



Raman scattering studies of the $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glassy system

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Abstract

Room temperature Raman spectra of samples on four serials within $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glassy system have been investigated systematically. Based on the analysis of the local coordination surroundings of Cs^+ ions, the similarities and changes of Raman spectra for glass $\text{Ga}_2\text{S}_3\text{--}2\text{CsCl}$ and bridged molecular GaCl_3 were explained successfully. With a profound consideration of the effect of Cs^+ ions on mixed anion units ($\text{GaS}_{4-x}\text{Cl}_x$) and bridged units ($\text{Ga}_2\text{S}_{6-x}\text{Cl}_x$) and the corresponding micro-structural model, the Raman spectral evolution of the samples within $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glassy system was reasonably elucidated.

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1. Introduction

Ga_2S_3 -based chalcogenide glasses have been considered as promising hosts for rare-earth (RE) doped active devices [1–3]. In addition, due to their higher optical non-linear coefficient and smaller two-phonon absorption, recently the Ga_2S_3 -based chalcogenide glasses have become a hot-point of research and development particularly for applications such as ultra-fast all optical switching [4]. Because the above-mentioned two properties all have an intimate relationship with the microstructure of Ga_2S_3 -based chalcogenide glasses, therefore, an understanding and utilization of the micro-structural research findings have practical importance.

Much research on the binary Ge–S and ternary Ge–Ga–S glasses has been done [5–7]. However, the micro-structural research about the $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glassy system is scarce. Based on the similarity of Raman spectra between

the $\text{CsGaS}_{1.5}\text{Cl}$ glass and GaCl_3 molecule, Tverjanovich et al. [8] proposed that the $\text{CsGaS}_{1.5}\text{Cl}$ glass is a one-dimensional chain structure formed by the double edge-sharing tetrahedral $(\text{ClS}_{1/2}\text{GaS}_2\text{GaS}_{1/2}\text{Cl})^{2-}$, but the differences between the two Raman spectra were not ascribed. Furthermore, in Ref. [9], they also reported the Raman spectra of samples on the compositional line $\text{CsGaS}_{1.5}\text{Cl}\text{--}0.15\text{Ga}_2\text{S}_3\text{--}0.85\text{GeS}_2$ within $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glasses. However, the evolution of microstructural units (m.u.) with compositional change was not further studied. Through further considering the local coordination of Cs^+ ions, Raman spectra of $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glasses were further discussed in this work.

2. Sample preparation and measurements

The samples were prepared by conventional melt-quenching techniques. Details of the preparations were similar to the procedure in our previous paper [10]. $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glassy samples on four composition serials

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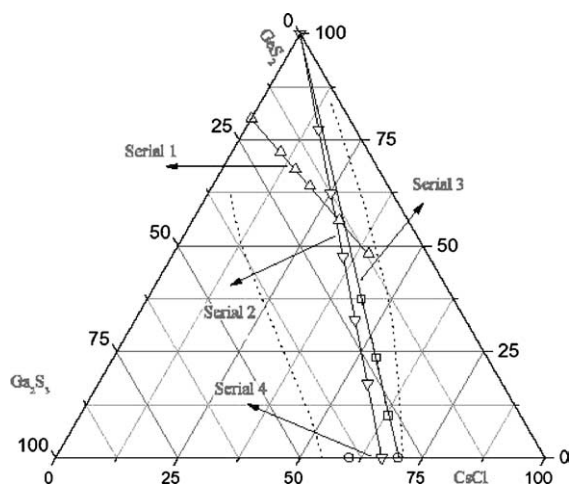


Fig. 1. GeS₂–Ga₂S₃–CsCl pseudo-ternary phase diagram [11] showing the glass-forming region and glass molar compositions investigated in this study. Serial 1: (0.8GeS₂–0.2Ga₂S₃)_{1–x}(CsCl)_x ($x=0, 0.1, 0.15, 0.2, 0.3, 0.4$). Serial 2: (GeS₂)_{1–1.5x}(Ga₂S₃)_{0.5x}–(CsCl)_x ($x=0.15, 0.25, 0.35, 0.45, 0.55, 0.6, 0.64, 0.667$). Serial 3: (GeS₂)_{1–10x/7}(Ga₂S₃)_{3x/7}–(CsCl)_x ($x=0.4, 0.537, 0.563, 0.7$). Serial 4: (Ga₂S₃)_{1–x}–(CsCl)_x ($x=0.6, 0.667, 0.7$).

were probed (Fig. 1). In addition, several samples (0.5GeS₂(orGeS)–0.5CsCl) were prepared according to the similar preparation process of GeS₂–Ga₂S₃–CsCl glasses.

The 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 with Cu K α radiation. Because of the poor water-resistance of samples with high CsCl content, the Raman measurement was conducted by focusing the laser into the sample within the silica ampoule in a back (180°) scattering configuration by the micro Raman Spectrometer (Type: Renishaw RM-1000) using the 632.8 nm laser line.

Table 1
Batch and analytical compositions of GeS₂–Ga₂S₃–CsCl glasses on serial 1

	Batch (mol%)	Ge (at.%)	Ga (at.%)	S (at.%)	Cs (at.%)	Cl (at.%)
1	80GeS ₂ – 20Ga ₂ S ₃	28 (26.7)	9 (8)	63 (65.3)		
2	72GeS ₂ – 18Ga ₂ S ₃ – 10CsCl	24 (24)	8 (7.2)	58 (58.8)	5 (5)	5 (5)
3	64GeS ₂ – 16Ga ₂ S ₃ – 20CsCl	23 (21.3)	6 (6.4)	52 (52.3)	10 (10)	9 (10)
4	56GeS ₂ – 14Ga ₂ S ₃ – 30CsCl	19 (18.7)	7 (5.6)	45 (45.7)	15 (15)	14 (15)

The values in brackets are calculated from the batch compositions. The error of compositional analysis is within $\pm 1\%$.

3. Experimental results and discussion

The amorphous GeS₂–Ga₂S₃–CsCl samples were optically homogeneous to the eye and according to the methods given above. The glassy compositions were determined with X-ray fluorescence spectroscopy. The analytical compositions of the GeS₂–Ga₂S₃–CsCl glasses on serial 1 are reported in Table 1. The results of the XRF analysis revealed that the difference in composition between a batch and the glass sample was within reasonable range. So, for the sake of clarity, the glasses will be labeled by their batch composition in the following text.

3.1. Ga₂S₃–CsCl pseudo-binary system

It is well known that (GaS₄) and (GaCl₄) tetrahedra have an edge-sharing tendency and mixed tetrahedra (GaS_xCl_{4–x}) can be formed easily [7,12,13]. In addition, Ramos etc. [14] pointed out that Cs⁺ exists as the form of (CsCl_{*n*}) clusters within Ga–La–S–CsCl glasses. Last, based on the m.u. within the CsGa_{1.5}SCl glass proposed in Ref. [8,9], it is reasonable to suppose that within Ga₂S₃–CsCl glasses, (GaS_xCl_{4–x}) clusters can be easily formed; these clusters can easily form edge-sharing dimmer when two of them border; these dimmers can be connected into chains through two coordinated sulfur atoms; and Cs⁺ ions are homogeneously dispersed in the glassy network as the Cl atoms for their nearest neighbor. So the addition of Cs⁺ mainly influences on the Ga–Cl bonds while less on Ga–S ones, especially, on the inner bridge sulfur bonds within (Ga₂S₂S_{2/2}Cl₂) m.u. Based on these deductions, later it will be verified that the Raman spectra evolution of Ga₂S₃–2CsCl glass and GaCl₃ can be successfully elucidated.

The strongest Raman peak of GaCl₃ is located at 413 cm^{–1} (Fig. 2), assigned to the ν_1 mode (Fig. 3) of the dimmer Ga₂Cl₆ [13]. But when it comes to the Ga₂S₃–2CsCl glass, this band shifts to 400 cm^{–1} and its intensity is not the strongest one. Considering the similarity of S and Cl, the structural difference between the Ga₂S₃–2CsCl glass and

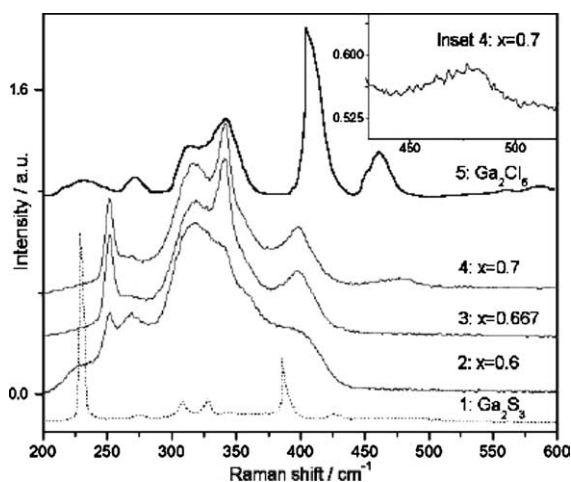


Fig. 2. Room temperature Raman spectra of samples within $(1-x)$ $\text{Ga}_2\text{S}_3-x\text{CsCl}$ system and GaCl_3 molecule.

Ga_2Cl_6 originates mainly from the Cs^+ ions. Compared to $\text{Cs}-\text{Cl}$ bonds, the $\text{Ga}-\text{Cl}$ bonds are more covalent, so the addition of Cs^+ certainly makes the $\text{Ga}-\text{Cl}$ bonds harden and weaken and displaces the chloric atoms towards the Cs^+ ions. In addition, according to the theory of molecular vibration [15], the oscillating frequency bears a relationship shown as follows

$$\nu \propto \sqrt{\frac{f}{\mu}} \quad (1)$$

where f is a constant related to bond strength, and μ is the discount mass. So it is due to the presence of Cs^+ that the ν_1 mode of $(\text{Ga}_2\text{S}_2\text{S}_{2/2}\text{Cl}_2)$ units shifts 13 cm^{-1} toward a lower wavenumber compared to the corresponding mode of the (Ga_2Cl_6) unit. Finally, due to the decreasing coupling which originates from the small difference between $\text{Ga}-\text{Cl}$ and $\text{Ga}-\text{S}$ bonds, the ν_1 mode of $(\text{Ga}_2\text{S}_2\text{S}_{2/2}\text{Cl}_2)$ units comes forth as a broad band between 370 and 430 cm^{-1} .

Furthermore, the variances of several other Raman modes between $\text{Ga}_2\text{S}_3-2\text{CsCl}$ glass and GaCl_3 also verified

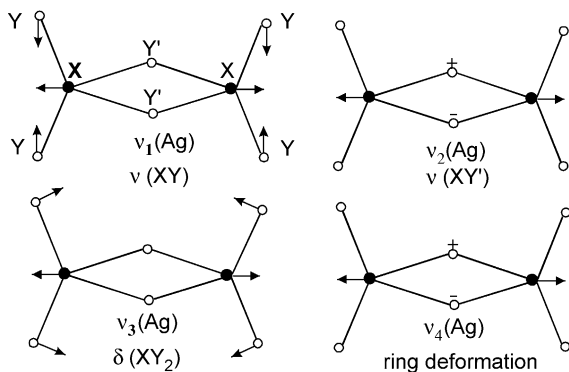


Fig. 3. Several normal coordination models of X_2Y_6 units.

the validity of the proposed model. First, nearly no change happens about the ν_2 mode located at about 318 cm^{-1} that is related to the vibrating of inner bridge bonds. Secondly, according to Ref. [8], the ν_4 mode of (Ga_2Cl_6) sited at about 167 cm^{-1} has a relationship with the vibration of inner bridge chlorines. On the spectra of $\text{Ga}_2\text{S}_3-2\text{CsCl}$ glass, the corresponding mode has small shift (located at about 165 cm^{-1}). Thirdly, the ν_3 mode of Ga_2Cl_6 locates at about 100 cm^{-1} that is ring in-plane bend vibrating [8]. While for the $\text{Ga}_2\text{S}_3-2\text{CsCl}$ glass, the corresponding mode shifts 14 cm^{-1} and locates at about 86 cm^{-1} . Fourthly, the peak at about 268 cm^{-1} which is $\nu_3^{(\text{Ag})} + \nu_4^{(\text{Ag})}$ on the Raman spectra of GaCl_3 shifts about 18 cm^{-1} when it comes to the glass $\text{Ga}_2\text{S}_3-2\text{CsCl}$. Finally, about the peak at about 340 cm^{-1} that is ν_{32}^* , no shift happens on the Raman spectra of the $\text{Ga}_2\text{S}_3-2\text{CsCl}$ glass and GaCl_3 .

Finally, the Raman spectra evolution of samples 2–4 further verified the correctness of the proposed model. On the Raman spectrum of sample 2, the broadband at about 233 cm^{-1} is ascribed to the characteristic Raman peak of the crystal Ga_2S_3 m.u. (Fig. 2(1)). It indicates that crystal Ga_2S_3 m.u. still exist when less CsCl is added. Moreover, the little peak at about 269 cm^{-1} is ascribed to the anti-symmetric stretching vibration of $(\text{S}_3\text{Ga}-\text{GaS}_3)$ ethane-like m.u. [5]. The emergence of the distinct prominence at about 360 cm^{-1} that is ascribed to the ν_1 mode of this ethane-like m.u. further verified the validity of the ascription. Following the addition of CsCl , the above-mentioned three bands decrease in intensity and shrink to nothing after the ratio of $\text{CsCl}/\text{Ga}_2\text{S}_3$ is equal to 2. So it can be concluded that with the addition of CsCl , other m.u. gradually substitute the Ga_2S_3 crystal and $(\text{S}_3\text{Ga}-\text{GaS}_3)$ ethane-like m.u.

Being separated by the crystal Ga_2S_3 and ethane-like m.u., many $(\text{GaS}_{4-x}\text{Cl}_x)$ mixed tetrahedra within sample 2 do not form bridged edge-sharing units. Based on the similarity of S and Cl, the strongest ν_1 mode of $\text{GaS}_{4-x}\text{Cl}_x$ also should locate at about 340 cm^{-1} and shift toward a lower wavenumber due to the $\text{Cs}-\text{Cl}$ bonds. In addition, the vibrational coupling ability of $(\text{Ga}_2\text{S}_2\text{S}_{2/2}\text{Cl}_2)$ edge-sharing units drops due to the effect of other m.u. So, compared to sample 3, the Raman spectrum of sample 2 manifest itself a broad peak and a little shoulder within the region $300-350\text{ cm}^{-1}$. Within the insert figure, there exist a prominence at about 477 cm^{-1} that can be ascribed to the vibration of S_8 rings and/or multi-sulfur bonds [5] and a shoulder at about 463 cm^{-1} that is the feature of the ν_{13} mode of (Ga_2Cl_6) . This can be explained as follows. When the ratio of $\text{Ga}_2\text{S}_3/\text{CsCl}$ is equal to 1:2, the glasses are completely composed of $(\text{Ga}_2\text{S}_2\text{S}_{2/2}\text{Cl}_2)$ edge-sharing units. Further increasing the content of CsCl , $\text{Ga}-\text{Cl}$ bonds can further replace the $\text{Ga}-\text{S}$ ones because of the larger affinity of $\text{Ga}-\text{Cl}$ atoms. The replaced S first, forms multi-sulfur bonds and finally leads to the forming of S_8 rings. The more Cl atoms within $(\text{Ga}_2\text{S}_{6-x}\text{Cl}_x)$ units will make the Raman spectra of sample 4 present more Raman characteristics of (Ga_2Cl_6) units. Lastly, sample 2 and 3 are colorless and transparent, while

sample 4 is pale yellow in color. Based on these facts, it can be speculated that the color of sample 4 should be ascribed to the reaction of Ga_2S_3 and superfluous CsCl which lead to the coming into being of S_8 rings.

3.2. $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ pseudo-ternary system

To study the interaction of CsCl with germanium and sulfur compounds, the pseudo-binary system GeS_2 (or GeS)– CsCl was probed. Raman spectra (Fig. 4) of two different points in the sample $0.5\text{GeS}\text{--}0.5\text{CsCl}$ are similar. The strongest peak at 300 cm^{-1} is due to the symmetric stretching vibrating of (Ge_4) tetrahedral [16]. The other broad peaks and shoulders are spectral characteristics of $\text{Ge}\text{--S}$ glass. No characteristic peaks of crystal GeS appear. That is to say, no GeS crystal m.u. appear even when the batch was conducted according to the GeS compound.

According to the Ref. [8], CsCl can not react with GeS_2 based on the $\text{GeS}_2\text{--CsCl}$ phase diagram. In Fig. 5, the broadband centered at about 780 cm^{-1} and the clear shoulder in the region $510\text{--}610\text{ cm}^{-1}$ are the Raman characteristics of GeO_2 glass [17], originating from oxygen contamination during the preparation procedure. On the Raman spectra of GeS_2 glass, the little peak at about 486 cm^{-1} is ascribed to the multi-sulfur bonds originating from the compositional fluctuation. Accordingly, the little prominence at about 255 cm^{-1} is originated from the $(\text{S}_3\text{Ge--GeS}_3)$ ethane-like m.u. The increased intensity of the peak at about 480 cm^{-1} indicates the existence of more S_8 rings in the yellow phase compared to the white phase. First, suppose that the addition of CsCl should have no effect on the (GeS_4) tetrahedra and no mixed tetrahedra $(\text{GeS}_{4-x}\text{Cl}_x)$ be formed. Then the S_8 rings in white and yellow phases should be ascribed to the sulfur that dose not react with the Ge . The shoulder centered at about 255 cm^{-1} should emerge due to the sulfur stoichiometric deficiency. But no such a distinct prominence appears for the white phase. In addition, the corresponding shoulder shifts to the site at

265 cm^{-1} when it comes to the yellow phase. So the addition of CsCl should have a certain effect on the (GeS_4) and less tetrahedral $(\text{GeS}_{4-x}\text{Cl}_x)$ be formed. But due to the larger forming probability of $(\text{GaS}_{4-x}\text{Cl}_x)$ units, it can be inferred that almost no mixed tetrahedra $(\text{GeS}_{4-x}\text{Cl}_x)$ be formed within $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ system.

The basic structural unit of GeS_2 glass is (GeS_4) tetrahedral [6]. The Raman spectrum of GeS_2 glass (Fig. 5) is comparable to those reported previously [6–8]. The strongest peak at 340 cm^{-1} is due to the symmetric stretching vibration of (GeS_4) . The shoulder at about 370 cm^{-1} is ascribed to the vibration of two edge-sharing (GeS_4) tetrahedra. The ascription of the band at 430 cm^{-1} is still a controversial problem till now [6–8]. The compositional fluctuation leads to the band sited at about 255 cm^{-1} originated from the vibrating of $(\text{S}_3\text{Ge--GeS}_3)$ ethane-like m.u. The addition of Ga_2S_3 into GeS_2 resulted in three distinct changes of the Raman spectra (Fig. 6). First, the low frequency peak gradually shifted from 255 to 270 cm^{-1} that is due to the appearance of $\text{S}_3\text{Ga--GaS}_3$ ethane-like units [5]. Secondly, the ν_1 mode of GeS_2 glass broadens resulting from the similarity of Ge and Ga . Lastly, the appearance of edge-sharing (GaS_4) tetrahedra leads to the redistribution of intensity in the region $350\text{--}440\text{ cm}^{-1}$.

Based on the above analysis, it can be proposed that within $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glasses, only the reaction for Ga_2S_3 and CsCl happens and $(\text{GaS}_{4-x}\text{Cl}_x)$ units are formed easily; when two $(\text{GaS}_{4-x}\text{Cl}_x)$ units meet the edge-sharing unit $(\text{Ga}_2\text{S}_2\text{S}_{2/2}\text{Cl}_2)$ is formed easily; the Cs^+ ions are also homogeneously dispersed in the glassy network as Cl for its nearest coordination. Later it will be verified that the Raman spectra evolution of $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--CsCl}$ glasses can be successfully elucidated in terms of these proposals.

Fig. 6 shows the Raman spectra of samples on serial 1. First, the two prominences centered at about 270 and 255 cm^{-1} gradually shrinks to nothing in intensity following the addition of CsCl . Based on the proposed model, this manifests itself as a sign of the gradual substitution of $(\text{Ga}_2\text{S}_{6/2})$ by two $(\text{GaS}_{3/2}\text{Cl})$ units. When the $\text{CsCl}/\text{Ga}_2\text{S}_3$ ratio is equal to two, complete substitution occurs. At the same time, the stoichiometric coordination of Ge is satisfied naturally. So the shoulder at 250 cm^{-1} also vanishes.

Secondly, the peak centered at about 480 cm^{-1} that can be ascribed to the vibration of S_8 rings and/or multi-sulfur bonds comes out on the spectrum of Sample 6. Certainly, this is an important proof that the $(\text{GaS}_{4-x}\text{Cl}_x)$ m.u. for $x > 1$ are formed because of the larger affinity of Ga--Cl atoms compared to Ga--S ones when more CsCl is added.

Thirdly, in the region $290\text{--}360\text{ cm}^{-1}$, a gradual spreading toward the lower wavenumber occurs from sample 1 to 4 (the content of CsCl is less than 20%) and no distinct extending toward high wavenumber can be observed. However, further adding CsCl , the broadband in this region splits into a shoulder at about 340 cm^{-1} and a peak centered at about 320 cm^{-1} that quickly strengthens in intensity. When less CsCl is introduced, the formed $(\text{GaS}_{4-x}\text{Cl}_x)$

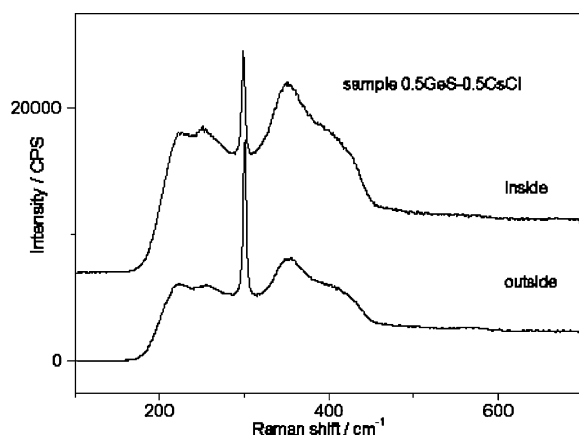


Fig. 4. Raman spectra of sample $0.5\text{GeS}\text{--}0.5\text{CsCl}$.

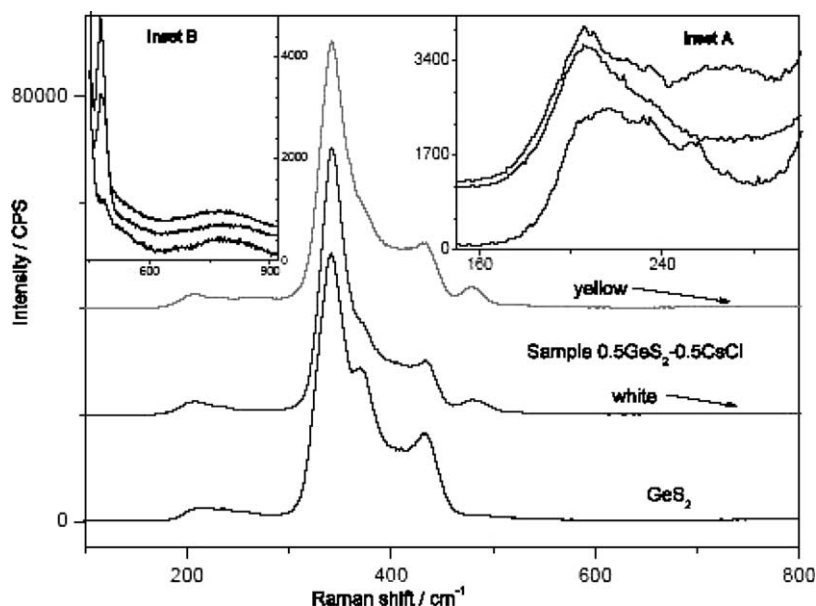


Fig. 5. Raman spectra of samples $0.5\text{GeS}_2-0.5\text{CsCl}$ and GeS_2 glass. The insert A and B are the spectra magnifying in Y-coordination within the region $150-300\text{ cm}^{-1}$ and $440-920\text{ cm}^{-1}$, respectively. The sample $0.5\text{GeS}_2-0.5\text{CsCl}$ is distinctly two phase separation to the eye.

tetrahedra, separated by the (GeS_4) tetrahedra, have less neighbor chance. So less $(\text{Ga}_2\text{S}_{6-x}\text{Cl}_x)$ bridged units can be formed. Because of the slight overweight for Ge compared to Ga, the ν_1 mode of (GaS_4) should have an appreciably larger Raman shift than the corresponding one of (GeS_4) . Furthermore, the ν_1 mode of $(\text{GaS}_{4-x}\text{Cl}_x)$ and (GaS_4) should have the same Raman shift due to the similarity of S and Cl. On the other hand, considering the effect of Cs^+ according to the proposed model, the ν_1 mode of $(\text{GaS}_{4-x}\text{Cl}_x)$ within the glasses should shift toward the lower wavenumber compared to the sole $(\text{GaS}_{4-x}\text{Cl}_x)$ units. Combining the above two aspects, the ν_1 mode of $(\text{GaS}_{4-x}\text{Cl}_x)$ within the

glasses probably has a less shift toward the lower wavenumber. So this successfully elucidates the slight shift of the broadband within this region when the amount of CsCl is less than 20%. Further increasing the content of CsCl, the chance for two $(\text{GaS}_{4-x}\text{Cl}_x)$ units meeting is enhanced. Important proof can be acquired from the evolution of the peak located at about 320 cm^{-1} that is a characteristic peak of $(\text{Ga}_2\text{S}_{6-x}\text{Cl}_x)$ bridged units.

Finally, the evolution of the shoulder within the region $400-460\text{ cm}^{-1}$ also verifies this. When the amount of CsCl is less than 20%, almost no change occurs within this region. But when the amount of CsCl is more than 20%, this

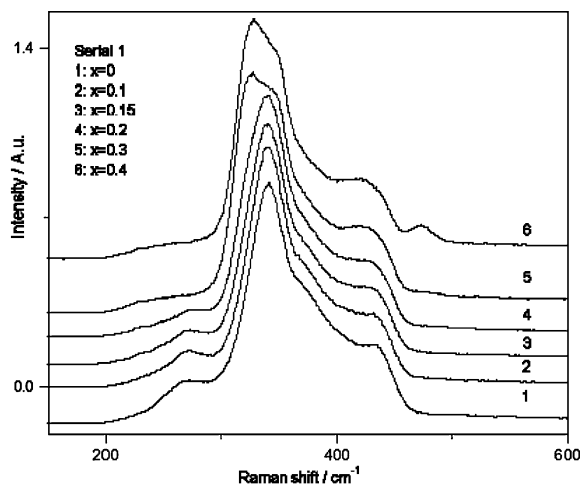


Fig. 6. Raman spectra of samples on serial 1 within $\text{GeS}_2-\text{Ga}_2\text{S}_3-\text{CsCl}$ system.

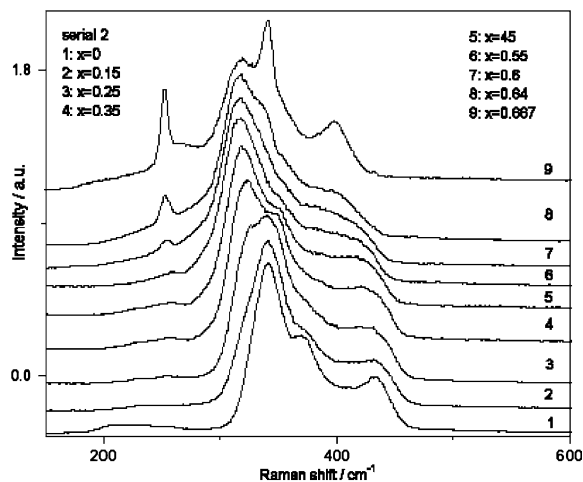


Fig. 7. Raman spectra of glasses on serial 2 within $\text{GeS}_2-\text{Ga}_2\text{S}_3-\text{CsCl}$ system.

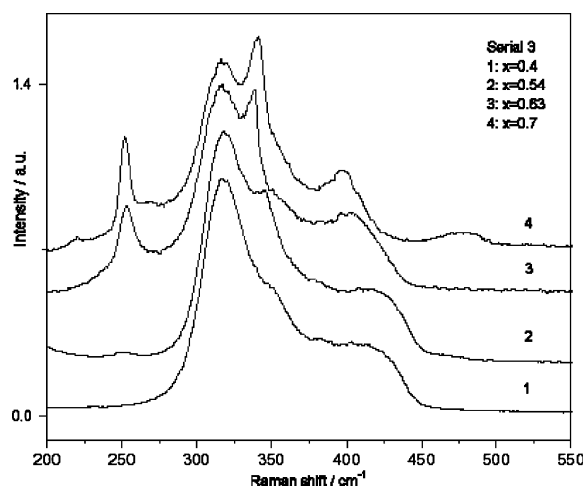


Fig. 8. Raman spectra of samples on serial 3 within $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ system.

shoulder quickly strengthens in intensity and shifts toward the lower wavenumber. This just can be ascribed to the contribution of the ν_1 mode of $(\text{Ga}_2\text{S}_{6-x}\text{Cl}_x)$ bridged units.

Fig. 7 presents the Raman spectra of samples on serial 2. It clearly reveals the evolution of spectra from a 3-dimensional network of GeS_2 glass to 1-dimensional chains of the $\text{Ga}_2\text{S}_3\text{-2CsCl}$ glass. Spectral evolutionary tendency of samples on serial 1 is exhibited more distinctly. Simultaneously, the evolutionary course of the peak sited at about 268 cm^{-1} that is ascribed to the mode of $\nu_3^{(\text{Ag})} + \nu_4^{(\text{Ag})}$ of $(\text{Ga}_2\text{S}_4\text{Cl}_2)$ bridged units also provides another important proof for the proposed micro-structural model.

The characteristic of samples on serial 3 is that the ratio of Ga_2S_3 and CsCl remains constant at 3:7. A similar evolution as seen on serial 2 can be found on this serial (Fig. 8). In addition, more Raman spectral characteristics of (Ga_2Cl_6) bridged units come out on the location at 221 and 468 cm^{-1} . Finally, the characteristic peak of S_8 rings is not presented on the spectra of samples 1–3. This suggests that multi-sulfur bonds are formed firstly following the substitutions of Ga-S bonds by Ga-Cl bonds. S_8 rings appear only after enough multi-sulfur bonds are formed.

4. Conclusions

Through considering the effect of Cs^+ ions on $(\text{GaS}_{4-x}\text{Cl}_x)$ mixed tetrahedral and $(\text{Ga}_2\text{S}_{6-x}\text{Cl}_x)$ bridged units, similarities and variances of Raman spectra between the $\text{Ga}_2\text{S}_3\text{-2CsCl}$ glass and GaCl_3 molecule are ascribed reasonably and the Raman spectral evolution of samples within $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ glassy system is elucidated successfully. At the same time, the following conclusions can be deduced:

1. The added Cs^+ ions are coordinated as the form of Cl^- ions for the nearest neighbor.
2. When the amount of CsCl is less than 20%, the $(\text{GaS}_{4-x}\text{Cl}_x)$ mixed tetrahedra are homogeneously dispersed in the glassy net mainly in the apex-sharing form through the two-coordination sulfur. Originating from the addition of CsCl , the ν_1 mode of $(\text{GaS}_{4-x}\text{Cl}_x)$ shifts towards a lower wave number.
3. Following the further addition of CsCl , when the content of CsCl is more than 20%, the bridged units $(\text{Ga}_2\text{S}_{6-x}\text{Cl}_x)$ are formed easily within the $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ glassy net.

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