

Structural analysis of As-S-Sb-Te polycrystalline nanostructured semiconductors

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The aim of this paper is to characterize the polycrystalline and vitreous phases in the $\text{As}_2\text{S}_3\text{-Sb}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ systems using several techniques such as XRD, SEM, EDS, and micro-Raman spectroscopy. The $\text{As}_{1.17}\text{S}_{2.7}\text{Sb}_{0.83}\text{Te}_{0.40}$, $\text{As}_{1.04}\text{S}_{2.4}\text{Sb}_{0.96}\text{Te}_{0.60}$, $\text{As}_{0.63}\text{S}_{2.7}\text{Sb}_{1.37}\text{Te}_{0.30}$, and $\text{As}_{0.56}\text{S}_{2.4}\text{Sb}_{1.44}\text{Te}_{0.60}$ semiconductor chalcogenide bulk glasses were examined using Scanning Electron microscopy (SEM), Energy-Dispersive Spectroscopy (EDS), X-Ray diffraction (XRD) and micro-Raman analysis. The EDS quantitative and mapping analysis showed that for each investigated area, the identified elements were sulfur (S), arsenic (As), antimony (Sb) and tellurium (Te). These elements are present in constant atomic percentages on the entire sample, showing a good homogeneity of the samples. The study of samples by the above-mentioned methods showed the presence of crystalline phases and amorphous phases with the polycrystalline inclusions corresponding to the structural units AsS_3 , Sb_2S_3 , and Sb_2Te_3 .

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1. Introduction

As_2S_3 , As_2Se_3 , Sb_2Te_3 , and Sb_2S_3 and its ternary and quaternary compounds are the most intensively studied and have been receiving immense research interest because of their ease of formation, excellent infrared transmission, resistance to atmospheric conditions and chemical stability. Chalcogenide glasses of As-S-Sb-Te system (the main average coordination number $Z=2.40$), are important for their contribution in semiconductor physics, as well as for a wide range of technical applications, such as infrared optics, acousto-optic and all-optical switching devices, ovonic devices, holographic recording media, diffractive optics, photonic crystals, gas sensors, etc. [1-2].

Even though As and Sb belong to the same group of the periodic table, As_2S_3 , As_2Te_3 , and Sb_2S_3 do not display the same glass forming tendency. The addition of As_2S_3 to Sb_2S_3 raises the glass-forming ability and makes it possible to form glasses in a mixed As-S-Sb systems [3]. The three-dimensional network of glassy As_2S_3 is made of trigonal pyramidal units $\text{AsS}_{3/2}$, which are interconnected through As-S-As bridges. The basic structural units of glassy Sb_2S_3 are the trigonal pyramidal arrangement $\text{SbS}_{3/2}$ bonded to each other by S atoms [4]. The crystal structure of Sb_2Te_3 exhibits the layered atomic arrangement in the rhombohedral structure, which consists of three quintuplet layers (QLs) and each quintuplet layer contains five atoms in the order of $\text{Te}^1\text{-Sb-Te}^2\text{-Sb-Te}^1$ [5]. From the analysis of the different Mössbauer spectra of the glasses $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{S}_3$, the hyperfine interaction parameters such as isomer shift (δ), quadruple coupling (Δ) and Line width (Γ) were determined [6].

The X-ray diffraction (XRD) and the Energy-dispersive spectroscopy (EDS) analysis were used to determine the stoichiometry of the proposed $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{S}_3$ glasses and the results

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obtained were compared with the theoretical one concerning the chemical composition [7]. The parameters for $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ compositions were calculated from their chemical formula obtained by EDS experiments [8]. Some optical and physical properties of $\text{As}_{11.2}\text{S}_{48.0}\text{Sb}_{28.8}\text{Te}_{12.0}$ and $\text{As}_{20.8}\text{S}_{48.0}\text{Sb}_{19.2}\text{Te}_{12.0}$ nano-structured polycrystalline semiconductors were reported in [9, 10].

The aim of this paper is to characterize the $\text{As}_2\text{S}_3\text{-Sb}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ systems from the morphological and compositional point of view by SEM, EDX, XRD and Raman techniques. The X-ray diffraction analysis elucidates the crystallinity of the samples.

2. Experimental

The different As-S-Sb-Te semiconductors such as: $\text{As}_{1.17}\text{S}_{2.7}\text{Sb}_{0.83}\text{Te}_{0.40}$ ($\text{As}_{23.0}\text{S}_{53.0}\text{Sb}_{16.0}\text{Te}_{8.0}$), $\text{As}_{1.04}\text{S}_{2.4}\text{Sb}_{0.96}\text{Te}_{0.60}$ ($\text{As}_{20.8}\text{S}_{48.0}\text{Sb}_{19.2}\text{Te}_{12.0}$), $\text{As}_{0.63}\text{S}_{2.7}\text{Sb}_{0.137}\text{Te}_{0.30}$ ($\text{As}_{12.6}\text{S}_{54.0}\text{Sb}_{27.4}\text{Te}_{6.0}$) and $\text{As}_{0.56}\text{S}_{2.4}\text{Sb}_{0.144}\text{Te}_{0.60}$ ($\text{As}_{11.2}\text{S}_{48.0}\text{Sb}_{28.8}\text{Te}_{12.0}$) were prepared from the preliminary synthesized compounds $(\text{As}_2\text{S}_3)_{0.35}(\text{Sb}_2\text{S}_3)_{0.65}$, $(\text{As}_2\text{S}_3)_{0.65}(\text{Sb}_2\text{S}_3)_{0.35}$, and Sb_2Te_3 , containing 6N purity elements (As, Sb, S, Te) by conventional melt quenching method.

The initial compounds were placed and mixed in quartz ampoules, which were then evacuated up to a pressure of $P \sim 10^{-5}$ Torr and sealed. At last, the mixtures were melted at 850-900 °C in rocking furnace during 10 hours for homogenization, and then quenched at the room temperature. The average mean coordination number for all samples is $Z=2.40$ as in the case of the binary components. Part of the synthesized ingots have been grinded into powders with a grain size of about $d=100$ nm and were used for the Micro-Raman measurements. The samples were analyzed using a Rigaku SmartLab Diffractometer (XRD) with a copper target ($\lambda_{\text{CuK}\alpha}=1.540598$ Å), a tube voltage of 45 kV and a tube current of 200 mA. The obtained diffractograms were fitted using SmartLab Studio Software from Rigaku and compared with existing data from the PDF2 database and scientific articles. The Raman study was carried out at room temperature by Confocal Micro - Raman Spectroscopy, using a LabRam HR800 system. All Raman measurements were performed by exposing the specimens with laser ($\lambda=632$ nm) for 100 s with a power of 2mW. The signal reflected from the sample was captured by a CCD detector using a grid of 600 lines/mm. The SEM-EDX analysis was performed on a Hitachi SU8230 Scanning Electron Microscope coupled with an Oxford Energy Dispersive Spectroscopy detector-analyzer. Several areas were studied for samples in a both states, bulk and powder. The EDS study was performed both as area elemental composition and as elemental mapping.

3. Results and discussion

Figure 1 shows the XRD patterns of polycrystalline bulk samples $\text{As}_{1.17}\text{S}_{2.7}\text{Sb}_{0.83}\text{Te}_{0.40}$ and $\text{As}_{1.04}\text{S}_{2.4}\text{Sb}_{0.96}\text{Te}_{0.60}$. The XRD diffractograms show that both investigated quaternary compounds have a polycrystalline structure with well-defined peaks.

In contrast, Figure 2 shows XRD patterns of $\text{As}_{0.56}\text{S}_{2.4}\text{Sb}_{0.144}\text{Te}_{0.60}$ and $\text{As}_{0.63}\text{S}_{2.7}\text{Sb}_{0.137}\text{Te}_{0.30}$ which present broad peaks that are specific for amorphous materials. The difference in crystallinity seen between the two types of samples could be generated by the As_2S_3 , Sb_2S_3 and Sb_2Te_3 structural units. The three-dimensional network of glassy As_2S_3 is built of trigonal pyramidal units $\text{AsS}_{3/2}$, which are interconnected through As-S-As bridges. The basic structural units of glassy Sb_2S_3 are the trigonal pyramidal arrangements $\text{SbS}_{3/2}$ and Sb_2Te_3 bonded to each other by S and Te atoms [3].

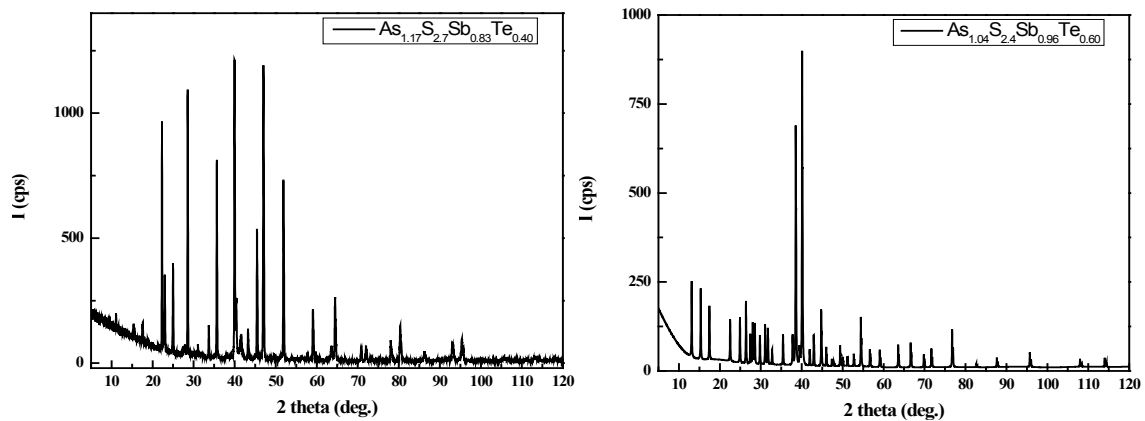


Fig. 1. X-Ray Diffraction patterns of $As_{1.17}S_{2.7}Sb_{0.83}Te_{0.40}$, and $As_{1.04}S_{2.4}Sb_{0.96}Te_{0.60}$.

The interplanar distance was calculated for the identified peaks in the diffractograms presented in Figure 1 using Bragg's Law:

$$n\lambda = 2d\sin\theta,$$

where n is the diffraction order, λ is the wavelength of the radiation, d – the interplanar distance and, θ is the Bragg angle. For the diffractograms presented in Figure 1, the interplanar distance were calculated for the predominant orientation peaks ($2\theta = 41.7$ deg.) and has been found to be 2.16 \AA . Given the amorphous characteristics of the samples presented in Figure 2, no interplanar distances were calculated.

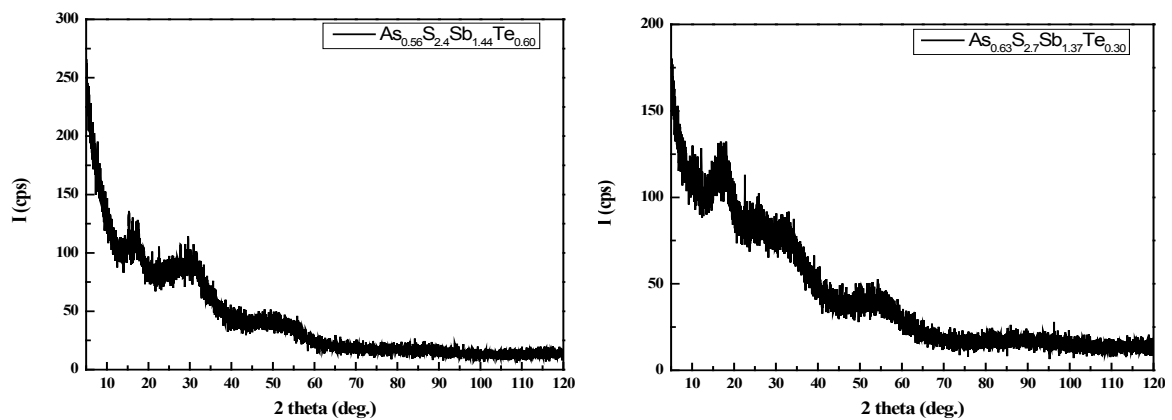


Fig. 2. X-Ray Diffraction patterns of $As_{0.56}S_{2.4}Sb_{1.44}Te_{0.60}$; and $As_{0.63}S_{2.7}Sb_{1.37}Te_{0.30}$.

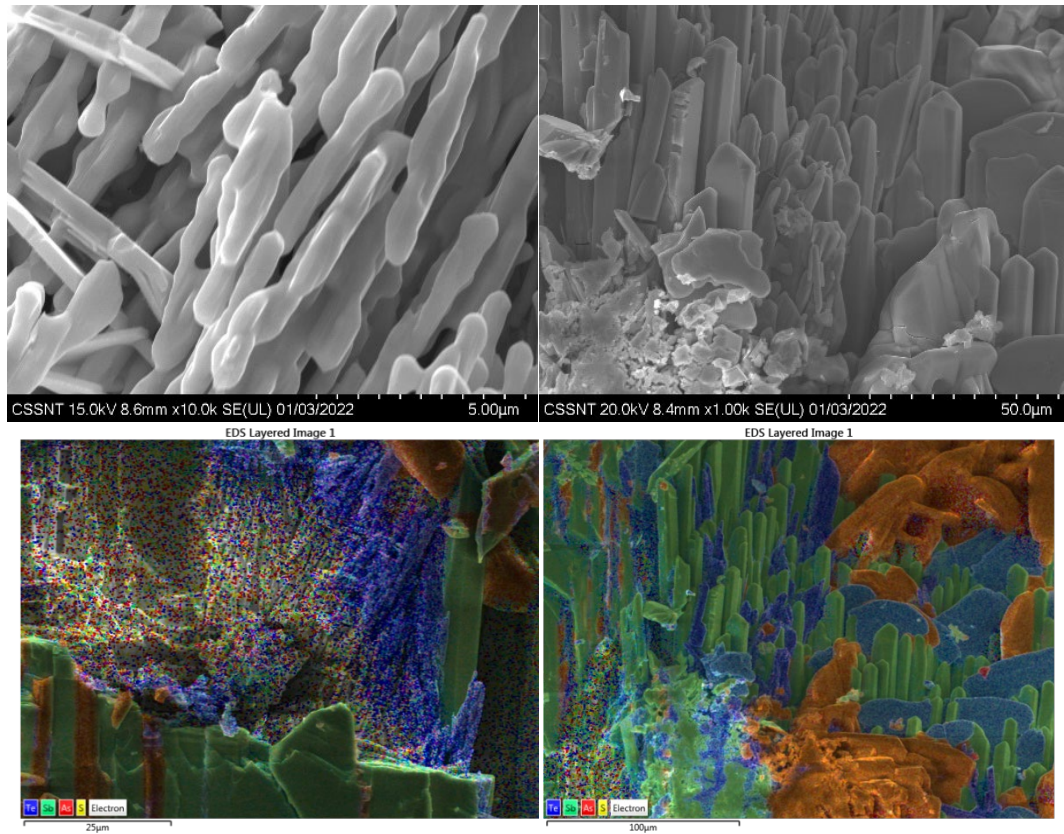


Fig. 3. SEM analysis and EDX mapping of the polycrystalline bulk samples $As_{1.17}S_{2.7}Sb_{0.83}Te_{0.40}$ (left) and $As_{1.04}S_{2.4}Sb_{0.96}Te_{0.60}$ (right).

From the SEM analysis showed in Figure 3 it can be observed that the investigated samples don't present a uniform morphology. This is clearly evidenced in the mapping analysis.

The Mapping analysis of elements distribution spectra (EDS) indicate that for each investigated area, the intensity corresponded to sulfur (S), arsenic (As), antimony (Sb) and tellurium (Te) remain practically unchanged. These spectra show the presence of all the initial elements (As, S, Sb, Te) with a slight deviation. But sometimes there was a high concentration of As and Te atoms. Different morphologies are observed depending on the content of the material present. Tellurium showed an acicular morphology while the regions containing more Sb are flatter.

Tables 1 and 2 present some results of Energy Dispersive X-Ray Spectroscopy for the bulk $As_{1.17}S_{2.7}Sb_{0.83}Te_{0.40}$ and $As_{1.04}S_{2.4}Sb_{0.96}Te_{0.60}$, which show that chemical composition corresponds to the average values of for all the investigated compositions. There is a significant difference in the composition of the samples. As it can be seen the region analyzed of the $As_{1.17}S_{2.7}Sb_{0.83}Te_{0.40}$ system, exhibit mainly tellurium while the content of S and As it's around 7-8 at.%, while the content of Sb remain the lowest, 3 at.%. By comparison, the $As_{1.04}S_{2.4}Sb_{0.96}Te_{0.60}$ bulk sample exhibit higher content of S and As, around above 34 at.%. Having, the content of Sb is 15 at.%.

Table 1. Quantitative analysis of the $As_{1.17}S_{2.7}Sb_{0.83}Te_{0.40}$ bulk sample.

Result Type	Atomic %
Spectrum Label	Spectrum 6
S	7.34
As	8.77
Sb	3.38
Te	80.51
Total	100.00

Table 2. Quantitative analysis of the $As_{1.04}S_{2.4}Sb_{0.96}Te_{0.60}$ bulk sample.

Result Type	Atomic %
Spectrum Label	Spectrum 1
S	36.76
As	34.57
Sb	15.75
Te	12.92
Total	100.00

According to the study presented in [11] the monocrystals Sb_2Te_3 , Sb_2Se_3 and Sb_2S_3 are well-known layered bulk structures with van der Waals interactions. It was shown, that, in the crystal structure of Sb_2X_3 (where $X=S, Se, Te$) each Sb atom is surrounded by six X atoms and each X atoms encompassed by four Sb atoms. The SEM images also show a layered structure of the investigated samples. Some structural investigations of the chalcogenide glasses of the Sb_2S_3 - As_2S_3 - Sb_2Te_3 and $(As_2S_3)_{1-x}(Sb_2S_3)_x$ systems have been reported in [6, 7].

Figure 3 illustrates the micro-Raman spectra of As-S-Sb-Te compounds as bulk (a) and powder (b) samples. The micro-Raman spectra of polycrystalline $As_{1.17}S_{2.7}Sb_{0.83}Te_{0.40}$ and $As_{1.04}S_{2.4}Sb_{0.96}Te_{0.60}$ semiconductors are similar and we can observe some strong bands located at $\nu=146, 187, 234, 273, 345 - 362 \text{ cm}^{-1}$, which are assigned with the vibration modes S, As_4S_4 , As-As, As_4S_3 , and $AsS_{3/2}$, respectively.

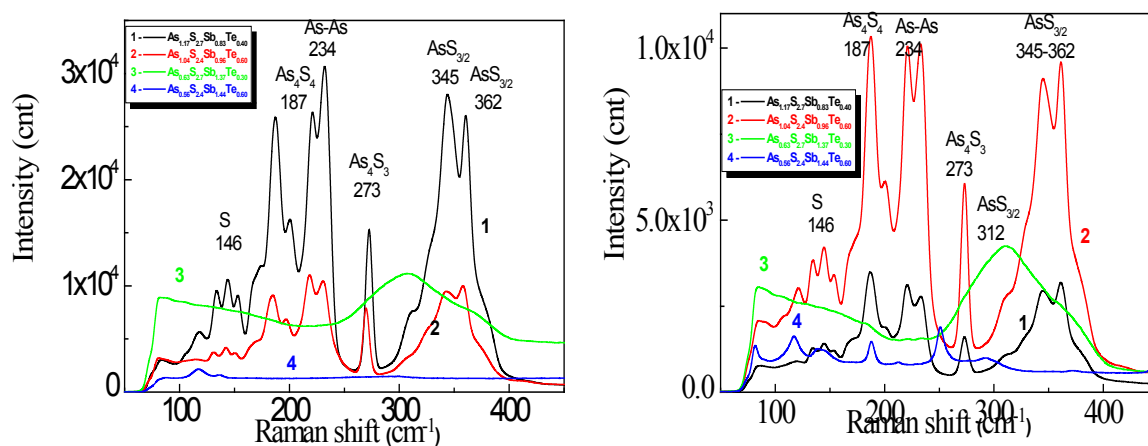


Fig. 3. Micro-Raman spectra of As-S-Sb-Te compounds as bulk (a) and powder (b) samples.

Some similar vibration bands were observed in As_mS_n and $(As_2S_3)_{0.95}(Sb_2S_3)_{0.05}$ chalcogenide optical fibers [8]. The vibration modes of Sb_2S_3 and Sb_2Te_3 is not observed in the micro-Raman spectra due to the inversion symmetry in the metastable cubic phase belongs to the F_{3m} space group [12]. The Raman spectra of sample $As_{0.63}S_{2.7}Sb_{1.37}Te_{0.30}$ exhibit a broad peak around 300 cm^{-1} associated to the vibration modes of $AsS_{3/2}$ and As_4S_3 . The presence of the broad

peak suggests the amorphous character of the sample. The $\text{As}_{0.68}\text{S}_{2.4}\text{Sb}_{1.44}\text{Te}_{0.60}$ sample present Te-Te (119 cm^{-1}), As_4S_3 (273 cm^{-1}) and Sb-O (258 cm^{-1}) associated peaks. Regarding the $\text{As}_{1.17}\text{S}_{2.7}\text{Sb}_{0.83}\text{Te}_{0.40}$, $\text{As}_{1.04}\text{S}_{2.4}\text{Sb}_{0.96}\text{Te}_{0.60}$ and $\text{As}_{0.63}\text{S}_{2.7}\text{Sb}_{1.37}\text{Te}_{0.30}$ systems, no significant differences could be observed in the Raman spectra where the samples are prepared as powder. However, a significant change is observed in the case of the $\text{As}_{0.68}\text{S}_{2.4}\text{Sb}_{1.44}\text{Te}_{0.60}$ system, which in powder form exhibit the peaks associated to S and As_4S_4 .

4. Conclusions

This paper identified the polycrystalline and vitreous phases in the As_2S_3 - Sb_2S_3 - Sb_2Te_3 systems using several characterization methods such as XRD, SEM, EDS, and micro-Raman spectroscopy.

The XRD, SEM, EDS, and micro-Raman analysis of nanostructured layered semiconductors of As-S-Sb-Te system has been performed. The XRD patterns for $\text{As}_{1.17}\text{S}_{2.7}\text{Sb}_{0.83}\text{Te}_{0.40}$ and $\text{As}_{1.04}\text{S}_{2.4}\text{Sb}_{0.96}\text{Te}_{0.60}$ compounds showed the presence crystalline phases while the $\text{As}_{0.63}\text{S}_{2.7}\text{Sb}_{1.37}\text{Te}_{0.30}$, and $\text{As}_{0.56}\text{S}_{2.4}\text{Sb}_{1.44}\text{Te}_{0.60}$ samples were shown to be amorphous phases with the main structural units AsS_3 , Sb_2S_3 , and Sb_2Te_3 . The EDX (quantitative analysis) and EDS (mapping analysis) analysis revealed that above mentioned bulk samples have all the initial elements (As, S, Sb, Te). The identified elements are present in constant atomic percentages on the entire sample, showing a good homogeneity of the samples. The micro-Raman spectra identified the positions of the main vibrational modes at $\nu=119\text{ cm}^{-1}$, $\nu=234\text{ cm}^{-1}$, $\nu=345\text{ cm}^{-1}$ and $\nu=310\text{ cm}^{-1}$ associated with Te-Te, As-As, $\text{AsS}_{3/2}$, and As-S bonds respectively.

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