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Structural, thermal and optical properties of $Ag(In_{1-x}Ga_x)_5Te_8$

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ABSTRACT

Ingots of the $Ag(In_{1-x}Ga_x)_5Te_8$ ($0 \le x \le 1$) system were prepared by direct fusion of the stoichiometric mixture of the elements in evacuated quartz ampoules. The analysis of the X-ray powder diffraction data showed the presence of a single phase with tetragonal structure at room temperature for all the studied compositions. The lattice parameters *a* and *c* were calculated. Melting temperatures, from 696 ºC for $AgIn_5Te_8$ to 775 ºC for $AgGa_5Te_8$, were obtained from Differential Thermal Analysis measurements performed on samples in evacuated quartz ampoules. Reflectance measurements were used to calculate the band gap energies and the real refraction indices. A direct band gap, slightly varying from 1.34 to 1.39 eV ($0 \le x \le 0.4$), was found in In-rich compounds, while an indirect band gap was found in all the studied compositions varying from 1.11 to 1.14 eV ($0 \le x \le 1$).

KEYWORDS

Semiconductors;
Powder diffraction;
Differential thermal analysis (DTA);
Optical properties;
Reflectance.

INTRODUCTION

The measurements on silver-based materials, having a large concentration of silver (at about 24%), show that these compounds are highly sensitive to optical and thermal stress and hence could be useful for device applications[1,2]. The ternary silver chalcogenides of the type Ag-In-VI (VI=S, Se, Te) are interesting materials because of their potential application in non-linear optics and solar cells. It has been found that they form very stable stoichiometric compounds with electrophysical properties independent of impurities[3-5].

Information about the Ag_2Te-Ga_2Te_3 phase diagram has been reported by few authors. Guittard et al[6] and Krämer[7] have reported the existence of $AgGa_5Te_8$ and other solid solutions in the vicinity of Ga_2Te_3. Julien et al[8] reported a description of the Ag_2Te-Ga_2Te_3 quasi-binary phase diagram and the role of oxygen in the creation of $AgGaTe_2$ and $AgGa_5Te_8$. They also reported on the electrical and optical properties of $AgGaTe_2$ and $AgGa_5Te_8$ single crystals. On the other hand, the Ag_2Te-In_2Te_3 phase diagram has been also described by few authors[9-11], showing the existence of different intermediate phases in the In-rich side of this pseudo binary system, but only $AgInTe_2$, $Ag_3In_{97}Te_{147}$ and $AgIn_5Te_8$ have been confirmed by more than one author. Sánchez et al[1] and Mora et al[3] have reported on the structural, optical and electrical properties of $AgIn_5Te_8$. Concern-

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ing to the variation of the properties of the polycrystalline $Ag(In_{1-x}Ga_x)_5Te_8$ ($0 \le x \le 1$) system no report has been published to date. The aim of this work is to examine some of the physical properties of this system, including the reflectance, by performing all the measurements on samples from the same ingot for each studied composition.

CRYSTAL GROWTH AND EXPERIMENTAL DETAILS

Ingots of the $Ag(In_{1-x}Ga_x)_5Te_8$ system at compositions x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0 were prepared exclusively for this work by direct fusion of the stoichiometric mixture of the elements of at least 5N purity in evacuated quartz ampoules ($\cong 10^{-6}$ Torr). The ampoules were heated in a vertical furnace. To minimize the risk of explosion due to exothermic reaction between group III elements and Te, the ampoules were heated very slowly at 5ºC/h up to 1050 ºC, kept at this temperature for 24 h were rocked manually at regular intervals to achieve a homogeneous mixing of the liquid phase of the reacting mixture and then were cooled to 600 ºC at a rate of 5ºC/h. Finally, they were cooled, at a rate of 30ºC/h, to 500 ºC where they were annealed for 4 days to reduce possible defects and to increase grain size. As observed by a simple thermal probe test, samples cut from the ingots showed p-type conductivity, except x=0.2 that showed n-type conductivity which could be due to a stoichiometric deviation. X-ray powder diffraction measurements were carried out using a Siemens D5005 diffractometer with copper anode (λ=1.54060 Å, α_2/α_1=0.5) and Bragg-Brentano geometry. All the patterns were obtained for $5^\circ \le 2\theta \le 100^\circ$ with a step size of 0.02º and a step time of 40.0s. The intensity and 2θ position of each reflection were determined using the Winplotr graphic interface. The indexation was made using the Treor90 program and the unit cell parameters were refined with the NBS program. A Differential Thermal Analysis apparatus, Shimadzu DTA-50, was used to determine the melting and the possible solid-solid transition temperatures. The equipment was previously calibrated with metals (Sn, Pb, Zn, Al, Ag and Au) in evacuated quartz ampoules to reproduce the running conditions of the studied samples, obtaining a maximum error of ±6ºC which can be considered a small error taking into account the presence of the bottom of the quartz ampoules between the sample and the thermocouple. The samples in the form of powder and weighing 80-90 mg were sealed in evacuated quartz ampoules. α-Al_2O_3 powder (80-90 mg) was used as inert reference material. Several heating and cooling rates were used and the melting and solid-solid transition temperatures were obtained from the extrapolation of the onset temperatures of DTA peaks to zero heating and cooling rates[12]. Onset temperatures were read from the maximum (cooling) or minimum (heating) peaks of the DTA signal first derivative. Transmittance and reflectance measurements were carried out at room temperature using a fiber-optics spectrophotometer Ocean Optics SD 2000. An integrating sphere was used for the reflectance measurements. For transmittance measurements, the samples were thinned down to a thickness of 100 μm and then polished to optical quality to about 50 μm with slurries of alumina powder of decreasing grid sizes (down to 0.3 μm) in deionized water. It was not possible to obtain thinner samples without breaking them. For reflectance measurements, rectangular pieces with surfaces of 10 mm^2 were thinned down to a thickness of 1 mm and polished to optical quality.

RESULTS AND DISCUSSION

The diffraction patterns of the $Ag(In_{1-x}Ga_x)_5Te_8$ compounds for different values of x are shown in Figure 1; only the most intense reflections are marked. From the analysis, it is observed that a single phase with tetragonal structure occurs across the whole composition range. The refined values of the unit lattice parameters a and c are shown in TABLE 1.

The values of the unit-cell parameters a and c obtained for the tetragonal structure of $AgIn_5Te_8$, 6.2125 Å and 12.456 Å, respectively, are in very good agreement with those reported by Mora et al[3] and Charoenphakdee et al[13]. The unit-cell parameters obtained for the tetragonal structure of $AgGa_5Te_8$ are a=5.961 Å and c=12.688 Å. Guittard et al[6] reported an orthorhombic structure for $AgGa_5Te_8$ with the values a=6.00 Å, b=12.02 Å and c=24.38 Å.

Charoenphakdee et al[13] also reported an orthorhombic structure for $AgGa_5Te_8$ with similar values for

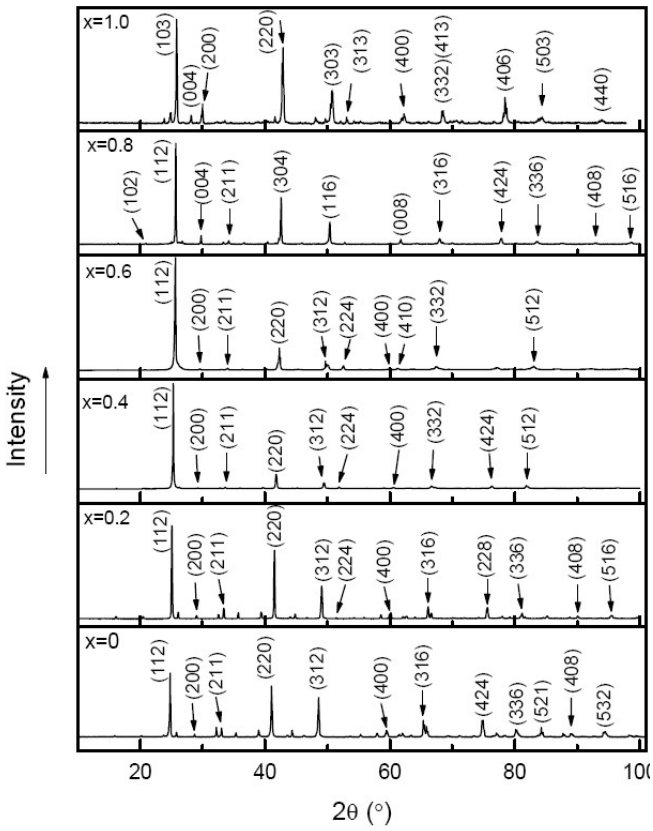

Figure 1 : X-ray powder diffraction patterns of $Ag(In_{1-x}Ga_x)_5Te_8$ compounds. Most intense reflections are shown with their respective Miller indices.

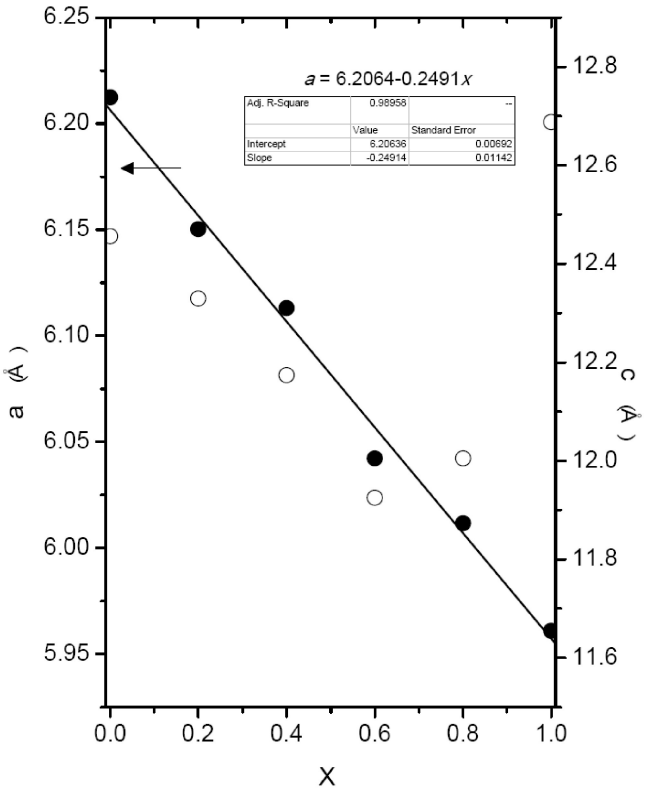

Figure 2 : Variation of lattice parameters *a* (full circles) and *c* (open circle) with composition for $Ag(In_{1-x}Ga_x)_5Te_8$ compounds. The solid straight line represents the linear fit of parameter *a*.

the lattice parameters. It can be noticed that half *b* and *c* lead to the values of the tetragonal structure obtained in this work. The parameters *a* and *c* are plotted as a function of the composition *x* in Figure 2.

It is found that parameter *a* follows the Vegard's linear rule; however, parameter *c* does not obey that rule. Substituting In atoms for smaller Ga atoms flatters the unit cell and reduces the lattice parameters until coulombian repulsion between cations makes parameter *c* increases again and the tetragonal thiogallate structure transits to tetragonal scheelite structure. This is estimated at x=0.73, as can be seen from the plot of the unit-cell volume vs. composition shown in Figure 3, where two linear regions are present.

DTA pattern of $AgIn_2Ga_3Te_8$ is shown in Figure 4 as an example of the DTA patterns obtained for all the

TABLE 1 : Unit cell lattice parameters of $Ag(In_{1-x}Ga_x)_5Te_8$ compounds.

Compound	*a*(Å)	*b*(Å)	*c*(Å)	*c*/*a*	*V*(Å^3)	Structure
$AgIn_5Te_8$	6.2125	6.2125	12.456	2.0049	480.7	Tetragonal/thiogallate
	6.1952[3]	6.1952[3]	12.419[3]	2.0046	476.7[3]	Tetragonal[3]
	-	-	-	-	-	Tetragonal/thiogallate[9]
	6.204 [13]	6.204[13]	12.423[13]	2.0024	478.2	Tetragonal[13]
$AgIn_4GaTe_8$	6.1503	6.1503	12.329	2.0046	466.4	Tetragonal/thiogallate
$AgIn_3Ga_2Te_8$	6.1130	6.1130	12.174	1.9914	454.9	Tetragonal/thiogallate
$AgIn_2Ga_3Te_8$	6.0423	6.0423	11.925	1.9736	435.4	Tetragonal/thiogallate
$AgInGa_4Te_8$	6.0117	6.0117	12.005	1.9970	433.9	Tetragonal/scheelite
$AgGa_5Te_8$	5.9610	5.9610	12.688	2.1284	450.8	Tetragonal/scheelite
	6.00[6]	12.02[6]	24.38[6]	-	-	Orthorhombic[6]
	8.415[8]	8.415[8]	47.877[8]	-	-	Tetragonal/scheelite[8]
	6.022[13]	12.113[13]	24.516[13]	-	-	Orthorhombic[13]

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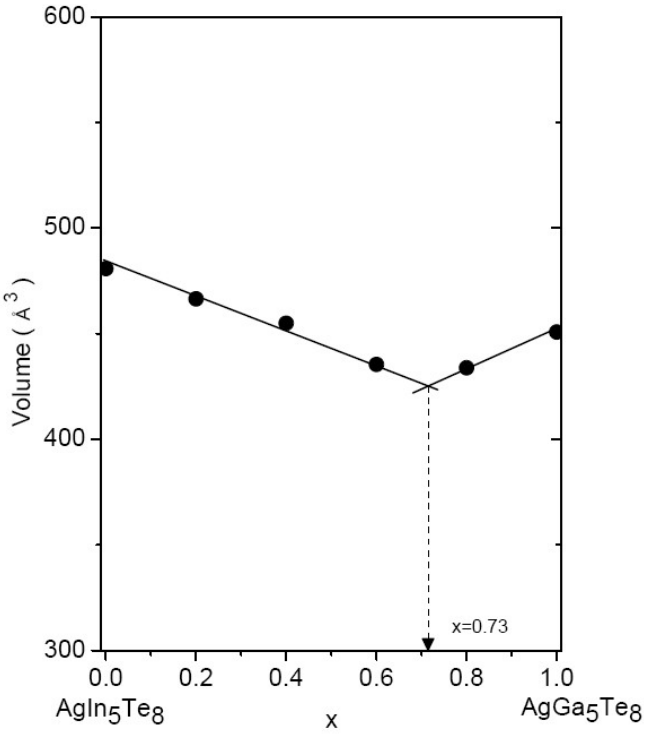

Figure 3 : Unit-cell volume vs. composition for $Ag(In_{1-x}Ga_x)_5Te_8$ compounds. The interception of two linear fits V_1=481.49-73.78*x* and V_2=365.99+84.85*x* occurs at *x*=0.73.

compositions. The values of phase transition temperatures for all the studied compositions, obtained as described early in section 2, are listed in TABLE 2. Figure 5 shows extrapolation to 0 ºC/min for $AgGa_5Te_8$.

TABLE 2 : Phase transition temperatures of $Ag(In_{1-x}Ga_x)_5Te_8$ compounds.

Compound	Heating T (ºC)	Cooling T (ºC)
$AgGa_5Te_8$	775	777
$AgInGa_4Te_8$	731	737
$AgIn_2Ga_3Te_8$	722	721
$AgIn_3Ga_2Te_8$	624, 701	703, 573
$AgIn_4GaTe_8$	704	699
$AgIn_5Te_8$	696	695

$AgIn_5Te_8$ melts congruently at 696 ºC, a lower temperature when compared with the congruent melting at 725 ºC reported by Mora et al[3], Palatnik and Rogacheva[9] and Bahari et al[10]. $AgGa_5Te_8$ melts congruently at 775 ºC. For this compound, Guittard et al[6] reported a peritectic decomposition at 450ºC and complete melting at 750ºC, while Kramer et al[7] reported melting at 780 ºC. The other studied compositions melt

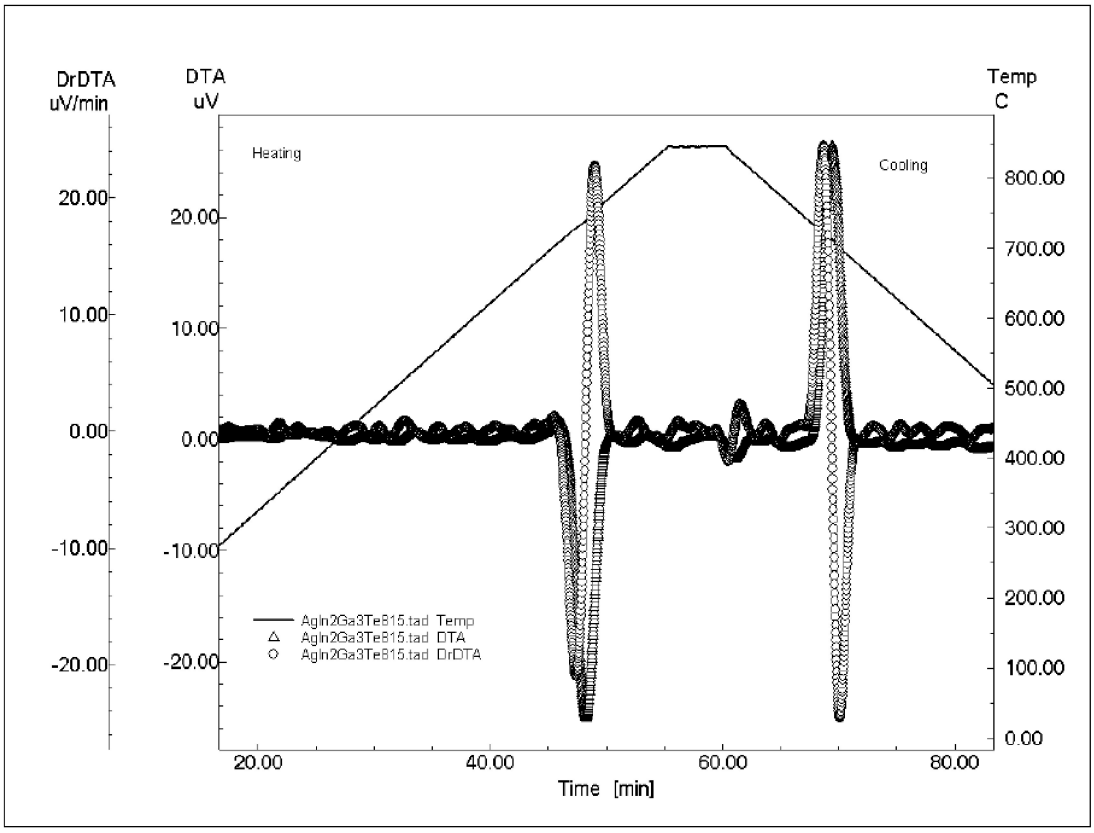

Figure 4 : DTA pattern of $AgIn_2Ga_3Te_8$ at 15ºC/min. Solid line represents temperature, open triangles represent DTA signal and open circles represent DTA signal first derivative.

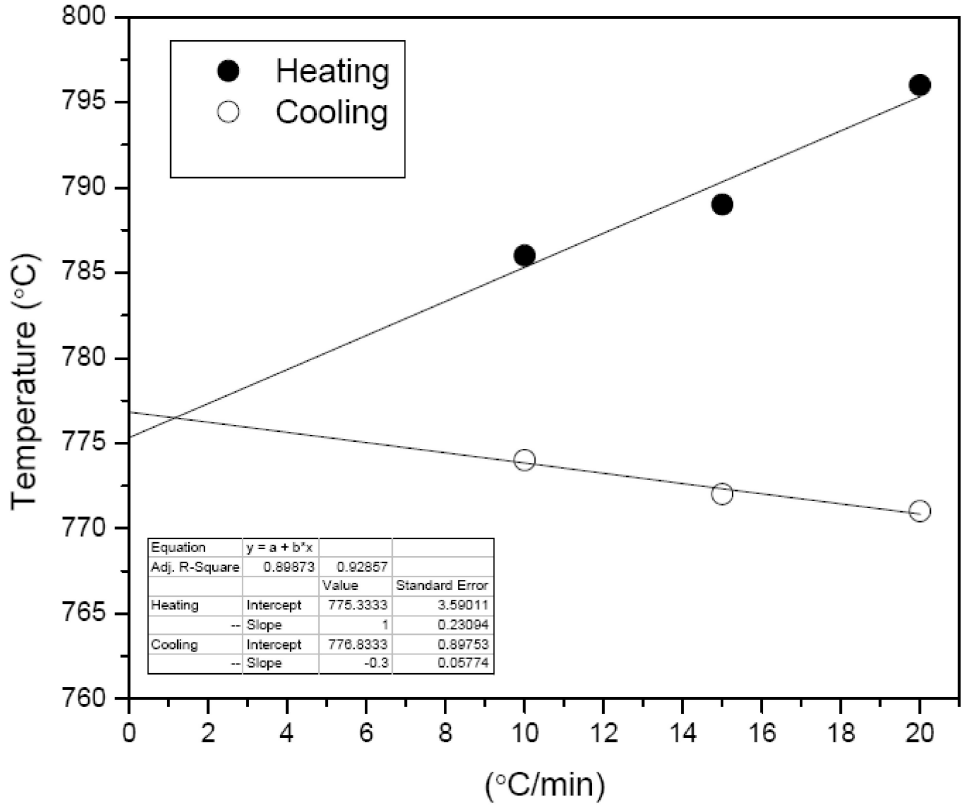

Figure 5 : Extrapolation to zero heating or cooling rate of the onset temperatures obtained for $AgGa_5Te_8$.

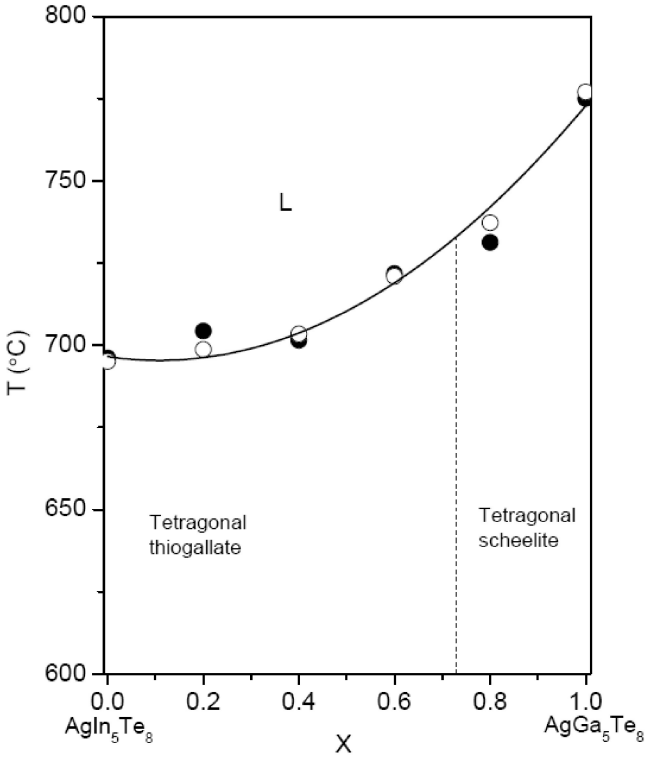

Figure 6 : T(*x*) vertical section of $Ag(In_{1-x}Ga_x)_5Te_8$ compounds. Full and open circles represent temperature values obtained from heating and cooling runs, respectively. The solid line shows how melting temperatures increase with composition *x*.

congruently, with melting temperatures increasing as *x* increases, as shown in Figure 6. Only $AgIn_3Ga_2Te_8$ shows a solid-solid transition between 573 ºC and 624ºC as previously reported[14].

The signals from the transmittance measurements resulted low and noisy and then useless for any analysis. This can be expected for thick samples (>50 μm) with high reflectivity, as is the case with the silver and tellurium-rich studied compounds[15]. On the other hand, reflectivity measurements resulted high and clear, as can be seen from Figure 7.

The tellurium content is high in the studied compounds, varying from 63.8 %*w* for $AgIn_5Te_8$ to 72.5 %*w* for $AgGa_5Te_8$, and the measured reflectivity values around 1 eV are in good agreement with the values reported for tellurium with normal incidence (0.606 with $E \parallel \hat{c}$ and 0.472 with $E \perp \hat{c}$)[15]. Several authors[16-18] have used reflectance measurements to estimate optical parameters of I-III-VI_2 compounds. Particularly, Diaz et al[19] developed a method to obtain the band gap energy values of bulk materials with direct or indirect band gaps.

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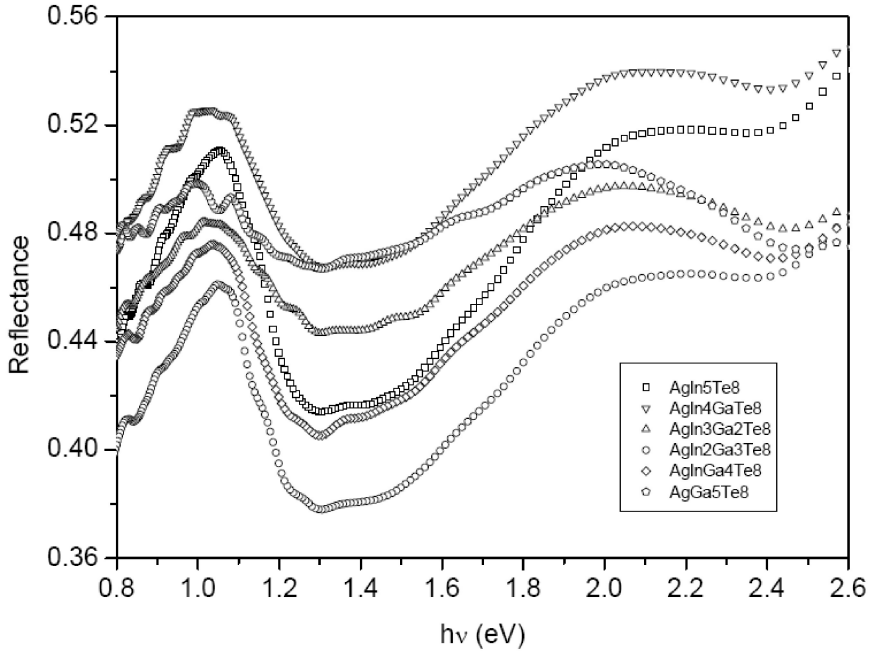

Figure 7 : Reflectance of $Ag(In_{1-x}Ga_x)_5Te_8$ compounds.

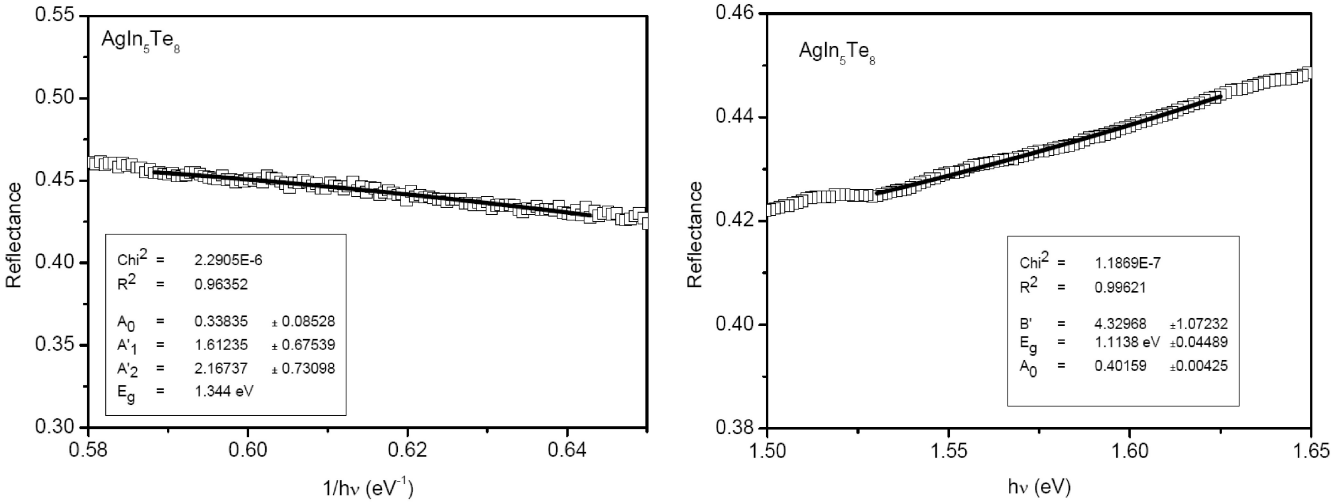

Figure 8 : Fitting of the reflectance for a) direct gap of $AgIn_5Te_8$ using Eq. (1) and b) indirect gap of $AgIn_5Te_8$ using Eq. (2).

TABLE 3 : Direct energy band gap values of $Ag(In_{1-x}Ga_x)_5Te_8$ compounds.

Compound	Direct Band Gap			
	Fitting region	Fitting Range (eV^{-1})	n	E_g(eV)
$AgIn_3Ga_2Te_8$	R↓ 1/hν↑ R^2=0.95503 Chi^2=2.3125E-6	0.5758 –0.6447 A_0=0.40548±0.04762 A'_1=1.03272±0.38392 A'_2=1.43609±0.41904	3.98-5.12	1.39
$AgIn_4GaTe_8$	R↓ 1/hν↑ R^2=0.94809 Chi^2=2.2558E-6	0.5325 –0.5766 A_0=0.28105±0.11868 A'_1=3.17792±1.15839 A'_2=4.3494±1.39206	2.35-4.44	1.37
$AgIn_5Te_8$	R↓ 1/hν↑ R^2=0.96352 Chi^2=2.2905E-6	0.5882 –0.6428 A_0=0.33835±0.08528 A'_1=1.61235±0.67539 A'_2=2.16737±0.73098	3.02-4.73	1.34 1.28[1]

TABLE 4 : Indirect energy band gap values of $Ag(In_{1-x}Ga_x)_5Te_8$ compounds.

Compound	Indirect Band Gap			
	Fitting region	Fitting Range (eV)	n	E_g(eV)
$AgGa_5Te_8$	R↑ hv↑ R^2=0.98548 Chi^2=1.3551E-7	1.5250 –1.6295 A_0=0.46516±0.06819 B'=2.4892±1.00366	5.25-5.33	1.14
$AgInGa_4Te_8$	R↑ hv↑ R^2=0.99858 Chi^2=2.7937E-8	1.5355 –1.6206 A_0=0.40174±0.00237 B'=4.29069±0.73872	4.43-4.49	1.13
$AgIn_2Ga_3Te_8$	R↑ hv↑ R^2=0.99562 Chi^2=6.2346E-8	1.5147 –1.6031 A_0=0.37217±0.00306 B'=3.52737±0.97949	4.10-4.16	1.12
$AgIn_3Ga_2Te_8$	R↑ hv↑ R^2=0.99965 Chi^2=2.249E-9	1.5678 –1.6147 A_0=0.42765±0.00345 B'=3.78286±0.83482	4.74-4.82	1.12
$AgIn_4GaTe_8$	R↑ hv↑ R^2=0.99674 Chi^2=3.671E-7	1.5058 –1.5859 A_0=0.45719±0.00281 B'=3.5419±0.95564	5.12-5.22	1.12
$AgIn_5Te_8$	R↑ hv↑ R^2=0.99621 Chi^2=1.1869-E7	1.5302 –1.6250 A_0=0.40159±0.00425 B'=4.32968±1.07232	4.41-4.51	1.11 1.11[1]

Using the data from reflectance measurements E_g is estimated from the fitting of the plot of (R vs. $1/h\nu$) for direct band gap or (R vs. $h\nu$) for indirect band gap. As established in the model, the fitting procedures were made using the following equations to obtain the direct or the indirect band gap energies, respectively:

$$\mathbf{R \cong A_0 + \frac{A_1'}{(h\nu)^2} - \frac{A_2'}{(h\nu)^3}} \quad \textbf{(1)}$$

where $A_0 = (n\text{-}1)^2/(n+1)^2$ and $E_g = A_2'/A_1'$, being n the real refraction index.

$$\mathbf{R = B' \frac{(h\nu - E_g)^4}{(h\nu)^4} + A_0} \quad \textbf{(2)}$$

where $A_0 = (n\text{-}1)^2/(n+1)^2$, $B' = (B^2c^2h^2)/[16\pi^2(n+1)^2]$ and

$$\mathbf{B = \frac{\pi e^2 h}{4ncm_e^2} \frac{C}{(2\pi)^3} \left(\frac{2m_v^*}{\hbar^2}\right)^{3/2} \left(\frac{2m_c^*}{\hbar^2}\right)^{3/2} n_p} \quad \textbf{(3)}$$

where C is a matrix element that connects initial and final states, n_p is the phonon occupation number, and m_v^* and m_c^* are, respectively, the effective masses of holes and electrons.

Figure 8a shows the fit of the reflectance of $AgIn_5Te_8$ to Eq. (1) for direct band gaps. The fitted reflectance decreases (R↓) when $1/h\nu$ increases ($1/h\nu$↑) between $2/3E_g$ and $1/E_g$ and the concavity of the fitted curve follows the concavity of the measured reflectance, just as described by Díaz[19]. Figures 8b shows the fit of the reflectance of $AgIn_5Te_8$ to Eq. (2) for indirect band gaps. In this case, the fitted values increase (R↑) with energy values $h\nu \geq E_g$ and the concavity of the fitted curve follows the concavity of the measured reflectance, following Diaz[19] criteria. TABLES 3 and 4 list all the values obtained from the different fittings. The fitting of the reflectance of Ga-rich compounds using Eq. (1) for direct band gaps resulted in too low R-square values (<0.5), indicating a non reliable fitting. The reflectance of all the studied compositions was fitted to Eq. (2) for indirect band gaps, obtaining good R-square values (>0.9). The direct and indirect band gap energies obtained for $AgIn_5Te_8$ are in good agreement with those measured by other authors[1] using transmittance and resistivity measurements. The values of the real refraction index n were obtained from the minimum and maximum A_0 values, being more reliable those obtained from indirect band gap fittings, which are in good agreement with the n values for tellurium for normal incidence with $E \perp \hat{\mathbf{c}}$ [15].

CONCLUSIONS

Ingots of $Ag(In_{1-x}Ga_x)_5Te_8$ were obtained by direct fusion of the stoichiometric mixture of the elements. The

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system showed p-type conductivity except for x=0.2 that showed an n-type conductivity. The X-ray powder diffraction patterns confirmed that a single phase with tetragonal structure occurs for the studied $Ag(In_{1-x}Ga_x)_5Te_8$ compounds. The variation of the unit-cell lattice parameters a and c were reported and a structural transition from tetragonal thiogallate to tetragonal scheelite was estimated at x=0.73. The melting temperatures increase with gallium composition. The band gap energy values and the real refraction indices were estimated from reflectance measurements. The fittings to obtain indirect band gap energies resulted more reliable than those to obtain direct band gap energies, authors suggest that Eq. (1) probably needs to consider the phonon contribution when the studied material has both direct and indirect band gaps.

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