ag sites which agree with molar volume in our results.

Values of ultrasonic wave velocities (longitudinal & shear), elastic moduli, and Poisson’s ratio of the investigated glasses are also listed in Table 2. Both longitudinal ($U_l$) and shear ($U_s$) wave velocities increased from $1028 \times 10^2$ and $647 \times 10^2$ (cm/s), respectively, to $1055 \times 10^2$ and $675 \times 10^2$ (cm/s) with the increase of copper on the expense of silver mol % content as shown in Table 2 and Fig. 1.

Fig. 1. Plot of ultrasonic wave velocities (longitudinal ($U_l$) and shear ($U_s$)) with $x$, Cu mol fraction in Cu$_x$Ag$_{1-x}$InTe$_2$ compounds.
In general, the increase of ultrasonic wave velocity is related to the decrease in inter-atomic spacing of the material. This increase in ultrasonic wave velocities can be explained by the decrease in molar volume (i.e. the decrease in the inter-atomic spacing), which means that the incorporation of copper instead of silver leads to the decrease in the average inter-atomic spacing (bond lengths and bond angles), supporting our results of molar volume and the results reported earlier [11, 16–18] for AgInTe$_2$, CuInTe$_2$ and Cu$_x$Ag$_{1-x}$InTe$_2$.

Table 3 gives the experimentally estimated values of the elastic moduli; longitudinal modulus ($L$), shear modulus ($G$) and Young’s modulus ($E$). As seen from Table 2, longitudinal, shear and Young’s elastic moduli values showed an increase from 6.396, 2.536 and 5.942 GPa, respectively to 6.726, 2.751 and 6.350 GPa, showing the same trend as ultrasonic wave velocities.

<table>
<thead>
<tr>
<th>X (Mol fraction)</th>
<th>L (GPa)</th>
<th>G (GPa)</th>
<th>E (GPa)</th>
<th>K (GPa)</th>
<th>σ</th>
<th>Gt (kJ/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>6.396 ± 0.025</td>
<td>2.536 ± 0.009</td>
<td>5.942 ± 0.002</td>
<td>3.02 ± 0.03</td>
<td>0.172 ± 0.009</td>
<td>11.79</td>
</tr>
<tr>
<td>0.25</td>
<td>6.468 ± 0.025</td>
<td>2.581 ± 0.009</td>
<td>6.030 ± 0.002</td>
<td>3.03 ± 0.03</td>
<td>0.168 ± 0.009</td>
<td>12.53</td>
</tr>
<tr>
<td>0.50</td>
<td>6.504 ± 0.025</td>
<td>2.606 ± 0.009</td>
<td>6.076 ± 0.002</td>
<td>3.03 ± 0.03</td>
<td>0.166 ± 0.009</td>
<td>13.00</td>
</tr>
<tr>
<td>0.75</td>
<td>6.628 ± 0.025</td>
<td>2.681 ± 0.009</td>
<td>6.221 ± 0.002</td>
<td>3.05 ± 0.03</td>
<td>0.160 ± 0.009</td>
<td>13.61</td>
</tr>
<tr>
<td>1.00</td>
<td>6.726 ± 0.025</td>
<td>2.751 ± 0.009</td>
<td>6.350 ± 0.002</td>
<td>3.06 ± 0.03</td>
<td>0.154 ± 0.009</td>
<td>14.20</td>
</tr>
</tbody>
</table>

Figure 2 shows the variation of bulk ($K$) modulus with molar volume of Cu$_x$Ag$_{1-x}$InTe$_2$ specimens under investigation. From this figure, it is noted that a decrease in volume should lead to an increase in bulk modulus with the increase in copper content. It is clear from the above results that the type of bonding in the network structure plays a dominant role in deciding on the rigidity of these structures, and the increase in elastic moduli is associated with the increase in covalence of bonds in these structures [11, 19]. EL-SAYAD et al. [11], reported that the structure of Cu$_x$Ag$_{1-x}$InTe$_2$ (0 ≤ x ≤ 1) is a tetragonal phase chalcopyrite-like compounds, and the refined unit cell parameters, bond distances and angles around the cations of tetrahedra in Cu$_x$Ag$_{1-x}$InTe$_2$ unit cell, were found to decrease with the increase in copper content. This is may be the reason for the increase in the rigidity of these structures. Moreover, the increased dissociation energy of bonds per unit volume ($G_t$) [14, 15] from 11.79 to 14.20 (kJ/mol) may contribute to the increased rigidity of these compounds (see Table 3). Furthermore, the increased values of micro-hardness from 0.555 to 0.634 GPa confirm the increased rigidity of these compound structures.

Table 3 gives the values of Poisson’s ratio ($σ$). Poisson’s ratio is formally defined for any structure as the ratio of lateral to longitudinal strain produced when tensile forces are applied. In solid materials, the tensile strain produced in the network is unaffected by the cross-links, while the lateral strain is greatly decreased with increasing covalence of bonds [20, 21]. The values of ($σ$) have decreased from 0.172 to 0.154 with copper con-
tent increasing from 0 to 1. Therefore, the decrease in Poisson’s ratio can be explained in terms of covalence bonds that have increased with copper content [21].

Values of $(E/G)$ ratio showed the same trend as Poisson’s ratio $(\sigma)$, they have decreased from 2.343 to 2.308 when copper mol fraction is increased from 0 to 1 confirming the decreased Poisson’s ratio.

The Debye temperature $(\theta_D)$ is an important parameter of solids, which represents the temperature at which nearly all the vibrational modes are excited. Calculated values of the mean ultrasonic velocity $(U_m)$, Debye temperature $(\theta_D)$ and acoustic impedance $(Z)$ of these compounds under study are collected in Table 4.

Table 4. Variation of mean ultrasonic velocity $(U_m)$, Debye temperatures $(\theta_D)$ and acoustic impedance $(Z)$ with Cu mol fraction.

<table>
<thead>
<tr>
<th>X Mol fraction</th>
<th>$U_m \times 10^2$ (cm/s)</th>
<th>$\theta_D$ (K)</th>
<th>$Z_i \times 10^{-6}$ (kg.m²/sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>713 ± 24</td>
<td>76 ± 3</td>
<td>43.11 ± 0.02</td>
</tr>
<tr>
<td>0.25</td>
<td>718 ± 24</td>
<td>77 ± 3</td>
<td>43.54 ± 0.02</td>
</tr>
<tr>
<td>0.50</td>
<td>722 ± 24</td>
<td>78 ± 3</td>
<td>43.69 ± 0.02</td>
</tr>
<tr>
<td>0.75</td>
<td>731 ± 24</td>
<td>80 ± 3</td>
<td>44.32 ± 0.02</td>
</tr>
<tr>
<td>1.00</td>
<td>741 ± 24</td>
<td>81 ± 3</td>
<td>44.80 ± 0.02</td>
</tr>
</tbody>
</table>

It can be observed from Table 4 that Debye temperatures increased from 76 to 81 K with the increase in copper mol fraction from 0 to 1. The increase in the mean ultrasonic
velocity and consequently, the increase in Debye temperatures [22] are mainly due to the decrease in molar volume and the increase in covalence of bonds.

The values of the acoustic impedance ($Z_i$) were found to increase from 43.11 to 44.80 (kg·m$^{-1}$·sec$^{-1}$) when the copper mol fraction increased from 0 to 1. The variation of the acoustic impedance resulting in higher impedance to the propagation of ultrasonic waves in these compounds [23].

5. Conclusions

Detailed measurements have clarified the fact that the structure of Cu$_x$Ag$_{1-x}$InTe$_2$ compounds becomes close-packed and more rigid with the substitution of Cu instead of Ag through the decrease in molar volume, increase in covalence bonds, the increase in ultrasonic velocities (longitudinal and shear) and consequently, the increase in elastic moduli.

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References


