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MICROSTRUCTURE AND MID-INFRARED REFRACTIVE INDEX DISPERSION OF $Ge(S_xSe_{1-x})_4$ GLASSES

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$Ge(S_xSe_{1-x})_4$ bulk glasses, which have the optimal constraint and glass-forming ability in Ge-S(or Se) binary glassy system, were prepared by the traditional melt-quenching method. In order to study the influence of the replacement of chalcogenide elements on the main Raman scattering frequency, we hold constant number of the topological constraints (n=3) in the studied glass series. The compositional evolution of the main Raman scattering frequency of $Ge(S_xSe_{1-x})_4$ bulk glasses was analyzed to investigate the structural changes following the replacement of Se for S. By adjusting the proportion of the chalcogenide elements, the evolution of mid-infrared refractive index dispersion of $Ge(S_xSe_{1-x})_4$ glasses was reasonably elucidated based on the structural variance of these glasses obtained from Raman spectra.

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1. Introduction

Chalcogenide glasses have the excellent optical properties such as high refractive index and large optical transmission ranges extending in the mid-infrared region. The properties found in chalcogenide glasses make them very interesting for technological applications, such as optoelectronics and chemical sensors, which leading to a very broad prospects for development in IF imager, information storage, national defense, military, biological engineering and medical fields [1-4]. Recently, Studies on chalcogenide glasses in the As-free Ge-S-Se system have received attention owing to their possible use as materials for IR technology [5-7], especially in atmospheric window of 3-5 μm. Numerous techniques have been used to investigate short- and medium-range orders in $Ge(S, Se)_2$ because it has become apparent that Raman spectroscopy is a simple, direct, and powerful probe of the molecular structure of chalcogenide glasses [8-10]. But much less attention has focused on the S, Se-rich multivariate chalcogenide glass like $Ge(S, Se)_4$ maybe due to its complex inner structure. By extending this work, we hold constant number of the topological constraints in the studied glass series of $Ge(S, Se)_4$, and then change the ratio of the chalcogenide component in order to explore the change of the property.

The refractive index is one of the most significant parameters for chalcogenide glasses in optical devices. Due to macro performance is depended on the internal atomic structure, investigation on chalcogenide glass internal structure is of very significance in order to find the best way to achieve the excellent performance. Raman scattering technique is regarded as a kind of efficient approach to research the micro-structure of chalcogenide glasses [11-13].

In this paper, S/Se-rich $Ge(S_xSe_{1-x})_4$ bulk glasses were prepared by the conventional melt-quenching method. The refraction index and the mid-infrared refractive index dispersion of these glasses were given. Through the investigation of Raman spectra, the microstructure of these

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glasses was analyzed and the origin of compositional evolution of mid-infrared refractive index dispersion was discussed.

2. Experimental details

Different compositions of bulk $Ge(S_xSe_{1-x})_4$ chalcogenide glasses with x = 0, 0.25, 0.5, 0.75 and 1, where x is the atomic ratio S/(S+Se), were prepared from high purity (99.999%) raw materials by the melt-quenching technique. The raw materials were sealed in evacuated (10^{-2} Pa) quartz ampoules. The rocking furnace was regularly shaken to ensure homogeneousness of the melt. The sealed quartz ampoules were heated for 24 hrs at the temperature range from 1123 K to 1223 K and then maintained at 923 K for 5 hrs without shaking before quenched into ice-cooled water to avoid crystallization. For the details, see the reference [14]. The chalcogenide glass bulks were annealed in order to relieve residual stress and then cut and polished into discs with 1 mm thickness.

Raman spectra were recorded using back-scattering configuration with the resolution of 4 cm^{-1} in the wave number range between 100 and 800 cm^{-1}. The spectra were collected with an Intelligent Fourier infrared spectrometer (Therno Nicolet, Nexus). The 1064 nm laser was used as the excitation light.

Refractive indexes of the samples were measured by the infrared ellipsometry (Type: IR-Vase; made by J.A. Woollam company in America).

3. Results and discussion

From the Raman spectra in Fig.1(a), we can see some information about the structure of $Ge(S_xSe_{1-x})_4$ glasses. The bands at 340, 370, 430 cm^{-1} can be clearly attributed to A_1 symmetric stretch vibrations of corner-sharing (GeS_4) tetrahedral units, A^c_1 companion vibrations of edge-sharing (GeS_4) tetrahedral units and the stretch vibrations of cluster edge S-S dimers or chains respectively [15-17]. The band observed at 475 cm^{-1} arises from the stretching of S-S bonds in short S_n chains or S_8 rings. The bands at 150 cm^{-1} and 220 cm^{-1} can be assigned to the A_1 mode and bending E_2 mode which are related to S_8 rings [18, 19]. Some symmetrical stretching vibration of S-Se under the curve is at about 300-400 cm^{-1}. The bands at 195 and 215 cm^{-1} have been attributed to the vibrations of corner-sharing ($GeSe_4$) tetrahedral units and edge-sharing ($GeSe_4$) tetrahedral units respectively [20]. The weak shoulder around 235 cm^{-1} is attributed to A_1 and E modes of Se chains. The broad and intense band at 255 cm^{-1} is associated to A_1 and E_2 modes of Se_n rings.

Some information about the process of structural change of $Ge(S_xSe_{1-x})_4$ were also showed in Fig.1(a). Upon a gradual substitution of Se for S, the bands related to (GeS_4) tetrahedral units, S_8 rings and S chains decrease gradually. Meanwhile, Se-rich structure like Se_8 rings, Se chains and $[Ge(S_xSe_{1-x})_4]$ tetrahedral units increase. Apart from GeS_4 and $GeSe_4$ system, the Raman spectra of $Ge(S_xSe_{1-x})_4$ glassy system are a bit complicated. There are five possible $Ge(S_xSe_{1-x})_4$ units. Among them, four units can contribute to stretching vibrational mode related to Ge-Se bond, namely $[GeS_3Se]$, $[GeS_2Se_2]$, $[GeSSe_3]$ and $[GeSe_4]$ and 363, 383, 392 cm^{-1} assigned to $\upsilon_1(A_1)$ of (GeS_3Se), (GeS_2Se_2), ($GeSSe_3$) tetrahedral units. Prof. Tao proposed that Microstructure of the present $Ge(S_xSe_{1-x})_2$ glasses can be described according to the chemical ordering random network model [20]. The chemical ordering random network model theory holds that S and Se can be replaced randomly in mixed Ge-S-Se system. Raman vibrational frequencies of $Ge(S_xSe_{1-x})_4$ are consistent with the change from vibration of Ge-S to vibration of Ge-Se. By comparing the peaks at 255 cm^{-1} shown in Fig.1, we found that with the replacement of S for Se in $Ge(S_xSe_{1-x})_4$ (x=0, 0.25, 0.5) glasses, the intensity of the peak which is associated to A_1 and E_2 modes of Se_n rings increased rather than decreased. And the intensity of the peak at 195 cm^{-1} which is associated to ($GeSe_4$) tetrahedral units decreased faster than Se content. We can therefore deduce that some mixed $Ge(S_xSe_{1-x})_4$ units swept under the curve and with the replacement of S for Se, GeS_4 unit turned into mixed $Ge(S_xSe_{1-x})_4$ units. These phenomena conform to the hypotheses of chemical ordering random network model.

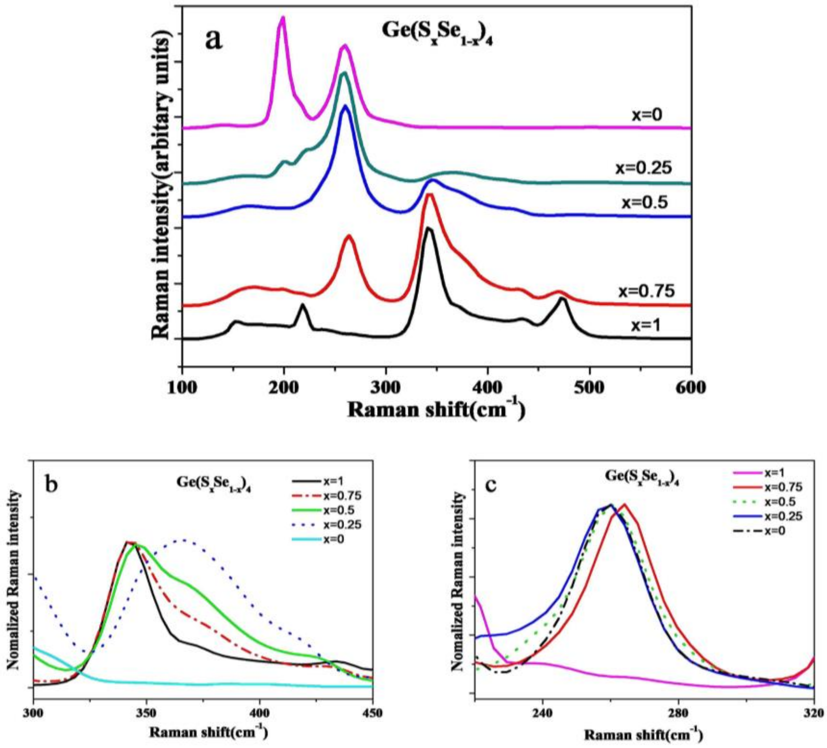

Fig.1 The experimental Raman spectra of the $Ge(S_xSe_{1-x})_4$ glassy system, x=0, 0.25, 0.5, 0.75, 1, b is obtained by normalization processing of peaks positing near 340 cm^{-1}, c is obtained by normalization processing of peaks positing near 260 cm^{-1}

The normalized peaks at about 340 cm^{-1} were showed in Fig.1(b). It is seen that the main Raman peak of (GeS_4) tetrahedral units gradually becomes wider and then shifts toward higher wave number. We consider that upon a gradual substitution of Se for S, (GeS_3Se) tetrahedral units were generated gradually and in abundance. Upon the gradual substitution of Se for S in $Ge(S_xSe_{1-x})_4$ glasses, we observe a slow but clear shift toward the higher wavenumber for the main vibrating modes of GeS_4 tetrahedra. According to the vibrational coupling theory, coupling of vibrating mode of intra- or inter- groups will lead to the shift of related Raman frequency of molecular clusters toward lower wavenumber [20]. Considering the coupling of inter-groups, the stepwise decreasing of environmental GeS_4 tetrahedra around the central GeS_4 group have both the same symmetry and approximately same energy to the central GeS_4 group. With the replacement of Se for S, more Ge-S bonds disappeared and the coupling weakened, then the frequency of central GeS_4 tetrahedra has a gradual increase.

Table.1 Probability of occurrences of S-S, S-Se, Se-Se

bonds	S	Se	S-S	S-Se	Se-Se
probability of occurrence	1	0	1	0	0
	3/4	1/4	9/16	6/16	1/16
	1/2	1/2	1/4	1/2	1/4
	1/4	3/4	1/16	6/16	9/16
	0	1	0	0	1

For S/Se-rich chalcogenide glasses, there are abundant S and Se to form Ge-S and Ge-Se bonds. According to random-network model, the problem of the combination of chalcogenide atoms can be resolved by random probabilistic model in Table.1. Without considering the impacts of $Ge(S_xSe_{1-x})_4$ mixed tetrahedral units, probability of occurrences of S-S, Se-Se are well fitted the peak areas of S-S, Se-Se in Fig.1(a). The symmetrical stretching vibration of S-Se swept under the curve at 300-400 cm^{-1} and can hardly be seen.

The normalized peaks at about 255 cm^{-1} were shown in Fig.1(c). The broad and intense band at 255 cm^{-1} is associated to A_1 and E_2 modes of Se_n rings. We can see that the peaks of $Ge(S_xSe_{1-x})_4$ (x=0.25, 0.5, 0.75) glass around 255 cm^{-1} have a blue shift. With the increase of S content, electronegativity of the surrounding environment of Se-Se, S-Se bonds enhanced and the average radius shortened. So the related stretching vibrations of center bond have a tendency of increase.

Table.2 Refractive index in 3-5 μm atmospheric window of $Ge(S_xSe_{1-x})_4$ glasses

Wavelength(μm)	x=1	x=0.75	x=0.5	x=0.25	x=0
3.00	1.929	2.041	2.144	2.248	2.398
4.00	1.916	2.029	2.134	2.233	2.363
5.00	1.908	2.016	2.116	2.214	2.357
Abbe number	44.715	41.122	39.548	35.865	33.301

The law of refractive indices of $Ge(S_xSe_{1-x})_4$ glasses following the change of composition are showed in Table 2. The values of n are between 1.9 and 2.4. With the increase of Se content, refractive index increases.

According to the following equation, the refractive index of glasses depends on molecular refraction and molecular volume [24]:

$$R_M = \frac{(n^2-1)}{(n^2+2)} \times V_M \tag{1}$$

Where n is refractive index, V_M is molecular volume. We can see that refractive index of glass depends on molecular refraction and molecular volume.

Molecular refraction R_M is proportional to ionic polarizability χ:

$$\mathrm{R_M} = (4\pi N_l / 3)\chi \tag{2}$$

In the formula, N_i is coordination number. Both R_M and n increased with the ionic polarizability. Due to the polarizability of negative ions are considerably bigger than positive ions, refractive index is mainly depends on polarizability of negative ions. Both Se and S belong to group element VIA, but the radius of Se is bigger. Ionic polarizability of Se is bigger than S, and R_M of Se is bigger.

Molecular volume of glass depends on composition and the compactly pile degree of structure units. From Raman spectra in Fig.1, with S substituted by Se, (GeS_4) tetrahedral substitute by $[Ge(S_xSe_{1-x})]$ tetrahedral firstly and then substitute by $(GeSe_4)$ tetrahedral. S_8 rings, S chains substituted by Se_8 rings, Se chains. All of the structure units are distributed evenly in the glass, so with the bigger structure units substituted by smaller structure, molecular volume of glass decreases.

Abbe number is always used to measuring the degree of dispersion in the visible region [25]. It is described as an equation below:

$$V_d = (n_d - 1)/(n_f - n_c) \tag{3}$$

Where V_d is Abbe number, n_c, n_d, n_f is the refractive index of c, d, f light respectively [26]. The Abbe value is essentially a measure of the median refracting action of a material for wavelengths of light across the visible spectrum compared to the difference in refracting action between the red and blue ends of the spectrum [27-29]. A larger Abbe number means a lower dispersion.

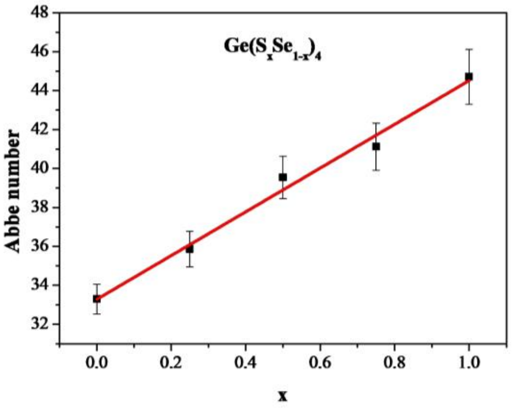

Fig.2 Abbe number in 3-5 μm atm*ospheric window of Ge(S_xSe_{1-x})$_4$ glasses,*
the standard error of slope is 0.6750

We use the similar method, retain the formula and substitute the value, to measure the degree of dispersion in infrared regions. We let c, d, f stand for the light of 3, 4, 5 μm. The computed results are shown in Table 2. With the increase of Se content, Abbe number decrease, so the dispersion is greater. A good fit was obtained as shown in Fig.2. The standard error of slope was 0.6750. It can be considered that the Abbe number decreases linearly with the increase of Se content. According to Fig.1(a) and Table 1, we know that the combination of negative ions, which contributed most to the refractive index, subject to chemical ordering random network model. So the linear relationship between dispersion and chalcogenide contents is working as expected.

4. Conclusions

Systematic measurements of compositional evolution of Raman scattering frequency of Ge(S_xSe_{1-x})$_4$ glassy samples have been conducted. Based on the proposed micro-structural model, all the Raman spectra can be reasonably ascribed and the spectral evolutions can be successfully elucidated. At the same time, the following conclusions can be deduced:

1. Microstructure of the present Ge(S_xSe_{1-x})$_4$ glasses can be well described according to the chemical ordering random network model.

2. With the replacement of Se for S, the main vibrating modes of GeS_4 tetrahedra has a slow but clear shift toward the higher wavenumber and the main vibrating modes of Se-Se has a gradual shift toward the lower wavenumber.

3. With the increase of Se content, refractive index and optical dispersion in the region of 3~5 μm increases gradually. And a linear relationship between optical dispersion and chalcogenide contents exists, which can be ascribed to their corresponding structural evolution following the replacement of Se for S.

Acknowledgments

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