Structural Analysis of Tm³⁺ Doped As-S-Ga Glasses by Raman and EXAFS spectroscopy

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ABSTRACT

Structural properties of Tm³⁺ doped As-S-Ga glasses were investigated using Raman spectroscopy and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy at As K-edge, Ga K-edge and Tm L₃-edge. The Raman spectra are interpreted on the basis of comparison with the well-known Raman spectra of As₂S₃ glasses the structure of which mainly consists of pyramidal [AsS_{3/2}] units interconnected by S-S chains. Incorporation of Ga₂S₃ in As₂S₃ glass matrix induced the dissociation of S-S chains in behalf of the formation of tetrahedra [GaS₄]. Moreover, introduction of Tm into As-S-Ga glasses forms Tm-S bonds through the further dissociation of [AsS_{3/2}] pyramidal units. The deficiency of S in the glasses is compensated with the formation of As₄S₄ structural units. The EXAFS results indicate that Ga-S bond distance in the tetrahedra [GaS₄] decreases from 2.29 Å to 2.26 Å with the increase of Tm concentration in the glass. Meanwhile, Tm-S bond distance increases from 2.66 Å to 2.71 Å approaching to that of crystalline Tm₂S₃ and simultaneously, the coordination number of Tm gradually decreases from 7 to 4.

Keywords: Raman spectra of As-S-Ga glasses, EXAFS study of Tm³⁺ doped chalcogenide glasses, As K-edge, Ga K-edge, Tm L₃-edge.

1. INTRODUCTION

Sulfides based chalcogenide glasses attract considerable interest thanks to their low phonon energy, high refractive index, good chemical durability and good glass-forming ability. A variety of sulfide glass systems has been studied based on gallium, germanium, arsenic sulfides and combinations of them [1-6]. Among all these systems the arsenic trisulfide (As₂S₃) is the best

known and the most explored system from the point of view of thermo-optical features and molecular structure [7]. When doped with rare earth (RE) ions [8-10], chalcogenide glasses open up the possibility of new transitions and significantly increased pumping efficiencies for fiber-optic amplifiers and infrared lasers. However, As_2S_3 glasses suffer from poor RE solubility [11], resulting the clustering of rare earth ions, which limits their applications as practical amplifiers or lasers.

According to the previous reports, the solubility of RE ions can be increased dramatically with the addition of gallium (Ga) to the host [12-14] due to the presence of edge-sharing $[\text{GaS}_4]$ tetrahedra which appear with the addition of Ga_2S_3 [15]. The increased solubility of RE is due to the fact that the incorporation of Ga provides compensation for the negative charge of free S^{2-} ions by forming chemical bonds with RE ions.

In our previous work, we explored different compositions of As-S-Ga glasses as host matrix for Tm^{3+} ions [16]. The luminescence properties of As-S-Ga:Tm glasses depending of Ga and Tm concentration were studied, as well as, their thermal and optical properties. It was found that the incorporation of Ga_2S_3 compound in the network of As_2S_3 glasses improved their RE solubility. Infrared emission spectra were recorded and strong emission bands at wavelengths around $1.2\mu\text{m}$ ($^1\text{H}_5 \rightarrow ^3\text{H}_6$), $1.4\mu\text{m}$ ($^3\text{H}_4 \rightarrow ^3\text{F}_4$) and $1.8\mu\text{m}$ ($^3\text{F}_4 \rightarrow ^3\text{H}_6$) were obtained under the excitation of a xenon lamp at 698nm and 800nm. A Tm^{3+} doped As-S-Ga glass fiber was also fabricated where all three emission bands were observed as in bulk samples.

The present work deals with better understanding of the structural changes created in the As_2S_3 glass matrix with the incorporation of Ga and Tm. A systematic structural study is performed in the As-S-Ga by varying the amount of Tm from 1 to 8%. To obtain structural information about the local environment in these glasses, Extended X-ray Absorption Fine Structure (EXAFS) analysis was performed at the As K-edge, Ga K-edge and Tm L_3 -edge. Structural information was also obtained through Raman analysis as a function of glass composition for different concentrations of Ga and Tm.

2. EXPERIMENT

The Tm^{3+} doped As-S-Ga glasses were prepared by melting Ga_2S_3 crystalline compound (99.999%), metallic Tm^{3+} and the pre-purified As_2S_3 glass. The glasses were synthesized in silica ampoules sealed under high vacuum (10^{-5} Torr). The ampoule is placed in a rocking furnace and heated at a rate of $1^\circ\text{C}/\text{min}$ up to 900°C . After being rocked for 12 hours (for homogenization),

the glass is quenched in the water at room temperature for few seconds and annealed at 160°C for 6 hours to remove the thermal stress.

The Raman scattering spectra were collected with a confocal Renishaw inVia spectrometer coupled to a Leica DM2700 microscope. A back-scattering geometry was used in the frequency range of 100-600 cm^{-1} . The excitation light source was a 17 mW vertically polarized 633 nm (He-Ne) laser. The laser beam was focused with a 50X long working distance objective, generating a sub-micron spot size containing a total power at the sample of approximately 5-10mW. The frequency uncertainty was estimated to be $\pm 2 \text{ cm}^{-1}$. The deconvolution of Raman spectra were performed using curve fit function of Wire 4.1 software.

EXAFS measurements were carried out at the Sector 10-BM-B (MRCAT) beamline at the Advanced Photon Source [17] (Argonne National Laboratory, Chicago). All measurements were performed using powdered samples at room temperature. The EXAFS spectra were collected at the As K-edge (11867eV), Ga K-edge (10367eV) and Tm L_3 -edge (8648eV). The Ga and Tm edges were measured in fluorescence mode using a 4 Element Vortex Silicon Drift detector. The As edge was measured in transmission mode, using Nitrogen (incident beam) and Argon (transmitted beam) filled ionization chamber detectors. The positions of the monochromator for As, Ga and Tm edges were calibrated using Au, Ta and Cu metal foils, respectively.

Structural parameters including coordination number (N), interatomic distance (r) and the Debye-Waller factor (σ) were obtained from least squares fitting in k-space, using theoretical phase and amplitude functions using the IFEFFIT-based software [18] packages Athena and Artemis [19].

3. RESULTS AND DISCUSSION

3.1. RAMAN SPECTROSCOPY

Figure 1 shows the Raman spectra of 0.2%Tm³⁺ doped $\text{Ga}_x\text{As}_{40-x}\text{S}_{60}$ ($0 < x < 4$) glasses as a function of Ga concentration as well as the Raman spectra of As_2S_3 glass as reference. The structure of As_2S_3 glasses has been extensively studied by several authors using Raman spectroscopy [20-23]. It is generally accepted that the three dimensional network of As_2S_3 glass is built of trigonal pyramidal units [$\text{AsS}_{3/2}$], which are interconnected through $\text{S}_2\text{AsS-SAsS}_2$ bridges [20,23,24], which give rise to two main bands centered at 342 cm^{-1} and 495 cm^{-1} . Such bands can be observed in the Raman spectra of As_2S_3 glass in figure 1a.

The addition of Ga_2S_3 to As_2S_3 glass matrix gives rise to two bands centered at 189 cm^{-1} and 233 cm^{-1} , which are ascribed to the presence of As-As homo-polar bonds [25] in As_4S_4

realgar molecules and to Ga-S-Ga bend [26] in $[\text{GaS}_4]$ tetrahedra, respectively. Besides, there are additional shoulders at approximately 365 cm^{-1} and 390 cm^{-1} (fig.1a) which have been associated to As_4S_4 cage-like nanocluster units [20,21,27] and to the symmetrical stretching vibration of $[\text{GaS}_4]$ tetrahedra [15,28], respectively. Moreover, the band at 495 cm^{-1} disappears with the incorporation of Ga (0.8 at%).

Fig. 1. a.) Normalized Raman spectra of 0.2% Tm^{3+} doped $\text{Ga}_x\text{As}_{40-x}\text{S}_{60}$ glasses. The inset represents the schematic structure of As_2S_3 glasses. b) Relative intensities of Raman bands for different structural units as a function of Ga content.

In order to better understand the role of the addition of gallium on the structural changes of the matrix of arsenic sulfide, the Raman spectra of studied glasses were deconvoluted with Gaussian peaks using least squares approach. A preliminary subtraction and a polynomial baseline were performed in the collected Raman spectra followed by the normalization at 342 cm^{-1} . The intensity of each band was calculated by integrating the surface of the corresponding peak for all Raman modes present in the spectra, which allowed us to quantify the contribution of the molecular constituents to Raman spectra. The resulting structural trends for each assigned structural units depending on Ga contents are presented in the figure 1b. It can be seen that the band associated with symmetric stretching of $[\text{AsS}_{3/2}]$ pyramids (342 cm^{-1}) decreases with the incorporation of Ga in the matrix, whereas the band assigned to As_4S_4 structural units (365 cm^{-1}) increases in amplitude. A slight increasing of $[\text{GaS}_4]$ tetrahedral units (390 cm^{-1}), Ga-S-Ga bonds (233 cm^{-1}) and As-As homo-polar bonds (189 cm^{-1}) is observed as well. Further increasing the Ga concentration did not show any significant changes in the band amplitudes, which is probably related to the fact that the glass formation region in this system is very small and up to 3.5at% of Ga can be incorporated in the glass [29]. This limits the observation of significant structural changes in the glass upon the increasing of Ga content.

Based on the above results, one can suppose that the sulfur, originally connecting $[\text{AsS}_{3/2}]$ pyramids, was removed to provide extra sulfur needed for the formation of $[\text{GaS}_4]$ tetrahedra. This trend is observed through the disappearance of the band centered at 495 cm^{-1} and the increase of the shoulder at 390 cm^{-1} (fig.1b). It is well known that the formation of $[\text{GaS}_4]$ tetrahedra from Ga_2S_3 results in a deficiency of sulfur in the glasses since the S/Ga ratio of Ga_2S_3 is 1.5 which is less than the 2 required to form tetrahedra [30]. Therefore, as we increase the amount of Ga_2S_3 in the glass matrix, $[\text{AsS}_{3/2}]$ pyramidal units started to be dissociated creating non-bridging sulphurs for Ga, which is visualised by the decrease of the 342 cm^{-1} band. Simultaneously, the migration of

sulfur from $[\text{AsS}_{3/2}]$ pyramids to $[\text{GaS}_4]$ tetrahedra results in the formation of metal-metal (As-As) bonds in the glass (forming As_4S_4 units).

So, we can consider that the molecular structure of our As-S-Ga glass matrix consists of $[\text{GaS}_4]$ tetrahedra and $[\text{AsS}_3]$ pyramids randomly linked by shared sulfur atoms surrounded by realgar-like As_4S_4 molecules (fig. 2).

Fig.2. Schematic representation of structural units formed in As_2S_3 glass with incorporation of Ga and hypothetical local structure model around Tm ions in As-S-Ga glasses

In our previous work [16] we observed that the incorporation of Ga in the As_2S_3 vitreous network allowed the solubility of Tm^{3+} ions and its corresponding emission bands were observed. Prior to addition of Ga, the Tm ions are described as clustered [31] and no emission was observed in As_2S_3 glasses. This behaviour may instead be due to a lack of solubility and random precipitation which avoid the luminescence [12]. With the introduction of Gallium, Ga complexes the RE-ion in the presence of chalcogen forming $[\text{RE}^{3+}\text{-S-Ga}^{\text{III}}]$ type species as already confirmed by Aitken et al. [32] in the sulfide glasses. We can suppose that the originally Tm cluster are dissolved into Ga site rather than in As regions and then become fully spread until proportions of such Ga regions reach a certain critical value (in our case, Ga=3.2 at% [16]). So, $[\text{GaS}_4]$ tetrahedra form a shell around the Tm ions (fig. 2), and the resultant complex is readily incorporated into the As_2S_3 glass with the same analogy as in silica glasses co-doped with Al_2O_3 to dissolve the rare earth element in the glass matrix[33].

As follow, we choose the sample already doped with Ga_2S_3 (namely $\text{Ga}_{0.8}\text{As}_{39.2}\text{S}_{60}$ glasses) where the process of As_2S_3 pyramidal units breakage already is placed, and we measure the Raman spectras of this matrix with different Tm^{3+} concentrations (1-8 at%). Results are presented in the figure 3. Raman spectrum of c- Tm_2S_3 is added as a reference. As we can see from the spectra, with the incorporation of Tm a new band appears at 224cm^{-1} , which is associated to Tm-S bonds [34] and with the increase of Tm concentration the intensity of this band increases slightly. The bands at 233 cm^{-1} (Ga-S-Ga) and 390 cm^{-1} ($[\text{GaS}_4]$ tetrahedral) stay almost constant upon the variation of Tm content in the glass (fig. 3b). Contrariwise, the band at 365cm^{-1} (As_4S_4) continues to increase. Simultaneously, the band at 342 cm^{-1} ($[\text{AsS}_3]$) decreases in amplitude. A slight increase of the band at 189cm^{-1} (As-As) is observed as well.

Fig. 3 a.) Normalized Raman spectra of Tm doped $\text{Ga}_{0.8}\text{As}_{39.2}\text{S}_{60}$ glasses. b.) relative intensities of Raman bands for different structural units as a function of Tm content $\text{Ga}_{0.8}\text{As}_{39.2}\text{S}_{60}$ glasses.

This behavior could indicate that the introduction of Tm into As-S-Ga matrix results in the formation of Tm-S bonds by breaking the As-S bond in $[\text{AsS}_3]$ pyramidal units, which increases the concentration of homo-polar (As-As) bonds due to the deficiency of sulfur. This would suggest that the formation of more As_4S_4 units is favored, which is associated to the increase of the band at 365 cm^{-1} . So, we could confirm that even a very small concentration of Ga atoms is able to facilitate the solubility of Tm-ions and enhance their fluorescence properties [16]. Despite the fact that with the increase of Tm concentration up to 8at% the band at 342 cm^{-1} ($\text{AsS}_{3/2}$) gradually decreases and the band at 224 cm^{-1} (Tm-S) continues to increase, the intensity of emission of Tm ions decreases at $\geq 4\text{at\%}$ [16], which could indicate that at higher concentrations, even if more Tm-S bonds are formed, the environment of Tm is no more favorable for the solubility of ions, and this leads to the decrease of luminescence.

These structural changes suggest that Tm ions act as a modifier in the As_2S_3 glass matrix. A similar mechanism was proposed by Pisarski et al. [35] based on visible and infrared spectroscopy data on Tm^{3+} ions in lead borate glass system.

3.2. EXAFS

In order to further investigate the structural modifications imported by Tm^{3+} ions in the $\text{Ga}_x\text{As}_{40-x}\text{S}_{60}$ glasses, EXAFS analysis at As K-edge, Ga K-edge and Tm L_3 -edge was performed. EXAFS spectra of As K-edge of As_2S_3 glass and Ga K-edge of Ga_2S_3 crystalline compound were also collected as references. The range of the Fourier Transform for As and Ga was $2\text{-}15\text{\AA}^{-1}$, and for Tm it was $2\text{-}10\text{\AA}^{-1}$. The range of the R-space fit was $1\text{-}3\text{\AA}$ for all three elements.

As K-edge

The k^3 -weighted $\chi(k)$ experimental EXAFS spectra of As K-edge, the corresponding Fourier transforms and their theoretical fits are shown in Fig. 4. The nominal compositions of glasses, studied with EXAFS spectroscopy, and the structural parameters for the first coordination shell are presented in Table 1.

Fig. 4. k^3 -weighted As K-edge EXAFS spectra (a) and the magnitudes of Fourier transformation (b). Black solid lines represent experimental data, red dash lines correspond to fit

	$N_{\text{As-S}}$ (± 0.2)	$r_{\text{As-S}}(\text{\AA})$ (± 0.005)	$\sigma^2(\text{\AA}^2)$ ± 0.001	R-factor
As₂S₃	3.0	2.280	0.003	0.004
Ga_{0.8}As_{39.2}S₆₀	2.9	2.279	0.003	0.005
Ga_{0.8}As_{39.2}S₆₀ : 1%Tm	3.0	2.279	0.003	0.006
Ga_{0.8}As_{39.2}S₆₀ : 2%Tm	2.9	2.279	0.003	0.006
Ga_{0.8}As_{39.2}S₆₀ : 4%Tm	2.9	2.279	0.003	0.005
Ga_{0.8}As_{39.2}S₆₀ : 8%Tm	2.8	2.281	0.004	0.005

Table 1: As K-edge EXAFS structural parameters (the coordination number N , the bond length r and Debye-Waller factor σ) for Tm doped Ga_{0.8}As_{39.2}S₆₀ glasses

The fitting of EXAFS spectra showed that the first neighbour of As is sulfur and yields the first-shell coordination numbers of $N \sim 3$ at $r = 2.28 \text{\AA}$, which reflects the As–S bonding distance. This value of As-S distance ($2.28 \text{\AA}$) is close to the mean As–S distance in crystalline As₂S₃ [36]. The present results are consistent with those reported by other authors [37], where the local atomic structure is formed of [AsS_{3/2}] units, and each arsenic atom is bound to three sulfur atoms with As-S bond lengths of $2.2701 \text{\AA}$, $2.2894 \text{\AA}$ and $2.2919 \text{\AA}$ [38].

The insertion of gallium (or thulium) in the As₂S₃ matrix did not show any modification in the pyramidal units [AsS_{3/2}], i.e. neither the average distance between As and S nor the coordination number of As were changed (table 1). Despite the fact that Raman spectra showed a formation of As-As bonds, no As-As bond was observed in the present EXAFS analysis. This could be related with the fact that these bonds are quite disordered in the glass and therefore the bands are overlapped in the spectra. So the contribution of As-As is not significant and only a single large peak is always obtained in spectra.

It must be noted that the disorder inherent in a glass and the similar electronic structures of Ga and As backscattering atoms do not allow to distinguish at least the nature of the second neighbour of As (or Ga) directly by EXAFS.

Ga K-edge

Fig. 5 shows the k^3 -weighted $\chi(k)$ spectra and Fourier transformed spectra of the Ga K-edge. The resulting fitting of the first coordination shell of Ga are summarized in table 2. It revealed that the Ga atoms in these glasses are surrounded by 4 sulphurs, like in the crystalline compound Ga₂S₃ which is in accordance with Goodyear et al. [39], where the structure of the Ga₂S₃ crystal is composed of [GaS₄] tetrahedral units. The interatomic distance Ga-S in the Ga_{0.8}As_{39.2}S₆₀ matrix is $2.27 \text{\AA}$, which is almost the same as in the crystalline Ga₂S₃ ($2.29 \text{\AA}$) [40].

The estimated standard deviation is about 0.01. Benazeth et al. [41] also studied the structure of bulk gallium lanthanum sulphide (GLS) glasses using EXAFS at the Ga K-edge and lanthanum L₃-edge. Their results showed as well that in the glass the gallium atoms exist in tetrahedral networks of GaS₄ and the Ga–S distances are identical to those existing in the crystalline form of Ga₂S₃. Upon the addition of Tm, the coordination number of Ga stays constant and the further changes in the Tm concentration do not lead to any additional changes in the coordination of Ga. However, at higher concentrations of Tm the bond distance of Ga-S becomes slightly shorter. So the increasing of the Tm concentration in the glass matrix leads to slight contraction of [GaS₄] tetrahedral.

The results are presented only for 1 and 2% of Tm. For the compositions with higher concentration of Tm the aberrations appear in the spectra, due the fact that bonding energies of Ga K-edge and Tm L₁-edge are very close.

Fig. 5. k^3 -weighted Ga K-edge EXAFS spectra and the magnitudes of Fourier transformation. Black solid lines represent experimental data, red dash lines correspond to fit

	$N_{\text{Ga-S}}$ (± 0.3)	$r_{\text{Ga-S}}$ (Å) (± 0.01)	σ^2 (Å ²) (± 0.001)	R-factor
c-Ga₂S₃	3.9	2.29	0.005	0.02
Ga_{0.8}As_{39.2}S₆₀	3.9	2.27	0.004	0.02
Ga_{0.8}As_{39.2}S₆₀ : 1%Tm	4.0	2.27	0.005	0.02
Ga_{0.8}As_{39.2}S₆₀ : 2%Tm	4.0	2.26	0.005	0.02

Table 2: Ga K-edge EXAFS structural parameters (the coordination number N , the bond length R and Debye-Waller factor σ) for Tm doped Ga_{0.8}As_{39.2}S₆₀ glasses

Tm L₃-edge

Figs. 6 shows the k^3 -weighted $\chi(k)$ spectra and Fourier transformed spectra of Tm³⁺ ions in Ga_{0.8}As_{39.2}S₆₀ glasses. The increase of Tm concentration resulted in significant changes in the shape of k^3 -weighted $\chi(k)$ and Fourier transformed R-space spectra, indicating modifications of local structure around Tm³⁺ ions. The two peaks between 3-5 Å are more prominent in the Tm spectra than in the As and Ga spectra which indicates that the Tm is in a more well-ordered environment at all concentrations.

Table 3 shows results of the fitting on the first coordination shell around Tm³⁺ ions. Current EXAFS analysis at Tm L₃-edge indicates that Tm ions are coordinated with sulfur ions, in accordance with the previous reports [42]. It can be observed that for small content of Tm³⁺ ions the coordination number is about 7.

Fig.6. k^3 -weighted Tm L_3 -edge EXAFS spectra and the magnitudes of Fourier transformation. Black solid lines represent experimental data, red dash lines correspond to fit

	$N_{\text{Tm-S}}$ (± 0.5)	$r_{\text{Tm-S}} (\text{\AA})$ (± 0.008)	$\sigma^2 (\text{\AA}^2)$ (± 0.001)	R-factor
Ga_{0.8}As_{39.2}S₆₀ : 1%Tm	6.5	2.666	0.016	0.003
Ga_{0.8}As_{39.2}S₆₀ : 2%Tm	5.4	2.695	0.011	0.001
Ga_{0.8}As_{39.2}S₆₀ : 4%Tm	4.9	2.716	0.011	0.005
Ga_{0.8}As_{39.2}S₆₀ : 8%Tm	4.2	2.713	0.011	0.003

Table 3: Tm K-edge EXAFS structural parameters (the coordination number N , the bond length R and Debye-Waller factor σ) for Tm doped Ga_{0.8}As_{39.2}S₆₀ glasses

However, upon the addition of Tm, the coordination environment of Tm³⁺ shows gradual changes, i.e. with the increase of the concentration of Tm³⁺ from 1% to 8%, the coordination number decreases from 7 to 4 and the Debye-Waller factor decreases from 0.016 to 0.011. Simultaneously, the distance between Tm and S becomes larger (from 2.66Å to 2.71Å). According to ref. [42] in the crystalline Tm₂S₃ the Tm-S distance is about 2.74Å, so the increase of Tm-S bond length in the glass and the decreasing of Debye-Waller factor could mean that crystalline units of Tm₂S₃ began to form in the glass matrix, when the concentration of Tm increases. This is in good agreement with X-ray diffraction spectra of Tm³⁺ doped Ga_{0.8}As_{39.2}S₆₀ glasses already reported in our previous work [16]. Meanwhile, the diminution of coordination number could be explained by the fact that at high concentrations the atoms of Tm become closer, leading to inhomogeneous distribution or clustering of Tm atoms. The Tm-Tm bond distance is known to be about 3.2-3.4 Å [43], but no Tm atom was observed in the first coordination shell of Tm. These bonds are significantly disordered in a glass and they could be simply not visible in the spectra.

In summary, the EXAFS analysis did not show any changes in the local environment of As with the incorporation of Tm. However, introduction of Tm³⁺ ions in the glass matrix leads to the contraction of Ga-S distance in the GaS₄ tetrahedra. Meanwhile, the formation of Tm₂S₃ crystalline units in the glass matrix is observed when the concentration of Tm became relatively high, which is reflected by the decrease of Debye-Waller factor, and the increase of Tm-S bond length.

As it was already mentioned above the maximum intensity of luminescence of Tm-ions in Ga_{0.8}As_{39.2}S₆₀ glass matrix was observed at 2at% of Tm [16], and it decreases with the further increase of Tm content. So we can conclude that at 2at%, despite the coordination number of Tm

decreases from 7 to 6, the concentration of homogenously distributed luminescent centers increases in the glass matrix, which promotes the increase of luminescence. However, starting from 4at% the coordination number of Tm decreases up to 5 and the environment of Tm becomes less favorable for the solubility of ions. Moreover, from 4at% the concentration of Tm ions is so high that the mean distance between ions could become small enough for spatial migration of the excitation energy, from one Tm-ion to a neighboring ion, becomes possible. This leads to depopulation of excited states and decrease of the luminescence.

4. CONCLUSION

The combination of the analyses of Raman spectra of Tm^{3+} doped $\text{Ga}_x\text{As}_{40-x}\text{S}_{60}$ glasses and EXAFS spectra at As K-edge, Ga K-edge and Tm L_3 -edge revealed that the atomic structure of initial As_2S_3 glasses matrix consist of pyramidal units of $[\text{AsS}_{3/2}]$ interconnected through As-S-S-As bridges. The As atoms are three fold coordinated with two fold-coordinated S atoms with the distance about $2.28\text{\AA}$. The incorporation of Ga_2S_3 leads to the formation of $[\text{GaS}_4]$ tetrahedra, by means of breaking both the As-S bond in AsS_3 of pyramidal units and the interconnecting S-S chains. The deficiency of sulfur is compensated by the formation of As_4S_4 realgar units, as the amount of Ga_2S_3 increases. Successively, the incorporation of Tm gradually breaks the $[\text{AsS}_{3/2}]$ pyramids and takes the role of charge compensators for non-bridging S ions forming Tm-S bonds. No dissociation of $[\text{GaS}_4]$ tetrahedra occurred with the incorporation of Tm. However, Ga-S bond length decreases from $2.29\text{\AA}$ to $2.26\text{\AA}$ with the increase of Tm concentration. The local environment of Tm undergoes significant changes upon the variation of its content in the glass. With the increasing of Tm content from 1% to 8% the coordination number gradually decreases from 7 to 4, and simultaneously the Tm-S bond distance increases from $2.66\text{\AA}$ to $2.71\text{\AA}$ approaching to that of crystalline Tm_2S_3 , which indicates the formation of crystalline units and Tm clusters in the glass at higher Tm concentration.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6