Microstructural analysis of Ga_2S_3–$2MCl$ ($M = K, Rb, Cs$) glasses using Raman scattering

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Abstract

Raman scattering spectra of Ga_2S_3–$2MCl$ ($M = K, Rb, Cs$) glasses have been conducted at room temperature. Based on the analysis of the local co-ordination surroundings of Cs^+ ions, the similarities and differences of Raman spectra for the glass Ga_2S_3–$2CsCl$ and the bridged molecular $GaCl_3$ were explained successfully. Through considering the effect of M^+ ions on mixed anion units $[GaS_{4-x}Cl_x]$ and bridged units $[Ga_2S_{6-x}Cl_x]$ and the corresponding microstructural model, the Raman spectral evolution of the Ga_2S_3–$2MCl$ ($M = K, Rb, Cs$) glasses was reasonably elucidated.
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1. Introduction

Rare-earth doped chalcohalide glasses are among the leading candidates for a high quantum efficiency rare-earth doped optical fiber amplifier at 1.3 μm [1,2] and optical fiber lasers in the mid-IR region [3,4]. A key for successful optical fiber laser design is the compositional selection providing the optimal match of several related parameters. Therefore, understanding and utilization of the microstructural studying findings have practical importance.

Raman scattering is a very useful vibrating spectroscopic method for detecting the microstructure of amorphous materials because very few unit cells of a definite structure are required for its detection [5]. The chemistry of Ga in alkali chloride melts is well known [6], but the chemistry of Gallium thio-chlorides is very little known. Based on the similarity of Raman spectra between the $CsGaS_{1.5}Cl$ glass and $GaCl_3$ molecule, Tverjanovich et al. [7–9] proposed that the $CsGaS_{1.5}Cl$ glass is a one-dimensional chain structure formed by the double edge-sharing tetrahedra $[ClS_{1/2}GaS_2GaS_{1/2}Cl]^{2-}$, but the differences between the two Raman spectra were not ascribed. Through further considering the local co-ordination of M^+ ions ($M = K, Rb, Cs$), Raman spectra of Ga_2S_3–$2MCl$ glasses were further discussed in this paper.

2. Experimental

2.1. Glass preparation

Samples of the Ga_2S_3–$2MCl$ ($M = K, Rb, Cs$) glasses were prepared by the conventional melt-quenching technique. Batches of Ga and S of 99.999% purity, and MCl ($M = K, Rb, Cs$) of 99.99% purity were weighted in appropriate quantity into fused quartz ampoules in a N_2 gas-filled glove box. The fused quartz ampoules were washed in advance with deionized water, soaked for 15 min in 25% HF acid, re-washed with deionized water, dried at 150 °C in an oven and then baked under vacuum at 1000 °C for 5 h. The ampoules containing the raw materials were sealed under vacuum with 10^{-1} Pa, which were then inserted into a

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rocking furnace. The regime is as follows: soaking at 600 °C (5 h) to assist the reaction while rocking, raising the temperature to 950 °C so as to completely melt the batches in 5 h, soaking at this temperature for 15 h, then decreasing to 700–850 °C in 3 h depending on the glassy composition, and then stopping the rock and preserving the temperature for 4 h, lastly cooling the melts by quenching in air (M = Cs), in ice–water mixture (M = Rb). But for M = K, in order to acquire amorphous materials, less amount of raw material and more quickly cooling (ice–water mixture containing NaOH) was necessary.

2.2. Measurements

The chemical compositions of glass samples were analyzed using an energy-dispersive XRF analyzer. Homogeneity and amorphous characteristic of the prepared bulk materials was confirmed by optical and electron microscopy and X-ray diffraction (XRD) patterns with Cu Kα radiation.

Because of the poor water-resistance of samples, 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: inVia) using the 632.8 nm laser line. The spectral resolution was of the order of 1 cm^{-1}. For details, see our previous work [10,11].

3. Results and discussion

According to the results of XRF analysis, the difference in composition between a batch and the glass sample is within ±0.5%. So, hereinafter, the samples are expressed by their batch composition.

The amorphous characteristics of the prepared samples were confirmed by XRD patterns that were diffuse and featureless. The amorphous Ga$_2$S$_3$–2MCl (M = K, Rb, Cs) samples were optically homogeneous to the eye and according to the methods given above (optical and electron microscopy).

According to the preparing procedure, the glass-forming ability of Ga$_2$S$_3$–2MCl glasses increases gradually with the increasing of alkali metal ion radius. Fig. 1 represents the Raman spectra of Ga$_2$S$_3$–2MCl glasses where M = K, Rb or Cs. The gradual changes of five bands or shoulders can be seen clearly in terms of the Raman spectra from Cs to K. Firstly, the peaks, which center at about 250 cm^{-1} and 340 cm^{-1}, reduce quickly in intensity; Secondly, the band centered at about 270 cm^{-1} stands out slowly; Lastly, the shoulder located at 400 cm^{-1} becomes weaker little by little; while the bands between 360 cm^{-1} and 400 cm^{-1} are enhanced gradually about the intensity.

Table 1 tabulates the frequencies of Raman bands and their assignments of the Ga$_2$S$_3$–2CsCl glass and the dimeric gallium trichloride. And in Fig. 2, several related normal vibrating modes, which will be analyzed, are listed.

It is well known that GaS$_4$ tetrahedra have a tendency to share edges [6]. And it is easy for Gallium to form mixed tet-
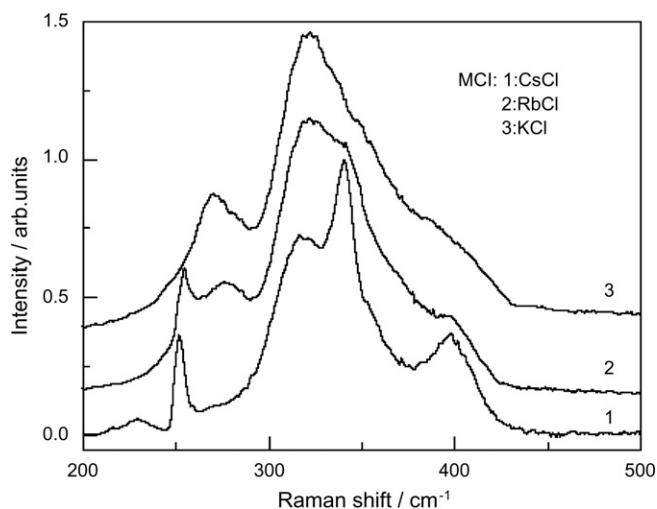

Fig. 1. Raman scattering spectra of the Ga$_2$S$_3$–2MCl glasses recorded at room temperature. The curves are shifted in parallel for clarity.

Table 1
Wave number and assignments of Raman bands of the Ga$_2$S$_3$–2CsCl glass and molten Ga$_2$Cl$_6$

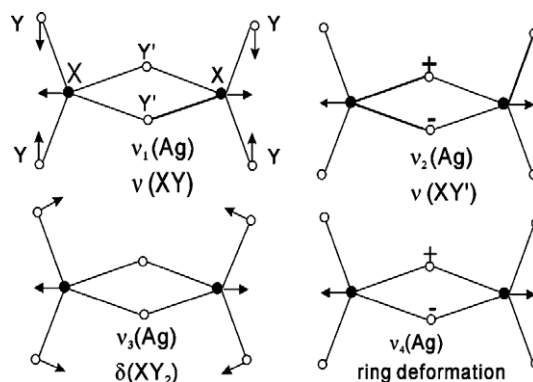| Ga$_2$S$_3$–2CsCl glass	Ga$_2$Cl$_6$ (molten)	Assignments [6–8]
215	215 (shoulder)	ν_{15} B$_{3g}$ symmetric twisting
228	230 (weak)	ν_6 B$_{1g}$ ring in-plane stretching
250	268 (weak)	ν_3 (A$_g$) + ν_4 (A$_g$)
318	318 (middle)	ν_2 A$_g$ ring breathing
342	344 (middle)	$\nu_3 * 2$ ring in-plane bend
400	413 (strong)	ν_1 A$_g$ symmetric stretching
462	462 (middle)	ν_{11} B$_{2g}$ anti-symmetric stretching

Fig. 2. Several normal co-ordination modes of X$_2$Y$_6$ bridged units.

rahedra with S and Cl atoms [7–9,12]. So it is reasonable to assume that within Ga$_2$S$_3$–2MCl glasses, new units [GaS$_{3/2}$Cl] are easily formed; and these units are easy to link into chains by sharing edges, i.e. bridged units [Ga$_2$S$_4$Cl$_2$] are easily formed within the Ga$_2$S$_3$–2MCl glasses. According to the reference [13], within the Ga–La–S–CsCl glasses, Cs exists in the form of [CsCl$_n$] clusters in the glassy network. Based on the Raman spectral analysis, we feel it rational to consider that the metal ions M$^+$ be dispersed in a disordered glassy network in the sole layer form of

chlorine atoms as its nearest neighbors; and following the reduction of ionic radius, larger clusters $[MCl_n]$ should be easier to form within Ga_2S_3–$2MCl$ glasses. As shown below, based on the above-mentioned microstructural model, through considering the local co-ordination of M^+ ions, the Raman spectral evolution of Ga_2S_3–$2MCl$ glasses can be explained successfully.

With the increase of ionic field strength, the larger ionic cluster $[MCl_n]$ will appear more easily within Ga_2S_3–$2MCl$ glasses. And this will lead to the inhomogeneous of glass microstructure. At the same time, the ethane-like structural units Ga_2S_6 will stand out in the glassy network. Based on the references [14,15], the peak at 270 cm^{-1} and the band at about 360 cm^{-1} are attributed respectively to the v_3 and v_1 (A_{1g}) vibrational modes of ethane-like structural subunits $[S_3Ga–GaS_3]$. The gradual enhancement of these two bands following the order of Cs, Rb, K on the spectra of Ga_2S_3–$2MCl$ glasses verified this speculation. In addition, because of the dissociative effect of $[S_3Ga–GaS_3]$ units within glassy network, the quantity of $[GaS_{3/2}Cl]$ non-edge-sharing units will be raised. In terms of the similarity of atomic weight for S and Cl, the v_1 stretching vibrational mode of these tetrahedral units $[GaS_{3/2}Cl]$ should located at about 340 cm^{-1} [9–12]. So, following the order of Cs, Rb, K, the increasingly broadening toward the high wave number about the peak 320 cm^{-1} can elucidate the gradual increase of quantity of the sole tetrahedra $[GaS_{3/2}Cl]$.

The strongest Raman band of the molten $GaCl_3$ is located at 413 cm^{-1} that is assigned to the v_1 symmetric stretching vibration (Fig. 2) [9]. But when it comes to the Ga_2S_3–$2CsCl$ glass, this shifts to 400 cm^{-1} and its intensity is not the strongest one. As to the Ga_2S_3–$2Rb(K)Cl$ glasses, this band further weakens in intensity, widens and shifts about its location to lower wave number with the reduction of M^+ radius. Considering the similarity of atomic weight for S and Cl, the structural differences of the molten Ga_2Cl_6 and Ga_2S_3–$2MCl$ glasses originate mainly from the presence of alkali metal cations M^+. Compared with the M–Cl bonds, the Ga–Cl bonds are more covalent, so the incorporation of M^+ cations certainly makes the Ga–Cl bonds hardening and weakening and displaces the chlorine atoms towards the M^+ ions. With the reduction of alkali metal ionic radius, the ionic field strength becomes stronger. So the Ga–Cl bonds of $[Ga_2S_4Cl_2]$ bridged units become weaker in the same order for Ga_2S_3–$2MCl$ glasses. In addition, according to the theory of molecular vibration [11], the oscillating frequency meets a relationship shown as follows:

$$v \propto \sqrt{\frac{f}{\mu}}, \tag{1}$$

where f is a constant related with bond strength, μ is the discount mass. Therefore, the larger shift of the v_1 mode of $[Ga_2S_4Cl_2]$ bridged units within Ga_2S_3–$2MCl$ glasses toward the lower wave number compared with that of Ga_2Cl_6 molecular should be ascribed to the effect of M^+ ions. Lastly, based on the above-mentioned analysis, M^+

ions exist in the form of chlorine atoms as its nearest co-ordination. Therefore, the Ga–S bonds within bridged units are little influenced by the M^+ ions. And it is just due to the effect of M^+ ions that the coupling capability of the v_1 mode greatly drops originated from the difference between Ga–Cl and Ga–S bonds. Correspondingly, the symmetric stretching vibrating mode of $[Ga_2S_4Cl_2]$ bridged units within Ga_2S_3–$2MCl$ glasses comes forth as a broad band between 370 and 430 cm^{-1}.

Furthermore, this effect can be verified by other vibrating modes of the Ga_2S_3–$2CsCl$ glass and $GaCl_3$ molecular: Firstly, the peak located at 318 cm^{-1}, which is ascribed to the inner Ga–S bond stretching vibration of bridged units $[Ga_2S_4Cl_2]$, changes little. In addition, the smaller shift of the v_3 mode from 167 to 165 cm^{-1} [7], which is ascribed to the XY_2 ring in-plane bending vibration of the bridged units $[Ga_2S_4Cl_2]$, can also confirm the rationality of the above-mentioned microstructural model. Lastly, the larger shift of v_4 from 100 to 86 cm^{-1} [7], which is ascribed to ring deformation and probably be influenced largely by the Ga–Cl bonds, explains the effect of introduced cations from another aspect.

In summary, it is the added alkali metal ions M^+ that makes the Raman spectra of Ga_2S_3–$2MCl$ glasses change systematically.

4. Conclusions

According to the further investigation by Raman scattering, the microstructure of Ga_2S_3–$2MCl$ glasses was considered to be that $[MCl_n]$ clusters were homogeneously dispersed in a disordered polymer network formed by $[GaS_{3/2}Cl]$ tetrahedra, $[S_3Ga–GaS_3]$ ethane-like units and $[Ga_2S_4Cl_2]$ bridged units interconnected by sulfur bridges. Through further considering the local co-ordination of M^+ ions, the similarities and changes of Raman spectra for the glass Ga_2S_3–$2CsCl$ and the bridged molecular $GaCl_3$ and the spectral evolution of the Ga_2S_3–$2MCl$ glasses were elucidated successfully.

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