# Synthesis and Crystal Structure Refinement of Sb$_2$Se$_{3-x}$S$_x$ Solid Solutions by Rietveld Analysis of X-Ray Powder Diffraction Data

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*Bulk materials of Sb$_2$Se$_{3-x}$S$_x$ solid solutions (x = 0, 1, 2 and 3) have been synthesized by fusion of the constituent elements in the stoichiometric ratios in vacuum-sealed silica tubes. The materials compositions were confirmed by using energy dispersive analysis of X-rays (EDAX). X-ray powder diffraction measurements were performed for all the prepared samples at 300 K. The analysis of X-ray data has indicated that all the prepared materials are polycrystalline of single-phase and belonging to the orthorhombic system with space group Pbnm (62). The crystal structural parameters were refined by Rietveld method using the FullProf program. The influence of the S-content in the ternary compounds on the structural properties was discussed. It was verified that the investigated compositions are formed of infinite puckered chains of stoichiometric composition indefinitely extended in the plane parallel to the c-axis. These larger chains are, in turn, bonded into sheets roughly perpendicular to the b-axis through sets of Sb-Se/S bonds, weaker than that within the chain. Finally, the sheets are held together to make the crystalline solid.*

## 1. Introduction:

Chalcogenide semiconductors of the chemical formula V$_2$-VI$_3$ have received considerable attention because of their interesting physical properties as well as their potential technological applications [1-7]. The importance of these materials arises from that they generally offer a wide range of optical, electrical and structural properties. By making suitable solid solutions among them, it is possible to obtain a new alloy with specific characteristics to meet a desired requirement.

$Sb_2Se_3$ and $Sb_2S_3$, which belong to the $V_2$-$VI_3$ family, are layer-structured semiconductors and they crystallize in the orthorhombic crystal structure. They are also of great interest as amorphous and crystalline materials. $Sb_2Se_3$ has received a great deal of attention due to its switching effects [8] and its excellent photovoltaic properties and high thermoelectric power [9], which could find potential applications in solar selective and decorative coating and thermoelectric cooling devices [10]. On the other hand, $Sb_2S_3$ has attracted attention for its applications as a target material for television cameras [11, 12], as well as in microwave [13], switching [14] and optoelectronic devices [3, 15, 16].

Previous studies have dealt with the preparation and crystal structure of $Sb_2Se_3$ and $Sb_2S_3$ [17, 18]. On the other hand, no information about their solid solutions was reported on ICDD [19]. So, the present work, aims to the preparation and crystal structure refinement of the bulk materials $Sb_2Se_{3-x}S_x$ ($x$ = 0, 1, 2 and 3) solid solutions in order to investigate the effect of S-content on their structural properties.

## 2. Experimental Procedure:

Polycrystalline ingots of $Sb_2Se_{3-x}S_x$ solid solutions ($x$ = 0, 1, 2 and 3) were prepared by using the constituent elements of 99.999% pure antimony, selenium and sulphur (obtained from Aldrich Chemical Co.) weighed in stoichiometric ratio. The mixture of each composition was taken in a pre-cleaned silica tube, sealed under a vacuum of $\sim 1 \times 10^{-3}$ Pa and placed into the uniform zone of an electric furnace for heating the mixture. The temperature of the furnace was first slowly increased at the rate of 10 K h$^{-1}$ up to 905 K (the melting temperature of antimony) and the mixture was left at such temperature for 12 h. Then, the temperature was increased at a rate of 40 K h$^{-1}$ up to 1273 K, at which the entire contents were melted. At this high temperature, the melt was subjected to occasional shaking for 2 h to ensure complete mixing and reaction of constituents to assure compound formation. The temperature was then decreased at a rate of 60 K h$^{-1}$ to temperature of 50 degrees above the melting temperature ($\sim$ 875- 935 K) and left for 12 h. Finally, the mixture was slowly cooled in the furnace to room temperature (300 K). The resulting ingots were ground and reduced to 200-300 mesh powders.

The elemental compositions of the prepared materials in powdered form on a polished surface of a graphite stub were determined by using an energy-dispersive X-ray spectrometer (EDXS) unit, interfaced to a scanning electron microscope (Philips XL) operating at an accelerating voltage of 30 kV.

X-ray powder diffraction data of the prepared compounds ($Sb_2Se_{3-x}S_x$, solid solutions) were collected at room temperature using a computer controlled Diano X-ray diffractometer. This instrument is equipped with Co X-ray tube operated at 10 mA and 45 kV using Fe filter to eliminate $K_\beta$ radiation and proportional counter. The diffraction patterns were collected in the angular 2θ range of 10-100º with step scanning mode of 0.02º 2θ and counting time of 5 sec/step. The XSPEX Diano software was used to establish the precise peak positions. Annealed quartz sample was used as an external standard material for determining the zero shift and the instrumental profile under exactly the same conditions conducted for the investigated samples.

## 3. Results and Discussions:

Figure (1) shows the energy dispersive X-ray spectrum of $Sb_2Se_2S$ composition as representative spectrum. The composition analysis of the prepared materials confirms the presence of antimony, selenium, and/or sulfur in the prepared samples with the average atomic percentages that are tabulated in Table (1). A chemical composition of $Sb_{1.988}Se_{3.012}$, $Sb_{1.905}Se_{2.103}S_{0.992}$, $Sb_{1.893}Se_{1.150}S_{1.957}$ and $Sb_{2.075}S_{2.925}$ were deduced from the obtained results. So, the deviation in stoichiometry was found to be comparable with the experimental errors and consequently the samples composition could be considered as very nearly stoichiometric.
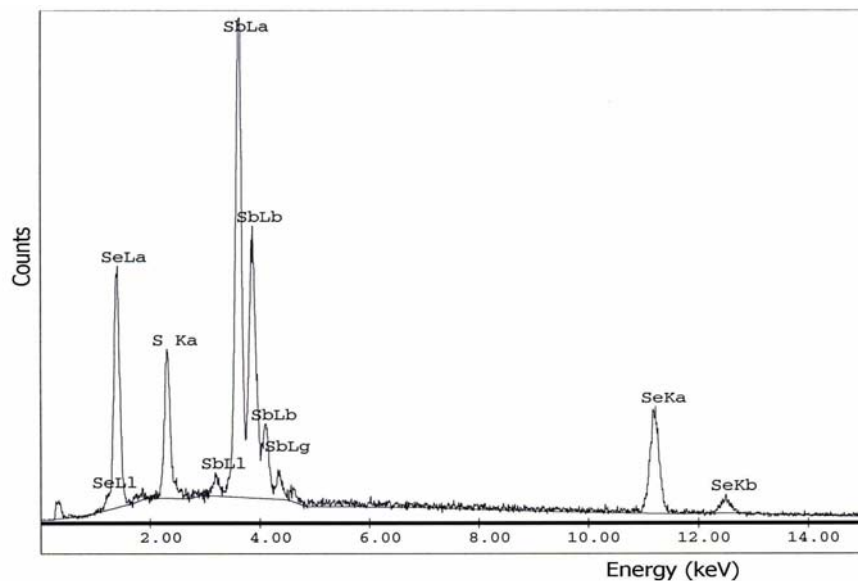


**Fig. (1):** Energy dispersive X-ray spectrum of powdered $Sb_2Se_2S$.

**Table (1):** Chemical analysis (EDAX) data of $Sb_2Se_{3-x}S_x$ solid solutions and calculated one.

| Element | Elemental composition (at%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | x = 0 | | x = 1 | | x = 2 | | x = 3 | |
| | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| Sb | 39.76 | 40 | 38.10 | 40 | 37.86 | 40 | 41.51 | 40 |
| Se | 60.24 | 60 | 42.07 | 40 | 23.01 | 20 | ------ | --- |
| S | ------ | --- | 19.83 | 20 | 39.13 | 40 | 58.49 | 60 |

Figure (2) shows the X-ray powder diffractograms of the synthesized materials. Although, the relative intensities in case of x = 3 are matched with the standard data, an enhancement of (hk0) peaks were observed in case of x= 0, 1 and 2. This enhancement in the peak intensity may be due to pressing the sample into the holder. It was found that the peak positions shift to higher 2θ-values as the value of x increases. The powder diffraction peaks was examined using ICDD data base [19] and no secondary phases were found corresponding to any precipitation of elements or binary alloys with other stoichiometry. This may indicate the complete solubility of the constituent elements of all synthesized compounds.
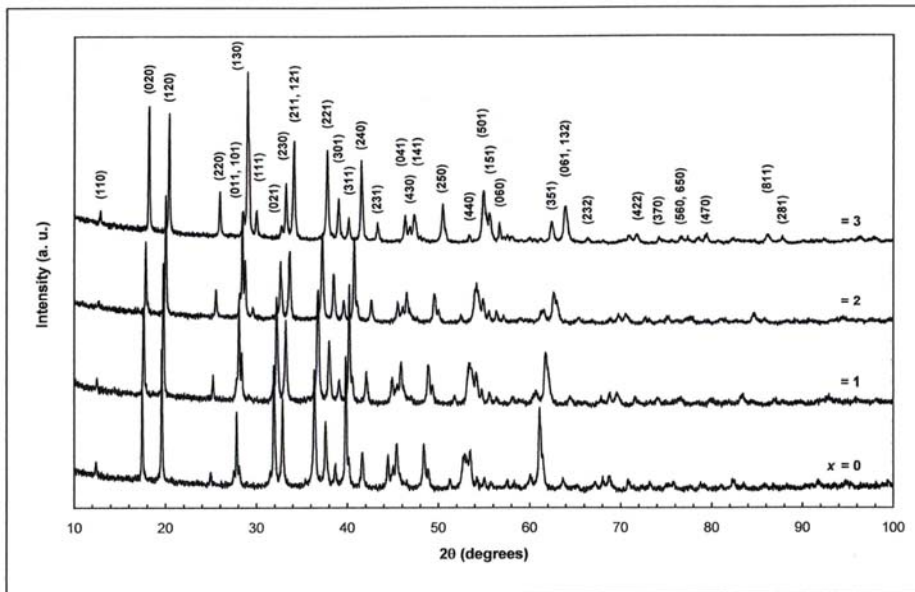


**Fig. (2):** X-ray powder diffractograms of $Sb_2Se_{3-x}S_x$ solid solutions.

The structure of the samples were refined by Rietveld method [20] using the FullProf program [21]. The lattice parameters obtained from the indexing calculations using DICOVOL91 program [22], the space group Pbnm and the atomic positions of the compound $Sb_2Se_3$ [23] were used as a starting parameters for the refinement, whereas all atoms occupy the 4c positions $\pm$ u, $\pm$ v, 1/4. A parameterized modified Thomson-Cox-Hasting pseudo-Voigt function [24] was used to fit the peak shape, a polynomial with 5 coefficients was used to model the background and preferential orientation was modeled using March's function [25, 26]. Fig. (3) shows the final Rietveld refinement for the $Sb_2Se_2S$ sample as representative one. The results of the Rietveld refinement with the criteria of the refinement are summarized in Table (2). The refined atomic coordinates are given in Table (3), while the bond lengths and angles are given in Table (4).
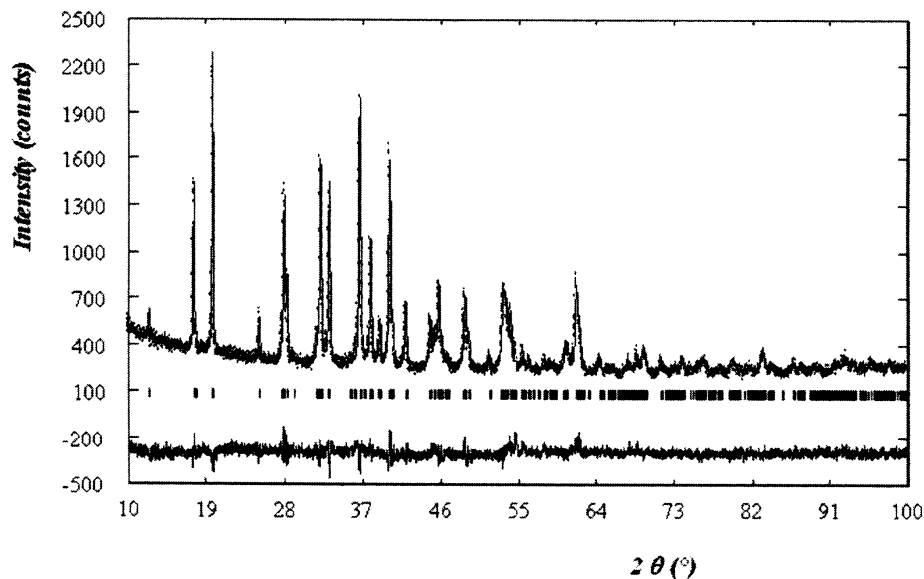


**Fig. (3):** Final Rietveld Refinement for $Sb_2Se_2S$ sample as representative one. The observed (closed circles) and calculated (solid line) X-ray diffraction profiles and the difference between them (on the bottom). Vertical bars refer to calculated Bragg peak positions.

Figure (4) represents the refined values of lattice parameters *a*, *b* and *c* showing how they depend on mole fraction, *x*. From this figure, it is clear that the substitution of Se by S lead to decrease of the lattice parameters and, consequently, the contraction of the unit cell (see Table 2). Bond lengths tend also to decrease as *x* increases. Both decrease of the unit cell and bond lengths may be due to the fact that the ionic radius of sulfur (1.84 Å) is less than that of selenium (1.98 Å) [27].

Table (2): The refined unit cell parameters and agreement factors of $Sb_2Se_{3-x}S_x$ solid solutions (Crystal System: Orthorhombic, Z = 4 and S. G.: Pbnm (62)).

| Sulphur content, x | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| $a$ (Å) | 11.6348 | 11.5330 | 11.3786 | 11.2275 |
| $b$ (Å) | 11.7879 | 11.6899 | 11.5273 | 11.3108 |
| $c$ (Å) | 3.9786 | 3.9356 | 3.8825 | 3.8359 |
| Volume ($Å^3$) | 545.66(1) | 530.60(1) | 509.25(1) | 487.13(1) |
| Calculated density ($gm/cm^3$) | 1.4618 | 1.3015 | 1.1928 | 1.1579 |
| $R_p$(%) | 27.2 | 26.7 | 26.6 | 21.4 |
| $R_B$ | 12.41 | 9.90 | 11.75 | 6.56 |
| $R_{wp}$(%) | 23.4 | 22.8 | 23.8 | 21.2 |
| $R_{exp}$(%) | 15.61 | 15.96 | 16.96 | 14.6 |
| $Chi^2$ | 2.25 | 2.04 | 1.97 | 2.12 |

**Table (3):** The atomic positions of $Sb_2Se_{3-x}S_x$ solid solutions.

| Sulphur content, x | | 0 | 1 | 2 | 3 |
|---|---|---|---|---|---|
| Sb1 | $x$ | 0.3268(2) | 0.3258(0) | 0.3251(2) | 0.3246(2) |
| | y | 0.0289(2) | 0.0302(0) | 0.0297(2) | 0.0277(2) |
| | z | 0.25 | 0.25 | 0.25 | 0.25 |
| Sb2 | $x$ | 0.5395(2) | 0.5362(0) | 0.5355(2) | 0.5365(1) |
| | y | 0.3536(2) | 0.3539(0) | 0.3521(2) | 0.3496(1) |
| | z | 0.25 | 0.25 | 0.25 | 0.25 |
| Se1/S1 | $x$ | 0.8729(3) | 0.8723(2) | 0.8723(4) | 0.8734(5) |
| | y | 0.0548(3) | 0.0567(4) | 0.0543(4) | 0.0502(4) |
| | z | 0.25 | 0.25 | 0.25 | 0.25 |
| Se2/S2 | $x$ | 0.5531(3) | 0.5577(0) | 0.5638(4) | 0.5580(5) |
| | y | 0.8721(2) | 0.8773(0) | 0.8803(4) | 0.8811(4) |
| | z | 0.25 | 0.25 | 0.25 | 0.25 |
| Se3/S3 | $x$ | 0.1945(4) | 0.1970(2) | 0.1977(5) | 0.1925(6) |
| | y | 0.2143(2) | 0.2124(1) | 0.2084(4) | 0.2045(4) |
| | z | 0.25 | 0.25 | 0.25 | 0.25 |

**Table (4)**: Bond lengths and angles in an orthorhombic unit cell of $Sb_2Se_{3-x}S_x$ solid solutions.

| Sulphur content, x | | Bond lengths (Å) and bond angles (°) | | | |
|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 3 |
| Sb2-(Se1/S1) | [a] | 2.582(4) | 2.595(2) | 2.556(5) | 2.484(5) |
| Sb1-(Se3/S3) | [a] | 2.674(4) | 2.596(2) | 2.518(5) | 2.490(6) |
| Sb1-(Se2/S2) | [a] | 2.697(3) | 2.617(9) | 2.538(3) | 2.546(4) |
| Sb2-(Se3/S3) | [a] | 2.802(3) | 2.813(1) | 2.768(4) | 2.668(5) |
| Sb2-(Se1/S1) | [b] | 2.980(3) | 2.921(1) | 2.895(4) | 2.884(4) |
| (Sb1-Se1/S1) | [a] | 3.214(3) | 3.181(1) | 3.123(4) | 3.065(4) |
| Sb1-(Se2/S2) | [c] | 3.217(4) | 3.217(1) | 3.216(5) | 3.101(5) |
| Sb2-(Se2/S2) | [d] | 3.492(3) | 3.514(1) | 3.495(4) | 3.408(4) |
| (Sb1-Se3/S3) | [d] | 3.716(3) | 3.725(1) | 3.713(5) | 3.660(5) |
| (Se2/S2)-(Se3/S3) | [a] | 3.690(5) | 3.602(2) | 3.491(6) | 3.530(7) |
| (Se1/S1)-(Se3/S3) | [a] | 3.825(4) | 3.795(2) | 3.684(5) | 3.539(5) |
| Sb1-Sb2 | [a] | 4.129(3) | 4.106(1) | 4.060(2) | 4.008(2) |
| (Se2/S2)-Sb1-(Se3/S3) | | 86.81(10) | 87.40(4) | 87.29(13) | 89.02(15) |
| (Se2/S2)-Sb1-(Se2/S2) | | 95.06(9) | 97.50(3) | 99.76(12) | 97.76(14) |
| (Se1/S1)-Sb2-(Se3/S3) | | 90.47(10) | 89.05(4) | 87.48(13) | 86.68(14) |
| (Se3/S3)-Sb2-(Se3/S3) | | 90.48(10) | 88.77(4) | 89.07(12) | 91.91(15) |
| Sb1-(Se2/S2)-Sb1 | | 95.06(9) | 97.50(3) | 99.76(13) | 97.76(15) |
| Sb2-(Se3/S3)-Sb2 | | 90.48(10) | 88.77(4) | 89.07(12) | 91.91(15) |
| Sb1-(Se3/S3)-Sb2 | | 97.88(11) | 98.67(5) | 100.24(14) | 101.93(17) |

[a] means within the same chain,

[b] between nearest pairs of chain,

[c] between next nearest pairs of chain (same sheet),

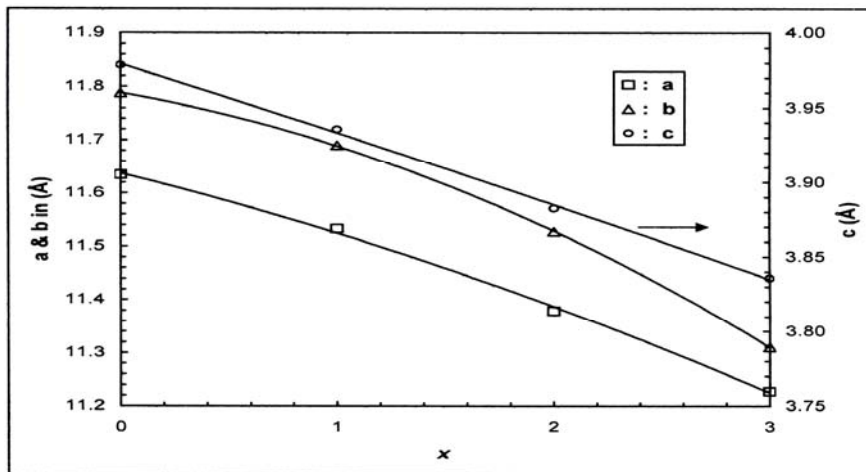[d] between chains in the neighbouring sheets.

**Fig. (4):** Variation of unit-cell lattice parameters *a, b,* and *c* with composition for $Sb_2Se_{3-x}S_x$ solid solutions. The points represent the experimental values and the solid line represents the empirical fit.

The present alloys are formed of infinite puckered chains of stoichiometric composition indefinitely extended in the plane parallel to the *c*-axis through a sets of strong bonds (Sb-(Se/S)) in the range from 2.484(5) Å for x = 3 to 2.813(1) Å for x = 1. In the chain, each antimony atom is coordinated to three atoms of (Se/S) with approximately trigonal pyramidal geometry in which (Se/S)–Sb–(Se/S) angles lay between 86.81(10)° for x = 0 and 99.76(12)° for x = 2. Projections of the structure of the chain on (010) and on (001) are shown in Fig. (5a, b). Pairs of these chains are fastened together along $2_1$ screw axes to form larger chains through sets of Sb-(Se/S) bonds weaker than that within the chain of length (2.884(4) Å, x = 3 to 2.980(3) Å, x = 0) as shown in Table (4). These larger chains [28] are, in turn, bonded into sheets roughly perpendicular to the *b* axis through sets of Sb-(Se/S) bonds, which are 3.101(5) Å, x = 3 to 3.217(4) Å, x = 0 in length. Finally the sheets are held together to make the crystalline solid through Vander Wall contacts, which are 3.408(4) Å to 3.660(5) Å and 3.514(1) Å to 3.725(1) Å for x = 3 and 1, respectively.

## 4. Conclusions:

Synthesis of very nearly stoichiometric $Sb_2Se_{3-x}S_x$ (*x* = 0, 1, 2, and 3) compounds from its constituent elements has been achieved. The X-ray powder diffraction data revealed that all the prepared materials are polycrystalline in nature and consists of single phase. The results of Rietveld refinement revealed that both of the unit-cell dimensions and the bond lengths decrease with increasing the S content. Also, it was found that the stereo configuration of the structure was not changed by the replacement of Se by S.
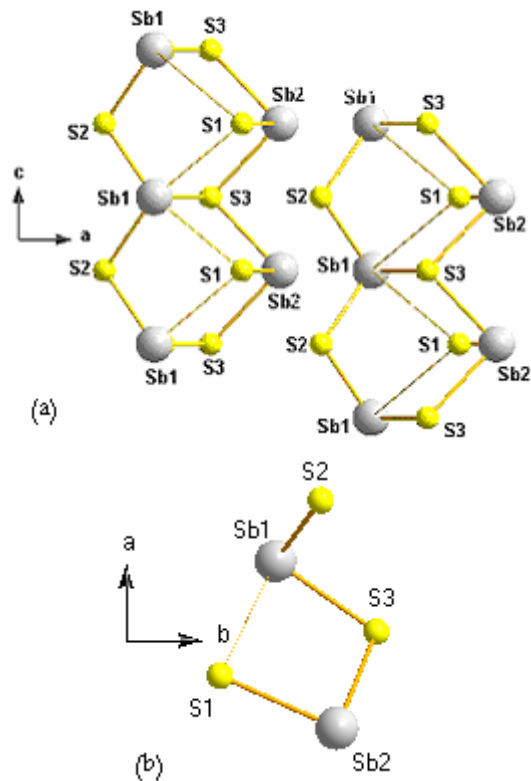
**Fig. (5):** Structure of the $Sb_2S_3$ chain as a representative example:
(a) projected on (010) and (b) projected on (001).

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