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Raman Spectra of Li_2O-SiO_2 Glasses Prepared by Rapid Quenching

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Raman spectra were measured of rapidly quenched Li_2O-SiO_2 glasses containing high Li_2O concentrations. The proportions of SiO_4 tetrahedral units with different numbers of non-bridging oxygen atoms per a silicon atom were determined for these glasses. It was found that silicates in the glass with the highest Li_2O content (63 mol% Li_2O) consist of large amounts of isolated SiO_4^{4-} and $Si_2O_7^{6-}$ ions.

Rapid quenching is one of the useful techniques to develop new glassy materials and to extend the composition range of glass formation. In the system Li_2O-SiO_2, we showed that the composition limit of glass formation is extended up to 66.7 mol% Li_2O,[2,3)] compared with 40 mol% Li_2O in the usual quenching method. These new glasses obtained as a result of the extension of the glass-forming region are attractive with respect to their glass structure since the "network" of glass former is predicted to be little formed in such a composition.

This paper reports the Raman spectra of rapidly quenched Li_2O-SiO_2 glasses in the composition range 41-63 mol% Li_2O (analyzed values).

Glasses were prepared with a rapid-quenching apparatus combining a thermal-image furnace and a twin roller, the details of which were reported elsewhere.[2)] The lithium contents of the obtained glasses were determined by atomic absorption analysis. Raman spectra were measured with a JASCO model R-800 double-grating spectrophotometer at a scattering angle of 90°. The excitation source was 5145 Å line of an NEC GLG-3300 mode Ar^+ ion laser at power levels from 300 to 400 mW. Each spectrum obtained was deconvoluted into several Gaussian peaks based on the least-squares procedure.

Figure 1 shows the Raman spectra of the Li_2O-SiO_2 glasses prepared by rapid quenching. In each spectrum several scattering peaks are observed at the two wavenumber regions, 500-750 and 800-1200 cm^{-1}. The peak at 500-750 cm^{-1}, assigned to the bridging Si-O-Si vibration[4)] and labeled as B in Fig.1, becomes weaker and shifts to higher wavenumbers with an increase in the Li_2O content. This means that the content of bridging oxygens present in the glasses decreases with an increase in the Li_2O content. In the region 800-1200 cm^{-1}, four peaks seem to overlap. These peaks are assigned to the stretching mode of the non-bridging Si-O vibration.[5)] It was shown that these peaks are attributable to the SiO_4 tetrahedral units with different numbers of non-bridging oxygen atoms (NBO) per a silicon atom in the units.[6,7)] The four peaks seen in the spectra at 1030-1100, 950-970, 900-930, and 850-890 cm^{-1} are associated with the SiO_4 units with 1,2,3, and 4 NBO's, respectively.[7)] The numerals given to the peaks in Fig.1 indicate NBO numbers in the units illustrated in the upper part of the figure. In glasses containing relatively small amounts of Li_2O, the main peaks are the absorption bands numbered as 1 and 2.

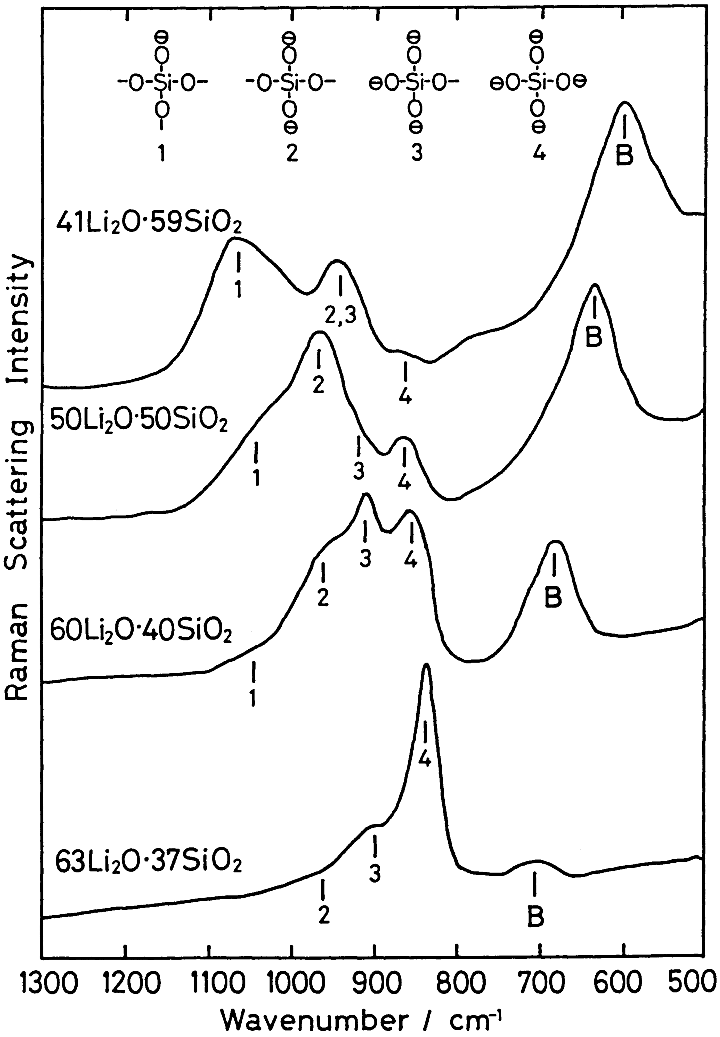


Fig. 1. Raman spectra of rapidly quenched Li_2O-SiO_2 glasses.

The spectra of these glasses are similar in shape to those of the Na_2O-SiO_2 glasses with the corresponding composition.[8,9] In glasses containing large amounts of Li_2O, on the other hand, the peaks 3 and 4 are mainly observed. These results indicate that the SiO_4 units with higher NBO/Si ratios increase with an increase in the Li_2O content. The glass with the highest Li_2O content, $63Li_2O\cdot37SiO_2$, is considered to consist of isolated silicate ions such as SiO_4^{4-} (NBO/Si=4) and $Si_2O_7^{6-}$ (NBO/Si=3) and Li^+ ions. These "isolated ion" structures may be related to the fact that the T_g/T_l ratios of the glasses largely deviate from the so-called "two-thirds rule."[3]

Each spectrum was separated into four Gaussian peaks attributed to SiO_4 units with different NBO numbers and the proportions of these units were determined, assuming that the area of each peak is proportional to the amount of corresponding SiO_4 unit.[5,10] Figure 2 shows the proportions of the four SiO_4 units as a function of the Li_2O content. The contents of the structure units numbered as 2 (NBO/Si=2) and 3 (NBO/Si=3) have maxima at the compositions 50 and 60 mol% Li_2O, respectively. These compositions correspond to Li_2SiO_3 (NBO/Si=2) and $Li_6Si_2O_7$ (NBO/Si=3), respectively. It is concluded that a structure unit maximizes at the composition in which the ratio NBO/Si is identical with that of the structure unit.

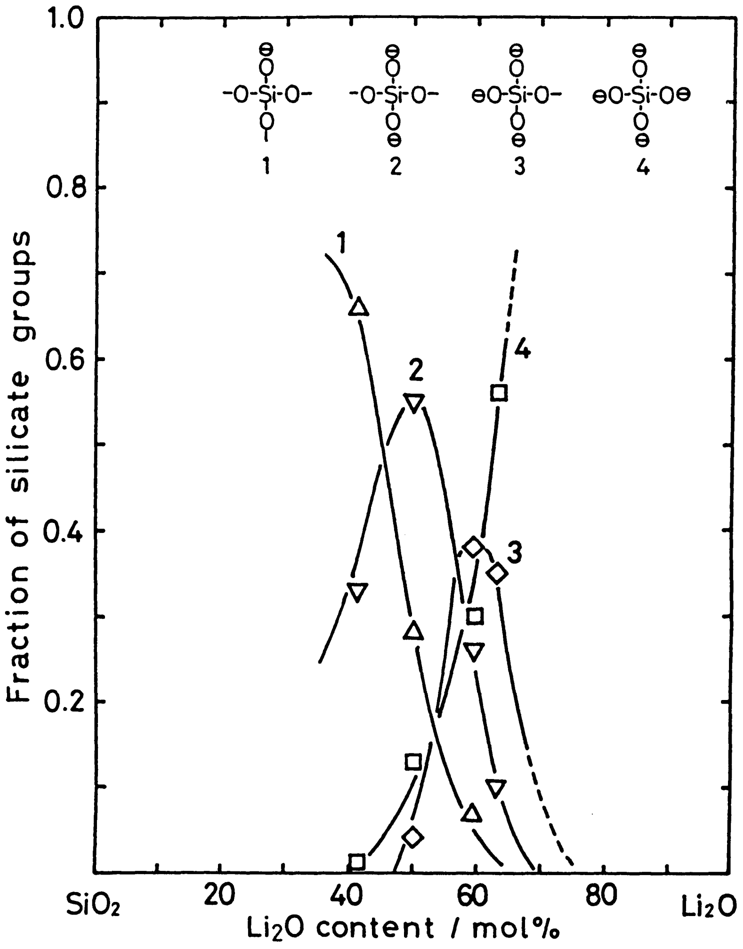
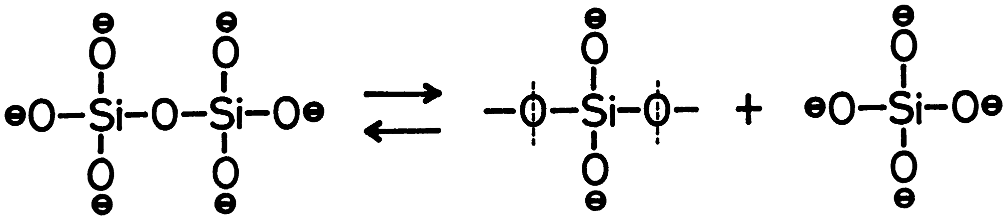


Fig. 2. Proportion of structure units present in Li_2O-SiO_2 glasses.

This figure also suggests that any glass is not composed of only one structure unit. For example, the glass $60Li_2O\cdot 40SiO_2$ is constructed not only by the structure unit 3 (NBO/Si=3) but also by significant amounts of the structure units 2 (NBO/Si=2) and 4 (NBO/Si=4). Such a glass structure is considered to arise from an equilibrium such as



This kind of equilibrium would be present in the melts to be quenched. A similar situation was also shown in Li_2O-B_2O_3 glasses.$^{10)}$

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