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Microstructural studies of GeS_2-In_2S_3-CsI chalcohalide glasses by Raman scattering

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Raman spectra of samples on three serials within GeS_2-In_2S_3-CsI pseudo-ternary system were probed systematically in this paper. XRD patterns and Raman spectra of Sample A ($1/3In_2S_3{\cdot}2/3CsI$) and B ($1/3InS{\cdot}2/3CsI$) reveal that $InS_{4-x}I_x$ new structural units are easily formed. The Raman spectrum of Sample B further indicates that bridged units $In_2S_{6-x}I_x$ ($x \geq 2$) are preferentially formed when two tetrahedra $InS_{4-x}I_x$ ($x \geq 1$) meet. The added Cs^+ ions are coordinated as I^- anions for their nearest neighbors which play the role of charge balance of $InS_{4-x}I_x$ tetrahedra. Based on this micro-structural model, Raman spectral evolution of GeS_2-In_2S_3-CsI glasses was reasonably explained.

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1. Introduction

In recent years, extensive research was focused on Ga_2S_3-based chalcohalide glasses due to their great potential for applications in the opt-communication field. Intensity, lifetime, and other radiative properties of the 1.3-μm emission from Dy^{3+} experience a great improvement because of the addition of alkali halides and Ga_2S_3 into GeS_2-based chalcogenide glasses maybe originated from the variation of local structure of Rare Earth ions [1, 2]. Figure of merits that have been proposed for evaluation of optical devices utilizing n_2 were effectively improved following the properly added alkali halides ascribed to their wider band gap compared with the corresponding As_2S_3-based ones[3-6]. Based on the similarity of chemical properties with Ga and In, it can be anticipated that In_2S_3-based Chalcohalide glasses also be the leading candidates in the above-mentioned fields. However, to our best knowledge, there are few reports about In_2S_3-based chalcohalide glasses.

Understanding of the basic relationship of composition, structure and properties has now, as before, been a key to further optimize the properties of materials. In this work, the microstructure and its compositional dependence of samples on three serials (see Fig. 1) within GeS_2-In_2S_3-CsI pseudo-ternary glassy system were discussed in detail.

2. Experimental procedure

The samples were prepared from particular high-purity materials (at least 99.9%) according to the well-established melt-quenching techniques in our lab. Details of the preparation were similar to the procedure in our previous works [7-9].

Homogeneities and amorphous characteristics of the prepared samples were confirmed by optical and electron microscopy and X-ray diffraction (CuKα radiation) measurements. And the chemical compositions of the prepared glasses were analyzed using an energy-dispersive XRF analyzer. Due to the poor water-repellency of samples with higher CsI content, Raman measurements were conducted using a 632.8 nm laser line by focusing the laser into the sample within the silica ampoule by a Laser confocal Raman Microscope (Type: inVia). For details see the refs [10-11].

3. Results and discussion

The prepared GeS_2-In_2S_3-CsI glasses were optically homogeneous to the eye and according to the methods given above. The results of XRF analyses revealed that the difference in composition between a batch and an actual one was within reasonable range. So, for the sake of clarity, the glasses will be labeled by their batch compositions in the following text.

To begin with, to better understand the microstructural units probably formed within the GeS_2-In_2S_3-CsI pseudo-ternary system, several pseudo-binary samples with the compositions $1/3In_2S_3{\cdot}2/3CsI$ (A), $1/3InS{\cdot}2/3CsI$ (B), $1/3GeS_2{\cdot}2/3CsI$ and $1/3GeS{\cdot}2/3CsI$ were prepared according to the procedure similar to GeS_2-In_2S_3-CsI glasses.

Similar to the results of our previous study about the GeS_2-Ga_2S_3-CsCl pseudo-ternary system [11], XRD patterns and Raman spectra of Sample $1/3GeS_2{\cdot}2/3CsI$ and $1/3GeS{\cdot}2/3CsI$ reveal that no new compounds come into being and a few quantity of $GeS_{4-x}I_x$ mixed tetrahedra comes forth following the addition of CsI.

Unexpectedly, no other peaks were observed except for the acute peaks of poly-crystal CsI on the XRD patterns of Sample A and B (see Fig. 2), which indicate that new microstructural units with larger glass-forming ability were formed. To further ascertain what these new microstructural units are, Raman spectra of Sample A and B were measured and presented in Figs. 3 and 4.

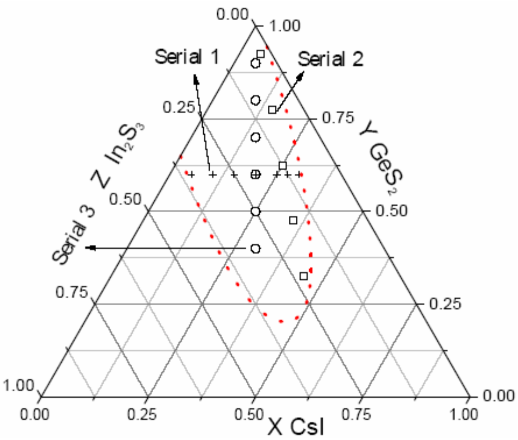

Fig. 1. GeS_2-In_2S_3-CsI pseudo-ternary phase diagram showing the glass-forming region and the molar composition of samples investigated in this work.

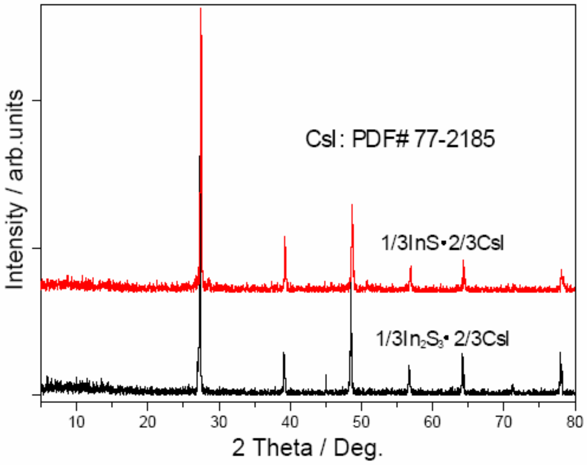

Fig. 2. X-ray diffractive patterns of the prepared samples with the compositions $1/3In_2S_3{\cdot}2/3CsI$ (A) and $1/3InS{\cdot}2/3CsI$ (B).

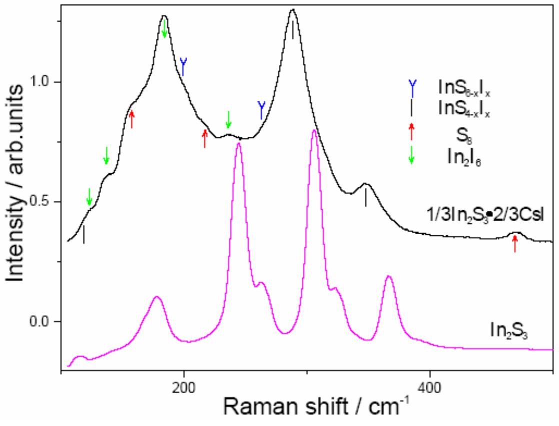

Fig. 3. Raman spectrum of the sample with the composition $1/3In_2S_3{\cdot}2/3CsI$ (A).

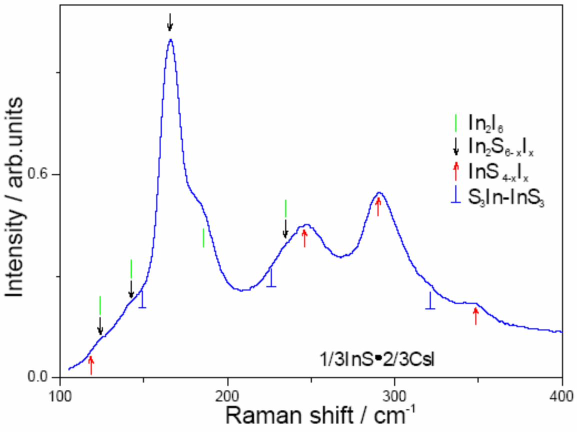

Fig.4. Raman spectrum of the sample with the composition $1/3InS{\cdot}2/3CsI$ (B).

Based on our previous microstructural study upon the GeS_2-Ga_2S_3-CsCl pseudo-ternary system (in which $GaS_{4-x}Cl_x$ mixed tetrahedra are easily formed and the added Cs atoms are coordinated by Cl atoms as its nearest neighbor) and the similarity of chemical properties of Ga and In atoms, it can be inferred that $InS_{4-x}I_x$ mixed tetrahedra can be easily formed and the added Cs atoms are coordinated by I atoms as its nearest neighbor that balanced the charge of $InS_{4-x}I_x$ tetrahedra. And this postulation provides us a primary clue to elucidate the Raman spectra of Sample A and B.

The strongest peak at 288 cm^{-1} in Fig. 3 for Sample A is considered to be due to the symmetric stretching (υ_1) vibration of InS_3I mixed tetrahedra based on the following considerations. Firstly, according to Ref.[12], the υ_1, υ_2, υ_3 and υ_4 modes of $InCl_4$ tetrahedra locate at 314, 93, 349 and 114 cm^{-1} respectively. According to the theory of molecular vibration[11], the υ_1 mode of InS_3I mixed tetrahedral units should locate at 292 cm^{-1} based on heavier atomic weight of I atoms compared with the S ones provided the similar force constants of In-I, In-Cl and In-S bonds. Secondly, based on the above structural model, the existence of Cs atoms will shift the υ_1 mode of InS_3I mixed tetrahedra toward the lower wave number originated from the stronger covalent nature of In-I bonds compared with the Cs-I ones that will make the In-I ones among Cs-I-In bonding configurations weaken, harden and displaces the iodine atoms towards the Cs ones. Therefore, it is the co-operation of the influence of Cs atoms upon InS_3I tetrahedra and the heavier atomic weight of I atoms compared with S ones that induces the large shift of 33 cm^{-1} toward the lower wave number about the υ_1 mode of InS_3I mixed tetrahedra compared with the isolated $InCl_4$ ones. According to the normal coordination analysis of the vibrating modes of tetrahedral units, little influence about the υ_3 and υ_4 modes originated from the above-mentioned two factors occurs. And this little influence can be confirmed by the location of υ_3 and υ_4 modes sited at 347 and 116 cm^{-1} respectively similar to the corresponding ones of $InCl_4$ tetrahedra. In addition, the formation of $InS_{4-x}I_x$ new units can be further verified by the appearance of characteristic peaks at 155, 217 and 470 cm^{-1} of S_8 rings

[11] because of the stoichiometric batch according to In_2S_3. And the appearance of characteristic peaks at 184(υ_1), 137(υ_2) and 236(υ_{11}) indicates the formation of In_2I_6 bridged units [14] because of the complete substitution of S atoms by I ones. Finally, based on the υ_1 mode of $InCl_6$ octahedra located at 277 cm^{-1}[13] and similar analysis, the little prominence at 264 cm^{-1} was ascribed to the υ_1 mode of InS_5I mixed octahedra which is consistent with the existence of InS_6 octahedra among In_2S_3 crystal[8]. And its much weaker intensity compared with the strongest one indicates its negligible amounts compared with InS_3I tetrahedra.

Similarly, the formation of new structural units InS_3I and bridged-units In_2I_6 within Sample 1/3InS·2/3CsI (B) can be confirmed by the appearance of corresponding Raman peaks (Fig. 4). But there are some differences for the Raman spectra of Sample A and B. Based on the molecular vibrating theory, the υ_1 mode of tetrahedra InS_2I_2 should located at about 260 cm^{-1} provided the similar force constants of In-S, In-Cl and In-I bonds. Based on this prediction together with the above-mentioned influence of Cs atoms upon In-I bonds, we feel it reasonable to ascribe the peak at 246 cm^{-1} to the υ_1 mode of tetrahedra InS_2I_2. In addition, the little prominences at 150, 225 and 320 cm^{-1} reveal the existence of less quantity of ethane-like units S_3In-InS_3 [8]. Finally, the strongest peak at 165 cm^{-1} can be ascribed to the υ_1 vibrating mode of $In_2S_{6-x}I_x (x \geq 2)$ bridged-uints. The shift of 23 cm^{-1} toward the lower wave number compared with the corresponding υ_1 mode of In_2I_6 similar units may be due to the fact that the Cs atoms mainly affect the outer In-I bonds while less influence upon the inner two In-S bonds.

Based on the above micro-structural analysis about several pseudo-binary samples, it can be concluded that within the GeS_2-In_2S_3-CsI pseudo-ternary system mixed tetrahedra $InS_{4-x}I_x$ can be easily formed following the addition of CsI and when two of them meet, bridged-units $In_2S_2I_4$ can be preferentially formed; the added Cs^+ ions are homogeneously dispersed in the glassy network as I atoms for its nearest coordination.

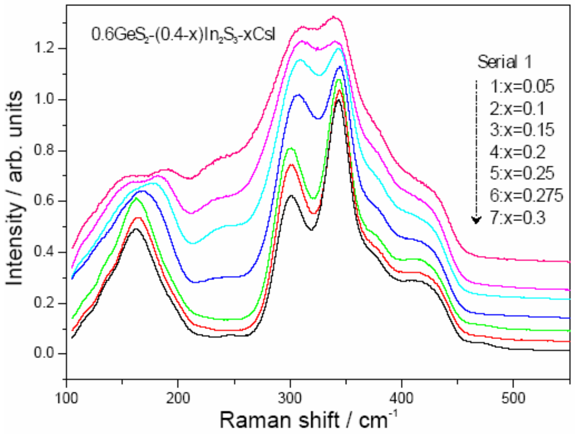

Fig. 5. Raman spectra of glasses on serial 1 within GeS_2-In_2S_3-CsI system.

To probe the effect of the added CsI upon GeS_2-In_2S_3 glasses, Raman spectra of samples on serial 1 whose characteristic is keeping the constant GeS_2 content are presented (Fig. 5). According to our previous research about the GeS_2-In_2S_3 glasses [8], the prominences in the region 210~260 cm^{-1} are ascribed to the vibrational modes of ethane-like units S_3In-InS_3 (225 cm^{-1}), S_3Ge-GeS_3 (255 cm^{-1}) and S_3Ge-InS_3 (240 cm^{-1}), and the peak at 310 cm^{-1} ascribed to the υ_1 mode of InS_4 tetrahedra. The formation of InS_3I tetrahedra can be clearly verified by the gradual shift of peak location from 310cm^{-1} (sample 1, x=0.05) to 300 cm^{-1} (sample 7, x=0.3) originated from the heavier atomic weight of I atoms compared with the S ones together with the influence of Cs atoms similar to the aforementioned analysis. Furthermore, the gradual decreasing of intensity of the prominences in the region 210~260 cm^{-1} with the addition of CsI together with its shrinking to nothing when the molar ratio of In_2S_3 and CsI tends to 1:2 can be deduced as a signature indicating the gradual substitution of S_3In-InS_3 ethane-like units by two InS_3I tetrahedra. And this substitution can be further testified by the following facts of spectral evolution. Firstly, the peaks at 150 cm^{-1} and 320cm^{-1} can be ascribed to the vibrating modes of S_3In-InS_3 ethane-like units and the peaks at 180 cm^{-1} and 360 cm^{-1} to the vibrating ones of S_3Ge-GeS_3 ones [8]. So the gradual vanishing of the peak at 150 cm^{-1}, 180 cm^{-1} and the gradual decreasing of intensity of the regions 310-325 cm^{-1}, 345-370 cm^{-1} and 320-345 cm^{-1} (the corresponding vibrational mode of S_3Ge-InS_3 should located at this situation[8]) can be seen as another proof of this substitution. Secondly, with the further addition of CsI after the molar ratio of In_2S_3:CsI arrives at 1:2, the further replacement of S atoms among InS_3I tetrahedra by I atoms occurs, which can be testified by the appearance of the peak at 250 cm^{-1} ascribed to the υ_1 mode of InS_2I_2 tetrahedra together with the emergence of the characteristic peak of S_8 rings at 470 cm^{-1}[11]. Finally, the spectral evolution in the region 100-200 cm^{-1} from two peaks to a very strong one at 165 cm^{-1} that is a characteristic peak of bridged-units $In_2S_{6-x}I_x$ verified the validity of our previous assumption that this bridged-unit can be preferentially formed when two $InS_{4-x}I_x$ tetrahedra meet.

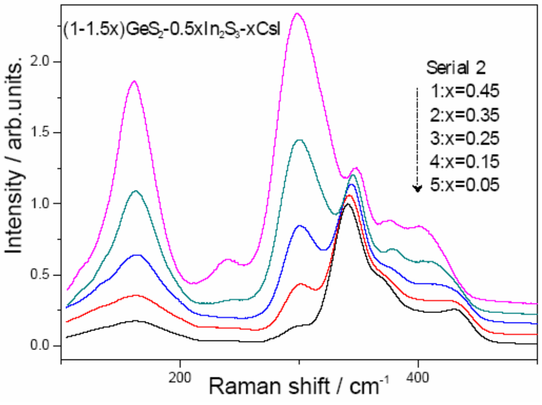

Fig.6. Raman spectra of glasses on serial 2 within GeS_2-In_2S_3-CsI system.

To further study the effect of CsI, Raman spectra of samples on serial 2 (the molar ratio of In_2S_3:CsI is equal to 1:2) were conducted (Fig. 6). To start with, after the molar content of CsI is bigger than 25 per cent, there is an increasing intensity about the prominence at about 240cm^{-1} following the further addition of CsI while no emergence of characteristic peaks of S_8 rings. So, we feel it reasonable to ascribe this peak at 240 cm^{-1} to the vibrational mode of $In_2S_{6-x}I_x$($x \geq 2$) bridged units based on the increasingly enhanced forming probability of this unit with the addition of CsI. Secondly, the increasing intensity of the peak at 160cm^{-1} with the addition of CsI that ascribed to the υ_1 mode of $In_2S_{6-x}I_x$($x \geq 2$) bridged units further verified the higher probability of formation of this bridged unit when two of $InS_{4-x}I_x$ tetrahedra meet. Lastly, with the addition of CsI, the probability of appearance of Ge-S-In bonding configurations increases, which will shift the S atoms toward the Ge atoms because of stronger covalency of Ge-S bonds compared with the In-S ones and this bonding configuration will lead to the strengthening of Ge-S bonds in one hand and the weakening of In-S ones in another hand. Therefore, according to the molecular vibrating theory [11], the change of bonding force constant of Ge-S and In-S bonds can well explained the spectral evolution of the shift of peak location about the υ_1 mode of GeS_4 tetrahedra from 340 cm^{-1} of Sample 5 (x=0.05) to 348 cm^{-1} of Sample 1 (x=0.45) together with the corresponding shift toward the lower wave number about the υ_1 one of InS_3I tetrahedra with the addition of CsI.

Similarly, the spectral evolution of samples on serial 3 (Fig.7) whose characteristic consists in the invariable ratio 1:1 of In_2S_3: CsI can be elucidated reasonably based on the above-mentioned analysis.

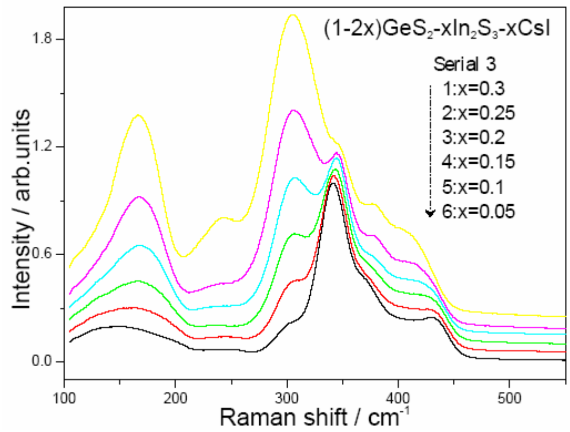

Fig. 7. Raman spectra of glasses on serial 3 within GeS_2-In_2S_3-CsI system

4. Conclusions

XRD patterns and Raman spectra of samples among GeS-CsI, GeS_2-CsI, InS-CsI and In_2S_3-CsI pseudo-binary systems were conducted. XRD patterns of these samples reveal that no new compounds come into being within samples of GeS-CsI and GeS_2-CsI pseudo-binary system while the formation of new structural units having better glass-forming ability was deduced among samples $1/3In_2S_3 \cdot 2/3CsI$ (A) and $1/3InS \cdot 2/3CsI$ (B). Further Raman investigations confirmed that the new structural units having better glass-forming ability are mainly $InS_{4-x}I_x$($x \geq 1$) mixed tetrahedra and when two of them meet $In_2S_{6-x}I_x$ ($x \geq 2$) bridged-units are easily formed.

Raman spectra of samples on three serials within GeS_2-In_2S_3-CsI pseudo-binary system were investigated systematically. Based on the elucidation of Raman spectral evolution, the following micro-structural information can be deduced: (1) Gradual substitution of ethane-like units such as $S_3In(Ge)$-$(Ge)InS_3$ by $InS_{4-x}I_x$ mixed tetrahedra occurs with the addition of CsI into GeS_2-In_2S_3 glasses. And the bridged units $In_2S_{6-x}I_x$ are preferentially formed when two of $InS_{4-x}I_x$ tetrahedra meet. (2) After the molar ratio of In_2S_3:CsI arrives at 1:2, further addition of CsI will lead to the appearance of less quantity of $InS_{4-x}I_x$ tetrahedra with x values larger than 2, multi-S bonds and even S_8 rings. (3) After the content of CsI is more than 25 molar percent, a great quantity of $In_2S_{6-x}I_x$ ($x \geq 2$) bridged units come into being within the glassy net.

Acknowledgements

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