The fundamental absorption edge of $CuGa_3Te_5$ ordered defect semiconducting compound

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Received 17 March 2017; accepted 31 July 2017

The analysis of the temperature variation of the optical absorption spectra of the ordered defect compound $CuGa_3Te_5$, a semiconducting material which crystallizes in a chalcopyrite-related structure with space group $P\bar{4}2c$, is made. It has been established that this compound has a direct-allowed band gap between parabolic bands which varies from 1.187 to 1.090 eV in the temperature range from 10 to 300 K. The mean temperature of the phonon involved in the direct band-to-band transition is $\theta \approx 125$ K. This is comparable with 3/4 $\theta_D \approx 156$ K, θ_D being the Debye temperature of the compound.

Keywords: Semiconductors; optical absorption; electronic band structure.

PACS: 71.20.Nr

1. Introduction

The conversion of heat and solar energy into electrical power could play a significant role in current efforts to develop alternative source energy to reduce the dependence both on fossil fuels and greenhouse gas emissions [1].

For this reason, search for new materials for Thermoelectric (TE) device applications is an active area of research [2,3]. Bulk semiconducting materials such as $CuGaTe_2$ [4-8] ternary chalcopyrite and the ordered defect compounds of the Cu_2Te-Ga_2Te_3 pseudo-binary system [9] such as $Cu_2Ga_4Te_7$ [4,10], $Cu_3Ga_5Te_9$ [4,11], $CuGa_3Te_5$ [4], and $CuGa_5Te_8$ [4], have attracted some attention recently as potential candidates for high-temperature TE materials. This is because these compounds have low carrier concentrations [12,13], which reduces their thermal conductivity, a condition required to obtain promising materials for TE applications [1-3]. In spite of this, the optical properties of these Cu-Ga-Te ODC's have not been studied in detail so far. $CuGa_3Te_5$, a member of these ODC's, has been studied with some interest and some reports on its electrical [12,14] and optical [14-18] properties have appeared in the literature. However, controversy exists on the nature of its fundamental absorption edge. Although a direct allowed band gap E_G, which is of about 1.09-1.15 eV, was originally reported for this material from the analysis of the optical absorption coefficient α at room temperature [14,15], a more recent study suggests that $CuGa_3Te_5$ has an indirect band-gap, of about $E_{GI} \approx 1.0$ eV, followed closely for a direct gap $E_G \approx 1.07$ eV [16,17]. Hence, to further understand the optical properties of this material and to clarify the discrepancy related to the nature of the band gap, in the present article, the optical absorption coefficient spectra of this compound as a function of temperature is studied.

2. Experimental details

Ingot of $CuGa_3Te_5$ was prepared by heating the stoichiometric mixture of at least 5N pure Cu, Ga, and Te sealed in an evacuated quartz ampoule, by using the vertical Bridgman-Stockbarger technique. Details are described elsewhere [14]. The obtained ingot was polycrystalline and black in color with polished surface. Circular shaped void free samples from the central part where cut for optical absorption study by slicing the ingot perpendicularly to the growth direction. X-Ray diffraction data analysis of these samples indicates that they crystallize in a chalcopyrite-related structure with space group $P\bar{4}2c$. The unit cell parameters were found to be $a = 0.59321(8)$ and $c = 1.1825(4)$ nm [14]. The optical transmittance spectra were measured with a Cary 17I monochromator using a 170 W tungsten lamp as a light source. The transmitted radiation was detected by a Ge photodiode detector. For the measurements of transmittance spectra, the sample was placed in a He_2 cryostat operating in the range from 10 to 300 K.

3. Results and discussion

3.1. Optical absorption spectra of $CuGa_3Te_5$

The absorption coefficient α was obtained from the measured transmittance through the relation $\alpha = (1/t)[\ln(I_0/I) + 2\ln(1-R)] - \alpha_R$, where t is the thickness of the sample, I_0 and I the incident and transmitted radiation, respectively, R is the reflectivity and α_R a nearly constant residual absorp-

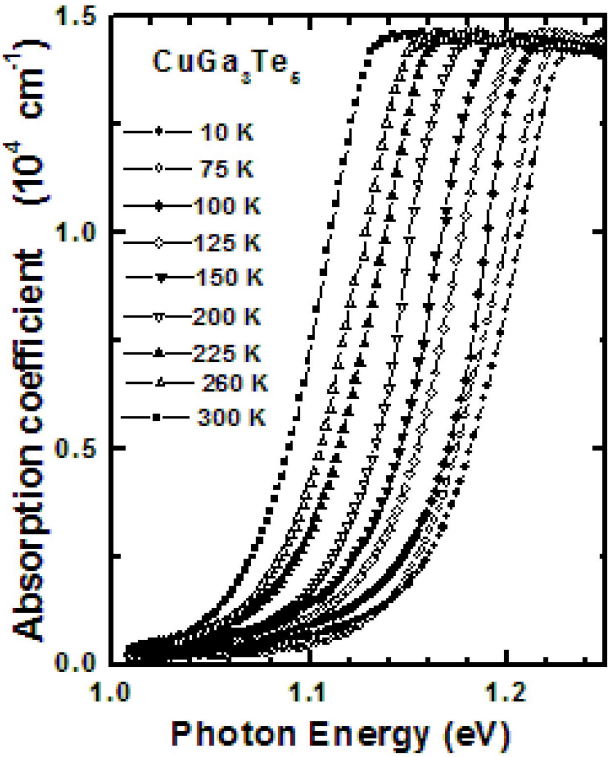

FIGURA 1. Absorption coefficient spectra of $CuGa_3Te_5$ between 10 and 300 K.

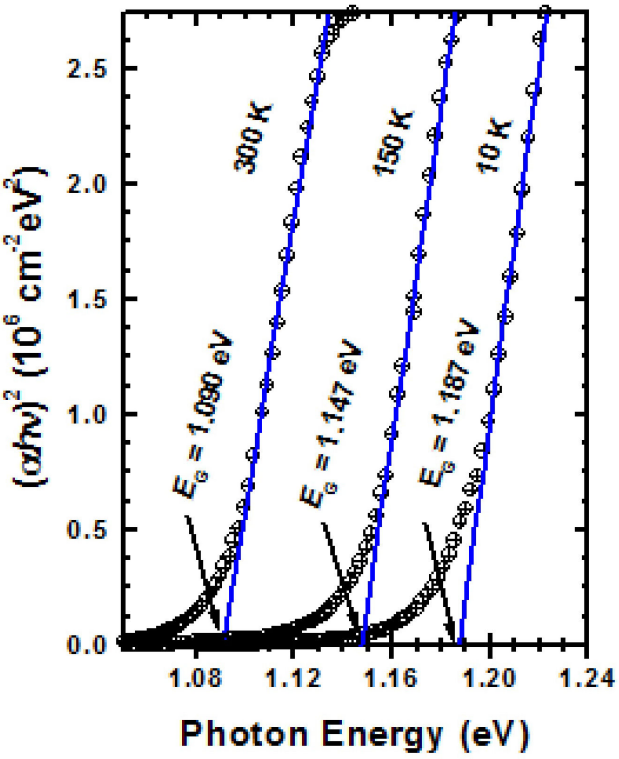

FIGURA 2. $(\alpha h\nu)^2$ vs. $h\nu$ for $CuGa_3Te_5$ at representative temperatures 10, 150, and 300 K.

tion observed in the low energy region of the spectra. R was estimated from the transmittance in the zero-absorption limit where it is expected that $T \approx (1-R)/(1+R)$. Typical values of T in this limit were found to of about 0.60. This gives $R \approx 0.25$.

In order to establish the nature of the fundamental energy gap in $CuGa_3Te_5$, the models for both direct and indirect band gaps should be considered. The theory of interband optical absorption transitions between parabolic bands in semiconductors [19] shows that near the fundamental absorption edge, α varies with the incident photon energy $h\nu$ according to the expression,

$$(\alpha h\nu)^m = A_G(h\nu - E_G), \tag{1}$$

where A_G is a parameter nearly independent of photon energy, E_G is the gap energy, and the value of the exponent m depends on the nature of the optical processes involved. This being 2 for allowed direct and 1/2 for allowed indirect transitions [19].

The absorption coefficient spectra $(\alpha h\nu)^2$ at different temperatures from 10 to 300 K of $CuGa_3Te_5$ are plotted in Fig. 1. Analysis of experimental data shows that $(\alpha h\nu)^2$ vs. $h\nu$ give a straight line for the spectra at each temperature indicating that this compound, like $CuGaTe_2$ [20], $CuIn_3Te_5$ [15], $CuIn_5Te_8$[15], and $Cu_3In_5Te_9$ [21], has a direct band gap. This is shown in Fig. 2, where $(\alpha h\nu)^2$ vs. $h\nu$ for representative temperatures 10, 150 and 300 K is plotted.

The value of the energy gap at each temperature was obtained by extrapolating the linear portion of each $(\alpha h\nu)^2$ vs $h\nu$ curve to $(\alpha h\nu)^2 = 0$. The temperature dependence of the energy gap E_G for $CuGa_3Te_5$, thus obtained, is plotted in Fig. 3. As can be noted, the present value of the energy gap at room temperature, $E_G = 1.090$ eV, is in good agreement with the value for this parameter reported in [14-17] which vary from 1.07 to 1.15 eV.

Several models have been employed in the literature to describe the temperature variation of the energy gap.

Varshni has proposed the following empirical expression [22]:

$$E_G(T) = E_G(0) - bT^2/(T+\beta), \tag{2}$$

where $E_G(0)$ is the value of the energy gap at 0 K and b and β are constants, β being of the same order as the Debye temperature θ_D.

On the other hand, Viña *et al.* [23] have proposed a more physically justified expression for the E_G vs T variation. This, based on Bose-Einstein phonon model, is given by

$$E_G(T) = E_B - a_b\{1 + 2[(\exp(\theta/T) - 1)]^{-1}\}, \tag{3}$$

where $E_B - a_b = E_G(0)$ is the value of the energy gap at 0 K, and θ an average phonon related to the Debye temperature.

Equations (2) and (3) were fitted to the $E_G(T)$ data of Fig. 3. Values of different parameters obtained by the fit are $E_G(0) = (1.189 \pm 0.001)$ eV, $b = (4.5 \pm 0.5) \times 10^{-4}$ eV/K,

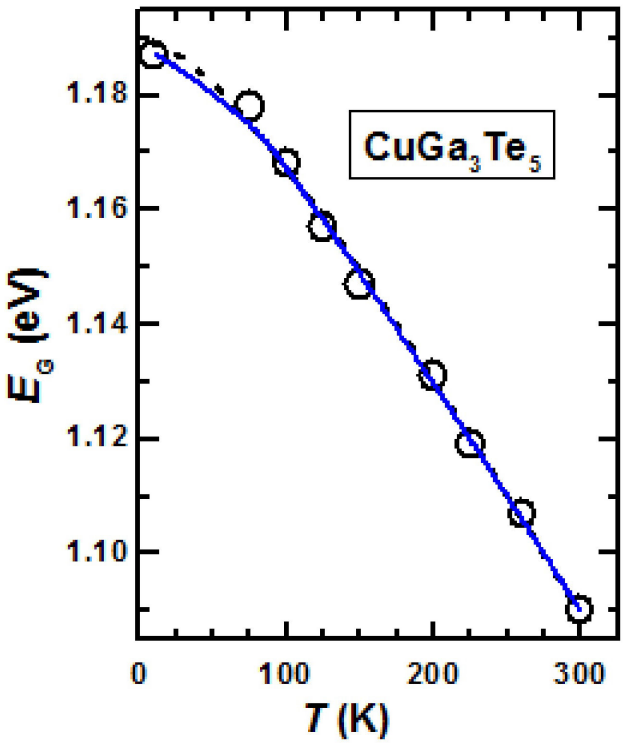

FIGURA 3. Variation of the energy gap E_G with temperature in $CuGa_3Te_5$. Doted and continuous lines represent the fits of Eqs. (1) and (2), respectively, to the E_G versus T data with the parameters $E_G(0)$, b, and β, from Eq. (2), and E_b, a_b, and θ, from Eq. (3), given in the text.

and $\beta = (102 \pm 18)$ K from Eq. (2), and $E_B = (1.213 \pm 0.003)$ eV, $a_b = (2.5 \pm 0.4) \times 10^{-2}$ eV, and $\theta = (125 \pm 20)$ K from Eq. (3). Theoretical curves from these equations are also shown in the same figure by dotted and continuous lines, respectively. The values of the energy gap at $T \to 0$, $E_G(0) = 1.189$ and 1.188 eV, predicted by these models, respectively, are in good agreement to each other. Also, as expected, the value of β obtained from Eq. (2) is slightly lower than θ obtained from Eq. (3). This is because these parameters should be related [24], according to the expressions $\beta \approx (3/8)\theta_D$, and $\theta_D \approx (3/4)\theta_D$. The Debye temperature θ_D of $CuGa_3Te_5$, as estimated from a semi-empirical model [25] that relates θ_D to the mean atomic weight per lattice site M and the mean atomic volume V, is (208 ± 20) K. By using $\beta \approx (3/8)\theta_D$ and $\theta \approx (3/4)\theta_D$, with this value of θ_D, one gets $\beta = (78 \pm 8)$ and $\theta = (156 \pm 15)$ K. This in comparable with $\beta = (102 \pm 18)$, and $\theta = (125 \pm 20)$ K, obtained from the fit of Eqs. (2) and (3), respectively, to the present E_G vs. T data.

4. Conclusion

From the analysis of the optical absorption spectra of $CuGa_3Te_5$ as a function of temperature, it is reconfirmed that this compound has a direct-allowed band gap between parabolic bands which varies from 1.187 to 1.090 eV in the temperature range from 10 to 300 K, respectively. The mean temperature of the phonon involved in the direct band-to-band transition is 3/4 $\approx$ 125 K which is comparable with 3/4 $\theta_D \approx 156$ K.

Acknowledgments

This work was supported by the Consejo de Desarrollo Científico, Humanístico, Tecnológico y Artístico of the Universidad de Los Andes (Grants C-917-98-05-A and C-918-98-05-E).

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