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Structural and optical properties of $AgIn_5Se_8$

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ABSTRACT

Compounds of the chalcogenide family Ag-In-VI (VI=S, Se, Te) are interesting materials because of their stoichiometric stability and potential application in non-linear optics and solar cells. For this work, an ingot of $AgIn_5Se_8$, an ordered vacancy compound, was prepared by direct fusion of the stoichiometric mixture of the elements in an evacuated quartz ampoule. The analysis of the X-ray powder diffraction data showed the presence of a single phase with tetragonal structure at room temperature. The lattice parameters *a* and *c* were calculated, giving 5.795224 Å and 11.627038 Å, respectively. Differential Thermal Analysis measurements were performed on samples in evacuated quartz ampoules. A solid–solid (order-disorder) transition was observed at 730 ºC, while the melting temperature was found to be 810 ºC. Transmittance and reflectivity measurements were used to calculate the absorption coefficient from which two energy gaps were estimated, 1.24 eV and 1.46 eV, indirect and direct, respectively. Alternatively, from the fit of the reflectivity, the indirect energy gap and the direct energy gap turned out to be 1.28 eV and 1.48 eV, respectively. The real refraction index, also obtained from the fit of the reflectivity, resulted to be 4.05.

KEYWORDS

Ordered vacancy compounds;
X-ray powder diffraction;
Differential thermal analysis (DTA);
Transmittance;
Reflectivity;
Energy gap;
Refraction index.

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]. The silver ternary chalcogenides of the type AgInVI (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 are very stable stoichiometric compounds and their electrophysical properties depend slightly on impurities[2-4].

In the systems Cu(In, Ga)VI and Ag(In, Ga)VI, in addition to the compounds $Cu(In, Ga)VI_2$ and $Ag(In, Ga)VI_2$, the compounds of the type $Cu(In, Ga)_5VI_8$ and $Ag(In, Ga)_5VI_8$ have also been studied. These are

known as Ordered Vacancy Compounds (OVC), since, according to the Grimm-Sommerfeld rule, present a cation deficiency (cation/anion ratio = 0.75 and valence electrons/atom ratio = 4.57)[5].

Information about $AgIn_5Se_8$ has been reported by some authors. Palatnik and Rogacheva[6] showed the existence of the compound in the pseudo binary phase diagram Ag_2Se-In_2Se_3. Lattice parameters and the temperature dependence of the optical energy gap were reported by Benoit et al[7], although the nature of the gap (direct or indirect) was not established. Razzini et al[8] and Peraldo et al[9] studied the photoelectrochemical behaviour of the compound and reported two energy gaps, one for an indirect transition and one for a direct transition. The structure and thermal stability of the $AgIn_5S_{8-x}Se_x$ system were reported by Haeuseler et al[10].

In this work, the authors report on some physical properties of $AgIn_5Se_8$, including the reflectivity, by performing all the measurements on samples from the same ingot.

CRYSTAL GROWTH AND EXPERIMENTAL DETAILS

An ingot of $AgIn_5Se_8$ was prepared exclusively for this work by direct fusion of the stoichiometric mixture of the elements of at least 5N purity in an evacuated quartz ampoule (≈10^{-6} Torr). The ampoule was heated in a vertical furnace. To minimize the risk of explosion due to exothermic reaction between In and Se, the ampoule was heated very slowly at 5ºC/h up to 1050 ºC, kept at this temperature for 24 h, it was rocked manually at regular intervals to achieve a homogeneous mixing of the liquid phase of the reacting mixture and then was cooled to 600 ºC at a rate of 5ºC/h. Finally, it was cooled at a rate of 30ºC/h to 500 ºC, where it was annealed for 4 days to reduce possible defects and to increase grain size. As observed by a simple thermal probe test, samples from the ingot showed n-type conductivity. 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. The diffraction pattern was obtained for 5º≤2θ≤100º 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 sample, obtaining a maximum error of ±6 ºC 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 sample, in the form of powder and weighing 80-90 mg, was 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[11]. Onset temperatures were read from the peaks maximum (cooling) or minimum (heating) of the DTA signal first derivative. Transmittance and reflectivity measurements were carried out at room temperature using a fiber-optics spectrophotometer Ocean Optics SD 2000. An integrating sphere was used for the reflectivity measurements. For transmittance measurements, the sample was thinned down to a thickness of 100 μm and then polished to optical quality to a thickness (*t*) of 30 μm with slurries of alumina powder of decreasing grid sizes (down to 0.3 μm) in deionized water. For

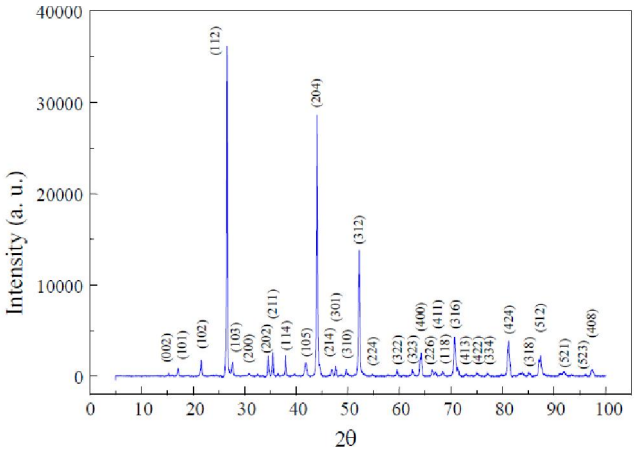

Figure 1 : X-ray powder diffraction pattern of $AgIn_5Se_8$. Most intense reflections are shown with their respective Miller indices

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TABLE 1 : Unit cell lattice parameters of $AgIn_5Se_8$

H K L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS
0 0 2	0.017556	0.017557	-0.000001	15.228	15.228	5.8137
1 0 0		0.017668			15.277	
1 0 1	0.022058	0.022057	0.000001	17.082	17.082	5.1866
1 0 2	0.035222	0.035224	-0.000002	21.634	21.635	4.1044
1 1 0		0.035335			21.669	
1 1 2	0.052919	0.052892	0.000027	26.599	26.592	3.3485
1 0 3	0.057165	0.057170	-0.000005	27.666	27.667	3.2218
2 0 0	0.070662	0.070671	-0.000009	s30.832	30.834	2.8978
1 0 4		0.087894			34.491	
2 0 2	0.088230	0.088227	0.000003	34.559	34.559	2.5933
2 1 0		0.088338			34.581	
2 1 1	0.092716	0.092728	-0.000012	35.455	35.458	2.5298
1 1 4	0.105552	0.105562	-0.000010	37.918	37.919	2.3710
2 1 2		0.105895			37.981	
1 0 5	0.127392	0.127397	-0.000005	41.822	41.823	2.1582
2 0 4	0.140891	0.140897	-0.000006	44.092	44.093	2.0522
2 1 4	0.158550	0.158565	-0.000015	46.929	46.932	1.9345
2 2 2		0.158898			46.984	
3 0 1	0.163376	0.163398	-0.000022	47.682	47.685	1.9057
3 0 2		0.176566			49.694	
3 1 0	0.176652	0.176677	-0.000025	49.707	49.711	1.8327
3 1 2	0.194211	0.194233	-0.000023	52.296	52.300	1.7479
2 2 4	0.211676	0.211568	0.000108	54.785	54.770	1.6743
3 1 4		0.246903			59.589	
3 2 2	0.247204	0.247236	-0.000033	59.629	59.634	1.5493
3 0 5		0.268738			62.450	
3 2 3	0.269123	0.269182	-0.000059	62.500	62.507	1.4849
4 0 0	0.282648	0.282683	-0.000034	64.234	64.238	1.4489
2 2 6	0.299357	0.299351	0.000006	66.341	66.341	1.4079
4 1 1	0.304766	0.304740	0.000026	67.016	67.013	1.3953
1 1 8	0.316227	0.316242	-0.000014	68.436	68.437	1.3698
3 1 6	0.334664	0.334687	-0.000022	70.690	70.693	1.3315
3 2 5		0.339409			71.266	
4 1 3	0.339783	0.339853	-0.000070	71.311	71.319	1.3215
4 0 4	0.352922	0.352909	0.000012	72.893	72.892	1.2966
4 1 4		0.370577			74.998	
4 2 2	0.370921	0.370910	0.000011	75.039	75.038	1.2648
3 3 4	0.388371	0.388245	0.000126	77.099	77.085	1.2361
4 2 4	0.423524	0.423580	-0.000056	81.202	81.208	1.1836
5 0 0	0.441628	0.441692	-0.000064	83.296	83.303	1.1591
5 0 1	0.446182	0.446081	0.000101	83.821	83.809	1.1532

H K L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS
3 1 8	0.457614	0.457583	0.000031	85.137	85.134	1.1387
5 1 2	0.476859	0.476916	-0.000058	87.347	87.354	1.1155
5 0 4	0.511853	0.511918	-0.000066	91.358	91.366	1.0767
5 2 1	0.516776	0.516752	0.000024	91.923	91.920	1.0715
5 1 4	0.529547	0.529586	-0.000039	93.388	93.392	1.0585
5 2 2		0.529919			93.431	
5 2 3	0.551877	0.551865	0.000012	95.955	95.954	1.0369
4 0 8	0.563555	0.563589	-0.000035	97.303	97.307	1.0261

a = 5.795224 ± 0.000111 Å α = 90.000000 ± 0.000000 DEG M(37)= 62 AV.EPS.= 0.0000317; b = 5.795224 ± 0.000111 Å β = 90.000000 ± 0.000000 DEG F 37 = 63(0.004132, 144); c = 11.627038 ± 0.000556 Å γ = 90.000000 ± 0.000000 DEG M CF. J.APPL.CRYST. 1(1968)108; UNIT CELL VOLUME = 390.49 Å^3 F CF. J.APPL.CRYST. 12(1979)60; NUMBER OF OBS. LINES = 37; NUMBER OF CALC. LINES = 49; M (20)= 113 AV.EPS.= 0.0000203; F 20 = 98(0.003165, 65); M (30)= 67 AV.EPS.= 0.0000303

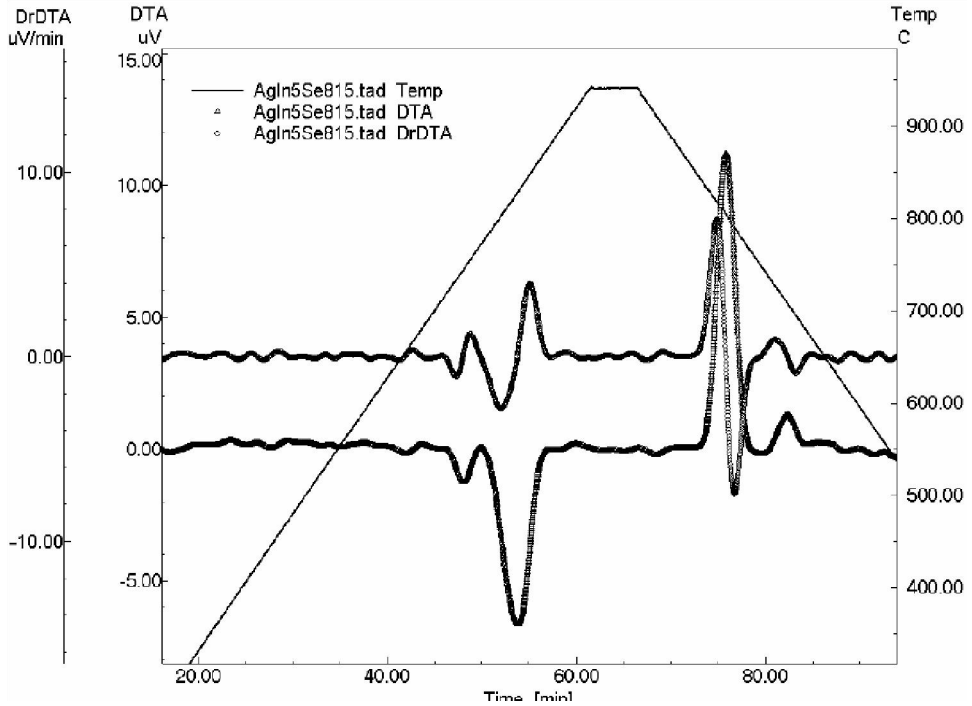

Figure 2 : DTA pattern of $AgIn_5Se_8$ at 15ºC/min. Solid line represents temperature, open triangles represent DTA signal and open circles represent DTA signal first derivative

reflectivity measurements, a rectangular piece with surface of 10 mm^2 was thinned down to a thickness of 1 mm and polished to optical quality.

RESULTS AND DISCUSSION

The diffraction pattern of $AgIn_5Se_8$ is shown in Figure 1, only the most intense reflections are marked. From the analysis, it was observed that a single phase with tetragonal structure occurs. The refined values of the unit lattice parameters a and c are shown in TABLE 1. For comparison, values reported by other authors are a=5.793 Å and c=11.622 Å[7], and a=5.7934 Å and c=11.6223 Å[8].

The DTA pattern of $AgIn_5Se_8$ at 15ºC/min is shown in Figure 2 as an example of the DTA patterns obtained for different heating or cooling rates. As described early in section 2, Figure 3 shows the extrapolation to 0 ºC/min for $AgIn_5Se_8$. The values of phase transition temperatures are 730 ºC for the solid-solid transition and 810 ºC for melting. These values are in good agreement with those reported

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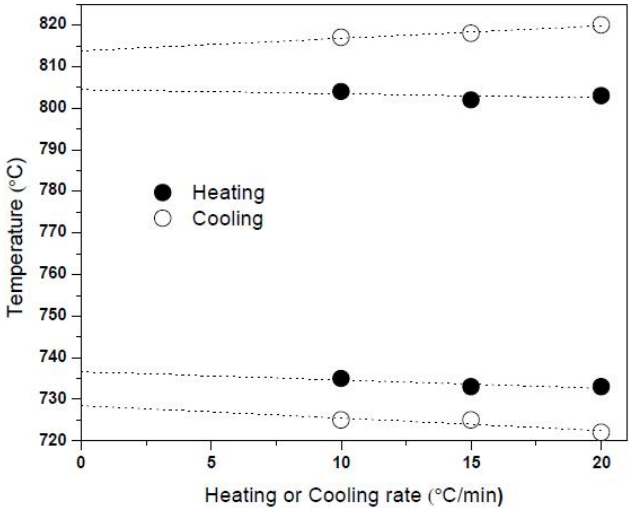

Figure 3 : Extrapolation to zero heating or cooling rate of the onset temperatures obtained for $AgIn_5Se_8$

by Palatnik and Rogacheva[6], who described a cation vacancy ordered structure (thiogallate structure) from room temperature up to 740 ºC and then a sphalerite structure melting at 815 ºC.

The transmittance (*T*) and reflectivity (*R*) spectra of $AgIn_5Se_8$ are shown in Figures 4 and 5, respectively. From these, the absorption coefficient α (Figure 6) can be calculated as[12]:

$$\alpha = \frac{2\ln(1-R) - \ln[a_T(T-T_{min})]}{t} \quad (1)$$

with

$$a_T = \frac{(1-R)^2}{T_{max}} \quad (2)$$

The inserts in Figure 4 and 6 show a second transition for $AgIn_5Se_8$. An indirect transition requires less energy, has a smaller probability and therefore it appears as a shoulder in the spectra. The indirect energy gap value can be obtained from the interception at α=0 of the fit to a straight line of the plot of $(\alpha h\nu)^{1/2}$. On the other hand, the direct energy gap value can be obtained from the interception at α=0 of the fit to a straight line of the plot of $(\alpha h\nu)^2$. This is shown in Figure 7. The values obtained are 1.24 eV and 1.46 eV, in good agreement with 1.27 eV and 1.47 eV reported by Razzini et al[8] and in the optimum range for solar energy conversion.

Several authors[13-16] have used reflectivity measurements to estimate optical parameters of I-III-VI_2 compounds. Particularly, Diaz et al[16] developed a method to obtain energy gap values E_g of bulk materials with direct and/or indirect transitions.

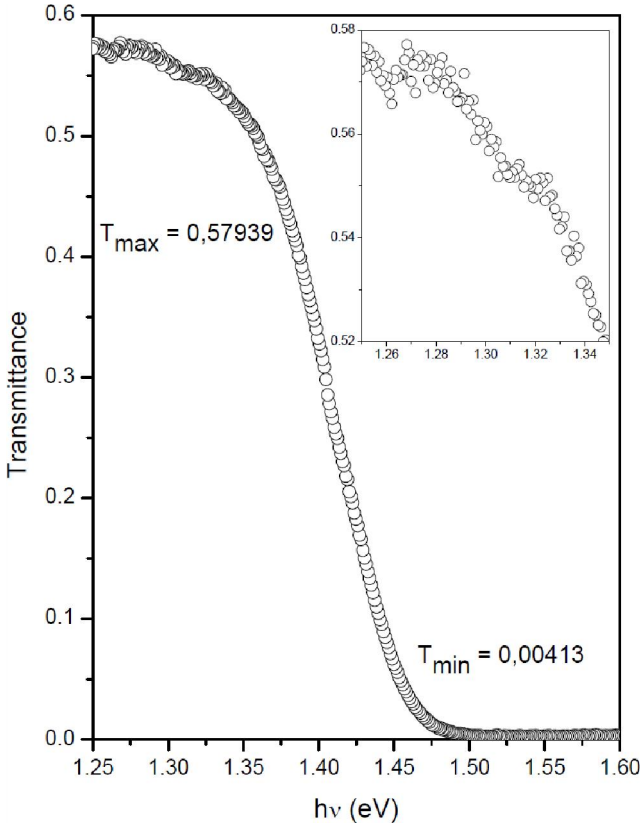

Figure 4 : Transmittance for $AgIn_5Se_8$. The insert shows a second transition

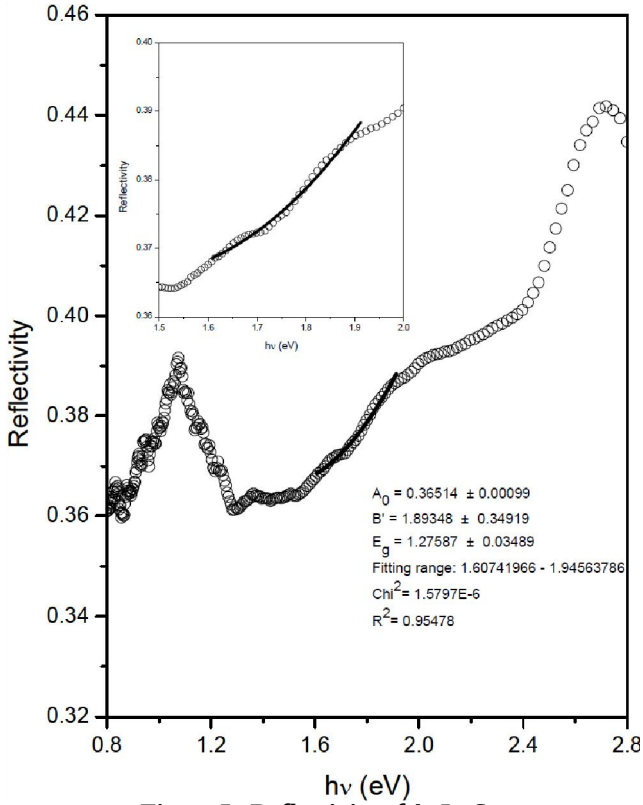

Figure 5 : Reflectivity of $AgIn_5Se_8$

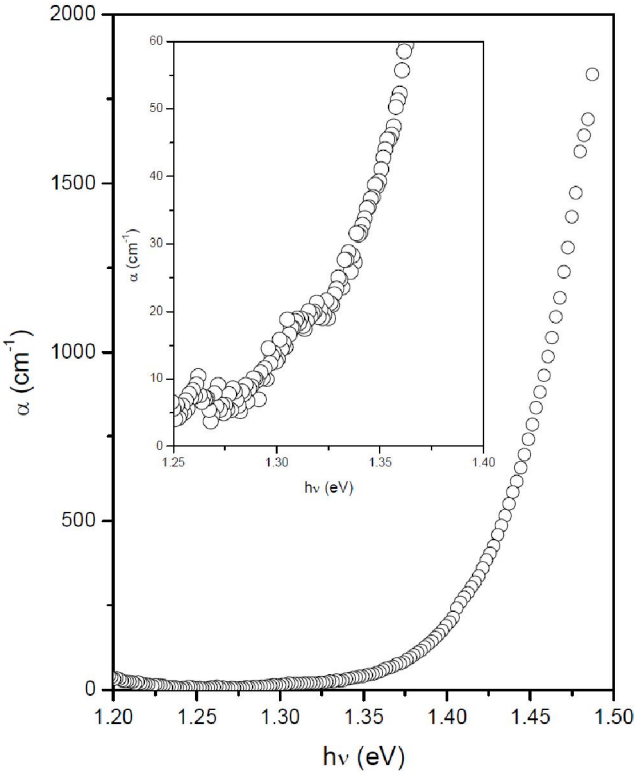

Figure 6 : Absorption coefficient α for $AgIn_5Se_8$. The insert shows a second transition

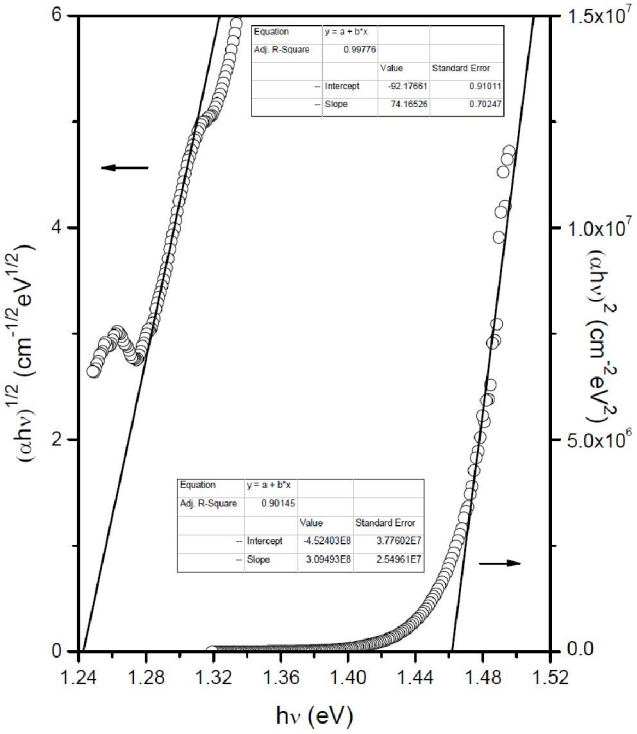

Figure 7 : Plot of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ for $AgIn_5Se_8$. The values obtained are 1.24 eV for the indirect energy gap and 1.46 eV for the direct energy gap

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

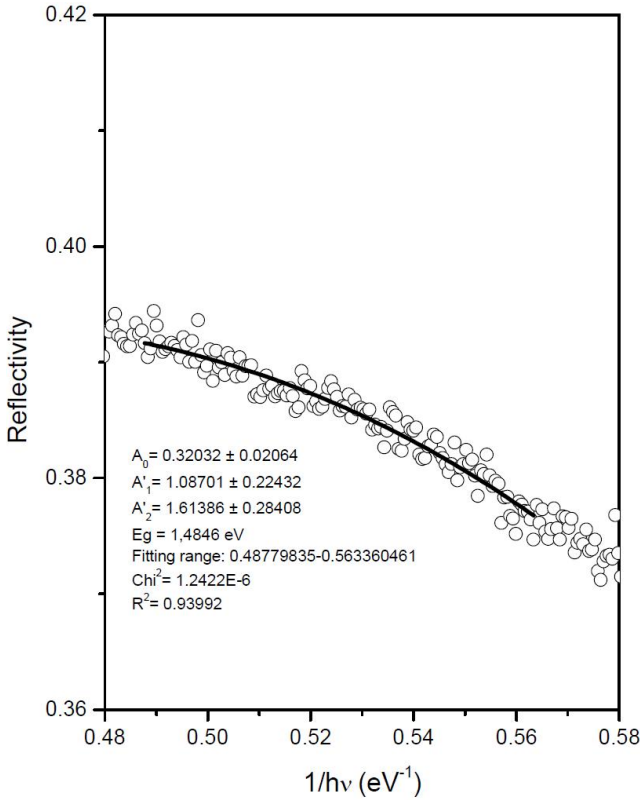

Figure 8 : Reflectivity vs 1/hν for $AgIn_5Se_8$

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

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

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

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

$$B = \frac{\pi e^2 h}{4ncm_e^2} \frac{C}{(2\pi)^3} \left(\frac{2m_v^*}{\hbar^2}\right)^{3/2} \left(\frac{2m_c^*}{\hbar^2}\right)^{3/2} n_p \quad (5)$$

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 8 shows the fit of the reflectivity of $AgIn_5Se_8$ to Eq. (3) for a direct gap. The fitted reflectivity

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 reflectivity, just as described by Díaz[16]. Insert in Figure 5 shows the fit of the reflectivity of $AgIn_5Se_8$ to Eq. (4) for an indirect gap. 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 reflectivity, following Diaz[16] criteria. From the value of A_0 in Figure 5, the real refraction index is calculated, giving 4.05.

CONCLUSIONS

An ingot of $AgIn_5Se_8$ was obtained by direct fusion of the stoichiometric mixture of the elements. The compound showed n-type conductivity. The X-ray powder diffraction patterns confirmed that a single phase with tetragonal structure occurs. The values of the lattice parameters a=5.795224 Å and c=11.627038 Å are in good agreement with those reported previously. A solid-solid transition at 730 ºC and the melting point at 810 ºC were confirmed. The existence of two optical transitions, one indirect and one direct, was also confirmed. The energy gap values and the real refraction index were estimated from transmittance and reflectivity measurements.

ACKNOWLEDGEMENTS

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