ppi 201502ZU4659
Esta publicación científica en formato digital es continuidad de la revista impresa
ISSN 0254-0770 / Depósito legal pp 197802ZU38

REVISTA TECNICA

DE LA FACULTAD DE INGENIERIA
UNIVERSIDAD DEL ZULIA

MARACAIBO - VENEZUELA

Una Revista Internacional Arbitrada
que está indizada en las publicaciones
de referencia y comentarios:

- Science Citation Index (SCIExpanded)
- Compendex
- Chemical Abstracts
- Metal Abstracts
- World Aluminium Abstracts
- Mathematical Reviews
- Petroleum Abstracts
- Current Mathematical Publications
- MathSci (online database)
- Revencyt
- Materials Information
- Periódica
- Actualidad Iberoamericana

Rev. Téc. Ing. Univ. Zulia. Vol. 41, No. 3, 140-146, 2018

Synthesis, thermal analysis and structural characterization of the ternary compound Ag_2SnTe_3

Delgado Gerzon-E[1], Pirela Maria[2], Velásquez Ana[2], Villarreal Manuel[3], Fernández Braulio[3], Grima-Gallardo Pedro[3,4]

[1]Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela
[2]Laboratorio de Materiales y Centro Multidisciplinario de Ciencias, Instituto Venezolano de Investigaciones Científicas, Caracas 1020 y Mérida 5101, Venezuela
[3]Centro de Estudios de Semiconductores, Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela
[4]Centro Nacional de Tecnologías Ópticas y Centro Investigaciones de Astronomía, Mérida 5101, Venezuela

e-mail: gerzon@ula.ve; mariapirelabracho21@gmail.com; avelasqu@ivic.gob.ve; mavu@ula.ve; braulio@ula.ve; peg1952@gmail.com

Abstract

The ternary compound Ag_2SnTe_3 has been synthesized and investigated by means of X-ray powder diffraction and its structure has been refined by the Rietveld method. The thermal differential analysis indicates a melting point of 343 ºC for this compound. The powder pattern was composed by 86.5% of the principal phase Ag_2SnTe_3 and 13.5% of a secondary phase identified as the binary SnTe. The compound Ag_2SnTe_3 crystallizes in the monoclinic space group Cc (Nº 9), Z = 4, with unit cell parameters a = 7.4420(1) Å, b = 12.8377(1) Å, c = 7.4025(1) Å, β = 109.54(1) °, and V =666.5(2) Å^3. The refinement of 36 instrumental and structural parameters converged to Rp = 8.1 %, Rwp = 9.6 %, Rexp = 7.1 %, S = 1.4, for 5501 step intensities and 290 independent reflections. The structure of Ag_2SnTe_3 can be described as an adamantane compound derivative of the sphalerite structure.

Key words: Chalcogenides; Chemical synthesis; Thermal analysis; X-ray powder diffraction; Crystal structure.

Síntesis, análisis térmico y caracterización estructural del compuesto ternario Ag_2SnTe_3

Resumen

El compuesto ternario Ag_2SnTe_3 ha sido sintetizado e investigado mediante difracción de rayos-X en muestras policristalinas y su estructura cristalina ha sido refinada utilizando el método Rietveld. El análisis térmico diferencial indica que su punto de fusión es 343 °C. El patrón de difracción se compone de 86,5 % de la fase principal Ag_2SnTe_3 y 13,5 % de una fase secundaria identificada como el binario SnTe. El compuesto Ag_2SnTe_3 cristaliza en el grupo espacial monoclínico Cc (Nº 9), Z = 4, con parámetros de celda unidad a = 7,4420(1) Å, b = 12,8377(1) Å, c = 7,4025(1) Å, β = 109,54(1) °, y V =666,5(2) Å^3. El refinamiento de 36 parámetros instrumentales y estructurales convergió a las figuras de mérito Rp = 8,1 %, Rwp = 9,6 %, Rexp = 7,1 %, S = 1,4, para 5501 intensidades y 290 refecciones independientes. La estructura del ternario Ag_2SnTe_3 puede ser descrita como un compuesto adamantano derivado de la estructura esfalerita.

Palabras clave: Calcogenuros; Síntesis química; Análisis térmico; Difracción de rayos-X en muestras policristalinas; Estructura cristalina.

Introduction

Ternary compounds belonging to the family Cu_2-IV-VI_3 (IV= Ge, Sn, VI = S, Se, Te) have interesting semiconducting and optoelectronic properties, mainly in applications as photovoltaic and acoustic-optic devices in the near infrared [1,2]. These materials belong to the normal structure compounds (I_2-IV-VI_3) derivatives of the II-VI binary semiconductors [3] and have low melting points which diminish with increments of the atomic number of the anions. The crystal structure of the ternaries Cu_2GeS_3 [4], Cu_2GeSe_3 [5], Cu_2GeTe_3 [6], Cu_2SnS_3 [7], Cu_2SnSe_3 [8] and Cu_2SnTe_3 [9] have been investigated by powder and single-crystal X-ray diffraction. These materials have received considerable attention recently for acousto-optic applications due to their low band gaps, low melting points, high mean atomic weights and high refractive indices [10-15]. On the other hand, silver-containing ternary compounds have been very little studied structurally and the limited information found in the literature is concerning some of their physical properties [16-20]. In particular for the ternary Ag_2SnTe_3, the synthesis, electrical and optical properties were reported [17], however its crystal structure was not characterized.

Therefore, in this work a complete structural analysis of the ternary compound Ag_2SnTe_3 is performed by using X-ray powder diffraction data.

Experimental

Synthesis

The sample was synthesized by using the direct fusion technique. Stoichiometric quantities of Ag, Sn and Te elements were charged in an evacuated and sealed quartz ampoule, which was previously subject to pyrolysis in order to avoid reaction of the starting materials with quartz. The fusion process was carried out into a furnace (vertical position) heated up to 1150 ºC at a rate of 60 ºC/hour. The ampoule was kept at this temperature for a period of 12 days. Finally, the sample was cooled to room temperature at a rate of 6 ºC/hour during 2 days. The furnace was then turned off and the ingot cooled down to room temperature.

Chemical Analysis (EDX)

Chemical analysis of the sample was carried out with a Hitachi S-2500 scanning electron microscope (SEM) equipped with a Kevex EDX accessory. Three different regions of the ingot were scanned and the average atomic percentages are: Ag (30.5%), Sn (17.2%) and Te (52.5%), which gave an atomic ratio close to the ideal value 2:1:3. The error in standardless analysis was around 5%.

Differential thermal analysis (DTA)

Differential thermal analysis (DTA) measurements were obtained, in the temperature range between 20 and 1150 ºC, using a Perkin-Elmer DTA-7 with aluminum and gold used as reference materials. The charge was of powdered alloy of approximately 100 mg weight. The error in determining these temperatures is of about ±10 °C.

X-ray powder diffraction (XRD)

For the X-ray analysis, a small quantity (~100 mg) of the sample was ground mechanically in an agate mortar and pestle. The resulting powder was mounted on a zero-background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data were collected at 295(1) K, in θ/θ reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (CuKα radiation: λ= 1.54059 Å; 30kV, 15mA) and a diffracted beam graphite monochromator. A fixed aperture and divergence slit of 1 mm, a 0.1 mm monochromator slit, and 0.6 mm detector slit were used. The specimen was scanned 10 to 120° 2θ, with a step size of 0.02° and a counting time of 45s. Quartz was used as an external standard.

Results and discussion

Figure 1 shows the DTA curve for the ternary compound Ag_2SnTe_3. A sharp endothermic peak observed at 343 °C corresponds to the compound melt (Tf). At a temperature 416 °C, one sharp endothermic peak occurred corresponding to the binary SnTe.

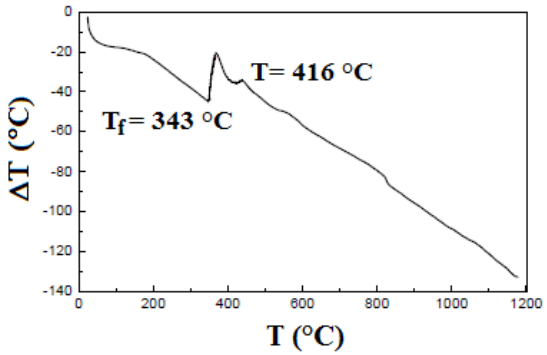

Figure 1. DTA curve for the ternary Ag_2SnTe_3

The X-ray diffractogram of Ag_2SnTe_3 is shows in Figure 2. A search in the ICDD-PDF database [21] using the software available with the diffractometer was performed, and one known phase present in small quantities were readily identified: SnTe (PDF N° 46-1210). The first intense peaks corresponding to the phase of interest were indexed in a monoclinic cell using the Dicvol04 program [22], with unit cell parameters a = 7.450 Å, b = 12.840 Å, c = 7.415 Å, β = 109.4 °. A detailed pattern examination of the main phase, taking into account the sample composition and unit cell parameters, established that this material is isomorphic with Cu_2SnSe_3 compound [8], which crystallize in a monoclinic cell, space group Cc (Nº 9).

The Rietveld refinement [23] of the Ag_2SnTe_3 structure was carried out using the Fullprof program [24]. Initial positional parameters were taken from those of Cu_2SnSe_3 [8] and unit cell parameters were those obtained above. Atomic positions of the binary SnTe compound [25] were included as secondary phase in the refinement. The angular dependence of the peak full width at half maximum (FWHM) was described by the Cagliotti's formula ($FWHM=(Utan^2\theta+Vtan\theta+W)^{1/2}$) [26]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function [27]. The background variation was described by a polynomial with six coefficients.

With the diffraction data available it was only possible to described the thermal motion of the atoms by one overall isotropic temperature factor. The refinement converged to the final profile agreement factors summarized in Table 1. The Rietveld semi-quantitative analysis [28] converged to the following weight fraction percentages: Ag_2SnTe_3 (86.7 %) and SnTe (13.3 %). The final Rietveld plot is shown in Figure 2. Unit cell parameters, atomic coordinates, isotropic temperature factor, bond distances and angles are shown in Table 2. Figure 3 shows the unit cell diagram of Ag_2SnTe_3.

The structure of Ag_2SnTe_3 can be described as derivative of the sphalerite structure. As expected for adamantane structure compounds [3], each anion is coordinated by four cations (Te1 by two Ag and two Sn, Te2 and Te3 by three Ag and one Sn) located at the corners of a slightly distorted tetrahedron. Ag and Sn cations are similarly coordinated by four anions. Figure 3 shows the tetrahedral coordination around the cations. The Ag-Te and Sn-Te bond distances compare quite well with those observed in other adamantane structures, such as $AgGaTe_2$ [29], $AgIn_5Te_8$ [30], Cu_2SnTe_3 [9], Mn_2SnTe_4 [31], $AgFe_2GaTe_4$ [32] and $AgInTe_2$ [33].

Table 1: Rietveld refinement details for Ag_2SnTe_3

Molecular formula	Ag_2SnTe_3	Diffractometer	Siemens D5005
Molecular weight (g/mol)	717.25	λ (Å)	1.54056 CuK_α
a (Å)	7.4420(1)	Data range 2θ (°)	10-120
b (Å)	12.8377(1)	Step size 2θ (°)	0.02
c (Å)	7.4025(1)	Counting time (s)	45
β (°)	109.54(1)	N°. step intensities	5501
V (Å3)	666.5(2)	N° independent refl.	290
Z	4	Peak-shape profile	Pseudo-Voigt
Crystal system	monoclinic	R_p (%)	8.1
Space group	Cc (N° 9)	R_{wp} (%)	9.6
D_{calc} (g/cm^{-3})	7.15	R_{exp} (%)	7.1
Temperature (K)	295	S	1.4

$$R_p = 100 \sum|y_{obs} - y_{calc}| / \sum|y_{obs}| \qquad R_B = 100 \sum_k|I_k - Ic_k| / \sum k |I_k|$$

$$R_{wp} = 100 [\sum w|y_{obs} - y_{calc}|^2 / \sum w|y_{obs}|^2]^{1/2} \qquad S = [R_{wp} / R_{exp}]$$

$$Rexp = 100 [(N+C) / \sum_w(y_{obs}^2)]^{1/2} \qquad N\text{-}P\text{+}C = \text{degrees of freedom}$$

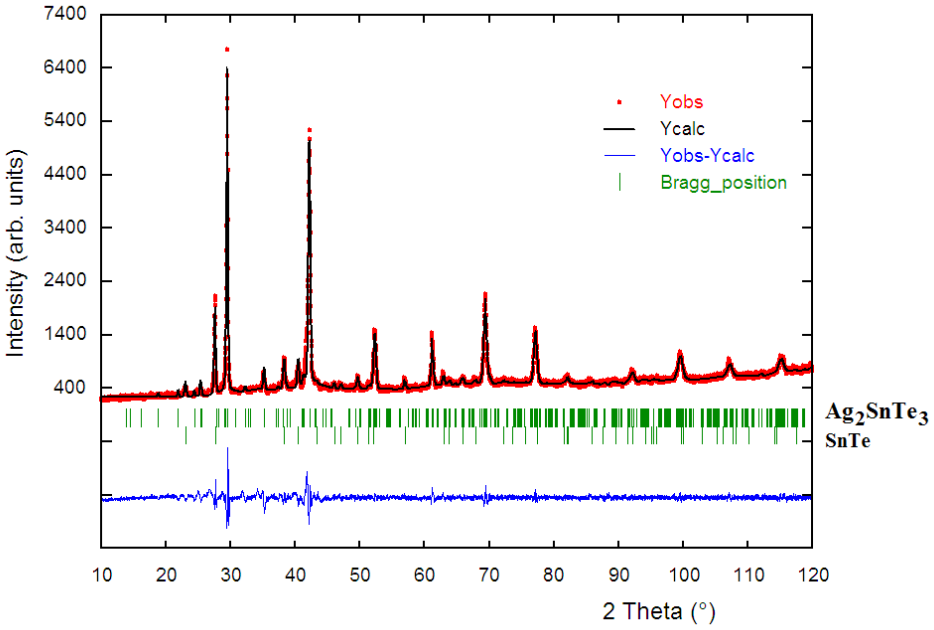

Figure 2. Observed (circles), calculated (solid line), and difference plot of the final Rietveld refinement of Ag_2SnTe_3

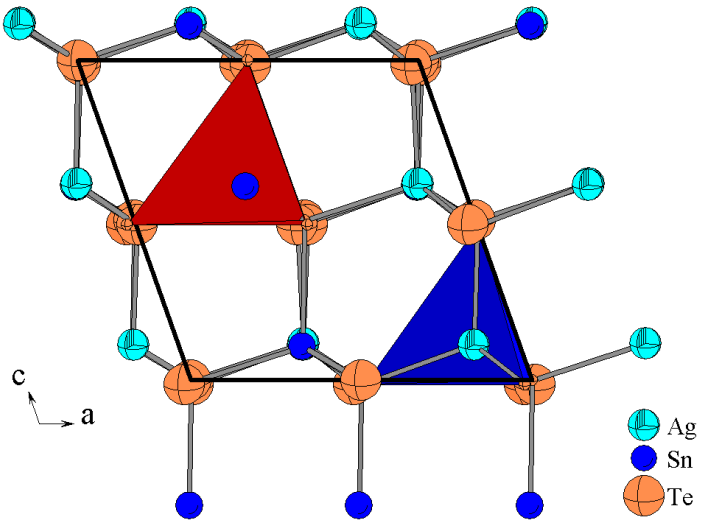

Figure 3. Unit cell diagram for the compound Ag_2SnTe_3, showing the tetrahedral coordination around the cations

Table 2
Atomic coordinates, isotropic temperature factors and geometric parameters (Å, °) for Ag_2SnTe_3

Atom	Ox.	Wyck.	x	y	z	foc	B (Å2)
Ag1	+1	4a	0.367(2)	0.251(1)	0.612(2)	1	0.7(5)
Ag2	+1	4a	0.370(1)	0.418(2)	0.116(1)	1	0.7(5)
Sn	+4	4a	0.363(2)	0.091(1)	0.107(1)	1	0.7(5)
Te1	-2	4a	0.00000	0.409(2)	0.00000	1	0.7(5)
Te2	-2	4a	-0.026(1)	0.078(1)	-0.014(1)	1	0.7(5)
Te3	-2	4a	0.503(2)	0.259(1)	-0.014(1)	1	0.7(5)

Ag1 - Te1^{i}	2.61(2)	Ag2 - Te1	2.59(1)	Sn - Te1^{i}	2.73(2)
Ag1 - Te2^{i}	2.54(3)	Ag2 - Te2^{i}	2.60(1)	Sn - Te2	2.77(3)
Ag1 - Te3^{ii}	2.61(2)	Ag2 - Te2^{iv}	2.50(3)	Sn - Te1v	2.74(1)
Ag1 - Te3^{iii}	2.56(2)	Ag2 - Te3	2.59(3)	Sn - Te3	2.68(2)
Te3^{ii} - Ag1 - Te2^{i}	106.8(6)	Te3^{iii} - Ag1 - Se1^{i}	108.8(6)	Te3^{ii} - Ag1 - Te3^{iii}	112.1(6)
Te3^{iii} - Ag1 - Te2^{i}	108.9(6)	Te2^{i} - Ag1 - Se1^{i}	111.4(5)	Te1^{i} - Ag1 - Te3^{ii}	108.8(5)
Te2^{i} - Ag2 - Te1^{i}	105.1(3)	Te2^{i} - Ag2 - Te2^{iv}	111.7(4)	Te1 - Ag1 - Te2^{iv}	109.9(4)
Te2^{i} - Ag2 - Te3	113.1(4)	Te3 - Ag2 - Te2^{iv}	107.4(1)	Te1 - Ag2 - Te3	109.7(5)
Te2 – Sn - Te1^{i}	108.9(3)	Te1^{v} - Sn - Te3	115.3(6)	Te2 - Sn - Te3	107.9(3)
Te2 - Sn - Te1v	107.8(5)	Te1^{i} - Sn - Te1^{v}	105.2(3)	Te1^{i} - Sn - Te3	111.3(5)

Symmetry codes: $^{(i)}$ 0.5+x, 0.5-y, 0.5+z; $^{(ii)}$ x, y, 1+z; $^{(iii)}$ -0.5+x, 0.5-y, 0.5+z; $^{(iv)}$ 0.5+x, 0.5+y, z; $^{(v)}$ 0.5+x, -0.5+y, z; $^{(vi)}$ -0.5+x, 0.5-y, -0.5+z; $^{(vii)}$ 0.5+x, 0.5-y, -0.5+z; $^{(viii)}$ -1+x, y, z; $^{(ix)}$ x, -y, -0.5+z; $^{(x)}$ -0.5+x, -0.5+y, z; $^{(xi)}$ x, 1-y, -0.5+z; $^{(xii)}$ -0.5+x, 0.5+y, z.

Conclusions

The ternary compound Ag_2SnTe_3 was synthesized by using the direct fusion technique. The thermal differential analysis indicates a melting point of 343 ºC for this compound. The refinement of the crystal structure of Ag_2SnTe_3 by Rietveld method from X-ray powder diffraction confirms that this compound crystallizes in the monoclinic space group Cc, and can be described as derivative of the sphalerite structure. The structure consists of a three-dimensional arrangement of slightly distorted $AgTe_4$ and SnTe4 tetrahedra.

Acknowledgements

This work was supported by CDCHT-ULA (Grants C-1885-14-05-B and NURR-C-606-15-05-B) and FONACIT (Grants LAB-97000821, PEII-1697 and project No 2011001341).

References

[1] Berger, L.I., Prochukhan, V.: "Ternary Diamond-Like Semiconductors", Consultant Bureau, New York, 1969.

[2] Coughlan C., Ibáñez M., Dobrozhan O., Singh A., Cabot A., Ryan K.M.: "Compound Copper Chalcogenide Nanocrystals", Chemical Reviews, Vol. 117, No. 9 (2017) 5865-6109.

[3] Parthé E.: Intermetallic Compounds, Principles and Applications. Vol. 1, In: J.H. Westbrook, R.L. Fleischer (eds), John Wiley & Sons, Chichester, UK (1995).

[4] Chalbaud L.M., Díaz de Delgado G., Delgado J.M., Mora A.E., Sagredo V.: "Synthesis and single-crystal structural study of Cu_2GeS_3", Materials Research Bulletin, Vol. 32, No. 10 (1997) 1371-1376.

[5] Parthé E., Garín J.: "Zinkblende-und wurtzitüberstrukturen bei ternären chalkogeniden der zusammensetzung 12463", Monatshefte fur Chemie, Vol. 102, No. 5 (1971) 1197-1208.

[6] Delgado G.E., Mora A.J., Pirela M., Villarreal M.A., Velásquez A., Fernández B.J.: "Structural refinement of the ternary chalcogenide compound Cu_2GeTe_3 by X-ray powder diffraction". Phys. Stat. Sol. (a), Vol. 201, No. 12 (2004) 2900-2904.

[7] Onoda M., Chen X., Sato, A., Wada, H.: "Crystal structure and twinning of monoclinic Cu_2SnS_3", Materials Research Bulletin, Vol. 35, No. 9 (2000) 1563-1570.

[8] Delgado G.E., Mora A.J., Marcano G., Rincón C.: "Crystal structure refinement of the semiconducting compound Cu_2SnSe_3 from X-ray powder diffraction data". Materials Research Bulletin, Vol. 38, No. 15 (2003) 1949-1955.

[9] Delgado G.E., Mora A.J., Marcano G., Rincón C.: "Crystal structure refinement of the ternary compound Cu_2SnTe_3 by X-ray powder diffraction". Crystal Research and Technology, Vol. 43, No. 4 (2008) 433-437.

[10] Rincón C., Marcano G., Marín G., Mora A.J., Delgado G.E., Herrera-Pérez J.L., Mendoza-Alvarez J.G., Rodríguez P.: "Raman scattering and X-ray diffraction study in Cu_2GeSe_3". Solid State Communications, Vol. 146, No. 1-2 (2008) 65-68.

[11] Lu X., Morelli D.T.: "Thermoelectric properties of Mn-doped Cu_2SnSe_3", Journal of Electronic Materials, Vol. 41, No. 6 (2012) 1554-1558.

[12] Raju C., Falmbigl M., Rogl P., Heinrich P., Royanian E., Bauer E., Mallik R.C.: "Thermoelectric properties of Zn doped Cu_2SnSe_3", Materials Chemistry and Physics, Vol. 147, No. 3 (2014) 1022-1028.

[13] Choi S.G., Kang J., Li J., Haneef H., Podraza N.J., Beall C., Wei S.-H., Christensen S.T., Repins I.L.: "Optical function spectra and bandgap energy of Cu_2SnSe_3", Applied Physics Letters, Vol. 106 (2015) 043902 (5 pp).

[14] Wubet W., Kuo D.-H.: "Effects of copper excess and copper deficiency on the structural and electrical properties of bulk $CuxSnSe_3$ with x=1.6–2.2", Journal of Solid State Chemistry, Vol. 226, No. 3 (2015) 120-125.

[15] Rincón C., Marcano G., Casanova R., Delgado G.E., Marín G., Nieves L., Sanchez-Perez G.: "Optical absorption, Raman spectra and electrical properties of Mn-doped Cu_2SnSe_3 semiconductor compound". Physica Status Solidi B, Vol. 253, No. 4 (2016) 697-704.

[16] Piskach L.V., Parasyuk O.V.: "The Ag_2GeS_3-CdS system", Polish Journal of Chemistry, Vol. 72, No. 6 (1998) 1112-1115.

[17] Dávila R., Fernández B.J.: "Electrical and optical properties of Ag_2SnSe_3 and Ag_2SnTe_3", Institute of Physics Conference Series, Vol. 152, No. 1 (1998) 531-533.

[18] Velásquez A., Belandria E., Fernández B.J., Avila R., Delgado G.E., Acosta G.D.: "Synthesis and characterization of the ternary compound Ag_2GeSe_3", Physica Status Solidi (b), Vol. 220, No. 1 (2000) 683-686.

[19] Belandria E., Avila R., Fernandez B.J.: "Synthesis and characterization of the ternary compound Ag_2SnS_3", Japanese Journal of Applied Physics, Vol. 39, Sup. 39-1 (2000) 132-133.

[20] Fedorchuk A.O., Zhbankov O.Y., Lakshminarayana G., Kityk I.V., Tokaichuk Y., Myronchuk G.L., Davydyuk G.Y., Yakymchuk O.V., Parasyuk O.V.: "Synthesis and spectral features of Ag_2SnS_3 crystals", Materials Chemistry and Physics, Vol. 135, No. 2-3 (2012) 249-253.

[21] International Centre for Diffraction Data (ICDD), Powder Diffraction File (Set 1-65). Newtown Square, PA, USA, 2013.

[22] Boultif A., Louër D.: "Powder pattern indexing with the dichotomy method". Journal of Applied Crystallography, Vol. 37, No. 5 (2004) 724-731.

[23] Rietveld H.M.: "A profile refinement method for nuclear and magnetic structures", Journal of Applied Crystallography, Vol. 2, No. 2 (1969) 65-71.

[24] Rodriguez-Carvajal J.: "Recent advances in magnetic structure determination by neutron powder diffraction", Physica B: Condensed Matter, Vol. 192, No. 1-2 (1993) 55-69.

[25] Rogacheva E.I., Gorne G.V., Laptev S.A., Arinkin A.V., Vesiene T.B.: "Concentration dependences of properties in the region of homogeneity of SnTe", Inorganic Materials, Vol. 22, No. 1 (1986) 34-37.

[26] Cagliotti G., Paoletti A., Ricci F.P.: "Choice of collimators for a crystal spectrometer for neutron diffraction", Nuclear Instruments, Vol. 3, No. 4 (1958) 223-228.

[27] Thompson P., Cox D.E., Hastings J.B.: "Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al2O3". Journal of Applied Crystallography, Vol. 20, No. 2 (1987) 79-83.

[28] Hill R.J., Howard J.C.: "Quantitative phase analysis from neutron powder diffraction data using the Rietveld method", Journal of Applied Crystallography, Vol. 20, No. 6 (1987) 467-474.

[29] Guittard M., Rivet J., Mazurier A., Jaulmes S., Fourcroy P.H.: "Systeme Ag_2Te-Ga_2Te_3. phases intermediaires. determinations structurales. diagramme de phase Ag_2Te-Ga_2Te_3 system intermediate phase", Materials Research Bulletin, Vol. 23, No. 2 (1988) 217-225.

[30] Mora A.J., Delgado G.E., Pineda C., Tinoco T.: "Synthesis and structural study of the $AgIn_5Te_8$ compound by X-ray powder diffraction", Physica Status Solidi (a), Vol. 201, No. 7 (2004) 1477-1483.

[31] Delgado G.E., Mora A.J., Contreras J.E., Betancourt L.: "Synthesis and characterization of ternary compound, Mn_2SnTe_4". Bulletin of Materials Science, Vol. 33, No. 3 (2010) 247-249.

[32] Delgado G.E., Quintero E., Tovar R., Grima-Gallardo P., Quintero M.: "Synthesis and crystal structure of the quaternary compound $AgFe_2GaTe_4$", Journal of Alloys and Compounds, Vol. 613, No. 1 (2014) 143-145.

[33] Delgado G.E., Mora A.J., Pineda C., Ávila R., Paredes S.: "X-ray powder diffraction data and Rietveld refinement of the ternary semiconductor chalcogenides $AgInSe_2$ and $AgInTe_2$". Revista Latinoamericana de Metalurgia y Materiales, Vol. 35, No. (1) (2015) 110-117.

Recibido el 17 de Junio de 2017
En forma revisada el 23 de Mayo de 2018

UNIVERSIDAD DEL ZULIA

REVISTA TECNICA

DE LA FACULTAD DE INGENIERIA
UNIVERSIDAD DEL ZULIA

Vol. 41. N°3, Septiembre - Diciembre 2018_____

Esta revista fue editada en formato digital y publicada el 31 de Agosto de 2018, por el ***Fondo Editorial Serbiluz, Universidad del Zulia. Maracaibo-Venezuela***

www.luz.edu.ve
www.serbi.luz.edu.ve
produccioncientifica.luz.edu.ve