Structural Investigation of Rapidly Quenched $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ Glasses by Raman Spectroscopy

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Glasses were prepared over a wide range of composition in the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ using a rapid quenching technique. The glass-forming region was extended up to the composition of 70 mol% Li_2O . Raman spectra of the glasses were measured; drastic spectral changes were observed in the glasses containing more than 50 mol% Li_2O whereas the spectra of the glasses with the smaller Li_2O content showed a close resemblance to each other. The spectra revealed that the main structural units were the six-membered borate rings with BO_4 units for the glasses with small Li_2O contents and the pyroborate and orthoborate groups for those with large Li_2O contents. Corrected Raman spectra were deconvoluted into six Gaussian lines ascribed to specific structural units and the relative amounts of the structural units were determined on the basis of each area of the Gaussian lines. The six-membered borate ring with BO_4 units and the pyroborate group were shown to have a maximum proportion at the compositions with 33 and 67 mol% Li_2O , respectively. A large amount of orthoborate groups, completely discrete anions, was also shown to be present even in the compositions with such a small Li_2O content as 25 mol%. The fraction N_4 of four coordination boron atoms present in the glasses was determined against the glass composition and compared with the results by NMR study. Although in both results a maximum of N_4 was observed in the composition region around 30 to 40 mol% Li_2O , the maximum value in this study was only a half of that by NMR study. This would be caused by the fact that every structural unit was assumed to have the same Raman scattering efficiency.

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ラマン分光法による超急冷 $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ ガラスの構造研究

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1. Introduction

The structure of borate glasses, being attractive because of their relation to the so called "borate anomaly", has been studied by infrared absorption¹⁾, X-ray diffraction²⁾, nuclear magnetic resonance³⁾, and so on. Raman scattering spectroscopy is also one of the most useful means to investigate the borate glass structure. Koni-jendijk et al.^{4),5)} showed that the Raman spectra could be used to identify the presence of certain structural units such as boroxol groups in the borate glasses. The Raman spectra, however,

have been measured only for the compositions containing less than 50 mol% alkali oxide in alkali borate glasses; 50 mol% alkali oxide is a limit composition for glass formation by the usual preparation procedure.

Rapid quenching is one of the useful techniques to obtain new glasses which are difficult to be prepared by the usual procedure⁶⁾. It is useful not only to prepare glasses in the systems without "glass formers"⁷⁾ but also to extend the glass-forming regions in the systems with "glass formers"⁸⁾. In the typical glass-forming system

$\text{Li}_2\text{O}-\text{SiO}_2$, for example, the limit of glass formation was shown to be extended by rapid quenching up to 66.7 mol% Li_2O from 40 mol% Li_2O in the usual procedure^{9),10)}. Much attention has been focused on such rapidly quenched glasses containing a large amount of Li_2O because of their unusual glass structure constructed not by "network"^{8),9)}.

In this paper, glasses were prepared over a wide range of composition in the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ by rapid quenching and their Raman spectra were measured. The relative amounts of component structural units present in the glasses of each composition were determined and the glass structure was discussed especially for the composition with high Li_2O contents.

2. Experimental procedure

The mixtures of reagent grade Li_2CO_3 and anhydrous B_2O_3 powders were melted in a platinum crucible at 700° to 1000°C, depending on composition, and the melts were poured into a rod-shaped mold made with a stainless steel plate. The rod-shaped samples were melted again in the thermal-image furnace and quenched rapidly by the twin roller for preparation of glasses; the rapid-quenching apparatus was previously described in detail⁹⁾. The samples obtained by rapid quenching were determined to be glassy by their transparency and by X-ray powder diffraction measurements.

Raman spectra were measured on a JASCO model R-800 double-grating spectrophotometer. Sample excitation was achieved by using the 4880 Å line of a NEC GLG-3300 mode Ar^+ ion laser with a source power of 400 mW. Spectra were obtained from the glass flakes prepared by rapid quenching. Scattered radiation was collected in the direction of 90° to the excitation beam. The deconvolution of the spectra was carried out for the digitized scattering data by using a micro-computer.

3. Results and discussion

3.1 Glass formation

Figure 1 shows the glass-forming region by rapid quenching for the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$. Open and closed circles denote glassy and crystalline samples, respectively. Glass preparation was tried for nine compositions containing more than 25 mol% Li_2O ; all the compositions here are the nominal ones. Only

Fig. 1. Glass-forming region in the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ by rapid quenching. ○ : Glassy, ● : Crystalline.

the composition containing 75 mol% Li_2O (corresponding to lithium orthoborate, Li_3BO_3) could not form glass and the glass-forming region was extended up to 70 mol% Li_2O . The present glass-forming region in this system agrees with that reported by Ota and Soga¹²⁾, who also determined the region by rapid quenching. Although the glass formation by the usual procedure was limited up to the composition with 43 mol% Li_2O ¹³⁾, which lies between the two compounds, lithium diborate $\text{Li}_2\text{B}_4\text{O}_7$ and lithium metaborate LiBO_2 , the rapid quenching made it possible to form glass for the compounds with extremely high Li_2O content such as lithium pyroborate $\text{Li}_4\text{B}_2\text{O}_5$.

Martin and Angell pointed out that the glass-forming region in the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system depended on the starting materials¹⁴⁾. The difference was shown between the glasses prepared from Li_2CO_3 and B_2O_3 and those from Li_2O and B_2O_3 ; the retention of CO_2 affected the glass formation in case of using Li_2CO_3 . Although, in the present study, the glass-forming region was also determined for the samples obtained from Li_2CO_3 and B_2O_3 , the glasses were considered to be free from the influence of retained CO_2 . This was confirmed by the fact that no difference in the Raman spectra was observed between the glass 67 $\text{Li}_2\text{O} \cdot 33 \text{B}_2\text{O}_3$ prepared from Li_2CO_3 and B_2O_3 and that from Li_2O and B_2O_3 .

3.2 Raman spectra

Figure 2 shows the Raman spectra of the glasses in the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ and the orthoborate crystal Li_3BO_3 (75 $\text{Li}_2\text{O} \cdot 25 \text{B}_2\text{O}_3$); "C" in parenthesis designates a crystalline sample. The spectra of the glasses with relatively small Li_2O contents of 25 to 40 mol% Li_2O show a close resemblance to each other. One strong and two weak peaks were observed near

Fig. 2. Raman spectra of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses and of Li_3BO_3 crystal.

770, 930 and 500 cm^{-1} , respectively. The 770 cm^{-1} peak becomes slightly weaker with an increase in Li_2O contents, whereas the other peaks remain constant. Drastic spectral changes were observed for the glasses containing more than 50 mol% Li_2O . In these glasses with higher Li_2O contents, two remarkable peaks near 930 and 840 cm^{-1} were seen together with the strong 770 cm^{-1} peak. The addition of Li_2O leads to the increase in the peaks near 930 and 840 cm^{-1} and the decrease in the 770 cm^{-1} peak. The 930 cm^{-1} peak, also observed in the crystal Li_3BO_3 ($75\text{ Li}_2\text{O} \cdot 25\text{ B}_2\text{O}_3$), becomes the most intense in the glass with the highest Li_2O content, i.e. in the glass $70\text{ Li}_2\text{O} \cdot 30\text{ B}_2\text{O}_3$. The 840 cm^{-1} peak, however, is the strongest at the glass composition $67\text{ Li}_2\text{O} \cdot 33\text{ B}_2\text{O}_3$, which corresponds to lithium pyroborate $\text{Li}_4\text{B}_2\text{O}_5$.

The structures of many crystalline borate compounds, which have already been determined, are known to consist of several structural units or groups. Borate glasses are also considered to be composed of such structural units or groups, the presence of which in the glasses results in their

Table 1. Wavenumbers of the Raman bands due to some borate structural units.

Borate Group	Structural Unit	Wavenumber/ cm^{-1}
1 Orthoborate		950 – 930
2 Pyroborate		850 – 830
3 Six-Membered Borate Ring with BO_4 Unit		785 – 760
4 Metaborate Chain Type		735 – 715
5 Metaborate Ring Type		670 – 650
6 Isolated Diborate		560 – 510

characteristic Raman bands. Some of these structural units and the corresponding wavenumbers of the Raman bands caused by them are listed in Table 1, which is made after Konijnendijk et al.^{4),5)} Based on this table the intense 770 cm^{-1} peak seen in the glasses with relatively low Li_2O contents is attributed to the six-membered borate rings with one and two BO_4 units; the former was called triborate and the latter di-triborate groups. On the other hand, the peaks near 930 and 840 cm^{-1} mainly observed in the glasses containing large amounts of Li_2O are attributed to orthoborate (BO_3^{3-}) and pyroborate ($\text{B}_2\text{O}_4^{2-}$) groups, respectively. The Raman bands caused by the six-membered borate groups, the main structural units in the composition of 25–40 mol% Li_2O , decrease with an increase in the Li_2O content in the high Li_2O glasses. When the Li_2O content is over 50 mol%, the main structural units are orthoborate and pyroborate groups. In the composition $70\text{ Li}_2\text{O} \cdot 30\text{ B}_2\text{O}_3$, especially, the glass structure is almost constructed not by a “network” but by the discrete borate anions, such as pyroborate and orthoborate groups.

3.3 Relative amounts of structural units

In order to determine the proportions of the structural units present in the glasses, the Raman spectra should be dealt with more quantitatively. Each spectrum can be deconvoluted into some Gaussian lines ascribed to specific structural units^{(15), (16)}. The curve fitting between the observed Raman spectra and the calculated ones with Gaussian line shapes was improved by use of the least squares method. Before doing the curve fitting analysis it is necessary to correct the observed spectra for the dependence of the scattered intensity on temperature and frequency. A correction factor R employed by Long⁽¹⁷⁾ was used,

$$R = \frac{\nu_0^3 \nu}{(\nu_0 + \nu)^4} \left[1 - \exp\left(-\frac{hc\nu}{kT}\right) \right] \quad (1)$$

where ν_0 and ν are the frequencies of the excitation line and the Raman shift, respectively. The measured intensities were multiplied by R to obtain a corrected spectrum.

The corrected spectra were deconvoluted into six Gaussian lines arising from the six structural units shown in Table 1. As an example, Fig. 3 shows the corrected Raman spectrum of the glass 60 Li₂O·40 B₂O₃ and the deconvoluted six Gaussian lines. The six Gaussian lines numbered 1 to 6 in Fig. 3 corresponds to the six structural units of 1 to 6 in Table 1. The residual curve in Fig. 3 indicates the difference between the observed and

Fig. 3. Corrected Raman spectrum of 60 Li₂O·40 B₂O₃ glass deconvoluted into six Gaussian lines.

the calculated curves; the difference lies within 10%.

The calculated Raman intensity I_R composed of six Gaussian lines is expressed by the following Eq. (2).

$$I_R = \sum_{i=1}^6 I_i \exp\left(-\ln 2 \left[\frac{2(\omega - \omega_i)}{\Delta\omega_i}\right]^2\right) \quad (2)$$

where I_i , ω_i and $\Delta\omega_i$ were the intensity, position and half width of the line i ($i=1-6$), respectively; they are so called the Gaussian line parameters. The area of this Gaussian line A_i is expressed by

$$A_i = \frac{1}{2} \sqrt{\frac{\pi}{\ln 2}} I_i \Delta\omega_i \quad (3)$$

The area of each Gaussian line should be related to the amount of corresponding structural unit and thus the relative amounts of each unit can be determined.

Figure 4 shows the relative amounts of three structural units, orthoborate, pyroborate and six-membered borate groups with BO₄ units, as a function of Li₂O content. The results for the other units were omitted to prevent the figure from being complicated. Six-membered borate rings with BO₄ units, which contain no non-bridging oxygens and form "network" structure, have a

Fig. 4. Relative amounts of structural units present in Li₂O-B₂O₃ glasses.

maximum amount at the composition 33 mol% Li_2O . The addition of more Li_2O reduced the amount. On the other hand, the orthoborate and pyroborate groups, which form no "network", increase with an increase in the Li_2O content. For the pyroborate group, a maximum was observed at the composition 67 $\text{Li}_2\text{O} \cdot 33 \text{B}_2\text{O}_3$ corresponding to the lithium pyroborate. Although the orthoborate group without bridging oxygens is a completely discrete anion, it is noteworthy that a large amount of this group is present even in the compositions with small Li_2O contents.

This figure also suggests that any glass is never composed of only one borate group. For example, the glass 67 $\text{Li}_2\text{O} \cdot 33 \text{B}_2\text{O}_3$ is constructed by not only pyroborate groups but also significant amounts of orthoborate groups and six-membered borate rings with BO_4 units. Such a structure is considered to arise from the equilibrium shown in Scheme 1 present in the melts before quenching.

3.4 Fraction N_4 of borons in a state of four coordination

The structure of borate glasses has been often discussed in terms of coordination state of borons. Bray et al. investigated the coordination state of borons in several alkali borate glasses by using nuclear magnetic resonance (NMR) techniques^{3),18)}. The composition dependence of N_4 was plotted against composition in Fig. 5. Open circles were determined by Raman spectra in this study and open triangles were taken from the NMR study by Bray et al.^{3),18)} Both results indicate that a maximum of N_4 was observed in the composition region around 30 to 40 mol% Li_2O . The N_4 values were calculated on the basis of the assumption that the 770 cm^{-1} peak was attributed to only ditriborate group. Even when the peak was attributed to triborate groups, the composition with the maximum N_4 was the same. Although the N_4 values decrease steeply with an increase in Li_2O content in the higher Li_2O region, the values near the limit composition for glass formation remain almost constant at about 0.1. This result is in contrast with the prediction that

Fig. 5. Fraction N_4 of four coordinated boron atoms in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses.

the N_4 value would be reduced to zero at the composition with 75 mol% Li_2O ¹⁸⁾. This indicates that several structural units including BO_4 units would be present also in the composition region with an extremely high Li_2O content. Although the composition with the maximum N_4 in this study is consistent with that by Bray et al., the maximum value is different; the value in this study is only a half of that by Bray et al. The assumption that every structural unit has the same Raman scattering efficiency would cause the deviation from the results by NMR. In fact, since the borate groups including BO_4 units are less symmetrical, the efficiency would be lower the more symmetrical units such as orthoborate groups. Such a difference in scattering efficiency results from the fact that the Raman bands discussed here are ascribed to the symmetrical stretching mode.

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