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Mössbauer and DTA Studies on the Structure of Semiconducting Sodium Vanadate Glasses

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Distinct decreases in the quadrupole splitting of the tetrahedral Fe^{3+} ions and the T_g suggest a gradual change from the layer structure composed of the VO_5 tetragonal pyramids to the chain structure composed of the VO_4 tetrahedra. It is also concluded that nonbridging oxygen atoms are present in the VO_4 tetrahedra.

Structural study of the crystalline V_2O_5 has been performed by Byström et al.[1] and Jansen and Sperlich.[2] They revealed that each V^{5+} ion is surrounded by five oxygen atoms making a distorted tetragonal pyramid, which can also be viewed as a distorted trigonal bipyramid, sharing edges and corners to form a layer structure. An IR study of several vanadate glasses performed by Dimitriev et al.[3] revealed that the introduction of alkali or alkaline earth oxides into the V_2O_5 matrix results in a destruction of the layer structure followed by a formation of tetrahedral VO_4 units. Dimitriev et al.[3] also elucidated that only the VO_4 units are present in the skeleton of metavanadate glasses. The same conclusion has been obtained in an NMR study of KVO_3 glass.[4] The crystal structure of the alkali metavanadate crystals including the KVO_3 is known to be composed of chains of VO_4 tetrahedra.[5] Dimitriev et al.[3] also revealed that the introduction of other kind of oxides which play a role of a network former, such as SiO_2, B_2O_3, GeO_2, and TiO_2, affects little structural change on the skeleton of the V_2O_5-based glass originally made of only VO_5 units.[1,2] On the other hand, a neutron diffraction study performed by Wright et al.[6] revealed that the coordination number of the vanadium is always 5 in P_2O_5-V_2O_5, BaO-V_2O_5, and PbO-V_2O_5 glasses irrespective of the glass composition, and that the skeleton of the vanadate glasses is composed of the interconnected and distorted VO_5 tetragonal pyramid. It should be noted that the neutron diffraction study by Wright et al.[6] has not been performed for alkali vanadate glasses. Similar conclusion has been obtained in a simultaneous EXAFS and XANES study of P_2O_5-V_2O_5 glass.[7] Besides the VO_4 and the VO_5 units described above, the presence of octahedral VO_6 units has been proposed based on the ESR measurements of the V^{4+} (VO^{2+}) ions.[8,9] Mössbauer spectroscopy has been utilized for the structural study of potassium vanadate glasses,[10] where the present authors revealed that all the Fe^{3+} ions are tetrahedrally coordinated by oxygen atoms at the substitutional sites of the V^{5+} or V^{4+} ions constituting the VO_4 tetrahedra.

The present Mössbauer study was carried out in order to elucidate the structure of the sodium vanadate glasses. DTA measurements were performed in order to know the structural change through the glass transition temperature (T_g), because the T_g is known to reflect a change in the coordination number of the network-forming atoms and a formation of nonbridging oxygen atoms.[10]

Experimental

Sodium vanadate glasses were prepared by fusing the individual mixtures (1 g) of commercially available Na_2CO_3, V_2O_5, and Fe_2O_3, of guaranteed reagent grade, at 950 °C for 1 h in an electric muffle furnace. After the fusion in the ambient atmosphere, each melt in a platinum crucible was quenched with ice-cold water. The vanadate glasses were tried to prepare in the compositional ranges of $0\ \text{mol\%} \leqslant Na_2O \leqslant 40\ \text{mol\%}$, $50\ \text{mol\%} \leqslant V_2O_5 \leqslant 90\ \text{mol\%}$, and $0\ \text{mol\%} \leqslant Fe_2O_3 \leqslant 30\ \text{mol\%}$. All the glass samples prepared in the present study are almost black in color. Mössbauer and DTA measurements were performed for the pulverized glasses similarly to the case of the potassium vanadate glasses.[10]

Results and Discussion

The glass-forming region for the ternary Na_2O-V_2O_5-Fe_2O_3 glass system is shown in Fig. 1, where open and closed circles indicate the formations of glass and non-glassy (devitrified) samples, respectively. A Mössbauer spectrum of the sodium vanadate glasses measured at room temperature is shown in Fig. 2, which indicates the presence of paramagnetic Fe^{3+} ions of high spin state.[11,12] The isomer shift and the linewidth of the absorption peaks are located in the ranges of 0.39—0.35 and 0.53—0.47 mm s^{-1}, respectively. As to the coordination number of the iron in glasses, earlier results are reviewed by Kurkjian[13] and Coey.[14] Recent Mössbauer results on the structure of

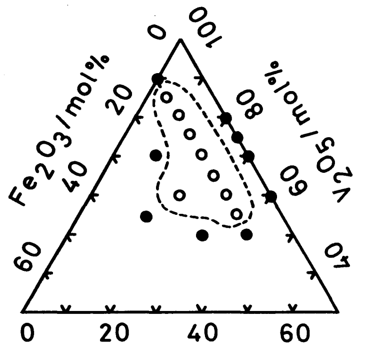

Fig. 1. Glass-forming region of the Na_2O-V_2O_5-Fe_2O_3 system.

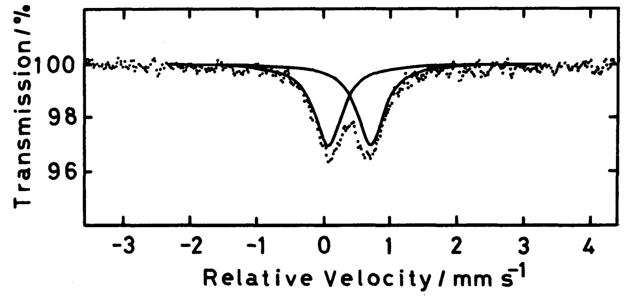

Fig. 2. Mössbauer spectrum of the $25Na_2O\cdot65V_2O_5\cdot10Fe_2O_3$ glass measured at room temperature.

glasses are reviewed by Müller-Warmuth and Eckert.[15] According to Coey, Fe^{3+} ions are reported to be present at the tetrahedral sites in borate and silicate glasses.[14] This is well consistent with the Mössbauer results of borate[16–18] and borosilicate[19–20] glasses, performed by the present authors, where the isomer shift ranges from 0.38 to 0.22 mm s^{-1} with respect to metallic iron. (The experimental error for the isomer shift is usually estimated to be ±0.01 mm s^{-1}.) Judging from the experimental results shown in those reviews[13–15] and papers,[16–20] the Fe^{3+} ions are concluded to be present at the tetrahedral environments in the sodium vanadate glasses. This conclusion indicates the presence of the tetrahedral VO_4 units, because the Fe^{3+} ions should be present either at the substitutional sites of the V^{5+} or V^{4+} ions constituting the glass matrix or at the interstitial sites of the glass matrix. These results are well consistent with the IR results obtained by Dimitriev et al.[3] and with the Mössbauer results of the potassium vanadate glasses.[10]

The composition dependency of the isomer shift is shown in Fig. 3, which shows a distinct decrease with increasing Na_2O content. Similar composition dependency has been observed in the case of the potassium vanadate glasses,[10] where the decrease in the isomer shift was ascribed to the formation of nonbridging oxygen atoms in the VO_4 tetrahedra. The composition dependency of the isomer shift is well consistent with that of the quadrupole splitting shown in Fig. 4, where the quadrupole splitting shows a distinct decrease with increasing Na_2O content. (The experimental error for the quadrupole splitting is usually estimated to be ±0.02 mm s^{-1}.) The decrease in the quadrupole splitting of the Fe^{3+} ions is ascribed to the increased symmetry around the Fe^{3+} ions, because the high-spin Fe^{3+} ions have a symmetric electron configuration of $3d^5$ in the outermost orbital. The present results of the isomer shift (Fig. 3) and the quadrupole splitting (Fig. 4) therefore indicate the formation of nonbridging oxygen atoms in the VO_4 tetrahedra constituting the skeleton of the sodium vanadate glasses. The decrease in the quadrupole splitting may be correlated with the decrease in the coordination number of the V^{5+} and V^{4+} ions from 5 to 4, because the electric field gradient (e^2qQ) is considered to be smaller in the case of the tetrahedral configuration.

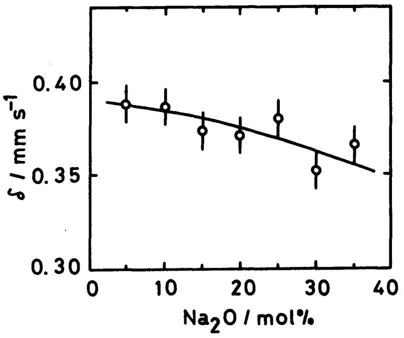

Fig. 3. Composition dependency of the isomer shift (δ) of the Fe^{3+} ions in the Na_2O–V_2O_5 glasses containing 10 mol% Fe_2O_3.

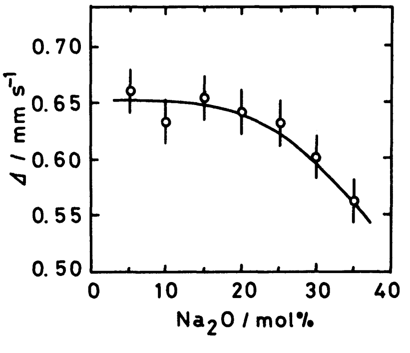

Fig. 4. Composition dependency of the quadrupole splitting (Δ) of the Fe^{3+} ions in the Na_2O–V_2O_5 glasses containing 10 mol% Fe_2O_3.

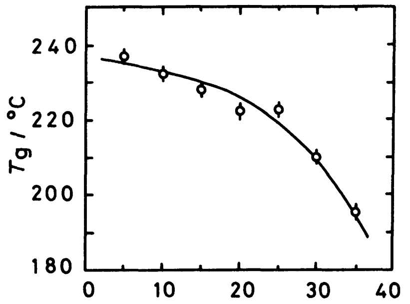

Fig. 5. Composition dependency of the glass transition temperature (T_g) of the Na_2O–V_2O_5 glasses containing 10 mol% Fe_2O_3.

Each DTA curve of the sodium vanadate glasses containing 10 mol% Fe_2O_3 consists of an endothermic peak due to glass transition and one or a few exothermic peak(s) due to crytallization. All the glass transition temperatures (T_g) are plotted in Fig. 5, where the T_g values are plotted against the Na_2O content. A Mössbauer and DTA study of potassium vanadate glasses[10] revealed that the T_g shows a distinct decrease when the coordination number of the V^{5+} or V^{4+} ions decreases from 5 to 4 and when the nonbridging oxygen atoms are formed in the VO_4 tetrahedra. The distinct decrease in the T_g from 237 to 195 °C (Fig. 5) is therefore ascribed to the gradual decrease in the coor-

Table 1. Glass Transition and Crystallization Temperatures of the Na_2O–V_2O_5 Glasses Containing 10 mol% Fe_2O_3

Composition	T_g[a]/°C	T_c[b]/°C
$5Na_2O\cdot85V_2O_5\cdot10Fe_2O_3$	237	254
$10Na_2O\cdot80V_2O_5\cdot10Fe_2O_3$	232	253
$15Na_2O\cdot75V_2O_5\cdot10Fe_2O_3$	228	247
$20Na_2O\cdot70V_2O_5\cdot10Fe_2O_3$	222	238
$25Na_2O\cdot65V_2O_5\cdot10Fe_2O_3$	223	250
$30Na_2O\cdot60V_2O_5\cdot10Fe_2O_3$	210	239
$35Na_2O\cdot55V_2O_5\cdot10Fe_2O_3$	195	213

a) Glass transition temperature. b) Crystallization temperature.

dination number of the V^{5+} and V^{4+} ions from 5 to 4 and to the formation of the nonbridging oxygen atoms in the VO_4 (and FeO_4) tetrahedra. All the T_g values obtained in the present study are summarized in Table 1, together with the individual crystallization temperatures (T_c). In Table 1, only one crystallization temperature corresponding to the main peak is given for each glass sample.

It is concluded that Fe^{3+} ions are present at the substitutional sites of the V^{5+} or V^{4+} ions constituting the VO_4 tetrahedra. It is also concluded that the introduction of Na_2O into the V_2O_5 matrix results in a gradual change from the layer structure composed of the VO_5 tetragonal pyramids (or trigonal bipyramids) to the chain structure composed of the VO_4 tetrahedra having nonbridging oxygen atoms.

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