

Preparation and electrical characterization of the compound CuAgGeSe₃

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Abstract. This work reports the synthesis and electrical characterization of the compound CuAgGeSe₃. This material was synthesized by direct melting of the constituent elements, in their stoichiometric ratio inside an evacuated quartz ampoule. The chemical analysis (EDX) confirmed the 1:1:1:3 stoichiometric ratios for the compound. The differential thermal analysis showed the existence of a principal phase that melts at 558°C and a second phase at 636°C. The X-ray powder diffraction analysis indicated that the compound crystallizes in the monoclinic system, space group Cc, with unit cell parameters: $a = 6.776(0)$ Å, $b = 11.901(5)$ Å, $c = 6.772(0)$ and $\beta = 108.2(0)^\circ$. The study of the electrical properties was realized in the temperature range from 80 to 300 K and under a magnetic field of 14 kG. Employing the Mott transition model, we were able to obtain the temperature dependence of the resistivity and we estimated that the activation energy is 25.3 meV in the low temperatures region. The mobility temperature dependence is analyzed by taking into account the scattering of charge carriers by acoustic phonons, polar optic phonons and thermally activated hopping. From the analysis, the activation energy is estimated to be around 38 meV and the characteristic temperature of the phonons is estimated to be around 400 K.

1. Introduction

Preliminary studies [1-8] of the family I₂-IV-VI₃ compounds show a high optical-acoustical efficiency for the infrared region application. These materials belong to two possible diamond-like structure families which derive from order 3 of the binary II-VI with two kinds of cations [9]. The derivation is made respecting the established rules for diamond-like compound of normal valence [2] and the substitution of the cations establishes four electrons for each atom and eight for each anion. Several previous structural studies of Cu₂GeSe₃ showed lots of controversy in regards to the unit cell. By means of a photographic study of a polycrystalline sample, Rivet [10] reports a sphalerite structure with $a = 5.445$ Å in this compound. In this work we found that the structure of the CuAgGeSe₃ is consistent with a monoclinic subcell of space group *C1c1* (9) determined by the strongest group reflections. Velásquez et al [11] reported the structure and cell parameters of Ag₂GeSe₃ which also belongs to the monoclinic system.

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Previous studies of the electrical properties [12] point out that Cu_2GeSe_3 exhibits semiconductor behaviour at liquid nitrogen and a metallic one at room temperature. In order to determine the quality as a semiconductor, we enterprise in this work the synthesis and electrical characterization of the compound CuAgGeSe_3 .

2. Experimental

The compound CuAgGeSe_3 was synthesized by direct fusion of the component elements weighted in the stoichiometric proportions 1: 1: 1: 3. The differential thermal analysis was made in a Perkin Elmer DTA-7 equipment. The chemical analysis of the CuAgGeSe_3 was made in a KEVEX EDX Delta-3 model equipment connected to a Hitachi S-2500 scanning electron microscope. In order to study the structural characteristics of CuAgGeSe_3 diffraction methods were employed in polycrystalline samples. The diffraction data of X-rays were taken at room temperature in a Siemens D5005 diffractometer equipped with $\text{CuK}\alpha$ ($\lambda = 1.54059\text{\AA}$ at 40 KV and 30 mA) radiation in configuration Θ/Θ , with a diffracted graphite beam monochromator. The angle (2Θ) measuring rank was of 10° - 100° , the scanning was of 0.020 and the counting time was 45 s/step.

Employing the Van der Pauw technique the resistivity and the Hall Effect were measured from 80 to 300 K under a magnetic field of 14 kG. Indium solder contacts were attached onto a clean and polished surface that was previously flux etched. The contacts were completely ohmic as deduced from the I-V characteristic taken from 1 to 20 mA, at 80 K and at room temperature.

3. Results and Discussion

Three different regions of the ingot were scanned and the average atomic percentages Cu (15.4%), Ag (11.6%), Ge (17.5%) and Se (55.5%), gave an atomic ratio close to the ideal value 1:1:1:3.

The thermogram of CuAgGeSe_3 is presented in the figure 1, it shows a well defined affluent tip at 558°C corresponding to his fusion point and another one of less intensity which can be described to a small secondary phase.

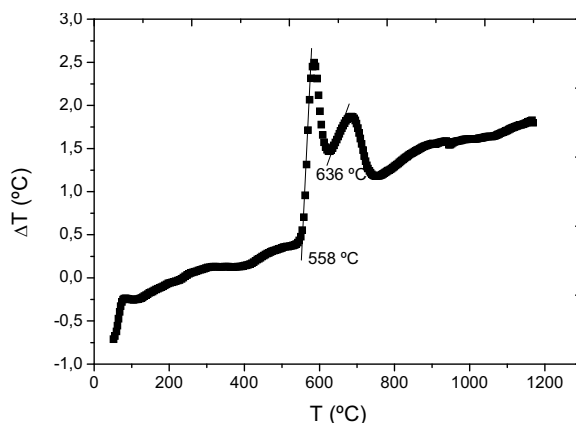


Figure 1. Thermogram of the compound CuAgGeSe_3

In figure 2 is given the X-ray powder diffraction pattern. The refinement of the unit cell was made with the program NBS* AIDS83, obtaining the following cell parameters: $a = 6.7760\text{\AA}$, $b = 11.9015\text{\AA}$, $c = 6.7720\text{\AA}$ and $\beta = 108.20^\circ$. Likewise as in the thermogram, in the X-ray diffraction it is also noticeable a secondary phase. A low intensity GeSe_3 phase is reported for Cu_2GeSe_3 in the reference file (PDF 71-117).

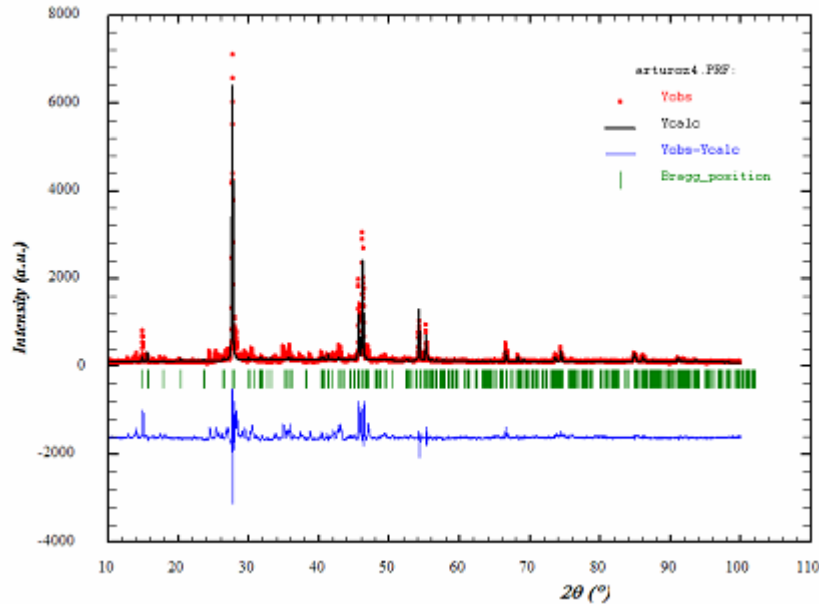


Figure 2. X-ray powder diffraction pattern. Generate with FULLprof Suite program.

The material CuAgGeSe_3 together with Cu_2GeSe_3 and Ag_2GeSe_3 all of them possess a common novel sphalerite superstructure. In the structure of CuAgGeSe_3 each tetrahedral is bonded to four anions, and conversely, each selenium atom is also tetrahedrally coordinated to four cations. This bonding scheme is consistent with the sphalerite-type subcell, a comparison between the refined atomic coordinate and the atom coordinate derived from sphalerite structure confirms the close structural relationship.

Table 1. Atomic coordinates and occupation factor, derived from the Rietveld refinement.

| Atoms | Oxid | Wyck | x | y | z | foc | Site |
|-------|------|------|-----------|-----------|-----------|------|------|
| Cu1 | +1 | 4a | 0.6222(6) | 0.4254(1) | 0.2443(1) | 0.5 | 1 |
| Ag1 | +1 | 4a | 0.1446(0) | 0.2447(5) | 0.2369(8) | 0.5 | 1 |
| Ge1 | +4 | 4a | 0.6381(4) | 0.0822(7) | 0.2179(1) | 0.5 | 1 |
| Se1 | -2 | 4a | 0.2571(9) | 0.4189(9) | 0.1033(9) | 0.35 | 1 |
| Se2 | -2 | 4a | 0.7909(4) | 0.4412(0) | 0.6419(9) | 0.18 | 1 |
| Se3 | -2 | 4a | 0.7711(5) | 0.2543(5) | 0.1185(0) | 0.18 | 1 |

Figure 3 shows the resistivity as a function of the inverse of temperature. At low temperatures below 170 K, the compound presents a behavior characteristic of an extrinsic semiconductor, meanwhile, at high temperatures between 170 and 300K the material behaves as a metal. This semiconductor-metal shift is known as a Mott transition [13] and it is ascribed to a shallow impurity band near the valence band. The intrinsic region is never reached; for this reason, a model similar to Friszsche's model was used to fit the data. A semiconductor-like and a metallike expression were combined to obtain:

$$\rho = \rho_0 \frac{T}{T_0} + \rho_1 e^{E_1 / K_B T} \quad (1)$$

In this formula we have assumed only one activation energy E_1 and $T_0 = 273 K$ as a fixed parameter.

The value for the activation energy obtained from a fit to the resistivity in the low temperature region was $E_1 = 25.3 \text{ meV}$ which corresponds to a $0^\circ C$ resistivity of $\rho_0 = 5.314 \Omega.cm$ and a resistivity $\rho_1 = 0.126 \Omega.cm$, used has fitting parameters.

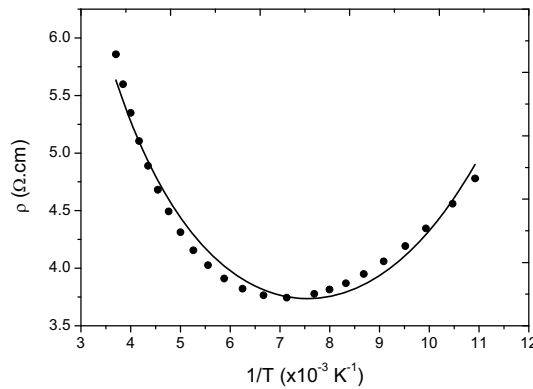


Figure 3. Resistivity of the compound CuAgGeSe_3 .

The mobility as a function of the inverse of temperature is shown in figure 5. This behavior is usually well explained using standard scattering processes. Thus, at low temperatures, according to the Cutler-Mott model [14] neutral and ionized impurities dominate. The Erginsoy and Brooks-Herring models are not suitable. At high temperatures, acoustic phonons ruled by the usual acoustic deformation potential model and optical polar phonons ruled by a phenomenological model of the form $\mu_{op} \propto (e^{\theta/T} - 1)$ are appropriate. To fit the data we used the Matthiessen rule.

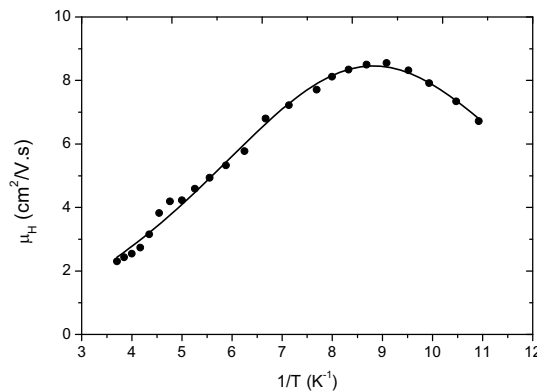


Figure 5. Mobility of the compound CuAgGeSe_3

To avoid parameter dependency, we define: $C_{II} = \rho v_{sl}^2$, $C_{ac} = m^{*5/2} E_{ac}^2$ and $A = x_d / m^{*3/2}$. Thus, using, C_{ac} , μ_0 , W , A and θ as adjustable parameters, the following values are obtained: activation energy $W = (38 \pm 2) \text{ meV}$, hopping factor $\mu_0 = (8,65 \pm 0,43)$, phonon characteristic temperature $\theta = (400 \pm 8) \text{ K}$ and elastic constant $C_{II} = 1.7 \times 10^{12} \pm 5.1 \times 10^{10} \text{ dynes/cm}^2$. The acoustic deformation

potential and dielectric constant they cannot be known due to the fact that the effective mass of the compound is not known.

As regards to the electrical resistivity and mobility we found a close behaviour between Cu_2GeSe_3 and CuAgGeSe_3 . However, in comparison to Ag_2GeSe_3 a different electrical behaviour has been reported [15].

Acknowledgements

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