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Author(s)	Iwamoto, Nobuya; Tsunawaki, Yoshiaki
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Raman Spectra of Na_2O-SiO_2-Al_2O_3 and K_2O-SiO_2-Al_2O_3 Glasses†

Nobuya IWAMOTO* and Yoshiaki TSUNAWAKI**

In order to clarify the structure of a solid, the informations have to be known such as chemical constitution, geometry of the atomic arrangement and the system of forces representing the interatomic bonds. It is considered that infra-red and Raman spectroscopy are favorable for the latter two knowledges as well as X-ray diffraction method. It remains, however, difficult in the case of glass that any mthods give precise informations due to the lack of long range order.

In infra-red absorption measurement of glass it is difficult to obtain a data with sufficiently large S-N ratio and high resolution because a lot of glasses have such intense absorption bands called "reststrahlen" that many of the components consisting glasses are used as cut-off filters in the far-infrared.[1] However, Raman scattering may be effective because not only a high intensity laser can be used as light source in the measurement but also glasses are sufficiently transparent for Raman scattering. Though the behaviour of Al^{3+} ions in glasses have been studied by several investigators[2~7], few measurements[8] of Raman scattering have been made. This note reports the Raman spectra of Na_2O–SiO_2–Al_2O_3 and K_2O–SiO_2–Al_2O_3 glasses.

According to the infra-red absorption measurements of Day and Rindone[2], the addition of Al_2O_3 to the Na_2O–SiO_2 glass resulted in a shift of the Si–O absorption band at about 1100cm^{-1} to lower frequency. However, for the glasses having an Al/Na ratio greater than unity, there is a small but detectable movement of this band to higher frequency. Moreover, in the infra-red spectra in the wavelength from 910 to 590 cm^{-1} the absorption band initially presents at 793 cm^{-1} gradually separated into two absorption bands with the absorption band at lower frequency (714 cm^{-1}) with the increase in intensity. When Al_2O_3 content exceeded the soda content, the second absorption band at lower frequency begins to decrease in intensity. These phenomena have been explained by the change of the average coordination number of Al^{3+} ions from 4 to 6 as the Al_2O_3 content increased.

Tarte[4] suggests that the absorption band caused by Al^{3+} ions of tetrahedral coordination appears in the frequency range from 700 to 800 cm^{-1}, on the other hand the band by octahedral Al^{3+} ions exists at about 500 cm^{-1} which have not been observed.

Suginohara and Yanagase[6, 7] denote in their infra-red measurements of various glasses that the band due to Si–O stretching vibrational mode shifts to a certain frequency with increasing Al_2O_3 content. In glasses which involve more alkaline or alkaline-earth oxides, this band consists of two peaks converging to one peak at a certain frequency when Al_2O_3 content is increased. They assumed that these peaks are caused by different complex silicate anoins.

The Raman spectra obtained in this study are shown in Figs. 1 and 2. They were obtained using K_2O–SiO_2–Al_2O_3 and Na_2O–SiO_2–Al_2O_3 glasses containing various amounts of Al_2O_3 under the condition that the ratio of M_2O (M=Na, K) to SiO_2 is constant, respectively.

The samples were prepared as follows. Analytical grade reagents, used as starting materials, were weighed and sufficiently. Each batch was held at about 1600°C in a platinum crucible. The melt, after sufficient degassing, was taken out and allowed to cool in air.

The laser Raman spectrometer used in this study was same as that described in Raman scattering measurements of K_2O–SiO_2 and K_2O–SiO_2–TiO_2 glasses.[9]

The both spectra in Figs. 1 and 2 are characterized by similar features. In alkaline-silica glasses without containing Al_2O_3, the spectra are characterized by two bands at about 500 and 1100 cm^{-1} which may correspond to a bending vibration of the $Si–O^-$ non-bridging oxygen group and to a bond stretching vibration of the $Si–O^-$ non-bridging or of the Si–O–Si bridging group, respectively.[9,10] When Al_2O_3 is added to M_2O–SiO_2 glasses, the band at about 780 cm^{-1} becomes broader as Al_2O_3 concentration increases. At the same time a band appears at about 1000 cm^{-1}. This band increases the intensity with increasing Al_2O_3 content. When the Al/Na ratio is greater than unity, this band becomes to be undistinguish-

† Received on Sep. 16, 1976
* Professor
** Research Instructor

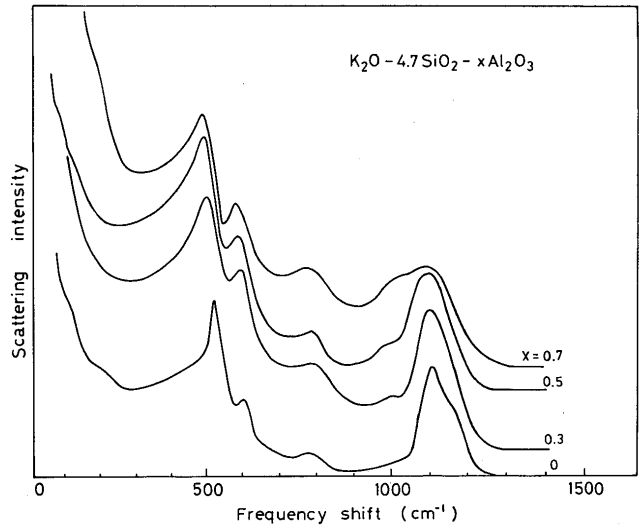

Fig. 1 Raman spectra of vitreous K_2O–SiO_2–Al_2O_3 glasses of various compositions. The scattering intensity is normalized to the intensity of the band near 500 cm^{-1}.

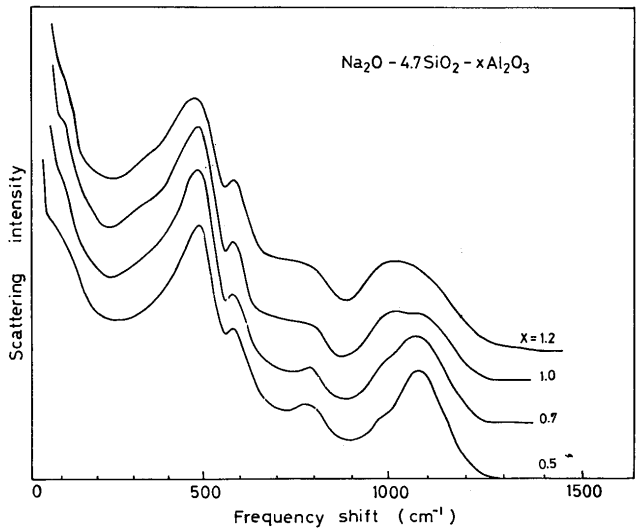

Fig. 2 Rama spectra of vitreous Na_2O–SiO_2–Al_2O_3 glasses of various compositions. The scattering intensity is normalized to the intensity of the band near 500 cm^{-1}.

able from the band at 1100 cm^{-1}.

It seems that these spectra show also the change of the features for the glasses of Al/Na ratio larger and smaller than unity. It is not, however, likely that the shift or the separation of bands pointed out by some investigators mentioned above.

Namely, the band at 780 cm^{-1} was not solved as Al_2O_3 content increased and new band at 500 cm^{-1} were not observed. Moreover, the higher frequency region, a

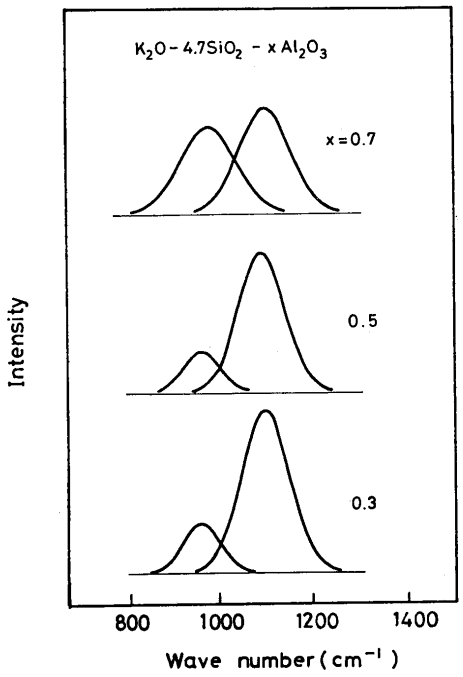

Fig. 3 Raman spectra separated into two Gaussian bands with the use of iterative least-square procedure. (K_2O–SiO_2–Al_2O_3 glasses)

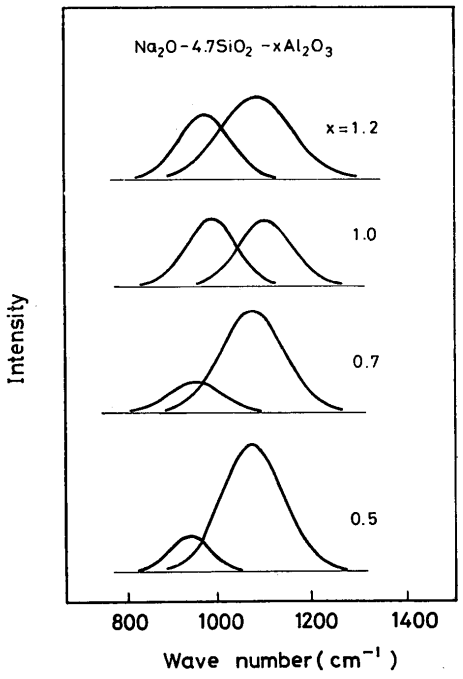

Fig. 4 Raman spectra separated into two Gaussian bands with the use of iterative least-square procudure. (Na_2O–SiO_2–Al_2O_3 glasses)

band appeared at 1000 cm^{-1} and increased in intensity Al_2O_3 content and both at 1000 and 1100 cm^{-1} may not shift in spite of a distinguishable broad band for the Al/Na>1.

To clarify especially the latter phenomenon, each spectrum was separated into two component bands as shown in Figs. 3 and 4 with the use of iterative least-square procedure under the condition that for every glasses the spectra consist of two Gaussian bands in the frequency range from 900 to 1200 cm^{-1}. It shows that two peaks shift only in the experimental error and the intensities change definitely as Al_2O_3 content increases.

Though this result does not give the enough discussion about the coordinate state of Al^{3+} ions in glasses, it shows that the measurement of laser Raman scattering will be powerful means. However, in order to obtain more reliable conclusions, further studies will be necessary on Raman spectra of various glasses containing Al_2O_3.

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