Artículo de Investigación Original

STRUCTURAL CHARACTERIZATION OF THE LAYERED COMPOUND Ag_2SnSe_3 FROM SCANNING AND TRANSMISSION ELECTRON MICROSCOPY AND SYNCHROTRON POWDER DIFFRACTION

R. Ávila-Godoy [a]*, D. Acosta-Najarro[b], G. Camargo-E[a], C. Magaña-Zavala[b], L. Nieves[c], S. Paredes-Dugarte[d], B. Hidalgo-Prada[d]

[a]Universidad de los Andes, Laboratorio de Análisis Químico Estructural de Materiales, Mérida, 5101, Venezuela.
[b]Instituto de Física, Universidad Nacional Autónoma de México, D.F.04510, México.
[c]Universidad de Los Andes, Centro de Semiconductores, Mérida, 5101, Venezuela.
[d]Laboratorio de Caracterización de Materiales, Instituto de Investigaciones en Biomedicina y Ciencias Aplicadas, Universidad de Oriente, Cumaná, Venezuela.

*Corresponding author, E-mail: rosario@ula.ve. Tel-+58 274 2401267

Recibido: Noviembre 2016. Aprobado: Junio 2018.
Publicado: Julio 2018.

ABSTRACT
In this paper, a study of structural characterization of the ternary semiconductor Ag2SnSe3 is presented. The experimental work was performed using Scanning Electron Microscopy (SEM), Selected Area Electron Diffraction (SAED) patterns, High Resolution Electron Microscopy (HREM), Annular Dark field imaging (ADF), and powder synchrotron X-ray Diffraction techniques. It was found that the semiconductor compound Ag_2SnSe_3 crystallizes in the monoclinic space group P2/m with cell parameters a = 7.977 Å, b = 7.912 Å, c = 13.023 Å, β = 101.734°, V = 804.79 Å^3.

Keywords: Ag_2SnSe_3, SEM, SAED, HRTEM, ADF, Synchrotron.

INTRODUCTION

Recent technological breakthroughs and the desire for new application generate an enormous demand for novel materials. Many of the well-established materials, such as semiconductors, can fulfill all technological desires for the various new applications, because of their great importance in the construction of electronic structures, such as light emitting diodes, photodetectors, highly efficient lasers, optical filters, and solar cells, and thermoelectric devices among other, have a reduced energy gap between 0.25 eV and 1.25 eV with low melting point [1-4].

The materials family I_2-IV-VI_3 belongs to one of two possible semiconductors ternary with diamond structure, derived from binary type IIVI. Some members of this family have been related with two orthorhombic superstructures, one sphalerite and another wurzite. In the case of Cu_2GeSe_3 and Cu_2SiS_3 [5]. The crystal structure for the compound Cu_2GeSe_3 belonging to space group Imm2, is considered the prototype of this family, while the structure for the Cu_2SiS_3 compound derived from wurtzite, belongs to $Cmc2_1$ space group, is the prototype. Studies of single crystal techniques, for compound Cu_2GeS_3, using a diffractometer with MoKα_1 radiation (λ = 0.7107 Å), established that the structure of this material exhibits monoclinic symmetry, space group Cc, with cell parameters a = 6.449 (2) Å, b = 11.319 (3) Å, c = 6.428 (2) Å and β = 108.37 (2)° [5]. In a recent study, [8] examined the crystal structure of Cu_2SnSe_3, using powder diffraction synchrotron X-rays, obtaining cell parameter a

= 6.9714 (2) Å, b = 12.0787 (5) Å, c = 13.3935 (5) Å, β = 99.865 (5) °, with space group Cc.

On the other hand, several studies have reported a monoclinic superstructure, which crystallizes as family members Ag_2-IV-VI_3. A monoclinic phase in the compound Ag_2GeSe_3, with parameters a = 7.7516 (1) Å, b = 10.874 (4) Å, c = 7,318 (9) and β = 115.82 (1) ° has been reported [6, 12]. For the compound Ag_2SnS_3, using a camera Guinier - de Wolff and a diffractometer, showed that the material crystallizes in the monoclinic system with cell parameters a = 8, 03 Å, b = 10,815 Å, c = 5,085 Å, β = 108.28° [7]. For ternary compounds Ag_2SnTe_3 and Ag_2SnSe_3 by X - ray powder diffraction using a Guinier Wolff camera [8], noticed that both compounds crystallize in a monoclinic system with space group Cc and cell parameters a = 11.506 (2) Å, b = 6.396 (1) Å, c = 6.437 (2) Å, β = 98.53 (2) ° for Ag_2SnSe_3 and a = 7.910(4) ▫, b = 6.044(3) ▫, c = 6.858(3) ▫, β= 117.57(5)° by Ag_2SnTe_3. A powder diffraction pattern for compound Ag_2SnSe_3, at room temperature, using a diffractometer obtained by [9]. They revealed that Ag_2SnSe_3, main phase crystallizes in the monoclinic system with space group Cc and unit cell parameters: a = 7, 18 Å, b = 10, 55 Å, c = 6, 70 Å, β = 111.98°.

Structural studies reported in the literature for compounds belonging to the family VI3 -IV- I2, as shown above, were performed using XRD diffractometric techniques for different photographic methods and in which there are few papers containing Ag (silver). Although studies have been reported for Ag_2SnSe_3 material and structure has not been established, this compound is a semiconductor that hardly few physical characteristics are known. Accordingly, in the present research work it was proposed to realize the study and characterization of the crystal structure of the semiconductor Ag_2SnSe_3 through the technique of polycrystalline samples, using Scanning Electron Microscopy, Selected Area Electron Diffraction patterns, High Resolution Electron Microscopy, Annular Dark field, and powder synchrotron X-rays Diffraction technique.

MATERIALS AND METHODS

The compound $Ag_2SnSe_3$was synthesized by direct fusion of the constituent elements with nominal purity of 999.999(6N).The elements were cleaned with nitric acid (HNO_3) and hydrochloric acid (HCl) for the Ag and Sn respectively in order to remove oxide layers. To perform the synthesis by the direct fusion method, the capsule was placed in a vertical furnace. The furnace was heated gradually from 25° C to a temperature of approximately 1000° C, in steps of 80 /100° C per day, for 20 days. Then slowly cooled at a rate 10° C / hour for a 48 hour time reaching 600° C, this temperature was maintained for a period of 7 days. Finally, the furnace was switched off and a dark grey ingot was obtained.

The morphological study of the samples and analysis of energy dispersive spectroscopy (EDX) were performed by scanning electron microscopy (SEM), in a JEOL SEM 5600 electron microscope equipped with a Noran EDS system. For the X-ray diffraction analysis a small quantify of the compound was ground in an agate mortar, avoiding any excess of pressure. The sample was placed in a capillary and the data were acquired by combining Debye Scherrer geometry and the beam focused on a microstrip detector 1D - II Mythen, to reduce the peak broadening caused by the capillary. The wavelength used was (λ = 0.61944Å) [10], at the high resolution powder diffraction station (beamline) of ALBA Synchrotron. For electron microscopy observations a very small piece of sample was ground in an agate mortar, the resulting powder was sprayed directly on a SEM holder. For transmission electron microscopy observations, the powder just mentioned, was dispersed in an ethanol aqueous solution to be deposited with a pipette on 200 mesh copper grids covered with a holey carbon film. The HREM, ADF and SAED micrographs were obtained in a JEOL 2010 FEG STEM microscope at 200 kV. The HREM images were

recorded with a slow scan GATAN camera and analyzed with the Digital Micrograph software.

RESULTS AND DISCUSSION

Chemical compositional analysis was performed on different regions of samples using the Energy-Dispersive X-Ray microanalysis technique. The following average atomic percentages were obtained: Ag (1.84), Sn (0.79) Se (3.37). These results are in good quality agreement with the nominal composition 2:1:3, the error in analysis was around 5%. The Figure 1 shows the Energy Dispersive X-ray Spectroscopy, which is based on the detection of characteristic X-rays emitted of elements present as a result of the de-excitation of core electron holes created by a high energy electron beam.

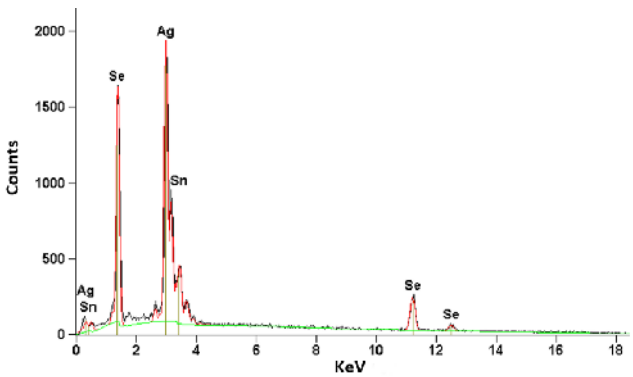

Fig. 1. EDS of Ag_2SnSe_3.

The use of synchrotron radiation allowed to obtain a diffraction pattern in which low angle reflections are recorded. The diffraction pattern shown in Figure 2, was analyzed and indexed using the computer program DICVOL91 [11] with figures of merit M (20) = 10.0 and F (20) = 41.8 (0.0092, 52). The first peak in the diffractogram obtained is in a 2θ~12 ° position and it does not correspond to the first Bragg reflection in the refinement [3]. This reflexion allowed to study in greater detail. By Rietveld refinement, it establishes the space group Cc for the compound Ag_2SnSe_3 [3].However, we have deferred this refinement because it is clear that the proposed theoretical model obtained. Moreover, in the diffractogram published by [6] for the compound Ag_2GeSe_3, which belong at the semiconductor family Ag_2SnSe_3,with diffraction lines sharper observed, however, the first peak is recorded at a position of 2θ~15°.

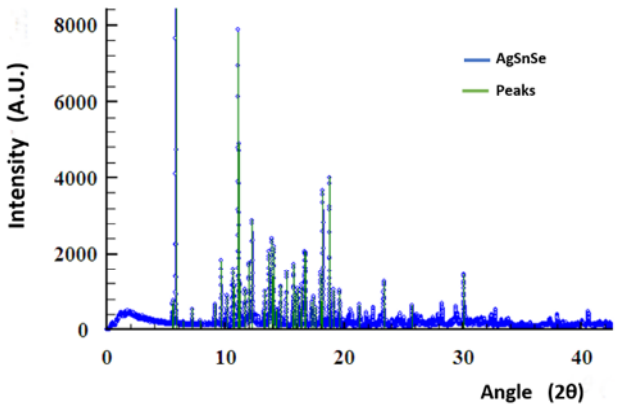

Fig. 2. XRD pattern obtained for Ag_2SnSe_3.

Table 1 contains the d(*hkl*) observed and calculated diffraction pattern in X-ray (synchrotron). The general reflection conditions applied to the whole three-dimensional set of reflections *hkl,* indicate what primitive cell was chosen. The unit cell is monoclinic with parameters a = 7.977 Å, b = 7.912 Å, c = 13.023 Å, β = 101.734°, V = 804.79 $Å^3$.

Table 1. XRD (synchrotron) powder data for Ag_2SnSe_3. Figures of merit: M (20) = 10.0 F20) = 41.8 (0.0092, 52).

H	K	L	DOBS	DCAL	DOBS-DCAL	2TH.OBS	2TH.CAL	DIF.2TH.
2	0	0	6.38868	6.34617	0.04251	5.558	5.595	-0.037
2	0	0	6.33914	6.34617	-0.00703	5.601	5.595	0.006
1	0	1	6.09138	6.10145	-0.01007	5.829	5.819	0.010
2	0	-1	5.49269	5.49746	-0.00477	6.465	6.459	0.006
2	1	0	4.94133	4.94654	-0.00521	7.187	7.180	0.008
2	0	1	4.48990	4.49548	-0.00558	7.911	7.901	0.010
0	0	2	3.90300	3.89445	0.00855	9.103	9.123	-0.020
0	0	2	3.89439	3.89445	-0.00006	9.123	9.123	0.000
2	0	-2	3.67139	3.67053	0.00086	9.678	9.681	-0.002
0	1	2	3.49307	3.49320	-0.00013	10.174	10.173	0.000
2	2	0	3.35116	3.35329	-0.00212	10.606	10.599	0.007
1	2	1	3.32946	3.31570	0.01376	10.675	10.720	-0.044
1	2	1	3.32013	3.31570	0.00442	10.705	10.720	-0.014
2	2	-1	3.20569	3.20792	-0.00223	11.089	11.081	0.008
4	0	-1	3.18108	3.17950	0.00158	11.175	11.180	-0.006
4	0	-1	3.17527	3.17950	-0.00422	11.195	11.180	0.015
2	0	2	3.06039	3.05748	0.00290	11.617	11.628	-0.011
2	2	1	2.96563	2.96766	-0.00203	11.989	11.981	0.008
3	2	0	2.89626	2.88971	0.00655	12.278	12.306	-0.028
2	2	-2	2.68923	2.68932	-0.00009	13.227	13.226	0.000

From all SEM micrographs, like the one presented in Figures 3-4, a layered configuration was observed for the Ag_2SnSe_3 samples at 5, 000X and 25,000X respectively. It

can be observed that the layer configuration is present in the rock type of the total volume of the material. Figure 3 shows void regions and the layer sequence in steps. At higher magnification (Figure 4) the thickness of the individual layers can be appreciated and, in some cases, this is in the order of 0.1 μm.

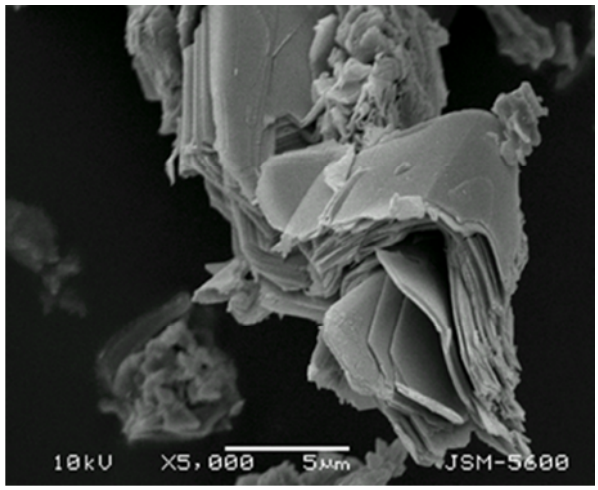

Fig. 3. SEM for Ag_2SnSe_3 showing the layer sequence in an irregular volume.

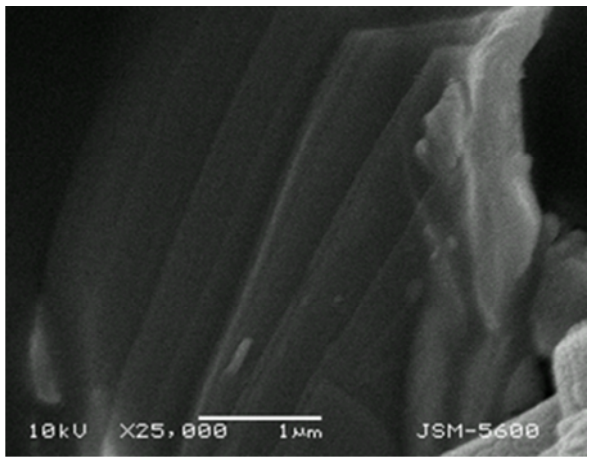

Fig. 4. SEM for Ag_2SnSe_3 showing layered sequence.

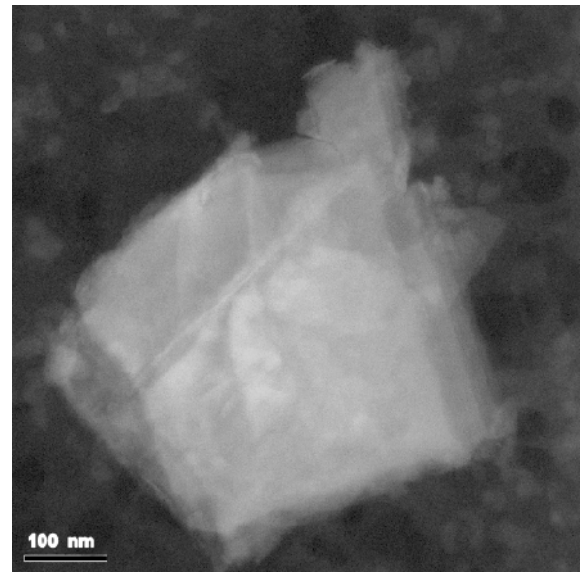

Fig. 5. Annular Dark Field (ADF) for Ag_2SnSe_3.

We have also investigated atomic resolution details using annular dark field image. The ADF image (Fig. 5) was formed by collecting electrons scattered at high angles. The micrograph in Figure 6 shows that the mass contrast is insensitive inside the sample and the layer structure is observed, with this structural analysis the volume of a single crystalline phase compound is evident.

The diffraction patterns were obtained by select area (SAED) through different crystallographic directions. These micrographs (Figures 6-7) show that the semiconductor compound is Ag_2SnSe_3 crystalline compound as well as the presence of double reflections due to the laminar morphology. The interplanar distance measure are in good agreement with the d(*hkl*) distances observed in the diffraction patterns of X-rays (synchrotron). The symmetry of space group of the compound is also imposed on the diffraction pattern; that is, through its Fourier transform (Figures 8-9), showing that the point symmetry group is 2 /m.

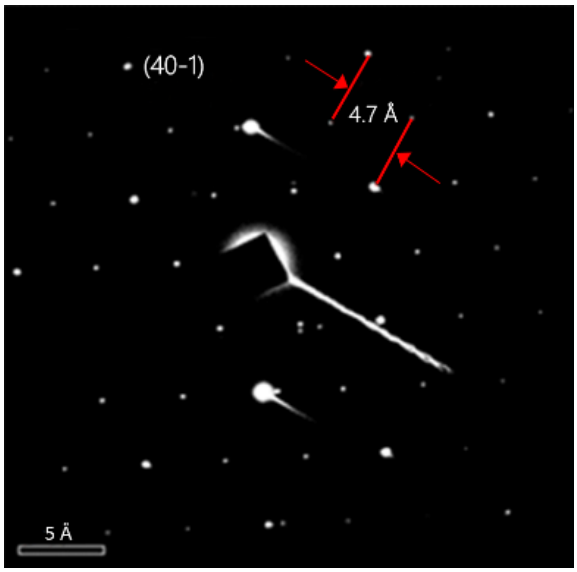

Fig. 6. SAED for Ag_2SnSe_3.

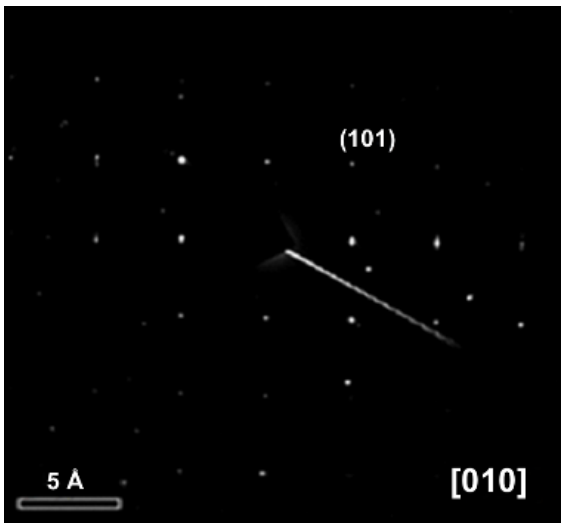

Fig. 7. SAED for Ag_2SnSe_3 along direction [010].

In Figures 8-10 HRTEM images, show that the semiconductor Ag_2SnSe_3 is highly crystalline. High-resolution images of samples clearly shows the well-defined atomic columns and the Fourier Transform of the reciprocal lattice, similar to that shown in the diffraction pattern of selected area, indicated in Figure 7, with the spacing along the [010] of order 4.6Å. Figure 10 shows different areas and crystalline defects (marked in box) which could be the grain boundary of a precipitate.

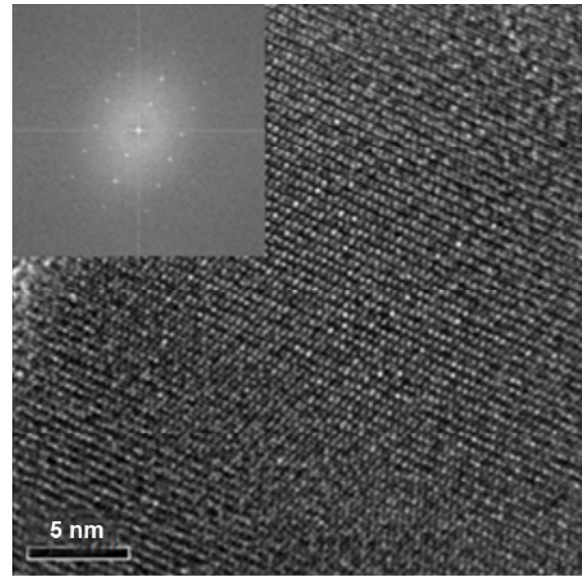

Fig. 8. HRTEM-FFT for Ag_2SnSe_3.

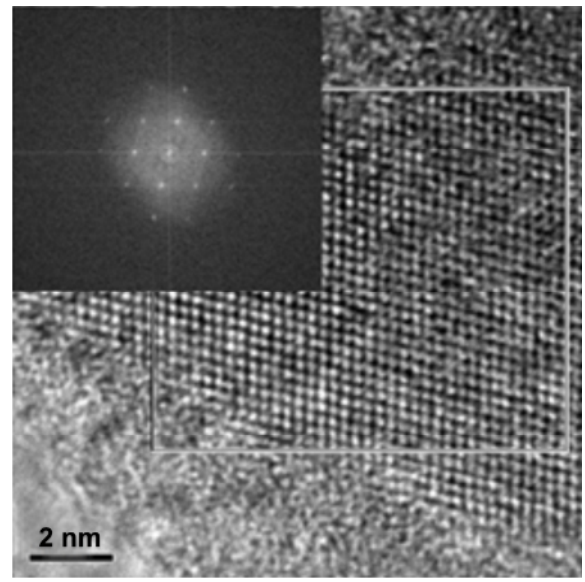

Fig. 9. HRTEM-FFT for Ag_2SnSe_3.

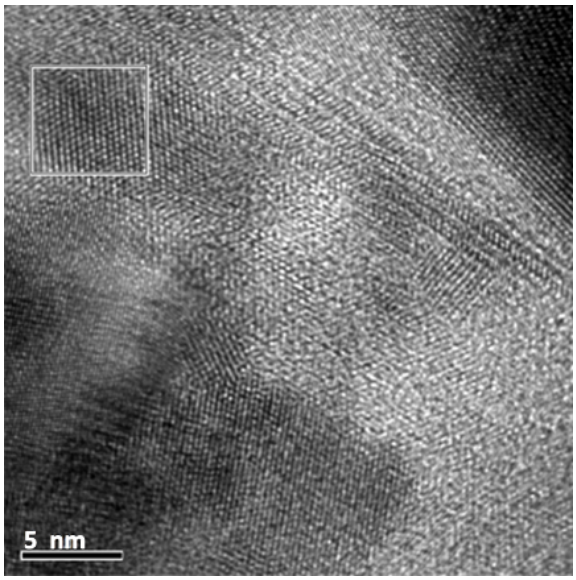

Fig. 10. HRTEM - FFT shows defects in the compound Ag_2SnSe_3.

CONCLUSIONS

Chemical analysis by Energy-dispersive X-ray spectroscopy showed the stoichiometry of the compound Ag_2SnSe_3, in agreement with the nominal composition 2: 1: 3. In the SEM micrographs it was observed that the material has a laminar layered structure.

The powder diffraction pattern obtained for the laminar compound semiconductor with synchrotron x-rays, showed that it crystallizes in the monoclinic system with especial group P2/m and the following cell parameters a = 7.977 Å, b = 7.912 Å, c = 13.023 Å, β = 101.734°, V = 804.79 Å. The electron microscopy images in the form of annular dark field show the laminar structure and the presence of a single phase in the material. The selected area diffraction pattern, taken along the [010] direction indicated that the point group symmetry of the semiconductor laminate is 2/m. The high-resolution micrographs obtained for the Ag_2SnSe_3laminar compound under study show the high degree of crystallinity and the sequence of interatomic planes observed in different areas. Also in some areas crystalline defects were observed.

ACKNOWLEDGEMENT

R.A.G. thanks Professor Jordi Rius for providing synchrotron radiations data (ALBA)-Catalonia-Spain.

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