

## Raman scattering studies of the Ge–In sulfide glasses

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### Abstract

Room temperature Raman scattering measurements of samples of the  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  ( $x=0.00-0.35$ ) system have been conducted together with the FTIR transmission spectra of partial samples. Based on the Raman scattering and FTIR transmission spectra of the prepared defect spinel polycrystalline  $\text{In}_2\text{S}_3$ , the additional peaks at 306 and  $245\text{ cm}^{-1}$  were ascribed to the local symmetric stretching vibration of  $\text{InS}_4$  tetrahedra and  $\text{InS}_6$  octahedra, respectively. According to the Raman scattering spectral evolution of the Ge–In sulfide glasses, the microstructure of the studied glasses was considered to be that  $\text{S}_3\text{Ge-GeS}_3$  and  $\text{S}_3\text{In-InS}_3$  ethane-like units originated from the sulfur deficient with the addition of  $\text{In}_2\text{S}_3$  are homogeneously dispersed in a disordered polymer network formed by  $\text{GeS}_4$ ,  $\text{InS}_4$  tetrahedra and a small quantity of  $\text{InS}_6$  octahedra interconnected by sulfur bridges.

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### 1. Introduction

Recently,  $\text{Ga}_2\text{S}_3$ -based chalcogenide glasses have attracted much attention because of their possible applications such as ultra-fast all optical switching, rare-earth doped  $1.3\text{ }\mu\text{m}$  fiber amplifier and, etc. [1–4]. In addition, based on the similarity of chemical properties with Ga and In, it can be anticipated that  $\text{In}_2\text{S}_3$ -based chalcogenide glasses also be the leading candidates in the above-mentioned fields. However, to our best knowledge, there are rare reports about the microstructure of  $\text{In}_2\text{S}_3$ -based chalcogenide glasses. Considering the intimate relations among the above-mentioned applications, microstructure and basic properties of materials, understanding and utilization of the basic studying findings are worthwhile from theoretical and practical viewpoints.

The understanding and utilization of the microstructure of the Ge–In sulphide glasses is a key clue to further elucidating the short range order of the  $\text{In}_2\text{S}_3$ -based chalcogenide glasses. The main objective of this work was to study the

microstructure of the  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  pseudo-binary glasses through the Raman scattering and FTIR technique.

### 2. Experimental procedure

The samples were prepared from particular high-purity elements (at least 99.9%) using the 10 mm inner-diameter silica tube by conventional melt-quenching techniques. For details see the Refs. [5,6].

Chemical compositions of the samples were analyzed using an energy-dispersive XRF analyzer. Homogeneity and amorphous characteristics of the prepared materials were confirmed by optical and electron microscopy and X-ray diffraction (XRD) with  $\text{Cu K}_\alpha$  radiation.

Raman scattering (RS) and Fourier-transform infrared (FTIR) transmission spectra were recorded at room temperature. The Raman measurements were performed in a  $180^\circ$  backscattering geometry using an inVia Laser Confocal Raman Microscope made by Renishaw PLC. The 632.8 nm line of a He–Ne laser was used and the spectral resolution was of the order of  $1\text{ cm}^{-1}$ . For the avoidance of local laser damage that could easily occur under the microscope and could locally crystallize the amorphous samples, a laser power not exceeding an approximate level of 2 mW was used. FTIR transmission spectra were recorded using a Nicolet Nexus Fourier-transform

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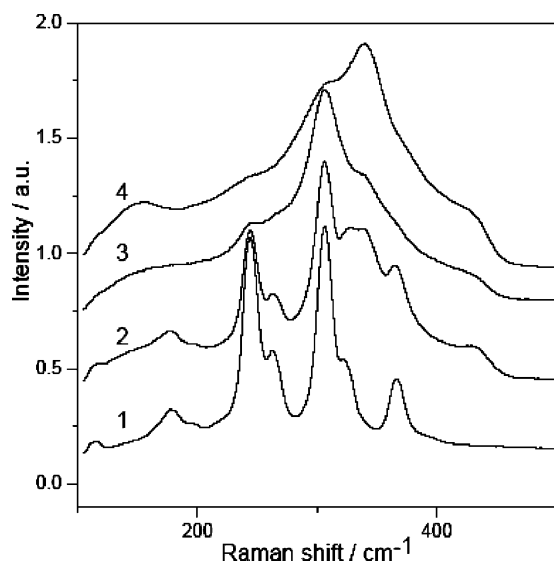


Fig. 1. Several sorts of typical Raman spectra of the sample 10 ( $0.65\text{GeS}_2-0.35\text{In}_2\text{S}_3$ ) under the microscope.

infrared spectrometer under the  $\text{N}_2$  gas atmosphere. Each FTIR spectrum is the average of 64 scans at a spectral resolution of  $4\text{ cm}^{-1}$ . The samples were ground, then dispersed in CsI, and pressed at 5 kPa into pellets to obtain far-infrared spectra in the range  $200-600\text{ cm}^{-1}$ .

### 3. Results

Samples with  $x$  up to 0.3 were confirmed to be optically homogeneous and transparent glasses to the eye and according to the methods given above. And these  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  ( $x=0.00-0.30$ ) glasses changed from pale yellow through tint red to deep red in color with the addition of  $\text{In}_2\text{S}_3$ . Based on the XRF analysis, the final glasses preserved their initial nominal

compositions except for negligible losses in sulfur concentration. So, hereinafter, the glass composition was expressed by the batch composition. Glass formation seemed to be limited to the range of  $x=0.00-0.30$  and several attempts made to prepare a glass with higher  $\text{In}_2\text{S}_3$  content failed. According to the XRD pattern, only the polycrystalline  $\text{In}_2\text{S}_3$  separates out within the sample 10 ( $x=0.35$ ). In addition, this sample is very inhomogeneous to the eye and several types of Raman spectra were obtained under the assistance of the microscope (Fig. 1).

Fig. 2 represents the Raman spectra of the  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  glasses (sample 0–9). Five spectral changes can be extracted following the addition of  $\text{In}_2\text{S}_3$  into the  $\text{GeS}_2$  glass. First, in the region  $100-200\text{ cm}^{-1}$ , the little prominence at  $150\text{ cm}^{-1}$  is gradually enhanced with the increased content of  $\text{In}_2\text{S}_3$ . Secondly, in the region  $200-270\text{ cm}^{-1}$ , a clear spectral evolution about the location of the dominating peak from  $255$  to  $245\text{ cm}^{-1}$  can be seen going with the gradual increasing about the intensity of the shoulder at about  $225\text{ cm}^{-1}$ . The third change is about the increasingly enhancement of the peak at  $306\text{ cm}^{-1}$  in the  $270-320\text{ cm}^{-1}$  range. Fourthly, the strongest peak at  $340\text{ cm}^{-1}$  is broadened little by little towards two sides with the increased content of  $\text{In}_2\text{S}_3$ . And the descending scattering intensity by inchmeal of the shoulder at  $370\text{ cm}^{-1}$  is the final change originated from the addition of  $\text{In}_2\text{S}_3$ . To further attain the micro-structural information, the FTIR transmission spectra of the glassy samples ( $x=0.00-0.25$ ) were presented in Fig. 3. However, no distinct spectral transformations are found except for the gradual descending of the characteristic absorption band of the  $\text{GeS}_2$  glass at  $377\text{ cm}^{-1}$ .

Finally, polycrystalline  $\text{In}_2\text{S}_3$  was synthesized by direct reaction of a stoichiometric mixture of the elements using the melt-quenching slowly method. The reaction led to a reddish powder that X-ray powder diffraction showed to be the pure defect spinel phase  $\text{In}_2\text{S}_3$  (JCPDF No: 84-1385). The Raman

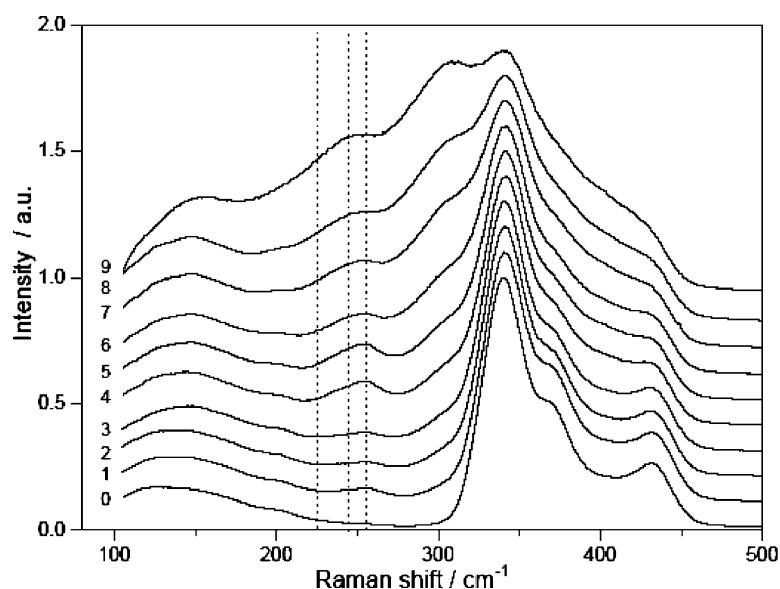


Fig. 2. Raman spectra of the  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  glasses. 0,  $x=0.00$ ; 1,  $x=0.01$ ; 2,  $x=0.025$ ; 3,  $x=0.04$ ; 4,  $x=0.07$ ; 5,  $x=0.10$ ; 6,  $x=0.15$ ; 7,  $x=0.20$ ; 8,  $x=0.25$ ; 9,  $x=0.30$ .

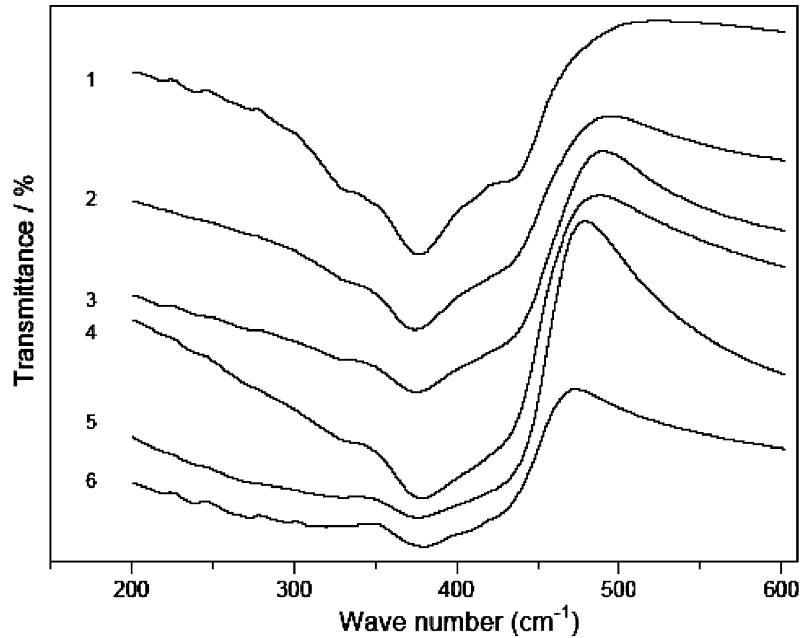


Fig. 3. FTIR spectra of the  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  glasses. 1,  $x=0.00$ ; 2,  $x=0.05$ ; 3,  $x=0.10$ ; 4,  $x=0.15$ ; 5,  $x=0.20$ ; 6,  $x=0.25$ .

and FTIR spectra of this polycrystalline sample were shown in Fig. 4. Group theoretical treatment of the spinel structure yields four infrared active modes of species  $F_{1u}$  and five Raman active ones, one each species  $A_{1g}$  and  $E_g$ , three of species  $F_{2g}$  [7]. According to the research of Lutz et al. [7,8], the Raman peak at  $366\text{ cm}^{-1}$  of the prepared polycrystalline  $\text{In}_2\text{S}_3$  can be ascribed to the  $A_{1g}$  mode, the peak at  $262\text{ cm}^{-1}$  to the  $E_g$  mode, and the peaks at  $117, 179, 322\text{ cm}^{-1}$  to the  $F_{2g}$  mode. As to the additional peaks at  $306$  and  $245\text{ cm}^{-1}$ , which are stronger than the Raman active modes originated from the spinel structure, it can be rationally presumed that these two additional peaks are so-called clustering modes caused by high density of states of distinct phonon branches at  $q \neq 0$ , which is Raman allowed

because of the breakdown of the translation symmetry. And this can be confirmed by the random distribution of indium on the octahedral and tetrahedral sites according to the JCPDF card together with the corresponding absorption bands of the FTIR spectrum.

In terms of our previous study [9], the  $A_{1g}$  breathing mode of  $\text{GaS}_4$  tetrahedra locates at about  $342\text{ cm}^{-1}$  in the  $\text{GeS}_2\text{-Ga}_2\text{S}_3$  pseudo-binary glassy system. Based on the similarity of chemical properties for Ga and In located in the same main family, it is reasonable to presume the same force constants among the  $\text{GaS}_4$  and  $\text{InS}_4$  tetrahedra. According to the theory of molecular vibration [10], then, the  $A_{1g}$  breathing mode of  $\text{InS}_4$  tetrahedra should locate at about  $315\text{ cm}^{-1}$  considering

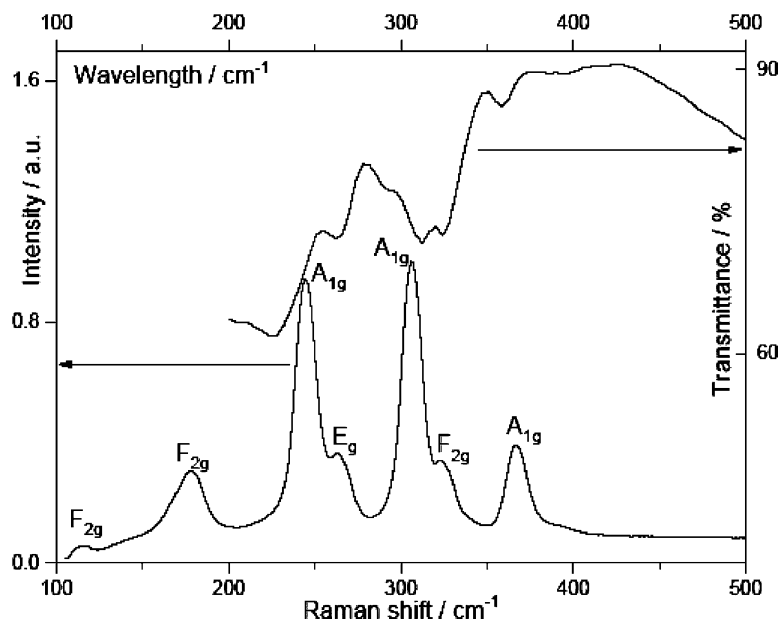


Fig. 4. Raman and FTIR transmission (CsI plate) spectra of the polycrystal  $\text{In}_2\text{S}_3$  sample.

the bigger weight of In compared with Ga. Furthermore, considering the less force constant of In-S bonds compared with Ga-S ones, the  $A_{1g}$  mode of  $\text{InS}_4$  tetrahedra should locate at the lower wave number than  $315\text{ cm}^{-1}$ . So it is rational to attribute the additional peak at  $306\text{ cm}^{-1}$  to the symmetric stretching vibration of  $\text{InS}_4$  tetrahedra.

According to the analysis about the Raman spectra of inverse and partially inverse indium sulfide spinels, Lutz et al. [7] ascribed the bands in the range 240–255 to the  $A_{1g}$  breathing mode based on the facts that the intensity of this band increases with increase in the degree of inversion of the spinels. So it is reasonable to ascribed Raman peak at  $245\text{ cm}^{-1}$  to the symmetric stretching vibrating of  $\text{InS}_6$  octohedra.

#### 4. Discussion

The Raman spectrum of the compound  $\text{GeS}_2$  glass in Fig. 1 (0) is similar to those reported previously [11–13]. Four bands can be distinctly observed at 115, 340 ( $A_1$ ), 370 ( $A_1^c$ ) and  $431\text{ cm}^{-1}$ . The broad band at  $115\text{ cm}^{-1}$ , superimposed on the high frequency tail of the boson peak, was ascribed ordinarily to the bond bending motions of S atoms in  $\text{GeS}_4$  tetrahedra, while Kotsalas, etc. [11] suggested that considerable contribution to this band may arise from intermolecular displacements of whole  $\text{GeS}_4$  structural units. The bands at 340 and  $370\text{ cm}^{-1}$  are strongly polarized and the former is attributed undoubtedly to the  $A_1$  symmetric stretching vibrations of  $\text{GeS}_4$  tetrahedra, while the latter is due to the symmetric stretch vibrations of S atoms in bridges of edge-sharing  $(\text{GeS}_{1/2})_4$  tetrahedra. The shoulder at  $431\text{ cm}^{-1}$  is relatively depolarized (to the  $A_1$  and  $A_1^c$  bands) and generally recognized to be due to the S-S and/or multi-sulfur bonds although there were some controversies [14]. And this gives a probable existence of small S-S chains in g- $\text{GeS}_2$  either as separate molecular units (inhomogeneities) or as interconnecting units between  $\text{GeS}_4$  units. In addition, the very weak Raman band at  $255\text{ cm}^{-1}$  (can be attributed to the vibrational mode of the ethane-like units  $\text{S}_3\text{Ge-GeS}_3$ ; and only can be seen clearly through local magnification of Raman spectra) give another proof that the microstructure of the stoichiometric  $\text{GeS}_2$  glass does not consist only of  $\text{GeS}_4$  tetrahedra.

According to the Fig. 1, the spectrum 1 exactly corresponds to the Raman spectra of the prepared polycrystalline  $\text{In}_2\text{S}_3$  which further verified the result of the XRD analysis. As to the spectrum 4, the characteristic bands of the  $\text{S}_3\text{In-InS}_3$  ethane-like units can be clearly distinguished based on the distinct broad peak at about  $153\text{ cm}^{-1}$  together with the small shoulders at about  $226$  and  $321\text{ cm}^{-1}$  [15]. In addition, the main peak at  $340\text{ cm}^{-1}$  is due to the symmetric stretching mode of  $\text{GeS}_4$  and the small prominence at about  $255\text{ cm}^{-1}$  can be ascribed to the vibrating of the  $\text{S}_3\text{Ge-GeS}_3$  ethane-like units. Furthermore, the bands at  $306$  and  $244\text{ cm}^{-1}$  can be attributed to the symmetric stretching vibrations of  $\text{InS}_4$  and  $\text{InS}_6$  units, respectively, based on the above-mentioned ascription. Lastly, the spectra 2 and 3 are intervenient between the spectrum 1 and 4.

Now let us see the spectral evolution of the  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  glasses ( $x=0-0.3$ ). Firstly, the clear evolution of the region  $270-320\text{ cm}^{-1}$  from a small shoulder to a distinct peak at  $306\text{ cm}^{-1}$  gives the direct proof about the existence of  $\text{InS}_4$  tetrahedra within the Ge-In sulfide glassy net. In addition, following the addition of  $\text{In}_2\text{S}_3$ , the similar transformation of the region  $225-255\text{ cm}^{-1}$  from a small prominence to a dominating peak at  $245\text{ cm}^{-1}$  within the region  $200-270\text{ cm}^{-1}$  indicates another coordination surroundings of In atoms, viz.  $\text{InS}_6$  octahedra. And the weaker scattering strength of the prominence at  $245\text{ cm}^{-1}$  compared with that of another one at  $306\text{ cm}^{-1}$  manifests itself that the added indium exists mainly in the form of  $\text{InS}_4$  tetrahedra. Secondly, the incremental quantity of the ethane-like units  $\text{S}_3\text{In-InS}_3$  with the addition of  $\text{In}_2\text{S}_3$  within the glassy net can be confirmed by the gradual enhancement of the characteristic bands at about  $150$  and  $225\text{ cm}^{-1}$  together with the slowly broadening of the main peak at  $340\text{ cm}^{-1}$  toward lower wave number aspect originated from another diagnostic band at  $321\text{ cm}^{-1}$  of the  $\text{S}_3\text{In-InS}_3$  units. Thirdly, the far weaker intensity of the prominence of the band at about  $225\text{ cm}^{-1}$  compared with that of another one at  $255\text{ cm}^{-1}$  gives us the information that the ethane-like units  $\text{S}_3\text{Ge-GeS}_3$  comes into being more preferentially than another similar units  $\text{S}_3\text{In-InS}_3$  when sulfur is deficient due to the addition of  $\text{In}_2\text{S}_3$ . And the gradually widening of the main peak at  $340\text{ cm}^{-1}$  toward the higher wave number aspect from sample 0–9 can be explained from the gradual enhancement of another characteristic band at about  $360\text{ cm}^{-1}$  [12] of the ethane-like units  $\text{S}_3\text{Ge-GeS}_3$ . Lastly, the descending scattering intensity by inchmeal of the shoulder at  $370\text{ cm}^{-1}$  is due to the descending amount of bridged units  $\text{Ge}_2\text{S}_6$  originated from the increasingly enhanced quantity of other units (e.g.  $\text{InS}_4$  and  $\text{InS}_6$ , etc.) following the addition of  $\text{In}_2\text{S}_3$ .

#### 5. Conclusion

The Raman scattering and FTIR transmission spectra of the prepared polycrystalline  $\text{In}_2\text{S}_3$  that belongs to the defect spinel-type structure was reported. The additional peaks at  $306$  and  $245\text{ cm}^{-1}$  were attributed to the local symmetric stretching vibrating of  $\text{InS}_4$  and  $\text{InS}_6$  microstructural units respectively.

The inhomogeneous nature of sample 10 ( $0.65\text{GeS}_2-0.35\text{In}_2\text{S}_3$ ) was clearly confirmed by the Raman scattering measurement. Based on the spectral evolution of the  $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$  glasses, the following micro-structural information can be deduced:

- (1) The added indium exists mainly in the form of  $\text{InS}_4$  tetrahedra together with a small quantity of  $\text{InS}_6$  octahedra within the glassy network.
- (2) With the addition of  $\text{In}_2\text{S}_3$ , the ethane-like units  $\text{S}_3\text{Ge-GeS}_3$  are more preferentially formed than the similar  $\text{S}_3\text{In-InS}_3$  units.

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