



## Raman spectroscopic study on the microstructure of $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$ glasses

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### Abstract

Raman spectra of  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  pseudo-ternary system glasses at room temperature in the air were investigated systematically in the  $150\text{--}500\text{ cm}^{-1}$  region. The systematical evolution of the Raman spectra of  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses was explained successfully through considering the interaction of  $\text{K}^+$  ions with  $[\text{GaS}_{3/2}\text{Cl}]$  units. Compared with the Raman bands of  $\text{Ga}_2\text{S}_6$ , some of the Raman bands shifted or weakened due to the interaction of alkali metal ions  $\text{K}^+$  and subunits  $[\text{Ga}_2\text{S}_{6/2}\text{Cl}_2]$ . Following the addition of KCl, gradual substitutions of ethane-like structural subunits  $[\text{S}_3\text{Ga--GaS}_3]$  by  $[\text{Ga}_2\text{S}_{6/2}\text{Cl}_2]$  subunits and/or two  $[\text{GaS}_{3/2}\text{Cl}]$  units occur. The microstructure of the studying system glasses is considered to be  $\text{K}^+$  ions in the form of Cl as the nearest coordination are homogeneously dispersed in a disordered polymeric network formed by  $\text{GaS}_{3/2}\text{Cl}$ ,  $\text{GeS}_4$ , etc. units interconnected by sulfur bridges.

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### 1. Introduction

$\text{Ga}_2\text{S}_3$ -based Chalcogenide glasses have been considered as promising hosts for rare-earth (RE) doped active devices, due to their good glass-forming abilities, lower non-radiative quenching of fluorescence transitions resulting from their low maximum phonon energy, large oscillator strengths and radiative transition probabilities originating from their high refractive indices [1–3]. In addition, due to their higher optical non-linear coefficient and smaller two-phonon absorption, recently the  $\text{Ga}_2\text{S}_3$ -based Chalcogenide glasses have become a hot-point of researching and developing particularly for the applications in the field of telecommunication signal processing such as ultra-fast all optical switching [4,5]. Because the two above-mentioned properties have an intimate relationship with the microstructure of  $\text{Ga}_2\text{S}_3$ -based Chalcogenide glasses, understanding and utilization of the microstructural study findings have practical importance.

The main objective of this investigation was to probe the microstructure of  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  pseudo-ternary system glasses by Raman scattering. Many researches on the microstructure of binary Ge–S glasses and ternary Ge–Ga–S glasses have been done [6–8], however, the study about microstructural effect following the addition of KCl into the pseudo-binary  $\text{GeS}_2\text{--Ga}_2\text{S}_3$  system glasses is scarce. So the main objective of this investigation was to probe systematically the microstructural changes with the gradually increasing amount of KCl in the pseudo-ternary  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses.

### 2. Experimental

#### 2.1. Glass preparation

Samples of  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses were prepared by the usual melt-quenching technique. Batches of Ge, Ga and S of 99.999% purity, and KCl of 99.99% purity were grounded and weighed in appropriate quantity into fused quartz ampoules in a  $\text{N}_2$  gas-filled glove box with  $<1$  ppm  $\text{H}_2\text{O}$  and  $\text{O}_2$  concentrations. The fused quartz ampoules were washed in advance with deionized water, soaked for

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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 rocking furnace. The regime was 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 within 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 the air or in the ice–water mixture.

## 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 (Tesla BS 340) and X-ray diffraction (XRD) patterns with Cu K $\alpha$  radiation at an output power 2 kW (40 kV and 40 mA).

Raman spectra of the GeS<sub>2</sub>–Ga<sub>2</sub>S<sub>3</sub>–KCl glassy samples were recorded at room temperature in back (180°) scattering configuration under a microscope, by using a Raman Spectrometer (Type: Renishaw RM-1000) made by Renishaw Company in United Kingdom. The spectrometer was coupled to a He–Ne laser. The 632.8 nm laser line was used to stimulate the samples. 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 2.2 mW was used. The resolution of the Raman spectra was 1 cm<sup>-1</sup>.

## 3. Results and discussion

The results of XRF analysis revealed that the difference in composition between a batch and the glass sample was within  $\pm 0.5\%$ . So, hereinafter, the glass composition is expressed by the batch composition.

The amorphous state of the prepared samples was confirmed by XRD and optical transmittance measurements. The amorphous GeS<sub>2</sub>–Ga<sub>2</sub>S<sub>3</sub>–KCl samples were optically homogeneous to the eye and according to the methods given above (optical and electron microscopy).

For systematically probing the Raman spectroscopic change with compositions, four lines in the ternary diagram were analyzed. The molar compositions of glassy samples prepared are shown in the pseudo-ternary diagram (Fig. 1).

For studying the microstructure of ternary GeS<sub>2</sub>–Ga<sub>2</sub>S<sub>3</sub>–KCl glasses, the microstructural understanding of GeS<sub>2</sub> glass and pseudo-binary GeS<sub>2</sub>–Ga<sub>2</sub>S<sub>3</sub> glass is very important. The Raman spectrum of GeS<sub>2</sub> in Fig. 4(1) is comparable to those reported previously [6,7]. The symmetric stretching vibration of GeS<sub>4/2</sub> tetrahedra leads

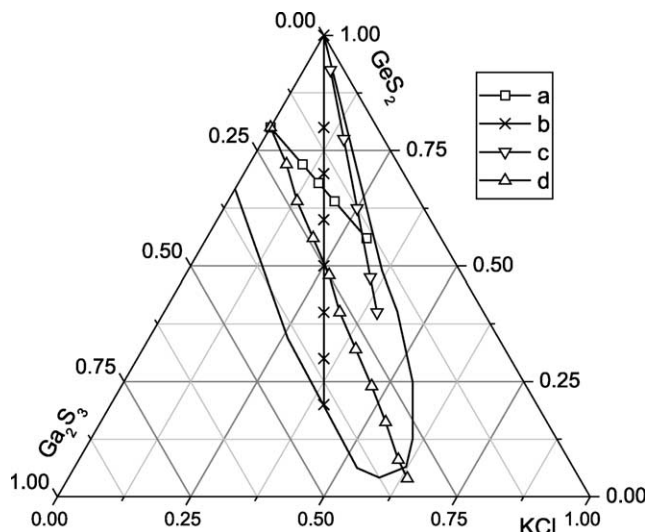


Fig. 1. Ternary phase diagram showing the glass-forming region and glass molar compositions investigated in this study. Line a:  $0.8(1-x)\text{GeS}_2-0.2(1-x)\text{Ga}_2\text{S}_3-x\text{KCl}$ . Line b:  $(1-2x)\text{GeS}_2-x\text{Ga}_2\text{S}_3-x\text{KCl}$ . Line c:  $(1-1.5x)\text{GeS}_2-0.5x\text{Ga}_2\text{S}_3-x\text{KCl}$ . Line d:  $(0.8-1.2x)\text{GeS}_2-(0.2+0.2x)\text{Ga}_2\text{S}_3-x\text{KCl}$ .

to the strongest band at about 340 cm<sup>-1</sup>. The distinct shoulders at about 370 and 430 cm<sup>-1</sup> are ascribed to the vibrational modes of two edge-shared tetrahedral Ge<sub>2</sub>S<sub>6</sub> although there has been some controversy [7]. In Fig. 2 (1:0KCl), we present the Raman spectrum of amorphous 0.8GeS<sub>2</sub>–0.2Ga<sub>2</sub>S<sub>3</sub>. A similar Raman spectral shape was obtained with  $x=0-0.4$  [8]. The spectra show that insertion of a relatively small amount of Ga<sub>2</sub>S<sub>3</sub> gives rise to two main changes only. On one hand, appearance of the lower frequency peak centered at about 270 cm<sup>-1</sup> and the shoulder located at about 250 cm<sup>-1</sup> were attributed, respectively, to the  $\nu_3$  (XX) normal vibrational mode of

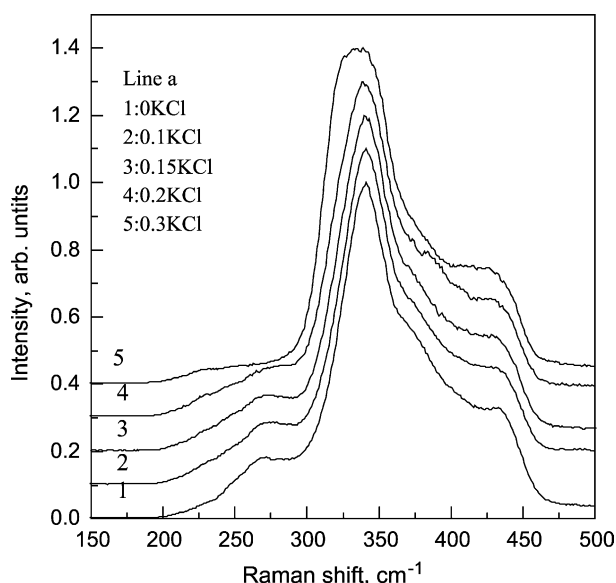


Fig. 2. Raman spectra of samples on Line a:  $0.8(1-x)\text{GeS}_2-0.2(1-x)\text{Ga}_2\text{S}_3-x\text{KCl}$  ( $x=0, 0.1, 0.15, 0.2, 0.3$ ). The curves are shifted in parallel for clarity.

the ethane-like structural subunit  $\text{Ga}_2\text{S}_6$  and  $\text{Ge}_2\text{S}_6$  [7,8]. On the other hand, the redistribution of intensity of bands between 310 and 420  $\text{cm}^{-1}$  are attributed to the appearance of edge-shared tetrahedral subunits  $\text{Ga}_2\text{S}_6$  in the glassy structure [8].

For the pseudo-binary system  $(1-x)\text{GeS}_2-x\text{KCl}$ , no change among the Raman spectra occurs following the change of  $x$  from 0 to 0.5 mol. The melt-cooling products are clear two-phase separation with yellow and white to the eye. And according to XRD measurements, no new phases were formed in the pseudo-binary system  $(1-x)\text{GeS}_2-x\text{KCl}$ . So we feel KCl does not interact with  $\text{GeS}_2$  at all. But for the pseudo-binary system  $(1-x)\text{Ga}_2\text{S}_3-x\text{KCl}$ , dramatic Raman spectroscopic changes occur with the addition of KCl (Fig. 3). And the melt-cooling products are homogeneous in color to the eye. Therefore, we assume that only KCl additions interact with  $\text{Ga}_2\text{S}_3$  in the pseudo-ternary  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses. Based on these facts, we assume that only the new unit  $[\text{GaS}_{3/2}\text{Cl}]$  is formed following the addition of KCl in the glasses for study. Furthermore, based on Ref. [9], the  $\text{GaS}_4$  has a tendency to share edges. So we further assume that the edge-sharing subunits  $[\text{Ga}_2\text{S}_{3/2}\text{Cl}]$  are easily formed in the ternary  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses. In addition, based on Ref. [10], in  $\text{Ga--La--S--CsCl}$  glasses, Cs exists in the glass network as the form of  $[\text{CsCl}_n]$  clusters. Because of the enhanced ion field strength compared to  $\text{Cs}^+$ , in the present studying glasses, K is supposed to exist as the form of K–Cl bonds, i.e. the chlorine atoms are the nearest coordination of  $\text{K}^+$  ions. As shown below, the above-mentioned assumptions are verified by our Raman spectra data.

For probing the effect of KCl in the ternary  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses, the samples along the Line a, which is the  $0.8\text{GeS}_2\text{--}0.2\text{Ga}_2\text{S}_3$  and KCl join were prepared. In Fig. 2, the Raman spectra of samples along the composition Line a are presented. With the increase of KCl molar

content, the peak centered at about 270  $\text{cm}^{-1}$  and the shoulder located at about 250  $\text{cm}^{-1}$  shrank to nothing in intensity when the molar ratio of KCl and  $\text{Ga}_2\text{S}_3$  is equal to or greater than 2. Based on the aforementioned analysis, the evolution of the peak 270  $\text{cm}^{-1}$  and the shoulder 250  $\text{cm}^{-1}$  that ascribed to the  $\nu_3$  mode of ethane-like structural subunits  $\text{Ga}_2\text{S}_6$  and  $\text{Ge}_2\text{S}_6$  [11] manifested itself as a sign of the gradual substitution of  $[\text{Ga}_2\text{S}_{6/2}]$  subunit by two  $[\text{GaS}_{3/2}\text{Cl}]$  units. Something that should be notified is that because of the similarity of Cl and S atomic weight, the peak that is located at about 340  $\text{cm}^{-1}$  can be ascribed partly to the breathing vibration of  $[\text{GaS}_{3/2}\text{Cl}]$  units. When the KCl/ $\text{Ga}_2\text{S}_3$  ratio is equal to 2, the subunits  $[\text{Ga}_2\text{S}_{6/2}]$  are completely replaced by  $[\text{GaS}_{3/2}\text{Cl}]$  units. At the same time, the stoichiometric coordination of Ge is satisfied naturally. So the shoulder 250  $\text{cm}^{-1}$  also vanished. In addition, the shrinking little by little of the band located at about 360  $\text{cm}^{-1}$  which is ascribed to the  $\nu_1$  normal vibrational mode of  $[\text{Ga}_2\text{S}_{6/2}]$  [11] is another proof of gradual substitution. Lastly, the slowly broadening towards the lower frequency side for the breathing mode of  $\text{GeS}_2$  (structural unit  $\text{GeS}_{4/2}$ , 340  $\text{cm}^{-1}$ ) and the gradual strengthening of the band between 390 and 420  $\text{cm}^{-1}$  is another two important characteristic of Raman spectral evolution following the addition of KCl. In order to further investigate the spectral evolution and more clearly drawing the information of misconstrue of the studied glasses, the samples along the Lines b, c, and d were prepared.

Fig. 4 shows the Raman spectra of samples along Line b with the fixed ratio 1:1 of KCl: $\text{Ga}_2\text{S}_3$ . Compared to Fig. 2, more clearer widening effect toward lower frequency of the peak located at about 340  $\text{cm}^{-1}$  stands out following the increasing enhancement in the intensity of the band between

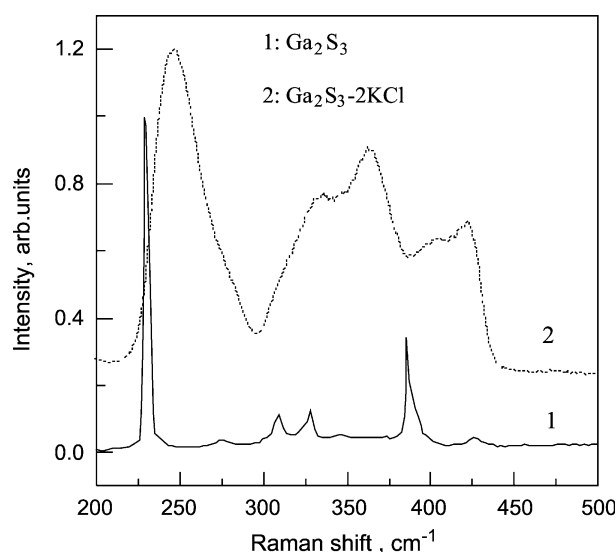


Fig. 3. Raman spectra of  $\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{S}_3\text{--}2\text{KCl}$ .

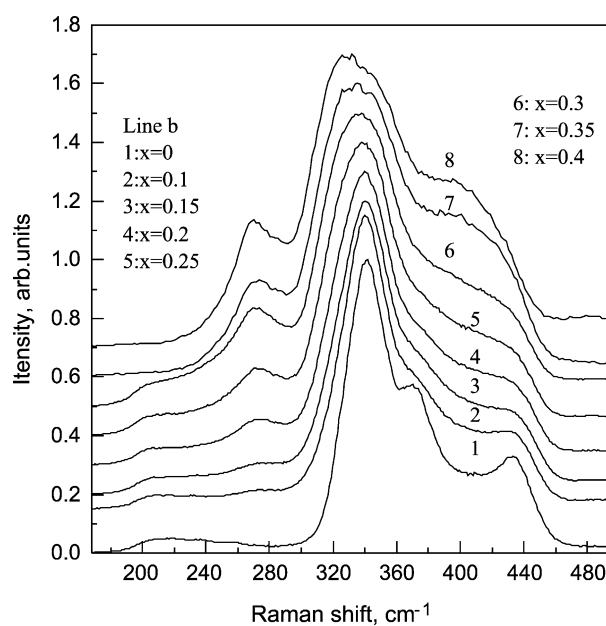


Fig. 4. Raman spectra of samples on Line b:  $(1-2x)\text{GeS}_2-x\text{Ga}_2\text{S}_3-x\text{KCl}$  ( $x = 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4$ ).

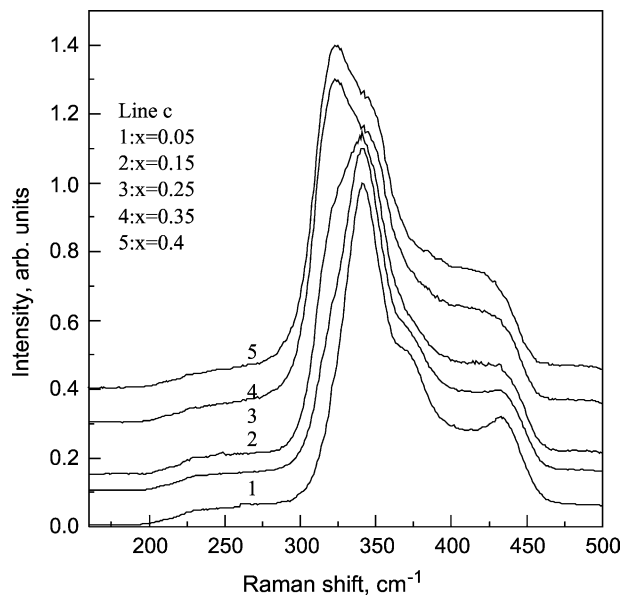


Fig. 5. Raman spectra of samples on Line c:  $(1 - 1.5x)\text{GeS}_2 - 0.5x\text{Ga}_2\text{S}_3 - x\text{KCl}$  ( $x = 0.05, 0.15, 0.25, 0.35, 0.4$ ).

380 and 420  $\text{cm}^{-1}$ . Because of the incomplete substitute of ethane-like structural subunits  $\text{Ga}_2\text{S}_6$  by  $[\text{GaS}_{3/2}\text{Cl}]$  units, the characteristic peak located at about 270  $\text{cm}^{-1}$  still appear and is enhanced gradually in amplitude following the descending of  $\text{GeS}_2$  content. In addition, according to Ref. [11], the  $\nu_1$  normal vibrational mode of ethane-like structural subunits  $\text{Ga}_2\text{S}_{6/2}$  should be located at about 360  $\text{cm}^{-1}$ . Following the shrinking of  $\text{GeS}_2$  content, the peak located at about 340  $\text{cm}^{-1}$  gradually broadens toward high wavenumber. While in Fig. 5, when the ratio of  $\text{Ga}_2\text{S}_3:\text{KCl}$  is equal to 1:2, no clear shift toward high wavenumber about the peak located at about 340  $\text{cm}^{-1}$  occurs. So we believe that the intensity of the peak at about 360  $\text{cm}^{-1}$  is increasingly enhanced with the descending of  $\text{GeS}_2$  content. And this is another proof that the content of ethane-like structural subunits  $\text{Ga}_2\text{S}_6$  is gradually increasing on Line b following the reduction of  $\text{GeS}_2$ .

In Fig. 5, because of the complete replacement of ethane-like structural subunits  $\text{Ga}_2\text{S}_6$  by  $[\text{GaS}_{3/2}\text{Cl}]$  units in the samples on the Line c, the peak located at about 270  $\text{cm}^{-1}$  and the shoulder located at about 360  $\text{cm}^{-1}$  have been fully get rid of. So more distinct evolution of the band between 280 and 360  $\text{cm}^{-1}$  can be manifested. Following the reduction of  $\text{GeS}_2$  content, the band between 280 and 360  $\text{cm}^{-1}$  changed into two peaks centered at about 340 and 320  $\text{cm}^{-1}$  step by step. Later we will elucidate that the peak sited at about 320  $\text{cm}^{-1}$  and the increasingly strengthening shoulder located at about 390  $\text{cm}^{-1}$  is due to the symmetric stretching vibration of inner bridging sulfur bonds and outer Ga–S and Ga–Cl bonds in the subunits  $[\text{GaS}_{3/2}\text{Cl}]$ , respectively. Furthermore, the aforementioned evolution can be more distinctly found from the Raman spectra of samples

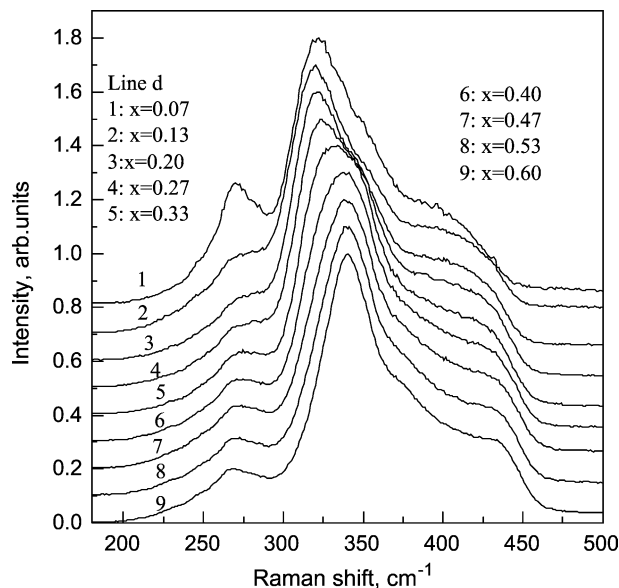


Fig. 6. Raman spectra of samples on Line d:  $(0.8 - 1.2x)\text{GeS}_2 - (0.2 + 0.2x)\text{Ga}_2\text{S}_3 - x\text{KCl}$  ( $x = 0.07, 0.13, 0.20, 0.27, 0.33, 0.40, 0.47, 0.53, 0.60$ ).

along the Line d, that is, the  $0.8\text{GeS}_2 - 0.2\text{Ga}_2\text{S}_3$  and  $\text{Ga}_2\text{S}_3 - 2\text{KCl}$  composition join in Fig. 6.

Based on our recent study on Raman scattering spectra of  $\text{Ga}_2\text{S}_3 - 2\text{MCl}$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) system glasses [13], all the spectral evolution can be interpreted correctly using a localized model considering the decoupled, weakly deformed subunits  $2\text{M}^+[\text{Ga}_2\text{S}_{4/2}\text{Cl}_2]^{2-}$ . Considering the similarity of  $[\text{Ga}_2\text{Cl}_6]$  and  $[\text{Ga}_2\text{S}_{4/2}\text{Cl}_2]$ , the coincidence of their Raman spectra should exist. In the Raman spectra of molten dimeric  $\text{Ga}_2\text{Cl}_6$  [12], the strongest Raman band is located at about 413  $\text{cm}^{-1}$  that is assigned to the  $\nu_1$  symmetric stretching vibration of the outer Ga–Cl bonds. Considering the similarity of S and Cl atomic weights, the structural difference of dimeric  $\text{Ga}_2\text{Cl}_6$  and  $2\text{M}^+[\text{Ga}_2\text{S}_{4/2}\text{Cl}_2]^{2-}$  originates mainly from the presence of alkali metal ions  $\text{K}^+$ . Compared to the K–Cl bonds, the Ga–Cl bonds are more covalent, so the introduction of  $\text{K}^+$  ions certainly makes the Ga–Cl bonds weaken and harden and displaces the chlorine atoms towards the  $\text{K}^+$  ions. Based on the above analysis, K is supposed to exist in the form of chlorine as its nearest coordination in our studying glass. So the Ga–S bonds are little influenced by the introduced  $\text{K}^+$  ions. So the peak sited at about 413  $\text{cm}^{-1}$  evolved into the broadening band between 380 and 420  $\text{cm}^{-1}$ . As for Sample 1 in Fig. 6, due to the appearance of larger clusters  $[\text{KCl}_n]$ , the characteristic peak manifesting the existence of ethane-like structural subunits  $\text{Ga}_2\text{S}_6$  stands out. According to Fig. 1, Sample 1 is sited outside the glass-forming range of  $\text{GeS}_2 - \text{Ga}_2\text{S}_3 - \text{KCl}$  glasses. Clearly, the bigger  $[\text{KCl}_n]$  clusters exist in Sample 1. So this manifested itself that alkali metal ions  $\text{K}^+$  are homogeneously dispersed in the polymeric network as the form of K–Cl coordination from another aspect.

#### 4. Conclusions

In summary, systematical Raman scattering probing about the  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses on the composition Lines a, b, c and d has been made. Based on the single reaction of  $\text{Ga}_2\text{S}_3$  and KCl in the  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  glasses and  $\text{K}^+$  ionic effect on the subunits  $[\text{Ga}_2\text{S}_{6/2}\text{Cl}_2]$ , the microstructural model of the studying glasses was presented. Based on the above-mentioned microstructural model, the satisfied interpretation about the evolution of Raman spectra in the  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KCl}$  pseudo-ternary system glasses was done.

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