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Structural Study of Potassium Gallate Glasses by Mössbauer Spectroscopy and Differential Thermal Analysis

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Mössbauer spectra of a series of potassium gallate (Ga_2O_3-based) glasses, containing 10 mol% Fe_2O_3 as a Mössbauer probe, consist of two types of quadrupole doublet peaks due to tetrahedral Fe^{3+} ions bonded with nonbridging and bridging oxygen atoms and those bonded only with bridging oxygen atoms. This indicates that all the Fe^{3+} ions are present at the substitutional sites of the tetrahedral Ga^{3+} ions constituting the skeleton of network structure. An increase in the K_2O content results in an increased fraction of the FeO_4 (and GaO_4) tetrahedra bonded with nonbridging oxygen atom(s). A Mössbauer spectrum of $70K_2O\cdot20Ga_2O_3\cdot10Fe_2O_3$ glass consists of only one quadrupole doublet peak due to the FeO_4 tetrahedra having nonbridging oxygen atom(s). This suggests that each of the Fe^{3+} (and also Ga^{3+}) ions is tetrahedrally bonded with at least one nonbridging oxygen atom. Structural information obtained from the Mössbauer measurements is confirmed by DTA measurements of the gallate glasses, T_g of which shows a drastic decrease from 647 to 555 °C when the K_2O content is changed from 35 to 70 mol%.

Recently, Dumbaugh and Tyndell[1,2)] and Kokubo et al.[3–5)] revealed that ternary gallate glasses are easily prepared by the conventional crucible-melting technique when alkali or alkaline earth oxides are incorporated into the Ga_2O_3 matrix with so-called middle oxides such as Nb_2O_5, Ta_2O_5, and TiO_2. It was also revealed that gallate glasses have an excellent optical transparency ranging from UV to IR (about 7 or 8 μm).[1–5)] Structural study of gallate glasses was performed using IR[3–5)] and Raman scattering,[6,7)] where most of the Ga^{3+} ions were reported to be tetrahedrally coordinated with oxygen atoms. In addition to the tetrahedral GaO_4 units, it was considered that a small amount of GaO_6 octahedra might be present in gallate glasses when the alkali or alkaline earth oxides content is low.[3–7)] In the IR[3–5)] and Raman[6,7)] studies it was discussed that so-called three-fold coordinated oxygen atoms will be present in gallate glasses. Besides the IR and Raman spectroscopies, often used for the structural study of glasses, ^{57}Fe-Mössbauer spectroscopy has been utilized for the structural study of several kinds of glasses, such as borate,[8,10)] borosilicate,[11–12)] and vanadate[13–15)] glasses. As a result, some useful information on the short-range (local) structure has been obtained, concerned with the coordination number of network-forming atoms and a formation of nonbridging oxygen atoms in BO_4, SiO_4, and VO_4 tetrahedra.[8–15)]

The present Mössbauer study was carried out in order to elucidate the short-range structure of potassium gallate glasses and a structural change caused by K_2O molecules incorporated into the Ga_2O_3 matrix. Potassium gallate glasses were chosen as one of the representative example of alkali gallate glasses. Differential Thermal Analysis (DTA) measurements were performed in order to examine the structural change in the gallate glasses, e.g., a change in the coordination number of Ga^{3+} ions and a formation of nonbridging oxygen atom(s).

Experimental

Potassium gallate glasses denoted by $xK_2O\cdot(90-x)Ga_2O_3\cdot10Fe_2O_3$ were prepared by fusing the individual mixtures (2g) of commercially available K_2CO_3, Ga_2O_3, and Fe_2O_3, of a guaranteed reagent grade, in an electric muffle furnace. Each mixture in a platinum crucible was fused in the ambient atmosphere at 1400 °C for 2.5 — 8.5 h, depending on the K_2O content. During the fusion, each of the platinum crucibles was covered with a piece of platinum foil to prevent the mixture from evaporating. The x value was changed from 30 to 75 at 5 intervals. Ten mol% Fe_2O_3 was incorporated into the individual mixture as a Mössbauer probe. After the fusion, each melt in a platinum crucible was quickly quenched by immersing the crucible into ice-cold water. As a result, homogeneous glass samples were prepared in the compositional region $35\leqq x\leqq70$. (Only glass-ceramics were obtained when x was 30 and 75.) All the gallate glasses obtained in this way are transparent and dark brown in color, being hygroscopic. Mössbauer measurements were performed on the pulverized glasses under a dry nitrogen atmosphere, according to the procedures shown in the previous papers.[8–15)] In the Mössbauer measurement, a piece of metallic iron foil enriched with ^{57}Fe was used as a reference of the isomer shift and for calibrating the velocity of the spectrometer. DTA measurements were performed under a nitrogen atmosphere, using Al_2O_3 powder as a standard material. Glass transition temperatures (T_g) were obtained from the DTA measurements performed in the range of room temperature to 800 °C. Each of the glass samples was heated with a heating rate of 5 °C min^{-1}.

Results and Discussion

Most of the Mössbauer spectra observed in the present study consist of two types of quadrupole doublet peaks, as indicated with broken lines in Fig. 1. No magnetic absorption peak is observed in the potassium gallate glasses, similarly to the case of several iron-containing oxide glasses so far studied by the present authors.[8–15)] In the case of potassium gallate glasses containing 10 mol% Fe_2O_3, it is

Table 1. Mössbauer Parameters of K_2O–Ga_2O_3–Fe_2O_3 Glasses

Composition	δ[a)] mm s^{-1}	Δ[b)] mm s^{-1}	Γ[c)] mm s^{-1}	A[d)] %
$35K_2O\cdot55Ga_2O_3\cdot10Fe_2O_3$	0.24	1.32	0.58	61.1
	0.32	0.78	0.58	38.9
$40K_2O\cdot50Ga_2O_3\cdot10Fe_2O_3$	0.23	1.32	0.59	55.2
	0.31	0.68	0.45	44.8
$45K_2O\cdot45Ga_2O_3\cdot10Fe_2O_3$	0.25	1.29	0.59	64.7
	0.34	0.72	0.40	35.3
$50K_2O\cdot40Ga_2O_3\cdot10Fe_2O_3$	0.23	1.26	0.52	66.1
	0.30	0.77	0.46	33.9
$55K_2O\cdot35Ga_2O_3\cdot10Fe_2O_3$	0.23	1.25	0.46	66.8
	0.32	0.71	0.43	33.2
$60K_2O\cdot30Ga_2O_3\cdot10Fe_2O_3$	0.23	1.28	0.59	69.2
	0.33	0.73	0.42	30.8
$65K_2O\cdot25Ga_2O_3\cdot10Fe_2O_3$	0.23	1.23	0.61	85.5
	0.29	0.65	0.42	14.5
$70K_2O\cdot20Ga_2O_3\cdot10Fe_2O_3$	0.23	1.17	0.68	100.0

a) Isomer shift. b) Quadrupole splitting. c) Linewidth. d) Absorption intensity (area).

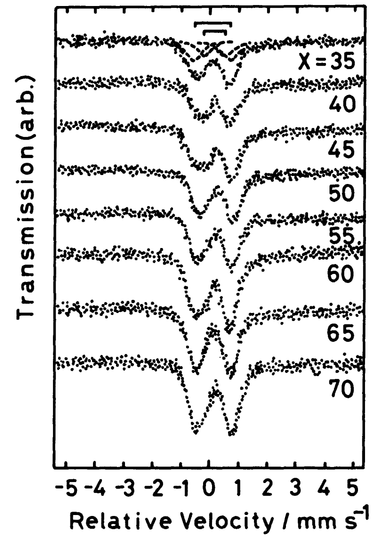

Fig. 1. Mössbauer spectra of $xK_2O\cdot(90-x)Ga_2O_3\cdot10Fe_2O_3$ glasses measured at room temperature.

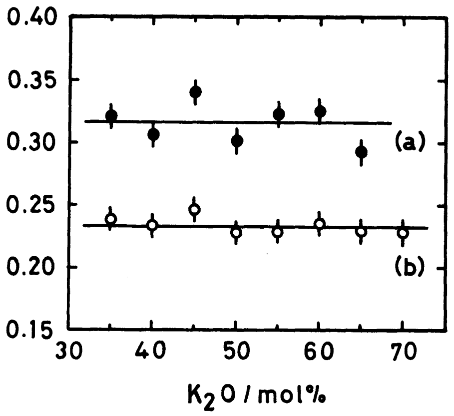

Fig. 2. Composition dependencies of the isomer shift (δ) of (a) inner and (b) outer doublet peaks shown in Fig. 1.

expected that all the iron (Fe^{3+} ions) should be present either at the substitutional sites of the Ga^{3+} ions constituting the skeleton of network structure or at the interstitial sites in the network structure. All the Mössbauer parameters obtained for the $xK_2O\cdot(90-x)Ga_2O_3\cdot10Fe_2O_3$ glasses are summarized in Table 1. It can be seen from Table 1 that the linewidth (FWHM), ranging from 0.40 to 0.68 mm s^{-1}, is characteristic of the absorption peak due to iron in glasses. This means that all the Fe^{3+} ions are homogeneously distributed in the glass matrix and are not forming a precipitate or aggregate which shows a magnetic hyperfine interaction. It is generally known that isomer shift indicates whether the Mössbauer nuclei (^{57}Fe in the present study) are present at the tetrahedral or octahedral environments.[8–18)] All the isomer shift values obtained for one or two types of quadrupole doublets are shown in Fig. 2. Figure 2 and Table 1 indicate that all the isomer shifts obtained for the $xK_2O\cdot(90-x)Ga_2O_3\cdot10Fe_2O_3$ glasses are much smaller than 0.39 or 0.40 mm s^{-1} which is the boundary of isomer shift between octahedral and tetrahedral Fe^{3+} ions.[8–18)] The experimental error of isomer shift is usually estimated to be ±0.01 mm s^{-1}. Experimental results shown in Fig. 2 and Table 1 suggest that all the Fe^{3+} ions are present at the tetrahedral environments. This means that all the Fe^{3+} ions are present at the substitutional sites of the tetrahedral Ga^{3+} ions in the skeleton of network structure. When the isomer shift indicates the presence of octahedral Fe^{3+} ions, we can conclude that such Fe^{3+} ions are present at the interstitial sites of network structure composed of several GaO_4 tetrahedra. It is easily understood from Fig. 2 that the skeleton of network structure of gallate glasses, other than $70K_2O\cdot20Ga_2O_3\cdot10Fe_2O_3$ glass, is composed of two types of FeO_4 (and GaO_4) tetrahedra having the isomer shifts of about 0.32 (inner doublet) and 0.23 mm s^{-1} (outer doublet). Figure 2 demonstrates that isomer shift values of inner (a) and outer

(b) doublets are constant irrespective of the K_2O content. Recently, Fukunaga et al.[6,7] revealed that several nonbridging oxygen atoms are present in the GaO_4 tetrahedra and each of the GaO_4 tetrahedra has at least one nonbridging oxygen atom when CaO content exceeds about 67 mol%, which corresponds to a composition $2CaO \cdot Ga_2O_3$. Taking into account the Raman results,[6,7] we can conclude that two types of the quadrupole doublets having different isomer shift values are concerned with the FeO_4 (and GaO_4) tetrahedra with and without nonbridging oxygen atoms.

This conclusion is consistent with the structural information obtained from composition dependencies of the quadrupole splitting (Fig. 3). The quadrupole splitting of outer doublets (b) shows a distinct decrease with increasing K_2O content. On the other hand, the quadrupole splitting of inner doublets (a) shows a less distinct decrease with increasing K_2O content. The experimental error of the quadrupole splitting is usually estimated to be ± 0.02 mm s^{-1}. Decrease in the quadrupole splitting of Fe^{3+} ions is ascribed to an increase in the symmetry of FeO_4 tetrahedra, because high-spin Fe^{3+} ion has a symmetric electron configuration of $3d^5$ in the outermost orbital. In such a case, the electric field gradient brought about by the neighboring oxygen atoms will primarily cause the quadrupole interaction (splitting).[8-15] It is generally considered that symmetry of the FeO_4 tetrahedra having nonbridging oxygen atom(s) is much higher than that of the FeO_4 tetrahedra bonded only with bridging oxygen atoms, because nonbridging oxygen atoms have higher degree of freedom. In the recent Mössbauer studies, the formation of nonbridging oxygen was observed as a decrease in the quadrupole splitting of Fe^{3+} ions.[8-15] The experimental results indicate that nonbridging oxygen atom(s) are present at less distorted sites than bridging oxygen. On the contrary, the quadrupole splitting of outer doublets (Fig. 3b) concerned with the nonbridging oxygen atom(s) is much greater than that of inner doublets (Fig. 3a) concerned only with bridging oxygen atoms. The large quadrupole splitting values observed for the outer doublets (Fig. 3b) may be concerned with so-called three-fold coordinated oxygen atoms proposed in IR[3-5] and Raman[6,7] studies. Three-fold coordinated oxygen atoms, if present, will greatly decrease the symmetry of the FeO_4 and GaO_4 tetrahedra because of higher distortion and lower degree of freedom. The FeO_4 and GaO_4 tetrahedra bonded with three-fold coordinated oxygen atom(s) will be present in more distorted (and highly energetic) states than those bonded with ordinary two-fold coordinated oxygen atoms. Therefore, it is concluded that large quadrupole splitting values of Fe^{3+} ions (Fig. 3b) are observed because the Fe^{3+} (and Ga^{3+}) ions are simultaneously bonded with so-called three-fold coordinated oxygen and nonbridging oxygen atoms. Further investigation will clarify the presence and role of the unfamiliar three-fold coordinated oxygen atoms. The continuous decrease in the quadrupole splitting of outer doublets (Fig. 3b) is concluded to be due to an increased fraction of nonbridging oxygen atoms in the FeO_4 (and GaO_4) tetrahedra. Small isomer shift values of the Fe^{3+} ions bonded with nonbridging oxygen atom(s) are ascribed to a decreased interatomic distance and therefore increased covalency between the Fe^{3+} ion and nonbridging oxygen atom. The peak assignment of the FeO_4 (and GaO_4) tetrahedra described above is confirmative when we see the distinct composition dependency of the relative absorption intensity of the Fe^{3+} ions bonded with nonbridging oxygen atom(s). This is shown in Fig. 4, where the relative absorption intensity (area) of the FeO_4 (and GaO_4) tetrahedra having nonbridging oxygen atom(s) (outer doublet) is increased with increasing K_2O content, and becomes 100% when the K_2O content is close to 70 mol%. A Mössbauer spectrum of $70K_2O \cdot 20Ga_2O_3 \cdot 10Fe_2O_3$

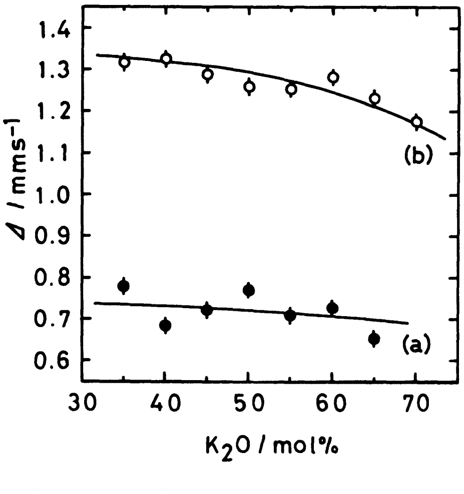

Fig. 3. Composition dependencies of the quadrupole splitting (Δ) of (a) inner and (b) outer doublet peaks shown in Fig. 1.

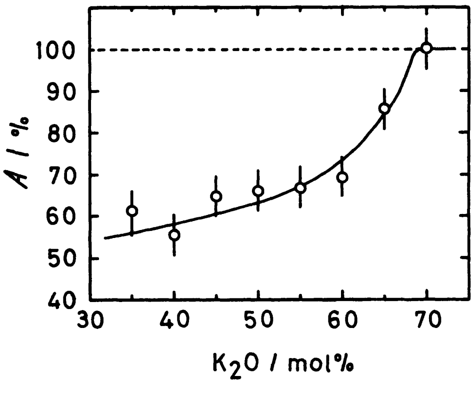

Fig. 4. Composition dependency of the relative absorption intensity of the outer doublets shown in Fig. 1.

glass is composed of only one quadrupole doublet corresponding to the outer doublet (Fig. 1). The experimental results on the formation and fraction of nonbridging oxygen atoms in the FeO_4 and GaO_4 tetrahedra are consistent with the Raman results recently obtained by Fukunaga et al.[6,7] In the Raman[6,7] and IR[3–5] studies, it was suggested that small amounts of octahedral GaO_6 units are present in the alkali or alkaline earth gallate glasses. In the present Mössbauer study, however, no absorption peak due to FeO_6 (and GaO_6) octahedra has been observed even in the low K_2O-content glasses. This is also in contrast to the ^{71}Ga-NMR results obtained by Zhong and Bray[19] recently, who elucidated that a large number of GaO_6 octahedra are present in caesium gallate glasses when the Cs/Ga ratio is smaller than unity. From the unambiguous NMR-spectral change of the caesium gallate glasses, Zhong and Bray[19] suggested that a gradual change of local structure from GaO_6 octahedra to GaO_4 tetrahedra was caused by caesium oxide molecules introduced into the Ga_2O_3 matrix. The NMR-spectral change is somewhat similar to the gradual change of Mössbauer spectra (Fig. 1), ascribed to the formation of nonbridging oxygen atoms in the FeO_4 and GaO_4 tetrahedra. If the NMR result of caesium gallate glasses[19] is taken into account, the absence of Mössbauer absorption peak due to FeO_6 (and GaO_6) octahedra in the present study may be responsible for the chemical property of iron in alkali gallate glasses. Fe^{3+} ions may be preferentially substituted for tetrahedral Ga^{3+} ions than octahedral Ga^{3+} ions. In such a case, a Mössbauer spectrum will be obtained only due to the tetrahedral FeO_4 (and also GaO_4) units. On the other hand, if Fe^{3+} ions are equivalently substituted for octahedral and tetrahedral Ga^{3+} ions, we can conclude that the fraction of GaO_6 octahedra in alkali (potassium) gallate glasses is too small to be detected by Mössbauer spectroscopy. Considering the precision of Mössbauer spectroscopy, we can estimate that the fraction of GaO_6 octahedra is less than several percent and that the skeleton of the $xK_2O\cdot(90-x)Ga_2O_3\cdot 10Fe_2O_3$ glasses is composed of only GaO_4 (and FeO_4) tetrahedra.

Each DTA curve of the potassium gallate glasses containing 10 mol% Fe_2O_3 consists of a weak endothermic peak due to glass transition and an exothermic peak due to crystallization. All the glass transition temperatures (T_g) of the $xK_2O\cdot(90-x)Ga_2O_3\cdot 10Fe_2O_3$ glasses are shown in Fig. 5, where the T_g shows a drastic decrease with increasing K_2O content. Similar composition dependency of T_g has recently been observed in K_2O–V_2O_5,[13] Na_2O–V_2O_5,[14] and Li_2O–V_2O_5[15] glasses containing 10 mol% Fe_2O_3. It should be noted that the decrease in T_g of potassium gallate glasses (Fig. 5) is much greater than that of alkali vanadate glasses.[13–15] In alkali vanadate glasses,[13–15] the decrease in T_g was ascribed to a formation of nonbridging oxygen atoms in VO_4 and FeO_4 tetrahedra, followed by a gradual change of the glass matrix from the two-dimensional layer structure, originally composed of VO_5 tetragonal pyramids, to the one-dimensional chain structure composed of VO_4 tetrahedra. Mössbauer and DTA results obtained for alkali vanadate glasses[13–15] suggest that the pronounced decrease in T_g of potassium gallate glasses (Fig. 5) is closely correlated with a formation of nonbridging oxygen atoms in GaO_4 (and FeO_4) tetrahedra. In alkali vanadate glasses,[13–15] a continuous decrease in T_g amounting to about 30—60 °C was observed when the alkali oxide content was changed from 0 to 35 mol%. On the other hand, a drastic decrease in T_g amounting to more than 120 °C is observed in the potassium gallate glasses when K_2O content is changed from 35 to 70 mol% (Fig. 5). This suggests that fraction of nonbridging oxygen atoms in the GaO_4 tetrahedra constituting alkali gallate glasses is much greater than that in the VO_4 tetrahedra constituting alkali vanadate glasses. In Fig. 5, the increasing fraction of nonbridging oxygen atoms in the GaO_4 and FeO_4 tetrahedra is observed as a drastic and apparently linear decrease of T_g. The formation of nonbridging oxygen atoms is considered to be equivalent to a depolymerization of the glass matrix. Regarding the relationship between the structure and physical properties of gallate glasses, it is speculated that high optical transparency of gallate glasses ranging from UV to IR[1–5] may be concerned with the extraordinarily high fraction of nonbridging oxygen atoms in the GaO_4 tetrahedra constituting the skeleton of network structure.

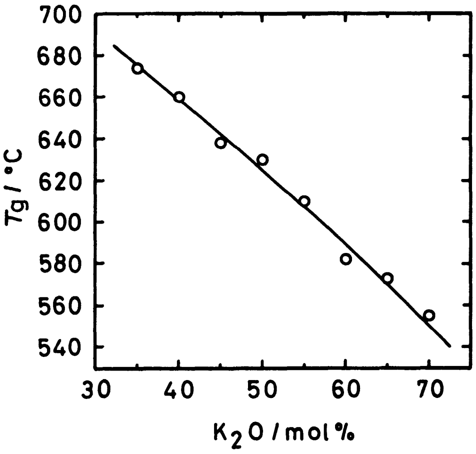

Fig. 5. Composition dependency of the glass transition temperature (T_g) of $xK_2O\cdot(90-x)Ga_2O_3\cdot 10Fe_2O_3$ glasses.

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