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STRUCTURAL CHARACTERIZATION OF THE SEMICONDUCTOR CHALCOGENIDE SYSTEM Ag-In-VI (VI = S, Se, Te) BY X-RAY POWDER DIFFRACTION

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The semiconducting system Ag-In-VI with VI = S, Se, Te, was studied by X-ray powder diffraction structure refinements using the Rietveld method. In Ag-In-S, three phases were simultaneously refined: $AgIn_5S_8$ cubic ($Fd\bar{3}m$) $AgInS_2$ tetragonal ($I\bar{4}2d$) and $AgInS_2$ orthorhombic ($Pna2_1$). In Ag-In-Se, the chalcopyrite phase $AgInSe_2$ with space group $I\bar{4}2d$ was found. In Ag-In-Te, the $AgIn_5Te_8$ phase was obtained, which crystallizes in the tetragonal space group $P\bar{4}2m$.

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1. Introduction

The ternary silver chalcogenides of the type Ag-In-VI (VI = S, Se, Te) form very stable stoichiometric compounds with potential application in non-linear optics and solar cells [1,2], due to its electro-physical properties independent of impurities [2]. Following the rules of formation of semiconductor compounds [3,4], in the system Ag-In-VI, stoichiometric compounds with three compositions can be form: $AgInVI_2$, $AgIn_3VI_5$ and $AgIn_5VI_8$, These materials belong to the normal structure compounds (I-III-VI_2) and the defect structure compounds (I-III_3-□-VI_5, I-III_5-$□_2$-VI_8), respectively [5]. Compositions of the type $AgIn_3VI_5$ has not been reported in the literature. In this work, we present the structural characterization of some members of the chalcogenide system Ag-In-VI, using X-ray powder diffraction.

2. Experimental

The samples were synthesized by the melt and annealing technique. Stoichiometric quantities of Ag, In and VI (S, Se, Te) were evacuated in sealed quartz ampoules and deposited into an one zone furnace, and then submitted to direct fusion. The detailed procedure is described elsewhere [6,7]. Chemical analysis of the resultant ingots were carried out with a Hitachi S-2500 SEM equipped with a Kevex EDX accessory. Three different crystals were scanned en each case with the following average atomic percentages results: Ag (18.1%), In (33.8%), S (48.1%) for Ag-In-S; Ag (24.4%), In (26.7%), Se (48.9%) for Ag-In-Se; Ag (7.1%), In (34.5%), Te (58.4%) for Ag-In-Te.

Small quantities of each the samples were ground mechanically in an agate mortar and pestle. The resulting fine powders were mounted on a flat zero-background holder. The X-ray powder diffraction data were collected at room temperature, in θ/θ reflection mode using a Siemens D5005 diffractometer (Bragg-Brentano) equipped with an X-ray tube (CuKα radiation; 40kV, 30mA) and a diffracted beam graphite monochromator. The powder patterns were analyzed by means of the Rietveld method [8] using the Fullprof program [9] and following the same

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procedure employed in the crystal structure analysis performed in the semimagnetic semiconductor compounds Cu_2SnSe_3 (Cc) [10], $CdGaCrS_4$ ($Fd\bar{3}m$) [11], Cu_2GeTe_3 (Imm2) [12], $Cu_2Cd_{0.5}Mn_{0.5}GeSe_4$ ($Pmn2_1$) [13], Fe_2CrSe_4 (I2/m) [14], $Cd_{(1-X)}Mn_XIn_2S_4$ system $Fd\bar{3}m$) [15], $CuFeInSe_3$ ($P\bar{4}2c$) [16], Cu_3TaSe_4 ($P\bar{4}3m$) [17], $CuFe_2InSe_4$ ($I\bar{4}2m$) [18], Cu_2SnTe_3 (Imm2) [19], $CuTaInSe_3$ ($P\bar{4}2c$) [20], $CuTa_2InTe_4$ ($I\bar{4}2m$) [21], $Zn_{0.5}Mn_{0.5}In_2Te_4$ ($I\bar{4}2m$) [22], $CuFeAlSe_3$ and $CuFeGaSe_3$ ($P\bar{4}2c$) [23], Mn_2GeTe_4 (Pnma) [24] and the diluted magnetic semiconductor $CuGa_{(1-X)}Mn_{(X)}Se_2$ ($I\bar{4}2d$) [25].

The whole diffraction data were used in each case. The angular dependence of the peak full width at half maximum (FWHM) was described by Caglioti's formula. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function and the background variations were described by polynomials with six coefficients.

3. Results and discussion

In the Ag-In-S system, three phases were simultaneously characterized from a single X-ray powder diffraction pattern. The structural Rietveld refinement converged to the figures of merit R_{exp} = 8.2%, R_p = 9.1%, R_{wp} = 11.4% and S = 1.4 [8]. The X-ray powder pattern was composed of $AgIn_5S_8$ (42.7%), $AgInS_2$ tetragonal phase (32.7%) and $AgInS_2$ orthorhombic phase (24.6%) [6]. Figure 1 shows the final Rietveld refinement plot and the unit cell diagram for each phase. The $AgIn_5S_8$ crystallizes in the cubic space group $Fd\bar{3}m$, Z = 8, with ***a*** = 10.8265(2) Å, in a spinel-type structure. The description of the structure of $AgIn_5S_8$ in this space group implies a random distribution of the Ag and In atoms among the tetrahedral sites. The $AgInS_2$ ternary compound crystallizes in two polymorphs: a tetragonal chalcopyrite-type phase ($I\bar{4}2d$), Z = 4, with unit cell parameters ***a*** = 5.8760(2) Å, ***c*** = 11.2007(7) Å, and an orthorhombic wurtzite-like phase ($Pna2_1$), Z =4, with ***a*** = 6.9972(6) Å, ***b*** = 8.2733(6) Å, ***c*** = 6.6939(6) Å. These structures can be described as a derivative of the sphalerite and the wurtzite structure, respectively. Ag-S and In-S average distances in both $AgInS_2$ structures are 2.58(5) Å and 2.44(5) Å, respectively.

For the Ag-In-Se system, a chalcopyrite-type structure was found with composition $AgInSe_2$. The Rietveld refinement converged to R_{exp} = 8.3%, R_p = 8.3%, R_{wp} = 10.4% and S = 1.4. Figure 2 shows the Rietveld plot and the unit cell diagram for $AgInSe_2$. This compound crystallizes with tetragonal symmetry ($I\bar{4}2d$) and unit cell parameters: ***a*** = 6.1010(8) Å, ***c*** = 11.708(2) Å. The Ag-Se bond distance is 2.621(2) Å and In-Se 2.593(2) Å. The complete powder diffraction dataset of $AgInSe_2$ was reviewed and the unit cell refined with the NBS*AIDS program [26] in the space group $I\bar{4}2d$. The unit cell parameters obtained were: ***a*** = 6.0988(2) Å, ***c*** = 11.7086(6) Å, with figures of merit M_{19} = 84.0 [27], and F_{19} = 40.7 (0.0071, 66) [28]. These powder data are improved that the two pattern with low quality (PDF 35-1099, 38-0952) reports for $AgInSe_2$ in the ICDD Powder Diffraction Files [29].

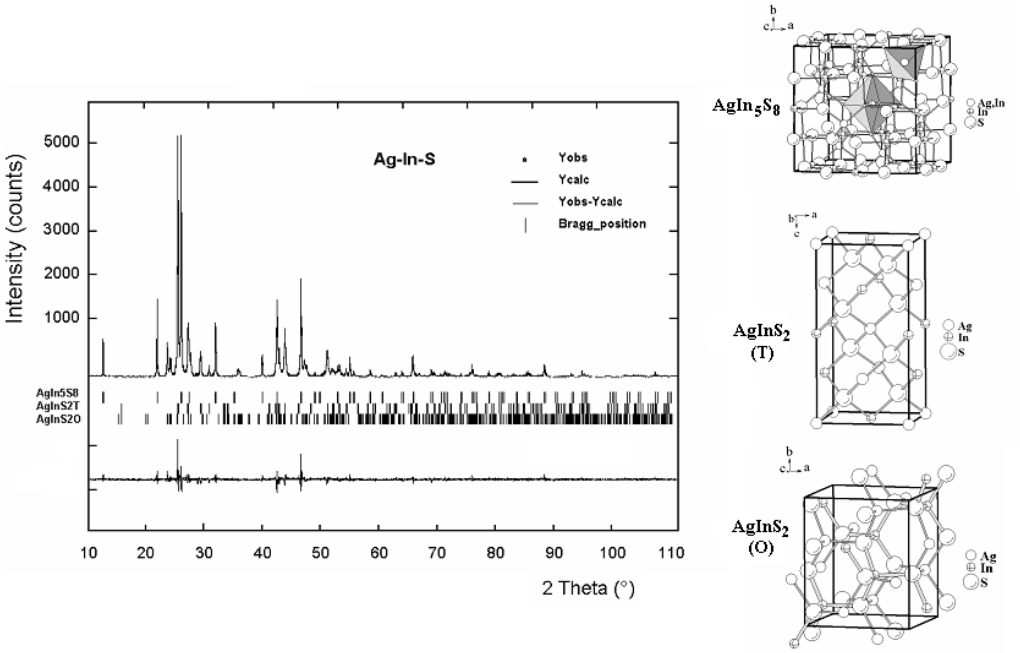

Fig. (1) Final Rietveld plot for the system Ag-In-S and Unit cell diagram for the phases $AgIn_5S_8$ (cubic), $AgInS_2$ (tetragonal) and $AgInS_2$ (orthorhombic), respectively.

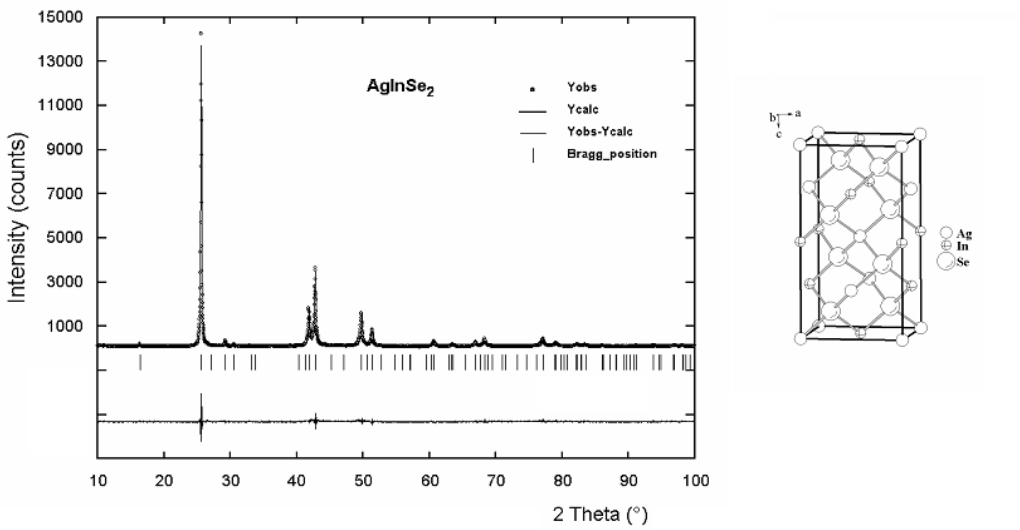

Fig. (2) Final Rietveld refinement plot and unit cell diagram for $AgInSe_2$.

For the Ag-In-Te system was found the $AgIn_5Te_8$ phase, which is isostructural with the $AgIn_5Se_8$ compound [30]. Figure 3 shows the unit cell diagram for Ag In_5Te_8 and the Rietveld refinement plot which converged to R_{exp} = 6.2%, R_p = 8.2%, R_{wp} = 11.6% and S = 1.7. This phase crystallize in the tetragonal space group $P\bar{4}2m$ with $\boldsymbol{a}$ = 6.1952(2) Å, $\boldsymbol{c}$ = 12.419(4) Å, and consists of a three-dimensional arrangement of distorted $AgTe_4$ and $InTe_4$ tetrahedra connected by common faces [7]. The Ag-Te [2.890(6) Å] and In-Te [2.764(7) Å] bond distances agree well with those observed in other adamantane structures found in the ICSD database [31].

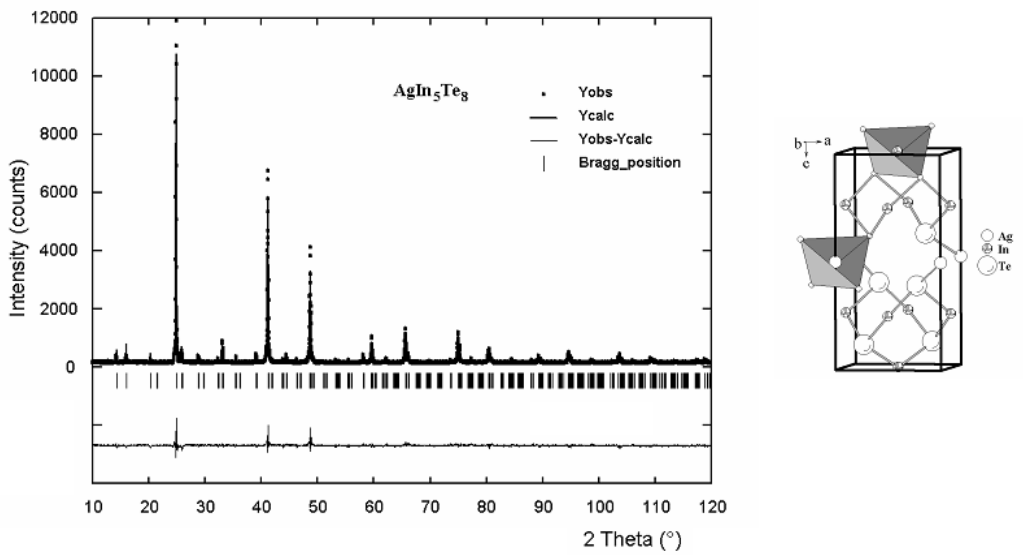

Fig. (3) Final Rietveld refinement plot for $AgIn_5Te_8$ and unit cell diagram showing the tetrahedral coordination around the cations.

4. Conclusions

The refinements of some members of the chalcogenide system Ag-In-VI were carried out by the Rietveld method using X-ray powder diffraction data. The Ag-In-S was composed by three different phases; $AgIn_5S_8$ and $AgInS_2$ in tetragonal and orthorhombic polymorphs. For the Ag-In-S and Ag-In-Te system only the phases $AgInSe_2$ and $AgIn_5Te_8$ were found, respectively.

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