crystals

$AgSn[Bi_{1-x}Sb_x]Se_3$: Synthesis, Structural Characterization, and Electrical Behavior

Paulina Valencia-Gálvez [1], Daniela Delgado [1], María Luisa López [2], Inmaculada Álvarez-Serrano [2], Silvana Moris [3,*] and Antonio Galdámez [1,*]

[1] Departamento de Química, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Chile; paulygav@uchile.cl (P.V-G.); dani.delgado.m@gmail.com (D.D.)
[2] Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid; marisal@quim.ucm.es (M.L.L.); ias@quim.ucm.es (I. A-S.)
[3] Centro de Investigación de Estudios Avanzados del Maule (CIEAM), Vicerrectoría de Investigación y Postgrado, Universidad Católica del Maule, Avenida San Miguel 3605, Talca 3480112, Chile
* Correspondence: smoris@ucm.cl (S.M.); agaldamez@uchile.cl (A.G.)

Supplementary Materials

Table S1. Final atomic parameters for $AgSnBiSe_3$ from Rietveld refinement Fullprof using XRD data using cubic model at room temperature. Selected Bond distances (Å) and angles (degrees).

Lattice (Å)	Atoms	Wyckoff	*x*	*y*	*z*	Occ.
a = 5.86180(6) Å	Se1	1a	0	0	0	1.0000
SpGR *Pm-3m*	Se2	3c	½	½	0	3.0000
	Ag1	3d	½	0	0	0.4173
	Bi1	3d	½	0	0	1.4173
*R*b = 3.32	Sn1	3d	½	0	0	0.9173
*R*wp = 4.44	Ag2	1b	½	½	½	0.5363
	Sn2	1b	½	½	½	0.3363
	Bi2	1b	½	½	½	0.2363

Bi1/Sn1/Ag1-Se1: 2.93090(3) Å Bi2/Sn2/Ag2-Se2: 2.93090(3) Å Se1-Ag/Sn/Bi-Se1: 180.0° Se1-Ag/Bi/Sn/-Se2

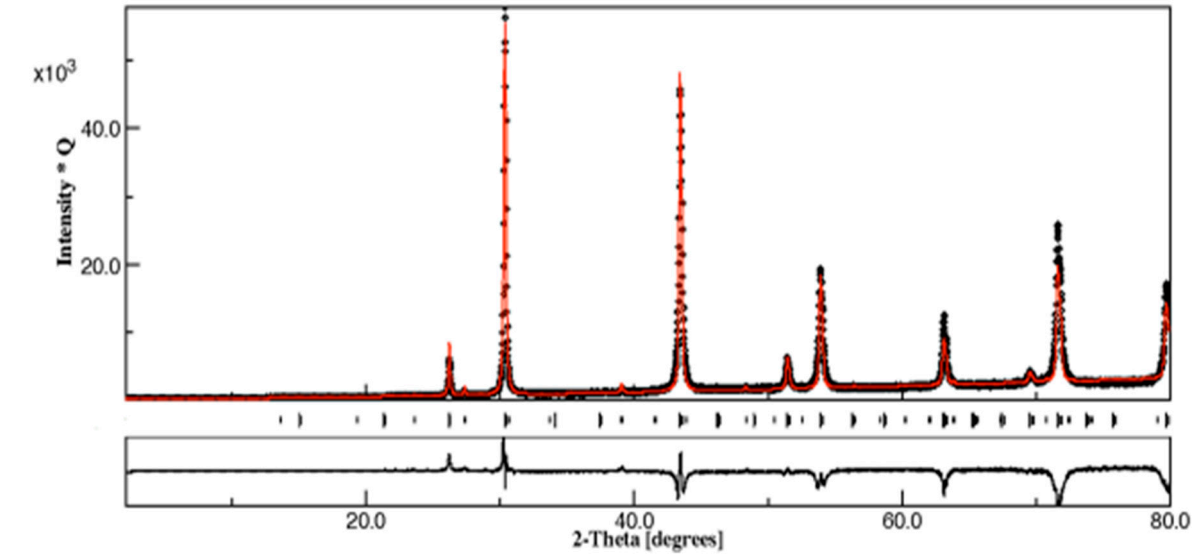
Table S2. Final atomic parameters for $AgSnBiSe_3$ from Rietveld refinement Fullprof using XRD data using tetragonal model at room temperature. Selected Bond distances (Å) and angles (degrees).

Lattice (Å)	Atoms	Wyckoff	*x*	*y*	*z*	Occ.
a = 4.14361(16) Å	Se1	1a	0	0	0	1.0000
c = 5.8633(4) Å	Se2	1d	½	½	½	1.0000
SpGR *P4/mmm*	Ag1	1b	1	0	½	0.1700
	Bi1	1b	1	0	½	0.4100
*R*b = 5.72	Sn1	1b	1	0	½	0.4200
*R*wp = 4.88	Ag2	1c	½	½	0	0.5000
	Sn2	1c	½	½	0	0.2400
	Bi2	1c	½	½	0	0.2600

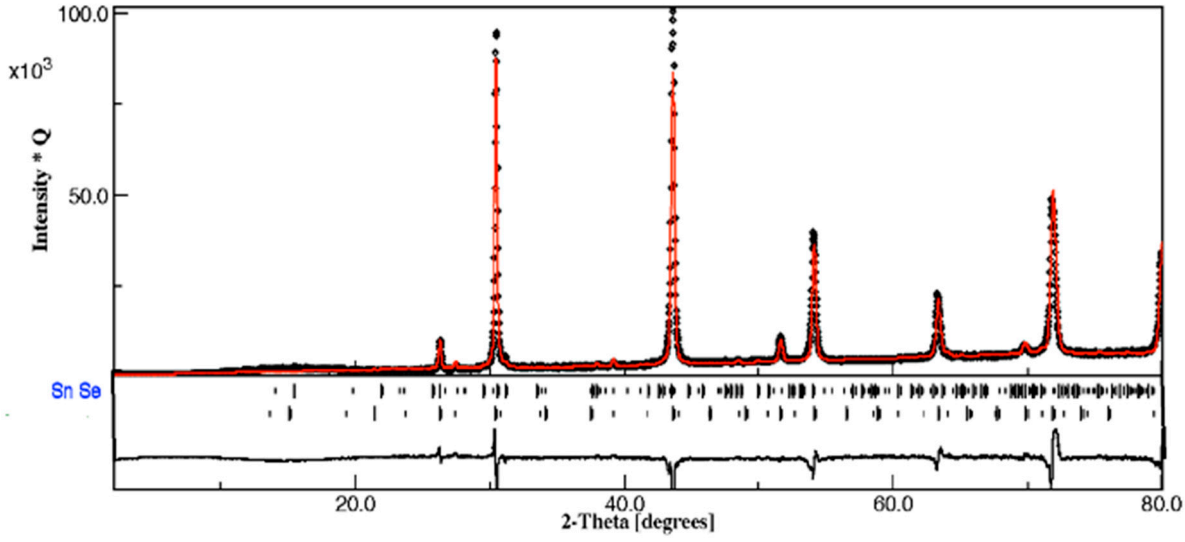
Bi1/Sn1/Ag1-Se1: 2.93165(20) Å Bi2/Sn2/Ag2-Se2: 2.93165(20) Å Se1-Ag/Sn/Bi-Se1: 180.0° Se1-Ag/Bi/Sn/-Se2

Table S3. Cell parameters of $AgSn[Bi_{1-x}Sb_x]Se_3$ and $AgSn_2[Bi_{1-x}Sb_x]Se_4$ systems indexed on cubic *Pm-3m* and tetragonal *P4/mmm* space groups.

Compound	a_c (Å)	V (cubic, Å^3)	$a_t = b_t$ (Å)	c_t (Å)	V (tetragonal, Å^3)
$AgSn_2Sb_{0.2}Bi_{0.8}Se_4$	6.013	217.5	4.252	6.020	108.8
$AgSn_2Sb_{0.8}Bi_{0.2}Se_4$	5.886	203.9	4.160	5.890	101.9
$AgSnBiSe_3$	5.861	202.1	4.144	5.863	101.3
$AgSnSb_{0.3}Bi_{0.7}Se_3$	5.851	200.5	4.135	5.853	100.1
$AgSnSb_{0.8}Bi_{0.2}Se_3$	5.846	199.8	4.133	5.847	99.89



(**a**)



(**b**)

Figure S1. Representative powder XRD data for $AgSn[Bi_{0.8}Sb_{0.2}]Se_3$ tetragonal model (**a**) and $AgSn_2[Bi_{0.2}Sb_{0.8}]Se_4$ cubic model (**b**) including profile fit, profile difference, and profile residuals from the corresponding Rietveld refinement using MAUD program. The intensities are plotted as the intensity *Q or Intensity to show low-intensity reflections as well. The extra reflection for $AgSn_2Sb_{0.2}Bi_{0.8}Se_4$ was indexed to SnSe (*Pnma* space group) with 3.0(4)–4.0(5) in weight %.

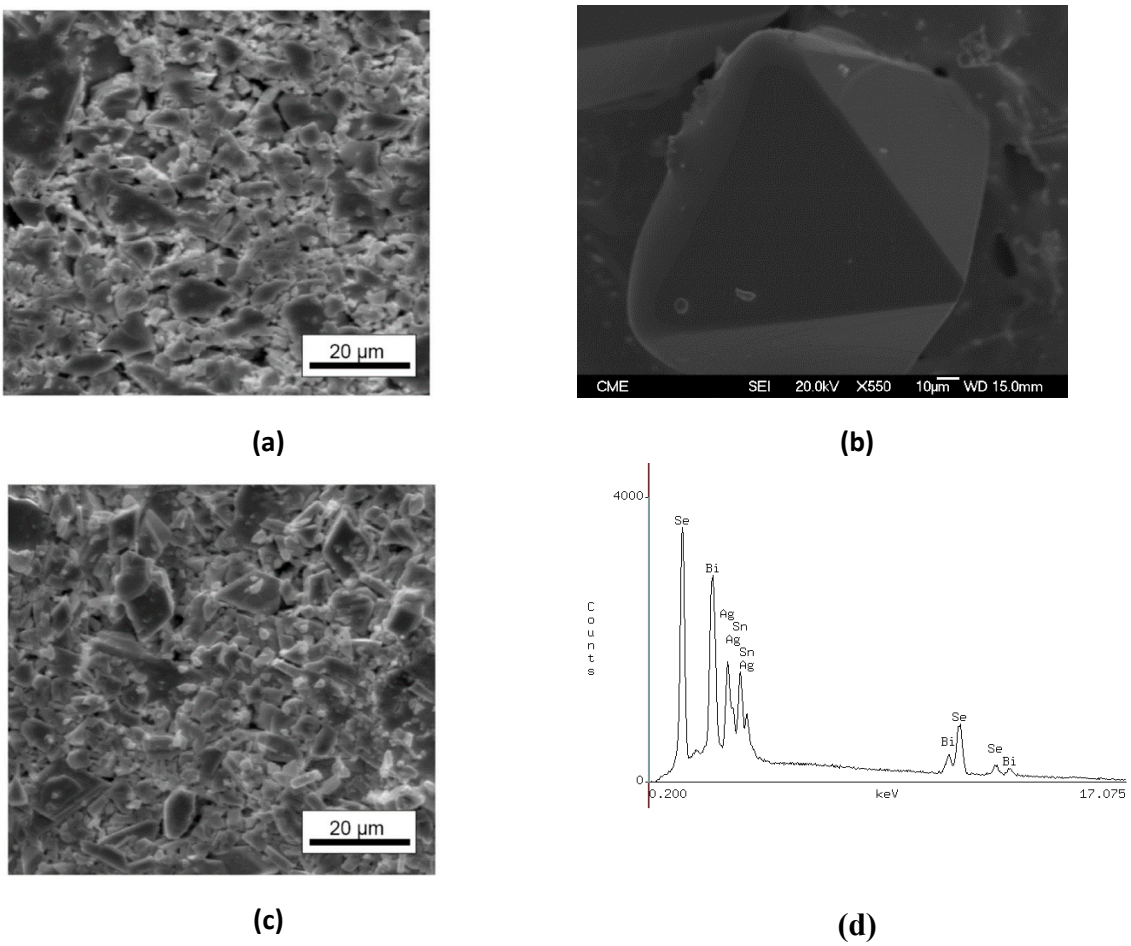


Figure S2. SEM micrographs of $AgSnBiSe_3$ sintered and (**a**) and $AgSnSbSe_3$ (**b**) sintered at 673 K 24 h and 973 K 12 h in argon atmosphere. SEM- BS image of crystal morphology (**c**) and EDS spectra (**d**) with Chi-sqd = 1.29, Livetime = 60.0 Sec., Volt= 20 kV, Take-off Angle=28.77 deg .

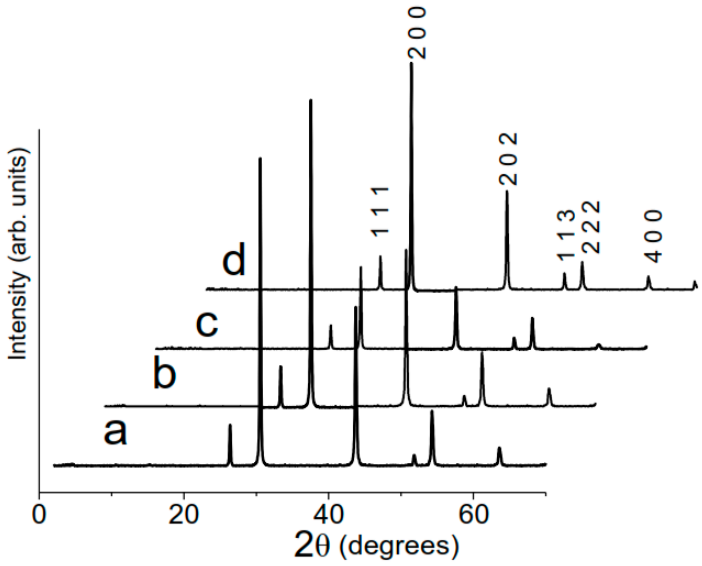


Figure S3. XRD patterns of $AgSnMSe_3$ (*a*) M = Sb (powder sample), (*b*) M = Bi sintered at 673 K in Ar during 12 h (*c*) M = Bi sintered at 923 K in air during 24 h (*d*) M = Bi (powder sample).

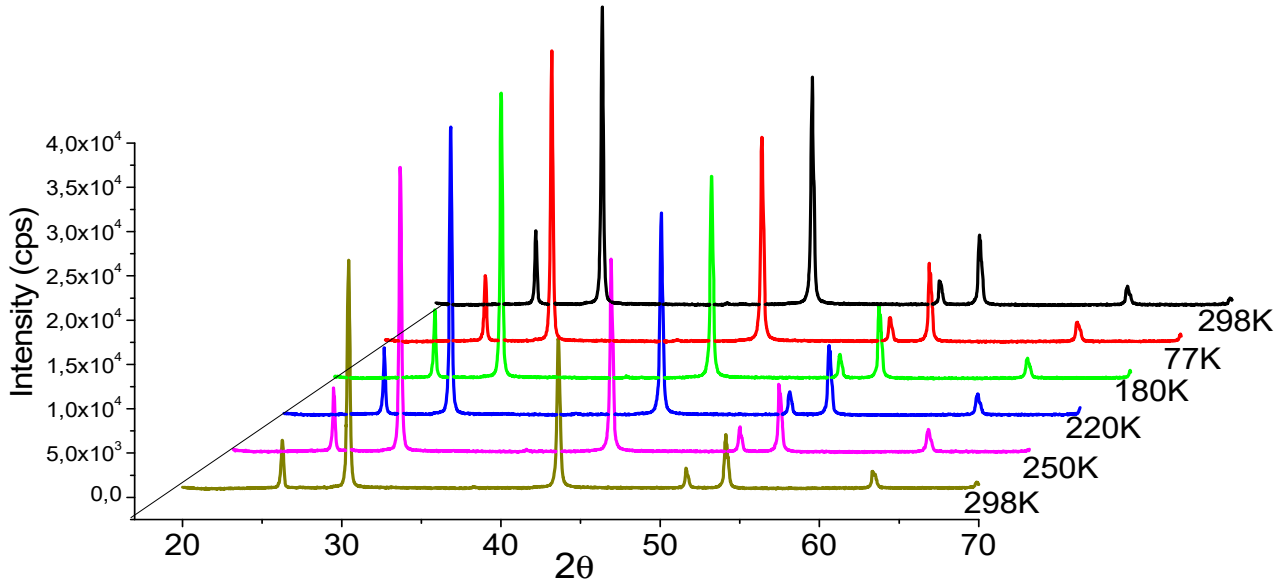


Figure S4. A representative XRD patterns heating/cooling from RT (bottom) up to 77 K of $AgSnBiSe_3$. The final heat treatment is shown in top XRD pattern at 298 K.

Supplementary Materials: The following materials are available online at www.mdpi.com/xxx/s1. Table S1 and S2: Final atomic parameters determined through Rietveld refinement using the Fullprof program; Figure S1: Powder XRD data obtained for the $AgSn_m[Bi_{1-x}Sb_x]Se_{m+2}$ samples from the corresponding Rietveld refinement data; Table S3: Cell parameters of $AgSn[Bi_{1-x}Sb_x]Se_3$ and $AgSn_2[Bi_{1-x}Sb_x]Se_4$; Figure S2: SEM–BS images and ED spectrum of $AgSnBiSe_3$; Figure S3: XRD patterns of the sintered samples; Figure S4: Representative XRD patterns of the samples obtained upon heating/cooling from RT (bottom) to 77 K.

Author Contributions: conceptualization, A.G. and S.M.; methodology and experiments, M.L.L., I. A-S., A.G., and D.D.; writing—original draft preparation, S.M., P.V-G., M.L.L., I. A-S., and A.G.; electrical measurements, M.L.L. and P.V-G. All authors have read and agreed to the final version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable

Informed Consent Statement: Not applicable

Data Availability Statement: The data presented in this study are available in the article.

Acknowledgments: This work was supported by Fondecyt No. 1190856. The authors also acknowledge the CAI center of UCM (HRTEM). We would like to thank Professors Daniela Ruiz and Daniela Herrera for their invaluable contributions to the synthesis of the samples and discussion of the experimental results.

Conflicts of Interest: The authors declare no conflicts of interest.