DYNAMICS OF Ge-Se GLASSES AT STIFFNESS TRANSITION

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Using the Raman scattering technique, we have investigated the thermal relaxation processes at various ranges of temperature in Ge_xSe_{1-x} glasses. Below 100 K, the reason why the peak position of the A_1 mode of GeSe_{4/2} tetrahedra shows a positive shift with temperature is that the network relaxes, caused by a thermal excitation of soft bending modes related to Se_n (n > 2) chain structures. This strengthens the remaining stretching modes. For rigid glasses (of average coordination number, $\langle r \rangle > 2.4$, or x > 0.20), few Se_n (n>2) units contained in the structure result in well mixed local vibrational modes. At the stiffness transition, the changes in peak positions with temperature in 100-300 K are the same, although the local modes differ markedly in frequency. In the temperature range 300-750 K including the glass transition temperatures $(T_{\rm o})$, relaxational modes, quasi-elastic contributions in the low-frequency region of 10-80 cm⁻¹, appear around the Tg only in the floppy (x ≤ 0.20) glasses, but it is undetectable in the rigid glasses ($x \ge 0.23$). We comfirm that the quasielastic contribution originates from the fast (B) process of relaxation. The compositional dependence of the guasielastic intensity is well explained by the constraint counting theory under the assumption that the origin of the relaxational modes is from the floppy modes. We attribute the relaxation modes mainly to the damping or jumping motions of the rotating Se_n segments, which could be regarded as the microscopic picture of the floppy modes in the Se-contained network glasses.

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1. Introduction

The covalent network glass system Ge-Se has been well studied and analyzed in terms of structural theories [1-13]. The mean-field constraint theory [1-4] for network glasses is proving to be useful in explaining many anomalous behavior around the critical composition of the rigidity transition threshold at an average coordination number, $\langle r \rangle = 2.4$, corresponding to x = 0.20 for Ge_xSe_{1-x} [5-13]. Short- and medium-range order in Ge_xSe_{1-x} glasses can be varied continuously to form both the floppy and rigid glass structures in the sense of the constraint theory, since, in the composition range $0.00 \le x \le 0.40$, the coordination numbers of Ge and Se are 4 and 2, respectively. According to the theory, the character of the network glass undergoes a qualitative change from being easily deformable at $\langle r \rangle < 2.4$ to being rigid at $\langle r \rangle > 2.4$.

Kamitakahara et al. [7] reported the dynamic density of state around 5 meV and showed the existence of the floppy mode ("zero-frequency" mode in floppy glass) by studying the inelastic neutron spectra of chalcogenide glasses. Recently, Boolchand et al. [11] demostrated that the results from Raman scattering, modulated differential scanning calorimetry, molar volumes and Mössbauer spectroscopy work provide evidence of a multiplicity of stiffness transitions, an onset point near $\langle r \rangle_{(1)} = 2.40$ and a completion point near $\langle r \rangle_{(2)} = 2.46$. We disuss the properties of bond-stretching, - bending and -rotating modes by studying the temperature dependence of optical bands, since the structural units relative to the bands are individually influenced by the nearby connectivity of the network. A microscopic structural explanation of the floppy mode is proposed as the damping or

jumping motions of the rotating Se_n (n > 2) segments. The criticality of the stiffness transition observed by Raman scattering is discussed from the point of view of a structural admixture of Se_n and $GeSe_{4/2}$ units.

The Dynamics of the glasses at the stiffness transitions is this review's subject that also contains the structural relaxations at glass transition temperature, T_g . The physical origin of a fast β process in glass material and its possible connection to the α relaxation are questions that are at present completely unclear. The structural relaxations around T_g are subjects of increasing interest in connection with the poorly understood glass transition phenomenon. It has been probed by infrared hole burning at cryogenic temperatures that topological effects rather than chemical ones must be considered to explain the energetic relaxations among glassy configurations in Ge-As-Se chalcogenides [14]. The relevance of the concept of $\langle r \rangle$ has also been explored in the liquid state [15 - 17]. These studies of ternary chalcogenide alloys have provided evidence for a correlation between the rigidity percolation and the departure from Arrhenius behavior, i.e., the fragility. However, it remains unclear whether another key aspect of the glass transition, viz., the structural relaxation also shows a systematic composition dependence. We discuss the structural relaxations at T_g through the investigation of temperature dependence of quasielastic contribution appearing in 10-80 cm⁻¹ in terms of network connectivity. A shapness of the transition, a first-order-like transition, of the relaxational dynamics from floppy to rigid is understood in terms of self-organization concept.

2. Experimental

The constraints per atom of Ge-Se glasses are varied by changing the Ge composition, because few dangling bonds are formed in samples obtained by conventional quenching method. Ge_xSe_{1-x} glasses were prepared from high purity Ge (99.9999%) and Se (99.999%) elements which were etched in CP4 (a solution of HNO₃, HF, and CH₃COOH in a volume ratio 8:10:5) and a KOH water solution, respectively. The etched elements were sealed in an evacuated (~ 10⁻⁶ Torr) silica ampoule in a desired molar ratio. The ampoule was slowly heated up to 960 °C (for Se glass up to 400 °C) in a rocking furnace and the melts were homogenized for at least 24 hours. Then, they were equilibrated at about 150 °C above the liquidus for an additional 24 hours before quenching in iced water. All the measured samples, with $\langle r \rangle = 2.00-2.70$ (x = 0-0.35), are picked from the as-prepared broken pieces with a typical dimension of 5x5x1 mm.

In noncrystalline materials, Raman scattering processes are allowed to occur from essentially all the vibrational modes of the material. Usually the intensity $I(\omega)$ of scattered light is proportional to the vibrational density of states (VDOS), $g(\omega)$. The experimental setup for Raman scattering is shown in Fig. 1. Raman scattering was measured in a backscattering configuration, excited by a DCM dye laser (1.83 eV) pumped by an Ar⁺ ion laser (Spectra-Physics Stabilite 2017). At the excitation energy or lower, resonant Raman effect is negligible. For avoiding light-induced events and restricting the sample temperature difference from the environment to less than 3 °C, excitation light was focused onto a rectangular region of about 2 × 0.2 mm² (line-focusing) with a low-power density less than 3 W/cm².

The back-scattered light is collected and anaylzed with a triple grating polychromator (JOBIN YVON T64000) and CCD detector in polarized and depolaried configurations. The samples were sealed in a silica tube in an argon gas atmosphere (~ 360 Torr) to avoid oxidation, and they were heated stepwise in an electric furnace. The temperature during the accumulation for each spectrum was fixed within ± 1 °C. The heating rate between the successive measured temperatures was about 3 °C/min. During the accumulation, 10 minutes or less for each spectrum, no change was observed in the spectra below T_g, and the changes were very small even above T_g except at the crystallization temperature. A temperature-programed cryostat (Oxford optistat) is employed for the low-temperature measurements. The glass transition temperature was measured by using a Perkin-Elmer model DSC-7 differential scanning calorimeter at a heating rate of 10 °C/min.



Fig. 1. Experimental setup for the high temperature Raman scattering measurement.

3. Results and discussion

3.1 Temperature dependence of Raman spectra

Stokes Raman spectra of Ge_xSe_{1-x} glasses for various composition at 80 K are shown in Fig. 2. In this paper, Raman spectra are reduced by $[n(\omega) + 1]$ and normalized to the maximum intensity, which for low Ge concentration is the peak at 255 cm⁻¹ or at 200 cm⁻¹ for high Ge concentration. In g-Se, the dominant peak at 255 cm⁻¹ and a shoulder at the lower frequency side are relevant to the bond-stretching modes of Se_n chains [18]. The weight of Se-chains related intensity decreases with increasing Ge concentration, which qualitatively reflects the changes in the vibrational density of states. It follows that the number of GeSe_{4/2} tetrahedra increases with increasing Ge content. A strong peak at lower or a weak one at higher energy side in the vicinity of 200 cm^{-1} is associated with the breathing mode of GeSe_{4/2} tetrahedra which are connected by sharing corners or edges, respectively [19]. It should be noted that even in the glass of Ge content of 8 percents a small amount of tetrahedra shares edges. For GeSe₂ and Ge₃₅Se₆₅, the Ge-Ge bond related band at 180 cm⁻¹ increases with Ge content. In GeSe2 glass, the Ge-Ge and Se-Se "wrong bonds" are assumed to release the exceeding tension or stress in the highly distorted network, since its mean coordination number $\langle r \rangle$ is 2.67. And the Se-Se vibrational bands are observed at 260 cm⁻¹ with the resonant Raman condition. Further discussion on the Ge-Ge and Se-Se "wrong" bonds in GeSe₂ glass will be done elsewhere [20].



Fig. 2. Polarized Raman spectra for Ge_xSe_{1-x} at 80 K. The resolution of the spectra is better than 1 cm⁻¹.

In Ge_xSe_{1-x} glasses, the basic structural units are Se_n chains and $GeSe_{4/2}$ tetrahadra. The former are floppy units that build floppy regions in the network; the latter are rigid units that construct rigid ones. Studying the temperature dependence of vibrational properties of Se-Se or Ge-Se bond for each unit will supply crucial information on the microstructure of the network. Fig. 3 shows Raman spectra for Ge_8Se_{92} glass from 20 K to room temperature. The spectrum at the successive higher temperature is plotted with the base line raised by the same value. To take systematic analyses, the line shape of the spectra in the range of 160-300 cm⁻¹ is fitted by one straight line and four Guassian curves, corresponding to two breathing modes of $GeSe_{4/2}$ tetrahedra and two Se-chain related modes.



Fig. 3. Raman spectra for Ge₈Se₉₂ glass at various temperatures. The spectra are obtained in a T-increasing sequence.

Here, we focus on temperature dependence of peak positions of $GeSe_{4/2}$ breathing mode, A₁, at 200 cm⁻¹ and Se-Se bond-stretching mode at 255 cm⁻¹, as shown in Figs. 4 (a) and (b). In the floppy glass of Ge_8Se_{92} , an anomalous peak shift of the A₁ mode, a positive shift with temperature, is observed below 100 K. This anomalous feature is hard understood without introducting a structural change at very low temperature.



Fig. 4. The temperature dependence of the A₁ breathing mode of tetrahedra and the Se-Se bond-stretching mode. Both are scaled by the frequency of each mode at the lowest temperature we meausred. (a) displays the typical case in floppy glasses and (b) the rigid glasses.

As we cool the glass down to 20 K (well below the T_g 's), each structural unit freezes at either critical temperature below which the unit is forbidden to change its topology in the network. In Ge-Se network, first the GeSe_{4/2}-unit rich region freezes, and at this time they might not be constraint or stressed. If all the atoms vibrate in limited spaces caused by the constraction of volume with decreasing temperature, a large number of stress or tension then should be induced since the glassy sample is not an ideal glass. Appending such stress or tension on the local structural units of $GeSe_{4/2}$ tetrahedra and Se_n chains, the structure of each unit must be distorted more or less (we can not expect an isotropic force in the microscopic region, though it is in a glass). The decrease in frequency of the A_1 mode during the cooling process suggests that the tetrahedra should depart from their regular structure under the anisotropic stress or tension. The similar stress or tension should influence the Sechain structure too. The reason why the Se-Se bond-stretching mode shows less temperature dependence than the A₁ mode does is probably because of the bending force of Se-Se bond much weaker than its stretching one. Most of the distortion in the Se_n (n>2) chains can cause a wide distribution of Se-Se-Se bond angle that makes the Se-Se bending mode broad as well. At present, however, it is unfortunate that we can only measure the \rest" stretching mode of Se-Se bond. In Ge_8Se_{92} glass, Se_n chains are the dominant structural units and $GeSe_{4/2}$ tetrahedra are probably isolated from each other. The structural units of Se_n (n>2) chains, as shown in Fig. 5, are assumed as the key units for the heavily distorted tetrahedra "relaxing" to the regular structure. We suppose that the rotating motion of Se(2) atom on the axis through the Se(1) and Se(3) atoms will completely freeze at 20 K. For the Se(3) atom, if there is a Se(4) atom next to it, the same discussion as for the Se(2) atom holds. With increasing temperature, the rotating mode of Se(2) atom could be thermally excited, since the relative force determined by the structure, consisting of two priori free dihedral angles, is fairly weak. Such thermally excited rotating motion supplies channels to leak the stress or tension by the way of changing the topology of network. The heavily distorted network then relaxes and make the "remaining" (or observed) A1 mode strengthened. When temperature is approaching to 100 K, the rotating modes is totally excited, and thereafter the vibrational peaks start to shift in negative behavior due to anharmonic effects.



Fig. 5. Schematic diagram for atom arrangements of Se_n chains. The Se(2) atom rotates on the axis through the Se(1) and Se(3) atoms. The rotating motion is constrained by two prior free dihedral angles consisting of the next nearest neighbor forces. The same rotating mode for the Se(3) exists with the Se(4) bonding to it.

In our measured samples, the most remarkable positive shift of the A_1 mode occurs in the Ge₈Se₉₂. For x < 0.08, although the positive shift (with the same origin) is expected, it might be difficult to figure them up strictly because of a smaller population of tetrahedra to form the vibrational density of states, which brings big errors in fitting the line shape of A_1 mode. The network could settle the stress or tension through the large floppy region consisting of Se_n chains surrounding the GeSe_{4/2}-rich region. While for Ge₁₅Se₈₅, the floppy region that surrounds the rigid region of GeSe_{4/2} units is not large enough to provide space for the distorted tetrahedra "relaxing". Nevertheless, we consider the rotating mode in Fig. 5 to be a probable microstructural explanation for the floppy modes in Secontained covalent network glasses. The same kind of rotating modes has been discussed in the computing analysis for modeling the flexible and rigid regions in proteins [12]. The easy excited dihedral angles that free the rotating motion of Se(2) and Se(3) in Fig. 5 is assumed as the bananas graphs proposed by Thrope et al. [4]. The soft constraint rotating modes (anyway glass is solid) could

be regarded as the floppy modes in a realistic floppy glasses. Most of properties of covalent glasses are discussed at room temperature or higher, at which such "constraint" (at low temperature) floppy modes are totally free. That is why the elegant constraint theory works so well [5-13], although the theory settles the problem of networks at 0 K.

With increasing *x*, the floppy glass is approaching to the rigidity percolation threshold of $\langle r \rangle = 2.4$ (x = 0.20). The stiffness transition behavior clearly appears in the temperature dependence of the vibrational modes between 100 K and room temperature where the anharmonic effects determine the essential rules. As shown in Fig. 4, large drops of the shifts for both the A₁ mode and the Se-Se mode at room temperature are observed in the floppy glasses. The room temperature is the temperature to which the samples were quenched (it should be 0 °C for an accurate discussion), and at which they rested for a long time. Between 100 K and 250 K, we can draw straight lines through the data for both of the two modes and get well linear fits. The slopes of lines as a function of x and mean coordination number $\langle r \rangle$ for both the A₁ mode and the Se-Se mode are plotted in Fig. 6. A nice convergence of the slopes, like the shifts themselves, comes to a common value at x = 0.22. This is the stiffness transition at which the number of degrees of freedom is equal to the number of constraints [11]. Apparently, all the observed modes shift together at this transition, because the network becomes almost ideally random to realize a maximum mixing of the different local modes.

For the rigid glasses, the fact that few Se_n (n > 2) units are included in the structure is the reason of admixture of all the local modes. Probably the same mixing of Se-Se bending motion goes into both the A₁ and Se-Se stretching modes. So although the local modes of the A₁ breathing and the Se-Se stretching have different frequencies, 200 cm⁻¹ and 255 cm⁻¹, respectively, the changes in those frequencies (scaled by their frequency at the lowest measured temperature) become the same. This kind of mixing should occure in a long-range scale and well detected by the light-probe technique.



Fig. 6. The slope of straight line obtained from the data of each modes in the temperature range of 100-250 K. The A₁ mode () has a fourth time large of the volume obtained from the Se-Se stretching mode (•) for $\langle r \rangle < 2.4$. While for $\langle r \rangle > 2.4$, they are similar. The lines are guide to the eye.

For the floppy glasses, the A_1 mode shifts much more than the Se-Se bond-stretching mode does. The probable reason is that the mixing of Se-Se bending motion into the bending of Se-Ge-Se permits all the bending modes mixing in the floppy glasses. In other words, the A_1 band is not a pure breathing mode because of the admixture of bending modes. Thus, the Se-Se stretching mode shows less temperature dependence than the A_1 one in which the soft bending modes are mixed.

3.2 Low-frequency spectra

Generally, low-frequency Raman spectra of glasses and supercooled liquids usually contain two contributions: relaxational (overdamped) and vibrational ones. Below T_g , the spectra are dominated by vibrational contributions termed the boson peak (BP). The Raman intensity I(ω) of the

vibrational part varies according to the Bose factor $n(\omega)$, i.e., $I(\omega) \propto n(\omega) + 1$ in many glasses [21,22]. The relaxational part of the dynamical structure factor varies with temperature more strongly than the Bose factor, and it becomes virtually dominating at temperatures higher than T_g [23-25]. As an example, we show the Stokes Raman spectra of Ge₁₀Se₉₀ in Fig. 7. The Raman spectra are normalized, for convenience, by the integrated intensity of optical modes between 170 cm⁻¹ and 330 cm⁻¹, including the A₁ mode of CST around 195 cm⁻¹, the breathing mode of EST around 211 cm⁻¹, and the stretching mode of Se-Se bonds around 255 cm⁻¹ [6,19]. The following discussion does not significantly effected by the normalization way; we focus on only the line-shape of the lowfrequency spectra. At 30 °C (the room temperature), the low-frequency spectra are dominated by a strong BP around 20 cm⁻¹. Since the Raman spectra are reduced by the temperature factor $[n(\omega, \omega)]$ T)+1]/w, the BP intensity should be independent of temperature. At 150 °C a quasielastic contribution arising from relaxational modes is superposed on the BP. The inset in Fig. 7 shows the depolarization ratio, defined as a ratio of the scattered intensity with propagation of the electric field parallel to the scattering plane (I_{VH}) to the corresponding vertical one (I_{VV}) . No sudden drop with decreasing the frequency to zero both at room temperature and above Tg confirms no Rayleigh line contribution in the low-frequency spectra.



Fig. 7. Raman spectra of $Ge_{0.10}Se_{0.90}$ glass at room temperature and above the glass transition temperature ($T_g = 100$ °C) in VV polarization configuration. The inset shows the depolarization ratio (I_{VH}/I_{VV}).

We inquire the composition dependence of the relaxational mode. Fig. 8 shows the normalized and reduced low-frequency Raman spectra of Ge_xSe_{1-x} glasses in the composition range $(0.07 \le x \le 0.35)$ covering the rigidity transition (x = 0.20). At room temperature, the low-frequency spectra are dominated by the BP around 20 cm⁻¹ in all the glasses. Around T_g quasielastic contribution resulting from relaxational modes appears in the "floppy" glasses ($x \le 0.20$), and it grows with temperature. The apperance of the relaxational modes in the threshold composition (x = 0.20) is due to breaking parts of the bond-bending constraint from Se atoms [9]. We regard the Ge₂₀Se₈₀ glass as floppy ones in the following discussion as well. On the other hand, the strong quasielastic contribution is not detected in the rigid glasses ($x \ge 0.23$) even above T_g. On the contrary to the floppy glasses, the intensity around the BP decreases with temperature. Such a decrease is related to structural changes occurring in rigid glasses, as we will discuss elsewhere [26]. Thus, it is found that the dynamics around T_g is distinctly different between the floppy glasses and rigid ones.

3.3 Relaxational modes

Mainly, two approaches to fit the low-frequency Raman data have been suggested, where the quasielastic (QE) and BP contributions are represented either as a convolution or as a superposition.



Fig. 8. Temperature dependences of the low-frequency Raman spectra of Ge_xSe_{1-x} in VV configuration. The spectra are reduced by the temperature factor $[n(\omega, T) + 1]/\omega$, and normalized to the integrated intensity of the optic modes (170-330 cm⁻¹).

The first approach, or the convolution model, relies on ideas originated from the "in-direct" scattering mechanism of Winterling [27], where it is assumed that the QE line represents a lowfrequency relaxation like part of the one phonon response function. In other words, the vibrational excitations are coupled to some relaxing variable that induces broadening to each frequency of the BP [28]. This way of interpretation of low-frequency Raman spectra has been essentially based on the following three putative similarities between the QE and the BP contributions. (i) The depolarization ratio is strictly constant, e.g., independent of the frequency in the whole region of both the QE line and the BP since the QE line is caused by the BP vibration. This constancy is not hold good in some glasses [29]. The Ge_xSe_{1-x} system is one of them. The depolarization ratio in that frequency region is not constant as shown in Fig. 9. (ii) There is a correlation between the strength of the fast dynamics described by the relative strength of the QE scattering and the BP [25] and the fragility (a dynamic character of an amorphous material). However, it has recently been shown that the correlation is not completely systematic [29]. (iii) The phonon-photon coupling coefficient $C(\omega)$ is constant in the frequency range from the QE line (~ 0 cm⁻¹) up to the BP maximum frequency (~ 20 cm⁻¹). Recent experimental determinations of the phonon-photon coupling coefficient, through the comparison of neutron and Raman-scattering data, have shown that the statement (iii) does not definitely hold [30]. Thus, the aforementioned statements, which are used as the stronger evidence in favor of the convolution model, are based on incomplete informations. From the above argumentation we will employ the second approach, or the superposition model, in the subsequent analysis.



Fig. 9. xpanded view of depolarization ratio of Ge_{0.10}Se_{0.90} glass.

In the superposition model, the spectrum is modeled [31] as a sum of two separate contributions: QE contribution described by a Lorentzian line and the BP contribution. We assume a very small QE contribution at room temperature and a temperature-independence of the BP intensity

in floppy glasses. These assumptions enable us to extract QE contribution by subtracting the spectrum at room temperature from those at high temperatures: $I^{qe}(T) = I^{exp}(T) - I_{BP}(30 \text{ °C})$, where $I^{exp}(T)$ and $I_{BP}(30 \text{ °C})$ are the experimentally measured intensities reduced by the Bose factor at $T(^{\circ}C)$ and 30 °C, respectively. Although the extraction from the lower temperature spectrum (< 30 °C) might be better, photoexcited carriers having the longer decay times at lower temperatures affect the spectrum more effectively in the Ge-Se system.



Fig. 10. Representative sets of extracted quasielastic spectra of Ge_xSe_{1-x} glasses, subtracted by BP. Each spectrum is well fitted by a single Lorentzian function (solid line).

Fig. 10 shows the extracted QE contribution (10-80 cm^{-1}) being well fitted by a Lorentzian function:

$$I^{qe} = I^{qe}_{0} (\Gamma / 2\pi) / [\omega^{2} + (\Gamma / 2)^{2}], \qquad (1)$$

where I_{0}^{qe} is the QE intensity and Γ is the damping rate. The resulting fit-parameters, I_{0}^{qe} and Γ are

presented in Fig. 11. In all the floppy glasses, the QE intensity I_{0}^{qe} increases with temperature. At T_g, the QE intensity progressively increases with increasing Se content. The structural units involving Se atoms should play an important role on the relaxational motions. The damping rate Γ is nearly independent of both temperature and composition. The temperature independence supports that the QE contribution originates from the fast (β) process of relaxation. From the inverse of the average damping rate, we can estimate the corresponding relaxation time in a first approximation. The estimated time of about 0.8 psec is consistent with the result of neutron spin echo measurement for amorphous Se. The fast relaxation time obtained by the measurement has been much shorter than 2 psec [32]. The composition independence of the relaxation time demonstrates that the relaxation mechanism itself does not change significantly with composition. Now we explore a quantity that corresponds to the QE intensity, I^{qe}, in the dynamical glass transition function F(t). The function has been calculated by the mode coupling theory (MCT) [33] and molecular dynamics simulation [34] in some glasses. F(t) can be experimentally obtained by neutron spin-echo experiments [32,35] and inelastic neutron scattering [36-39] as well.



Fig. 11. Quasielastic intensity I_{0}^{qe} and damping rate Γ obtained by a Lorentzian fit to the low-frequency spectra (10-80 cm⁻¹) of floppy Ge_xSe_{1-x} glasses. Temperature is normalized to T_g.

Fig. 12 shows the schematic view of a typical shape of F(t) curves at various temperatures. Each curve consists of a slow relaxation component (α relaxation) and a fast relaxation component (β relaxation). Historically, the slow component has been described by the empirical Kohlrausch-Williams-Watts formula [40]:

$$F(t) = f_0 \exp(-t / \tau_{slow})^{\beta}, \qquad (2)$$

where τ_{slow} is the characteristic slow relaxation time, β is the Kohlrausch stretch exponent typically ranging between 0.3 and 0.9 for structural glasses, and f_0 is the extrapolation to t = 0 of the slow relaxation component. The complement of f_0 , namely, $1 - f_0$, is the relative "weight" of the fast relaxing part of the correlation function. The weight increases from a finite value at T_g to 1 far above T_g without a large change of the fast relaxation time. One notices that the quantity $1 - f_0$ behaves like I_0^{qe} . The density fluctuations can induce susceptibility fluctuations. Since the Fourier transformation of the space-time correlation function of the susceptibility fluctuations is generally proportional to the Raman scattering intensity, the fast relaxing weight of $1 - f_0$ should qualitatively reflect in the QE intensity I_0^{qe} . The weights of the fast and slow components correspond to the number of the degrees of freedom of atomic motions relaxing fast and slow, respectively. The QE intensity increasing with temperature will be due to the increase of the fast relaxing degrees of freedom.



Fig. 12. Schematic view of the time-dependent density-density correlation function F(t) shown in a semilogarithmic plot. F(t) is normalized to F(0) = 1. Each curve consists of a fast relaxation (thick solid line) and a slow relaxation component (thin solid line).

We now identify the structural units mainly responsible to the relaxational motions. The QE intensity at T_g decreases with increasing Ge content x. The relaxational modes do not appear at and above x = 0.23. The threshold composition is close to the rigidity transition threshold of $\langle r_c \rangle = 2.4$.

By considering a Kirkwood-Keating type of potential [41,42], the floppy networks, in which the number of degrees of freedom per atom (that is 3 in a three dimensional space) is larger than the number of constraint per atom, have low-frequency (ideally, zero-frequency) floppy modes [3, 43]. The fraction of floppy modes available in a network is $f = 2 - (5 \langle r \rangle = 6)$; the fraction decreases to zero at $\langle r_c \rangle$ with increasing $\langle r \rangle$. The composition dependence of the floppy modes is very similar to that of the QE intensity. Thus, one arrives at the following picture; a part of the motions in the floppy modes causes relaxational (damping or jumping) motions around and above T_g , which couple with light to result in the QE scattering. In other words, the number of relaxing degrees of freedom in the floppy modes corresponds to the weight of the fast relaxing component.

In Ge-Se system, the rotating motion of the Se_n (n > 2) segments, as shown in Fig. 13, has been proposed as the probable microstructural explanation for the floppy modes [44,45]. The segments have locally larger degrees of freedom than the number of constraints. This kind of rotating modes has been discussed in computer similations for modeling the flexible and rigid regions in the Se-containing network glasses and proteins [4,12]. We propose that the Se_n segments cause the relaxational motions involving damping or jumping motions around and above T_g. Such motions of the Se_n segments should play an essential role on the relaxational modes.



Fig. 13. Schematic view for atomic arrangements of Se_n segments (n = 3) having rotational degrees of freedom. The damping (a) and / or the jumping (b) motions of the segments are proposed for the dominant motions contributing to the QE scattering.

Next we discuss an interesting connection of the increase of the QE intensity with the free volume model [46]. The free volume model is one of the conventional theoretical approaches for the liquid-glass transition, which can successfully describe the change of viscosity as well as the thermodynamic quantities, specific heat and thermal expansion at the liquid-glass transition. According to the theory, a glass-forming system consists of solid-like and liquid-like cells. When the temperature increases, the fraction of the liquid-like cells p increases. When p is larger than a percolation threshold p_c , there is an infinite, connected, liquid-like cluster and the material turns into the liquid state. When p is less than p_c , it lies in the glass state. Thus, the liquid-glass transition is treated as the percolation of the liquid-like cells. On the other hand, the rigidity transition is also treated as a percolation problem [3]; in floppy networks, floppy units percolate while rigid units do not, as shown in Fig. 14. We assume that, with increasing temperature, the floppy units become the liquid-like cells in which the atomic motions relax or damp. Since the floppy units percolate in floppy glasses, it follows that the liquid-like cells percolate around T_g . The percolation of the liquid units arising from the floppy units should achieve the strong QE line in our spectral range. We suppose that both of the increases of fast relaxing degrees of freedom and the number of the liquid-like units with temperature lead to the increase of the QE intensity. On the other hand, in our spectral range, the QE contribution is hardly observed in rigid glasses. This will be due to no "remaining" degrees of freedom in rigid units according to constraint counting theory; the number of constraints is larger than that of degrees of freedom. Then, even though the rigid units can become liquid-like cells, the relaxational motions of the liquid-like rigid units will be quite different with floppy ones; the characteristic time may be beyond our spectral range.



Fig. 14. Schematic illustration of floppy and rigid regions. In floppy network (a) the floppy regions percolate while in rigid one (b) the rigid regions percolate. There is a intermediate phase between the floppy and rigid networks, in which the network is a well admixture of floppy regions and rigid ones.

3.4 Self-organization

We emphasize again that the relaxational modes observed in Se-rich glasses ($x \le 0.20$) become hardly observed when the Ge content is slightly increased from x = 0.20 to 0.23. We feel that

the transition for the appearance of the relaxational modes is surprisingly sharp beyond the expectation from the mean-field constraint theory.

Boolchand et al. [11] have suggested that the rigidity transition is richer in nature than that predicted by the previous mean-field constraint theory [1-3], based on the measurements of Raman scattering, Mössbauer spectroscopy, modulated differential scanning calorimetry, and molar volumes. They have proposed the existence of an intermediate phase that starts near $\langle r_{(1)} \rangle = 2.40$ (x = 0.20) and is completed near $\langle r_{(2)} \rangle = 2.46$ (x = 0.23). Recent numerical simulations [47] have shown that the glasses in the intermediate phase are "self-organized" at some level. The network in the intermediate phase is rigid, but is formed with less (or no) overstressed region with the help of self-organization. With the self-organization processing, some constraints are removed from the overstressed region to apply on some floppy units. This process decreases the global constraints on the overconstrained region through sacrificing the degrees of freedom of the floppy region locally.

As displayed in Fig. 8, when the relaxational modes do not appear, the BP intensity decreases with temperature. The decrease of the BP intensity is caused by structural changes, as we will discuss elsewhere [26]. The structural changes occurring in the intermediate phase (x = 0.23) should have a tendency to self-organize the network. The self-organization process moving the constraint on the overconstrained units to floppy ones should decrease the local degrees of freedom of some floppy units. By this process, the number of responsible units for the relaxational modes, which may still be slightly remained in the x = 0.23 glass, is reduced to an undetectable number in our system. Thus, the self-organization process can sharpen the transition from floppy to rigid in the relaxational dynamics.

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