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Structural investigation of rapidly quenched Li_3BO_3–Li_4GeO_4 glasses

M. TAKAHASHI, H. TOYUKI
Osaka Municipal Technical Research Institute, 6-50, 1 Chome, Morinomiya, Joto-ku, Osaka 536, Japan

M. TATSUMISAGO, T. MINAMI
Department of Applied Materials Science, Osaka Prefecture University, Sakai, Osaka 593, Japan

Glasses were prepared in the pseudobinary system Li_3BO_3–Li_4GeO_4 by a rapid quenching technique in the composition range of 8–80 mol % Li_4GeO_4. The structure of the glasses was examined by Raman spectra, X-ray diffraction analysis and molecular dynamics simulation. The coordination number of germanium atoms with respect to oxygen atoms in the glasses Li_3BO_3–Li_4GeO_4 was shown to be higher than four by the X-ray diffraction analysis. The Raman spectra showed that not only monomer ions of BO_3^{3-} and GeO_4^{4-}, but also dimer $B_2O_5^{4-}$ ions and six-coordinated GeO_6^{8-} ions were present in these glasses over the whole glass-forming region. The presence of these ions was also confirmed from molecular dynamics simulation.

1. Introduction

The structure of rapidly quenched glasses with compositions combining two kinds of lithium ortho-oxosalts was studied. The glass systems Li_4SiO_4–Li_3BO_3 [1, 2] and Li_4SiO_4–Li_2WO_4 [3–5] are examples of such glasses. These glasses have been found to be inapplicable to typical theories of glass formation such as the random network concept, due to an extremely high concentration of Li^+ ions. Moreover, these systems contain one type of an element which is known to change the oxygen coordination number around this element depending on the composition; a boron atom can take three- or four-coordination to oxygen atoms [6], and a tungsten atom can take four- or six-coordination to oxygen atoms [7]. The structural units present in these glasses were investigated by X-ray diffraction (XRD) analysis and Raman spectra.

The structure of the Li_4SiO_4–Li_3BO_3 glasses was found to consist not of a network structure (as with the diborate and triborate groups with four-coordinated boron, or other units such as the boroxol group), but to consist of SiO_4^{4-} and BO_3^{3-} ions only [1, 2]. On the other hand, the glasses in the system Li_4SiO_4–Li_2WO_4 were found to contain condensed structural units such as $Si_2O_7^{6-}$ ions and WO_6 groups with bridging oxygen atoms in addition to the ortho-oxoanions of SiO_4^{4-} and WO_4^{2-} [3–5], both of which were four-coordinated monomer structural units. Although these two systems contain one type of element which can change its coordination, only tungsten atoms change the coordination number, and boron atoms remain unchanged. Glass structure is believed to be determined by the acid–base reaction which takes place in the melt at high temperatures [8]. In these systems the formation of the structural units in the glasses could be explained by the reaction among the component oxides, such as SiO_2, B_2O_3 and WO_3 as acids and Li_2O as a base. Oxides with strong acidity preferentially combine with Li_2O to form Li-rich structural units. The acidity of WO_3 is greater than that of SiO_2, which leads to the formation of WO_6 groups and subsequently forms $Si_2O_7^{6-}$ ions, in addition to SiO_4^{4-} and WO_4^{2-} ions in the glasses Li_4SiO_4–Li_2WO_4. In contrast, neither SiO_2 nor B_2O_3 preferentially combines with Li_2O, as the acidity of SiO_2 and B_2O_3 is not so strong and is similar in each case, leading to the formation of only SiO_4^{4-} and BO_3^{3-} ions in the glasses Li_4SiO_4–Li_3BO_3.

The glass systems Li_4SiO_4–Li_3BO_3 and Li_4SiO_4–Li_2WO_4 contain silicon atoms which take only four coordination with respect to oxygens. It is of interest to study the structure and coordination number for the glasses containing two kinds of element, which can change the coordination number. In the present study, the Li_3BO_3–Li_4GeO_4 system has been selected; boron atoms can take three or four, and germanium atoms can take four or six [9] as the coordination number. The coordination number and the presence of condensed structural units have been studied with Raman spectra, XRD analysis and molecular dynamics (MD) simulation.

2. Experimental procedure

The starting materials used for glass preparation were

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reagent-grade Li_2CO_3, B_2O_3, and GeO_2 powders. Glass preparation by a twin-roller quenching apparatus with a thermal-image furnace has previously been described in detail [10].

XRD measurements for the glasses were carried out with MoK_α ($\lambda = 0.07107$ nm) radiation under 50 kV, 120 mA. The diffraction intensities were collected from $\theta = 3°$ to $70°$ at 0.25° intervals by the step-scanning technique. The modified radial distribution function, $D(r)/r$, calculated from the intensities, was fitted into Gaussian peaks based on the least squares procedure for the determination of the coordination number of the atoms i around an atom j, $N_{i/j}$. The details of measurement and of the calculation method have been reported elsewhere [11].

Raman spectra were measured with a 514.5 nm excitation line of Ar^+ ion laser at a source power level of 300–450 mW. Scattered radiation from the glasses was collected at 90° to the excitation line. For quantitative estimation of the structural units present in the glasses, the Raman spectra were corrected for temperature and frequency dependences according to the method reported by Long [12], and were then deconvoluted into Gaussian peaks [13]. The curve fitting of the Raman spectra between the observed and the calculated summation of Gaussian peaks was improved on the basis of the least squares method.

The procedure for the MD simulation has been described elsewhere in detail [14]. The pair potential function used in this study is assumed to consist of a simplified Coulombic and a repulsive term:

$$U_{ij} = Z_i Z_j e^2/r + f_0(b_i + b_j) \times \exp\left[(a_i + a_j - r_{ij})/(b_i + b_j)\right] \qquad (1)$$

where Z_i is the ionic charge, e is the charge of electron a and b the parameters related to the radius and the compressibility of each ion, respectively, and f_0 an arbitrary constant (taken to be 6.742×10^{-11} N). U_{ij} is the pair potential and the quantity r_{ij} is the distance between the ions i and j. The proper choice of potential parameters is of primary importance for the MD calculation. We have adopted the parameters which reproduce the structures of several crystals such as Li_2SiO_3, B_2O_3, and GeO_2. The parameters used in this calculation are given in Table I.

The calculations were performed for compositions at a 20 mol % interval. To start the calculation, lithium, boron, germanium and oxygen atoms were randomly dispersed within a basic cell. A total of about 400 atoms was melted at 4000 K, stabilized to eliminate the strain force due to the abnormal starting configuration of the atoms, and then cooled through 2000 and 1000 to 300 K. The molecular dynamics glasses (MD-glasses) were obtained for the Li_3BO_3–Li_4GeO_4 system after stabilization at 300 K.

TABLE I Potential parameters used in the MD calculation

	Atoms			
Parameters	B	Ge	O	Li
a	0.720	1.072	1.629	0.930
b	0.080	0.080	0.085	0.080

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the $D(r)/r$ curves of the glasses in the system Li_3BO_3–Li_4GeO_4. There are several peaks at about 0.13, 0.17, and 0.22 nm in any curves. The first peak at about 0.13 nm corresponds to the shortest distance of B–O pairs of the glasses. The second and the third peaks at ~ 0.17 and 0.22 nm correspond to the shortest distances of Ge–O and Li–O pairs. The intensity of the peak due to Ge–O pairs increased with an increase in the Li_4GeO_4 content. The number of oxygen atoms around a germanium atom $N_{O/Ge}$ in the glasses could be evaluated from an analysis of the $D(r)/r$ curves. Quantitative discussion of the B–O and the Li–O pairs is omitted here because the X-ray scattering factors of boron and lithium atoms are very small and accurate analysis of these pairs is thought to be difficult. The coordination numbers of germanium, $N_{O/Ge}$, are listed in Table II. $N_{O/Ge}$ takes a value between 4.6 and 5.2, showing the presence of six-coordinated GeO_6 [9] groups along with isolated GeO_4^{4-} ions in the glasses.

3.2. Raman spectra

Fig. 2 shows the Raman spectra of the glasses in the wavenumber range from 600 to 1100 cm^{-1}. For comparison, the spectra of crystals Li_3BO_3 and Li_4GeO_4 are also shown in the figure. The Raman spectra of the glasses in the system Li_3BO_3–Li_4GeO_4 exhibit two

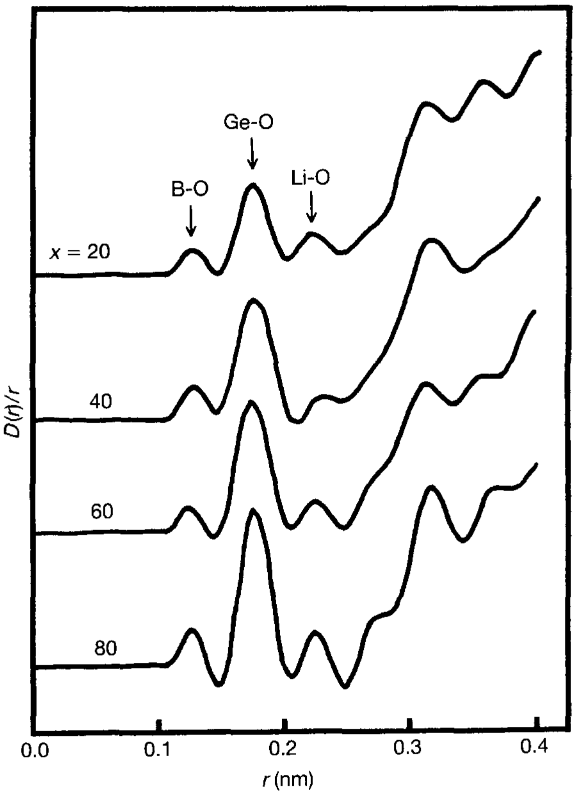

Figure 1 $D(r)/r$ curves of the glasses in the system Li_3BO_3–Li_4GeO_4.

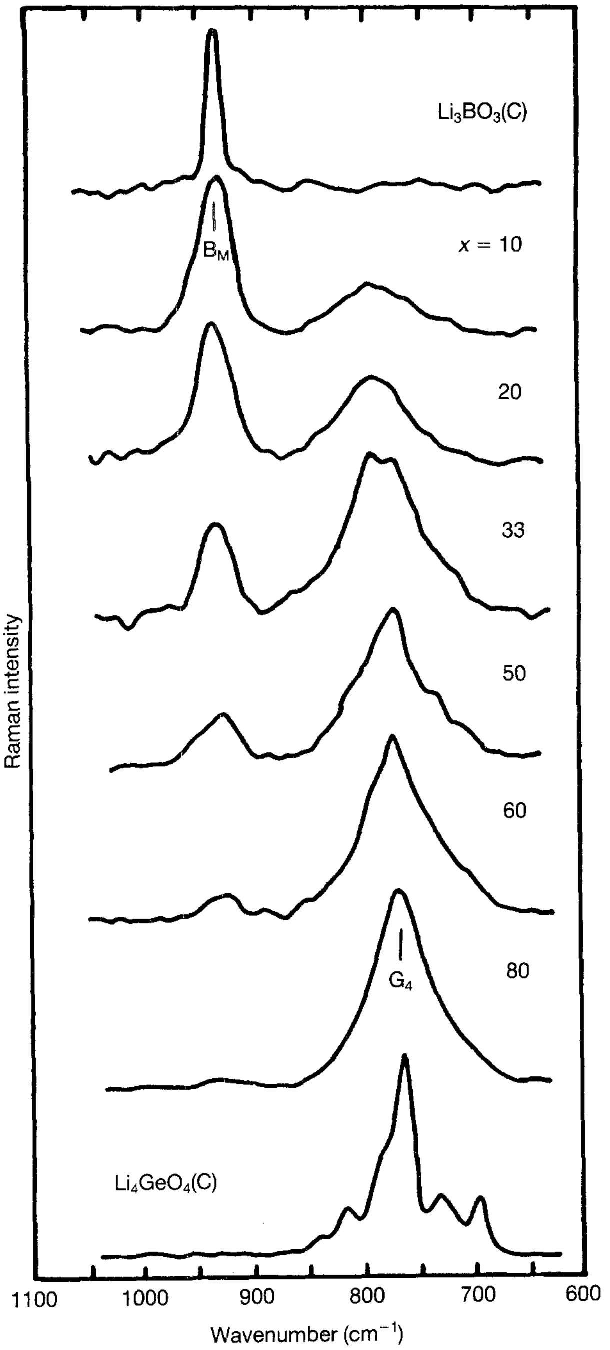

Figure 2 Raman spectra of the glasses in the system Li_3BO_3–Li_4GeO_4.

TABLE II Coordination numbers of germanium, $N_{O/Ge}$, for the glasses in the system $(100\text{-}x)Li_3BO_3 \cdot xLi_4GeO_4$ determined by XRD, MD simulation and Raman spectra

Li_4GeO_4 content (mol %)	$N_{O/Ge}$		
	Raman	XRD	MD
20	4.3	5.1	5.1
33	4.6	—	—
40	—	5.2	4.6
50	4.3	—	—
60	4.3	4.6	4.4
80	4.5	4.6	4.6

intense peaks at about 930 and 770 cm^{-1}. The peak at about 930 cm^{-1} is weakened and the peak at about 770 cm^{-1} is strengthened with increasing Li_4GeO_4 content. The intense peak at 930 cm^{-1} marked by B_M is also observed in Li_3BO_3 crystal, and the peak at 770 cm^{-1} marked by G_4 is also observed in the Li_4GeO_4 crystal. These peaks may be due to the orthoborate monomer ions BO_3^{3-} [1], abbreviated as B_M, and that of ortho-germanate monomer ions GeO_4^{4-} with four-coordinated germanium atoms [15], abbreviated as G_4, respectively. Thus the glasses are mainly composed of isolated BO_3^{3-}, GeO_4^{4-}, and Li^+ ions.

For quantitative estimation of the structural units, the spectrum (corrected for the dependence of scattered intensity on temperature and frequency) was fitted with the summation of some Gaussian peaks. Figs 3 and 4 show an example of deconvolution of the Raman spectrum for a glass $80Li_3BO_3 \cdot 20Li_4GeO_4$. Fig. 3a shows the fitted profile with two Gaussian peaks and the residual, Δ, between the calculated summation of the Gaussian peaks and the observed peaks; one is due to GeO_4^{4-} ions (G_4) and the other due to BO_3^{3-} monomer ions (B_M). The residual (Δ), however, shows remarkable amplitudes at around 830 and 720 cm^{-1}. Fig. 3b shows the relative intensities of the areas of the peaks caused by G_4 against the nominal weight fraction of the GeO_4^{4-} ions, calculated from the chemical composition of the glasses. The relative intensities show a large discrepancy from the straight line, which is the proportional variation to the nominal weight fraction. This is caused by the remarkable amplitudes of the residual at 830 and 720 cm^{-1}, indicating the presence of other peaks at about 830 and 720 cm^{-1}. These peaks are tentatively marked as B_D and G_6, respectively. Two more peaks at about 830 cm^{-1} (B_D) and 720 cm^{-1} (G_6) were taken into consideration, in addition to the peaks of B_M and G_4, for the much finer agreement between the calculated and observed spectra.

Table III lists the Gaussian peak parameters for the four peaks and the relative intensities of the areas of these peaks. As an example of the deconvolutions, the curve fitting of the spectrum for the glass $80Li_3BO_3 \cdot 20Li_4GeO_4$ with four Gaussian peaks is shown in Fig. 4a; the observed spectrum is the same as in Fig. 3a. The fit with the summation of the peaks at 830 cm^{-1} (B_D) and 720 cm^{-1} (G_6), in addition to the peaks at 930 cm^{-1} (B_M) and 770 cm^{-1} (G_4), becomes much better compared with Fig. 3a. The amplitude of the residual (Δ) decreases remarkably. The peak at 820 cm^{-1}, marked B_D, is due to dimer pyroborate ions, $B_2O_5^{4-}$ [1]. The peak at about 740 cm^{-1}, marked G_6, is assigned to six-coordinated GeO_6 groups (assigned with a peak of the Raman spectrum of Li_4GeO_4 crystal). The relative intensities of the peak areas due to the germanate ions (summation of G_4 and G_6) are found to be proportional to the nominal weight fraction of the GeO_4^{4-} ions, as shown in Fig. 4b. It is thus concluded that the deconvolution of the spectrum by the four peaks is favourable, rather than by the two peaks, suggesting the coexistence of structural units such as $B_2O_5^{4-}$ and GeO_6 groups in glass other than the units BO_3^{3-} and GeO_4^{4-} expected to be present from the chemical composition of the glasses.

TABLE III Peak parameters and relative peak areas of the four Gaussian peaks determined by deconvolution of the Raman spectra for rapidly quenched Li_3BO_3–Li_4GeO_4 glasses

Li_4GeO_4 content (mol %)	Peak position* (cm^{-1})				Relative peak area* (%)			
	B_M	B_D	G_4	G_6	B_M	B_D	G_4	G_6
8	930	810	775	735	63.0	10.4	18.2	8.5
10	930	813	780	736	59.7	11.7	19.5	9.1
20	930	817	782	740	49.9	16.2	28.1	9.8
33	930	815	780	740	22.0	17.6	39.9	20.5
50	928	810	773	730	14.8	44.1	44.1	21.6
60	930	810	773	728	7.1	18.1	50.3	24.5
80	928	810	770	727	2.8	13.9	61.6	21.7

* B_M, monomer BO_3^{3-} ions; B_D, dimer $B_2O_5^{4-}$ ions; G_4 monomer GeO_4^{4-} ions; G_6, GeO_6^{8-} ions.

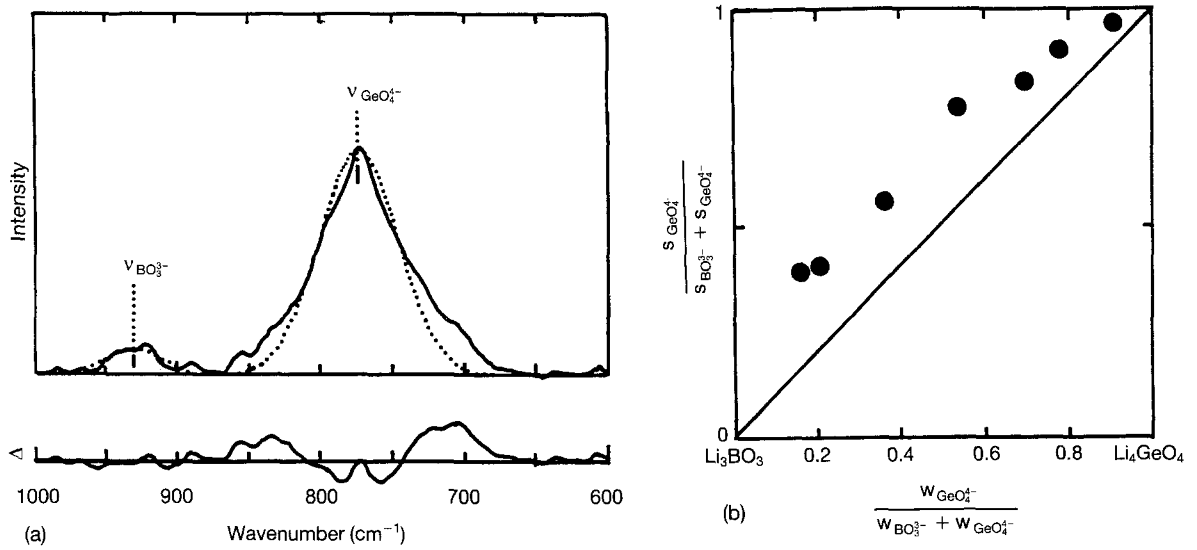

Figure 3 Deconvolution of the Raman spectrum for a rapidly quenched glass $80Li_3BO_3 \cdot 20Li_4GeO_4$ into two Gaussian peaks; residual curves, Δ, indicate the difference between the observed spectrum and the calculated summation of the Gaussian peaks (a), and relative intensities of the peak areas caused by G_4 against the nominal weight fraction of the GeO_4^{4-} ions (b).

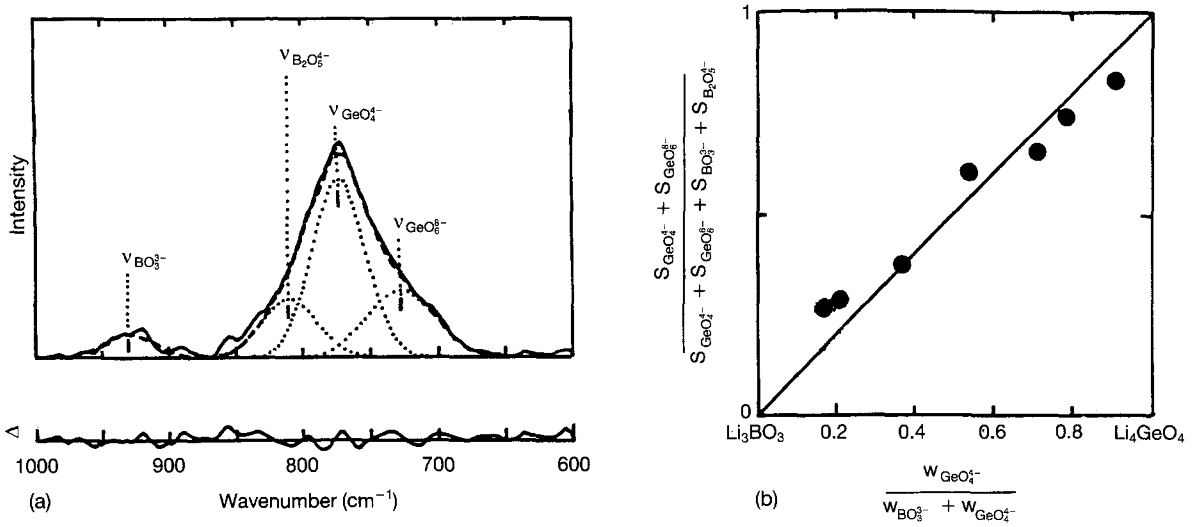

Figure 4 Deconvolution of the same Raman spectrum as shown in Fig. 3 for a rapidly quenched glass $80Li_3BO_3 \cdot 20Li_4GeO_4$ into four Gaussian peaks; residual curves indicate the difference between the observed spectrum and the calculated summation of the Gaussian peaks (a), and relative intensities of the peak areas caused by summation of G_4 and G_6 against the nominal weight fraction of the GeO_4^{4-} ions (b).

The high-temperature XRD measurement of the glass $80Li_3BO_3 \cdot 20Li_4GeO_4$ revealed that the high-temperature phase of lithium germanate, Li_8GeO_6 crystal, containing GeO_6^{8-} units was observed in the crystallized sample. It is thus thought that the groups of GeO_6 are in the form of GeO_6^{8-} structure.

The presence of such structural units as $B_2O_5^{4-}$ and GeO_6^{8-} ions can be explained by the occurrence of the equilibrium reaction in the melt according to Equation 2.

$$4BO_3^{3-} + GeO_4^{4-} \rightleftarrows 2B_2O_5^{4-} + GeO_6^{8-} \qquad (2)$$

The analysis of the Raman spectra, which shows the coexistence of structural units of $B_2O_5^{4-}$ and GeO_6^{8-} along with BO_3^{3-} and GeO_4^{4-}, agrees well with the result derived from the XRD analysis, which shows that the coordination number of germanium, $N_{O/Ge}$, takes a value between 5.1 and 4.4.

3.3. MD simulation

Fig. 5 shows the structure factor, $S \cdot I(S)$, derived from the XRD study of the rapidly quenched glasses at room temperature (a) and that derived from the three-dimensional configuration for the MD-glasses at 300 K (b) for the compositions $(100\text{-}x)Li_3BO_3 \cdot xLi_4GeO_4$ ($x = 20$, 40, 60, 80). The $S \cdot I(S)$ curves of the MD-glasses do not agree well with that of the rapidly quenched glasses, partly because a fully ionic potential was used and partly because the quenching rate in the MD calculation was extremely high. However, the periodic profiles at least resemble each other, suggesting that MD simulation basically reproduced the actual rapidly quenched glass structure.

Fig. 6 shows the running coordination numbers, $N(r)$, of B–O and Ge–O atomic pairs in the glass $80Li_3BO_3 \cdot 20Li_4GeO_4$. The $N(r)$ curves have a plateau at approximately 3.1 for the B–O pair, and 5.1 for the Ge–O pair. An inflection point is observed at about 0.18 nm in the curve for the Ge–O pair, showing the presence of two kinds of germanium atoms in different coordination of oxygen. It can be thought that boron atoms in glasses are mainly three-coordinated; half the numbers of germanium atoms are four-coordinated; and the other half are six-coordinated by oxygen.

Fig. 7 shows a 'snapshot' of a MD-glass of composition $40Li_3BO_3 \cdot 60Li_4GeO_4$ at 300 K as an example. Two kinds of germanium atoms and two kinds of boron atoms can be observed in the figure; mainly GeO_4^{4-} and BO_3^{3-} ions and to some extent GeO_6^{8-} and $B_2O_5^{4-}$ ions are observed. The fact that these ions are present in glasses is in good agreement with the results derived from XRD analysis and Raman spectra of the rapidly quenched glass.

The coordination numbers of oxygen atoms around a germanium atom in the glasses Li_3BO_3–Li_4GeO_4 determined by Raman spectra, XRD and MD simulation are summarized in Table III. The $N_{O/Ge}$ takes a value between 4.3 and 4.6 by Raman spectra, 4.6–5.2 by XRD analysis, and 4.4–5.1 by MD simulation. A general tendency of composition dependence was not observed in the three methods. However, the presence of six-coordinated germanium is suggested to be present in glasses by all three methods.

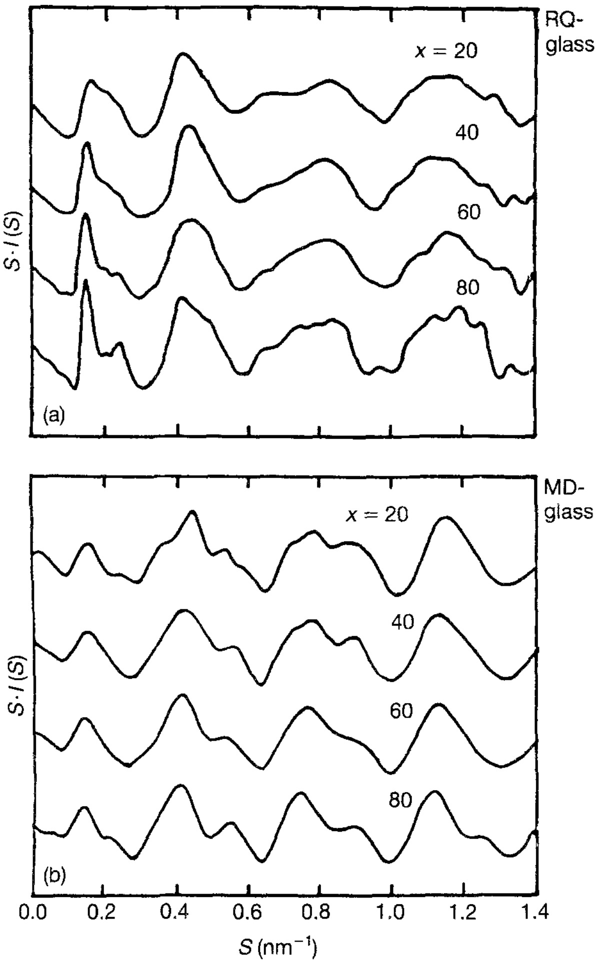

Figure 5 Structure factors for the glasses $(100\text{-}x)$ $Li_3BO_3 \cdot xLi_4GeO_4$ ($x = 20$, 40, 60, 80). (a) Rapidly quenched glasses at room temperature; (b) MD-glasses at 300 K.

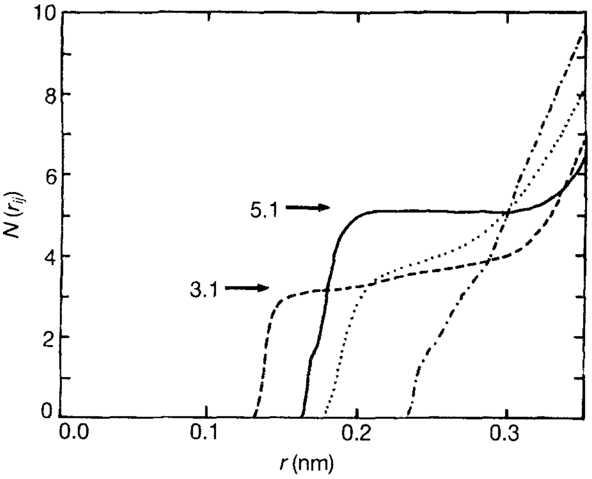

Figure 6 The running coordination numbers, $N(r_{ij})$, of B–O (– – –) and Ge–O (——) atomic pairs in a glass $80Li_3BO_3 \cdot 20Li_4GeO_4$ Li–O (· · ·); O–O (–·–).

3.4. Generation of structural units

Glass structure is believed to be determined by the acid–base reaction which takes place in the melt at high temperature [8]. In the case of Li_4SiO_4–Li_2WO_4 glasses, WO_3 which shows greater acidity than SiO_2 is preferentially combined with Li_2O to form Li-rich structural units containing higher coordination numbers such as WO_6^{4-}, as mentioned in the introduction. In the Li_3BO_3–Li_4GeO_4 system, the reaction expressed in Equation 2 is found to have progressed to the right hand side to some extent, to form GeO_6^{8-} units. From the experimental results in this study, the acidity of GeO_2 is expected to be higher than that of

B_2O_3. However, the acidity of GeO_2 is known to take a close value to B_2O_3 [8]. This shows that the oxides having strong acidity do not always preferentially combine with Li_2O to form Li-rich structural units containing higher coordination numbers.

The compounds most abundantly containing lithium atoms at room temperature, ortho-oxosalts, are known to be Li_3BO_3, Li_4GeO_4, and Li_2WO_4 in the binary systems Li_2O–B_2O_3, Li_2O–GeO_2, and Li_2O–WO_3, respectively. The high-temperature phases, Li_4WO_5 and Li_8GeO_6, however, contain lithium atoms more abundantly than the compounds Li_4GeO_4, and Li_2WO_4. These high-temperature compounds contain higher oxygen coordinated units. In contrast, such a high-temperature phase containing the units of higher coordination number is not present in the system Li_2O–B_2O_3. The formation of the six-coordinated structural units in the glasses Li_4SiO_4–Li_2WO_4 and Li_3BO_3–Li_4GeO_4 is thought to be concerned with the presence of such high-temperature phases in the systems Li_2O–WO_3, and Li_2O–GeO_2. It shows that six-coordinated structural units are liable to be formed at high temperature from a viewpoint of ionic radii or a preferential crystallographic orientation. This liability progresses the reaction expressed in Equation 2 to the right-hand side.

On the other hand, generally the more the temperature of the melt is increased, the more the low coordinated structural units are liable to be formed in the melt. From this general empirical principle, the reaction expressed in Equation 2 progresses to the left-hand side at high temperature. Competition of these two liabilities to the progress toward both sides resulted in an equilibrium of the reaction and the coexistence of BO_3^{3-}, $B_2O_5^{4-}$, GeO_4^{4-}, and GeO_6^{8-} ions in melt. Freezing of the melt structure by rapid quenching resulted in the coexistence of the ions BO_3^{3-}, $B_2O_5^{4-}$, GeO_4^{4-}, and GeO_6^{8-} in the Li_3BO_3–Li_4GeO_4 glasses.

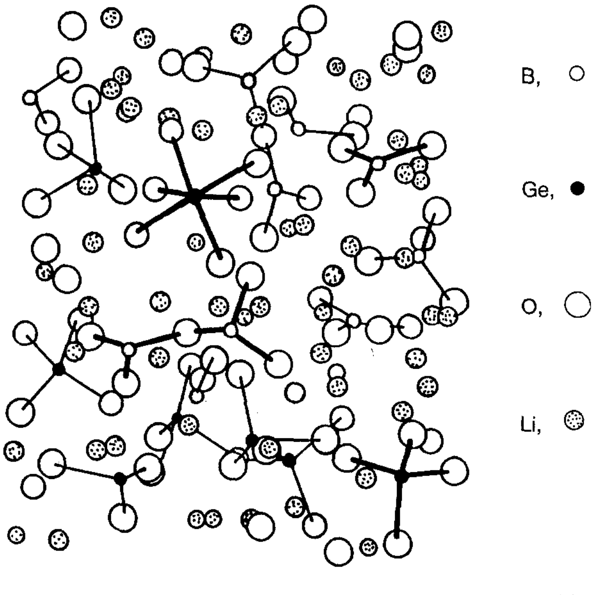

Figure 7 'Snapshot' of a MD-glass of composition $40Li_3BO_3 \cdot 60Li_4GeO_4$ at 300 K.

4. Conclusion

Glasses were prepared in the pseudobinary system Li_3BO_3–Li_4GeO_4 by a rapid quenching technique in the composition range of 8–80 mol % Li_4GeO_4.

The oxygen coordination number of germanium atoms in the glasses was verified to be higher than four by XRD analysis, which showed the presence of six-coordinated germanium atoms along with four-coordinated germanium atoms by oxygen. Furthermore, structural units of BO_3^{3-}, $B_2O_5^{4-}$, GeO_4^{4-}, and GeO_6^{8-} are found to be present in the glasses by Raman spectra and MD simulation. Both four-coordinated and six-coordinated germanium atoms are thought to be liable to form at high temperature by the ionic radii or a preferential crystallographic orientation and the general empirical principle. An equilibrium reaction among these structural units, expressed in Equation 2, has taken place in melt at high temperature, and freezing of the melt has caused the coexistence of BO_3^{3-}, $B_2O_5^{4-}$, GeO_4^{4-}, and GeO_6^{8-} ions in the glasses Li_3BO_3–Li_4GeO_4.

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