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To cite this version:


HAL Id: jpa-00222450

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Submitted on 1 Jan 1982

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SHORT RANGE STRUCTURE AND SOME PHYSICAL PROPERTIES OF THE GLASSES IN THE SYSTEM Na$_2$O-Ga$_2$O$_3$-SiO$_2$

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Abstract. - The glass-forming region in the system Na$_2$O-Ga$_2$O$_3$-SiO$_2$ was determined, and the density, hardness and thermal expansion coefficient were measured. The glass-forming region in this system was found to be much wider than that in the Na$_2$O-Al$_2$O$_3$-SiO$_2$ system. The properties showed a sudden change at the composition of Ga/Na ratio = 1. This anomaly is similar to that observed in the Na$_2$O-Al$_2$O$_3$-SiO$_2$ system. The results of IR spectra, X-ray emission spectra and X-ray diffraction patterns suggest that the non-bridging oxygens existing in sodium silicate glasses change into bridging oxygens with the addition of Ga$_2$O$_3$ at Ga/Na ratio less than 1 and then appear again along with the formation of Ga-O-Ga bond with further addition of Ga$_2$O$_3$ over the Ga/Na ratio of 1.

1. Introduction. - Previous studies on Na$_2$O-Al$_2$O$_3$-SiO$_2$ glasses revealed that many of their physical properties change abnormally at or near the composition of Al/Na ratio of 1/1,2/. In view of similarity between aluminum and gallium ions, it is expected that the physical properties of Na$_2$O-Ga$_2$O$_3$-SiO$_2$ glasses show similar anomalous changes to those of Na$_2$O-Al$_2$O$_3$-SiO$_2$ glasses. In order to verify this expectation, the glass-forming region in the system Na$_2$O-Ga$_2$O$_3$-SiO$_2$ was determined and various physical properties of the glasses were measured. To make the structural interpretation of the cause of these anomalies, the infrared spectra, X-ray emission spectra and X-ray diffraction patterns were obtained.

2. Experimental methods. - The reagent grade SiO$_2$, Na$_2$CO$_3$ and 8-Ga$_2$O$_3$ were used as the starting materials to obtain the following two series of glasses: A series; xGa$_2$O$_3$ \cdot $(100-x)$(Na$_2$O·2SiO$_2$)/3, B series; xGa$_2$O$_3$ \cdot $(100-x)$(Na$_2$O·SiO$_2$)/2, where x is the mole percent of Ga$_2$O$_3$. The
dendity, Vickers hardness number and thermal expansion coefficient were determined in the same manner as reported previously/3,4/. The infrared absorption spectra for the glasses and some related crystals were measured by the KBr pellet method from 250 to 4000 cm\(^{-1}\). SiK\(_8\) X-ray emission spectra were obtained with an electron probe X-ray microanalyzer. X-ray diffraction measurement was carried out with the use of a diffractometer with parafocusing reflect geometry and monochromatized MoK\(_\alpha\) radiation.

3. Results and Discussion.

3.1. Glass-forming region. - The glass-forming region in the system Na\(_2\)O-Ga\(_2\)O\(_3\)-SiO\(_2\) is shown in Fig. 1. Also shown is the glass-forming region in the system Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)/5/. The glass-forming region in the former system is much wider than that in the latter system.

3.2. Physical properties.- Various physical properties of the present glasses are shown in Fig. 2 as a function of Ga\(_2\)O\(_3\) content. Clearly, they change abnormally at or near the composition of Ga/Na ratio of 1.

3.3 Infrared spectra, X-ray emission spectra and X-ray diffraction. - In sodium silicate glasses, four infrared absorption bands appeared at or near 1100, 900, 760 and 480 cm\(^{-1}\). When Ga\(_2\)O\(_3\) was added, the two bands 1100 and 900 cm\(^{-1}\) became one band around 950 cm\(^{-1}\). At the same time, the band 760 cm\(^{-1}\) disappeared and the band at 480 cm\(^{-1}\) became small, as new three bands appeared at 730, 620 and 540 cm\(^{-1}\). Carnegie and nepheline-type compounds containing Ga\(^{3+}\) in place of Al\(^{3+}\) gave the same IR bands at 950, 730, 620 and 540 cm\(^{-1}\). From the structures of these compounds, these bands are considered to be associated with the vibrational modes of Si-O bond and Ga-O bond in Si-O-Ga bond. These results suggest the formation of Si-O-Ga bonds (in place of Si-O-Si and/or Si-O\(^-\)) with addition of Ga\(_2\)O\(_3\) to sodium silicate glasses. When the Ga/Na ratio became more than 1, new bands appeared at 700 and 500 cm\(^{-1}\) in addition to the above four bands. These two bands are observable also for \(\beta\)-Ga\(_2\)O\(_3\) crystal. This suggests the formation of the Ga-O-Ga bonds when the Ga/Na ratio becomes more than 1. The nature of oxygen connected to Si may be discussed through the chemical shift of SiK\(_8\) emission spectrum, which is known to change with the amount of the non-bridging oxygen/6/. The re-
Results of the chemical shifts for A and B series glasses are plotted as a function of Ga$_2$O$_3$ content in Fig. 3. The chemical shifts become smaller with increasing Ga$_2$O$_3$ content up to Ga/Na ratio 1. Further increase of Ga/Na ratio causes an increase in chemical shift. This means that the non-bridging oxygens decrease with increasing Ga$_2$O$_3$ up to Ga/Na ratio 1 and then increase with further addition of Ga$_2$O$_3$ to the glasses. The same conclusion was obtained from the result of band width of SiK$_\beta$ emission spectra. The band width of SiK$_\beta$ emission spectrum becomes wider when oxygen changes from the bridging oxygen to the non-bridging oxygen.$^6$ As shown in Fig. 4, the band width becomes narrowest at Ga/Na ratio 1. The X-ray diffraction study gives direct informations about the short range structure. The radial distribution function (RDF) observed for A-25, B-10, B-30 and B-45 glasses are shown in Fig. 5. The first peak at 1.77-1.83 Å is due to the nearest neighbour ionic pairs Si-O and Ga-O. This peak has a good symmetry and cannot be deconvoluted into two peaks of Si-O and Ga-O. So, the data were analyzed as the mixed T-O (T=Si,Ga) ionic pair. The second peak at 2.34-2.41 Å is due to the nearest neighbour Na-O ionic pair. The third peak at 3.14-3.33 Å is due to the T-T ionic pair. The short range parameters for the nearest neighbour are summarized in Table 1. The coordination number of T ions ($N_{T/O}$) is near four, 

![Graph](image-url)
which indicates that the coordination number of Ga ions is also four. The Na-O distance ($r_{Na-O}$) and the coordination number of Na ions ($N_{Na/O}$) for the B series glasses show the maxima at the Ga/Na ratio of 1. Imaoka/7/ has reported from the analysis of RDF that the basic structures for Na$_2$O·2SiO$_2$ and Na$_2$O·SiO$_2$ glasses are the layer and chain structure, respectively, and that the coordination number of Na ions is three for Na$_2$O·2SiO$_2$ and four for Na$_2$O·SiO$_2$ glass. Taylor et al./8/ has suggested that Na$_2$O·Al$_2$O$_3$·2SiO$_2$ glass has the six-membered ring structure and $N_{Na/O}$ is six. In view of their suggestions, it may be considered that the layer or chain structure of sodium silicate glass changes into six-membered ring with the addition of Ga$_2$O$_3$ to sodium silicate glasses. Thus, a structural model based on three dimensional six-membered rings was constructed and examined using the Debye scattering equation/9/ for A-25 glass, which has the same composition with the carnegiette-type crystal. In Fig.6, the $D(r)$ curve calculated from $S(r)$ for this carnegiette-like structural model is shown and compared with the observed $D(r)$ curve for A-25 glass. A reasonable agreement between the observed and calculated $D(r)$ curves can be seen. As given in Table 1, $N_{Na/O}$ for B-45 glass is smaller than that for B-30 glass. This seems to indicate that the three dimensional network structure breaks down when the amount of Ga$_2$O$_3$ becomes more than 1.

From these results of infra-red spectra, X-ray emission spectra and X-ray diffraction patterns, it is concluded that the non-bridging oxygens existing in sodium silicate glass change into bridging oxygens with the addition of Ga$_2$O$_3$ by forming GaO$_4$-Na$^+$ units when Ga/Na ratio is less than 1, but they appear again along with the formation of Ga-O-Ga bond with further addition of Ga$_2$O$_3$ over the Ga/Na ratio of 1.

References.

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