A Linear Relationship between the Glass Transition Temperature and Local Distortion of Calcium Gallate, Barium Gallate, and Calcium Aluminate Glasses

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The isomer shift in the ^{57}Fe-Mössbauer spectra of xCaO·(90−x)Ga_2O_3·10Fe_2O_3 (x=40—60) and xBaO·(90−x)Ga_2O_3·10Fe_2O_3 (x=65—70) glasses decreases gradually from 0.28 to 0.16 mm s^{-1} with increasing CaO or BaO contents. This indicates a formation of nonbridging oxygen atoms in the GaO_4 and FeO_4 tetrahedra. Large quadrupole splitting (Δ) values ranging from 0.98 to 1.24 mm s^{-1} indicate a noticeable distortion of the GaO_4 and FeO_4 tetrahedra. Mössbauer parameters of xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses (x=55—60) are comparable to those of the xCaO·(90−x)Ga_2O_3·10Fe_2O_3 glasses, suggesting that the local structures are essentially the same with each other. The glass transition temperatures (T_g) of the calcium gallate, barium gallate, and calcium aluminate glasses are 702—728, 580—583, and 750—773 °C, respectively. It is found that the T_g of several oxide glasses is proportional to the Δ, being expressed by $T_g=a\Delta+b$, where "a" is 680 °C mm^{-1} s and "b" is −180 °C when the Fe^{3+} ions are present at substitutional sites of the network former (NWF). The "T_g–Δ rule" is also applicable to the Fe^{3+} ions present at interstitial sites, in which case "a" and "b" are 35 °C mm^{-1} s and 260 °C, respectively. These findings indicate that the T_g is primarily determined by the distortion of NWF-oxygen polyhedra.

Gallate glasses have attracted much attention because they have highly optical transparency over the wide range of wavelength up to IR region (ca.7 μm).[1-5] Structural studies of gallate glasses have been performed by use of IR,[2-4] Raman,[5] NMR,[6] and Mössbauer[7] techniques. It was reported that Ga^{3+} ions constitute GaO_4 tetrahedra in the gallate glasses.[2-7] The IR[2] and NMR[6] studies revealed that small amounts of GaO_6 octahedra, besides the GaO_4 tetrahedra, constitute the gallate glasses when the alkali or alkaline earth oxides content is low. In the IR[3,4] and Mössbauer[7] studies, however, no evidence of the GaO_6 octahedra was obtained. It is known that gallate glasses have so called "three-fold coordinated" oxygen atoms,[3-5] which may cause a great local distortion.

It is reported that aluminate glasses also have a highly optical transparency in the visible to IR region.[4,8,9] Hafner et al.[8] proposed a relationship between the IR absorbing frequency and the chemical bond strength or reduced mass of the cations constituting aluminate glasses. This finding was further extended by Kokubo et al.[4,9] They elucidated that the cut-off wavelength (ca. 6 μm) in the IR region increased with increasing mass of cations and with decreasing single bond strength between the cations and oxygen atoms. Kokubo et al.[4] also reported that aluminate glass (45K_2O·35Nb_2O_5·20Al_2O_3) had an optical transparency similar to that of gallate glass (45K_2O·35Nb_2O_5·20Ga_2O_3). A structural study of alkali and alkaline earth aluminate glasses was performed by use of IR technique,[4,9] and it was suggested that AlO_4 tetrahedra constituted the glasses. The structure of aluminate glasses was previously discussed by Stanworth,[10] who suggested that calcium aluminate glass would be composed of AlO_4 tetrahedra. His idea was based on the fact that 12CaO·7Al_2O_3 crystal was composed of AlO_4 tetrahedra with and without nonbridging oxygen (NBO) atoms. On the other hand, it was reported that CaO·Al_2O_3 crystal comprised AlO_6 octahedra.[11]

This study was carried out for elucidating the local structure of calcium gallate, barium gallate, and calcium aluminate glasses and a relationship between the structure and the physical properties such as glass transition temperature (T_g) and highly optical transparency in the IR region. These glasses include small amounts (10 or 5 mol%) of Fe_2O_3 for the Mössbauer study. DTA measurements were made in order to obtain the T_g, since it is known that T_g reflects the structural changes of glass matrix.[7,12-23] A brief summary on the Mössbauer spectroscopy and DTA is given by Nishida,[23] relating to the structure and electrical conductivity of oxide glasses.

Experimental

Calcium and barium gallate glasses denoted by xCaO·(90−x)Ga_2O_3·10Fe_2O_3 and xBaO·(90−x)Ga_2O_3·10Fe_2O_3 were prepared by melting individual mixtures (0.5 g) of commercially available $CaCO_3$ or $BaCO_3$, Ga_2O_3, and Fe_2O_3, of guaranteed reagent grade. Each mixture in a platinum crucible was melted for 0.5 to 1.5 h at 1400 and 1350 °C in the cases of calcium and barium gallate glasses, respectively. Calcium aluminate glasses denoted by xCaO·(95−x)Al_2O_3·5Fe_2O_3 and xCaO·(90−x)Al_2O_3·10Fe_2O_3 were prepared by fusing individual mixtures (1 g), composed of $CaCO_3$, $Al(OH)_3$, and Fe_2O_3, at 1400 °C for 2 to 10.5 h. After the fusion in air, each melt was quenched by quickly immersing the bottom of the platinum crucible into ice-cold water. As a result, transparent and brown glasses could be obtained in the regions $40 \leqq x \leqq 60$ and $65 \leqq x \leqq 70$ in the cases of xCaO·(90−x)Ga_2O_3·10Fe_2O_3 and xBaO·(90−x)Ga_2O_3·10Fe_2O_3 glasses, respectively. In the case of

xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses, transparent and light brown glasses could be prepared in the region $55 \leqq x \leqq 60$. Only the 60CaO·30Al_2O_3·10Fe_2O_3 glass sample could be prepared in the xCaO·(90−x)Al_2O_3·10Fe_2O_3 series. Mössbauer measurements were made on pulverized samples at room temperature by using a constant acceleration method. Cobalt-57 (10 mCi) diffused into a palladium foil was used as the Mössbauer source. As the reference of isomer shift, a piece of metallic iron foil enriched with iron-57 was used. The iron foil was also used for calibrating the velocity scale of the spectrometer. Each Mössbauer spectrum was analyzed into a quadrupole doublet peak having an equal linewidth by use of a least-squares method. DTA measurements of the gallate and aluminate glasses were made at a heating rate of 5 °C min^{-1}, ranging from room temperature to 900 °C. Alpha-Al_2O_3 powder was used as the standard in the DTA measurements.

Results and Discussion

Mössbauer spectra of typical gallate and aluminate glasses are illustrated in Fig. 1. All the Mössbauer spectra studied in this paper consist of quadrupole doublet peaks. Some of them are shown in Fig. 1. The doublet peaks indicate the presence of paramagnetic iron species homogeneously distributed in the glass matrix. We can understand from Fig. 1 that the position and splitting width (quadrupole splitting) of the doublet peaks depend on the composition. The Mössbauer parameters of gallate and aluminate glasses are summarized in Table 1, together with the glass transition temperatures (T_g). The isomer shift (δ) indicates that Fe^{3+} ions are tetrahedrally coordinated with oxygen atoms, because each δ value is smaller than 0.4 mm s^{-1} as was observed in several kinds of oxide glasses.[7,15–23] It is therefore considered that the Fe^{3+} ions are forming FeO_4 tetrahedra at substitutional sites of the GaO_4 or AlO_4 tetrahedra. The presence of GaO_4 and AlO_4 tetrahedra has already been proposed in the IR[3,4,9] and Mössbauer[7] studies. Figure 2 indicates that an increasing CaO or BaO content results in a continuous decrease in the δ. This is ascribed to an increased s-electron density at the iron nucleus caused by a formation of NBO atoms in the GaO_4 and AlO_4 tetrahedra. The formation of NBO in BO_4 and/or SiO_4 tetrahedra has been observed in borate[24,25] and borosilicate[26] glasses in the form of a decrease in the δ of Fe^{3+} ions. In the case of potassium gallate glasses, $x$$K_2O$·(90−$x$)$Ga_2O_3$·10$Fe_2O_3$,[7] the formation of NBO was clearly observed as an increase in the absorption area (fraction). Figure 2 indicates that a curve drawn for the composition dependency of δ for the calcium gallate glasses (Fig. 2a) holds for the results of barium gallate glasses (Fig. 2b). We can speculate from Fig. 2a and 2b that the structural change of calcium gallate glasses is essentially the same as that of barium gallate glasses. Figure 2c indicates that the δ of calcium aluminate glasses is a little smaller than that of the calcium gallate glasses (Fig. 2a). This finding suggests that the Al^{3+}(Fe^{3+})-oxygen bond is more covalent than the Ga^{3+}(Fe^{3+})-oxygen bond because of the smaller ionic radius of Al^{3+} ion (0.050 nm[27]) and therefore shorter Al^{3+}-oxygen bond length. (The ionic radius of Ga^{3+} ion is reported to be 0.062 nm.[27]) The similar com-

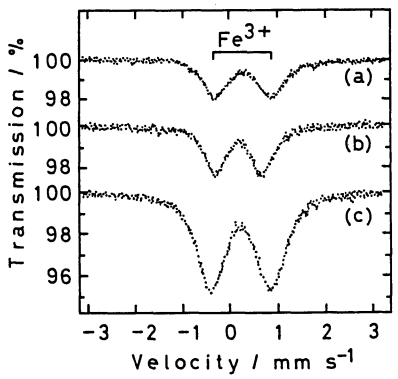

Fig. 1. Mössbauer spectra of (a) 40CaO·50Ga_2O_3·10Fe_2O_3, (b) 65BaO·25Ga_2O_3·10Fe_2O_3, and (c) 55CaO·40Al_2O_3·5Fe_2O_3 glasses measured at room temperature.

Table 1. Mössbauer Parameters and Glass Transition Temperature of Gallate and Aluminate Glasses

Composition	δ[a]	Δ[b]	Γ[c]	T_g[d]
	mm s^{-1}	mm s^{-1}	mm s^{-1}	°C
40CaO·50Ga_2O_3·10Fe_2O_3	0.28	1.20	0.61	702
45CaO·45Ga_2O_3·10Fe_2O_3	0.28	1.23	0.66	708
50CaO·40Ga_2O_3·10Fe_2O_3	0.25	1.23	0.65	710
55CaO·35Ga_2O_3·10Fe_2O_3	0.24	1.21	0.64	720
60CaO·30Ga_2O_3·10Fe_2O_3	0.21	1.24	0.62	728
65BaO·25Ga_2O_3·10Fe_2O_3	0.16	0.98	0.53	580
67.5BaO·22.5Ga_2O_3·10Fe_2O_3	0.16	0.98	0.50	580
70BaO·20Ga_2O_3·10Fe_2O_3	0.18	1.01	0.57	583
55CaO·40Al_2O_3·5Fe_2O_3	0.19	1.26	0.66	750
58CaO·37Al_2O_3·5Fe_2O_3	0.20	1.29	0.69	767
60CaO·35Al_2O_3·5Fe_2O_3	0.18	1.30	0.67	773
60CaO·30Al_2O_3·10Fe_2O_3	0.19	1.28	0.63	761

a) The isomer shift. The error is estimated to be ±0.01 mm s^{-1}. b) The quadrupole splitting with the error of ±0.02 mm s^{-1}. c) The linewidth (FWHM) with the error of ±0.02 mm s^{-1}. d) The glass transition temperature. The error is ±5 °C.

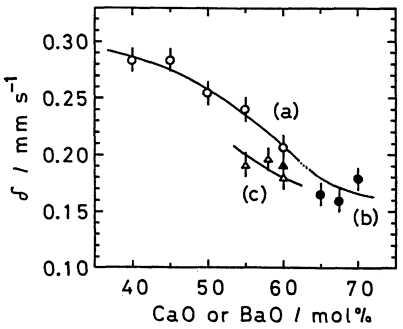

Fig. 2. The isomer shift (δ) of (a) xCaO·(90−x)Ga_2O_3·10Fe_2O_3, (b) xBaO·(90−x)Ga_2O_3·10Fe_2O_3, and (c) xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses plotted against the CaO or BaO contents.

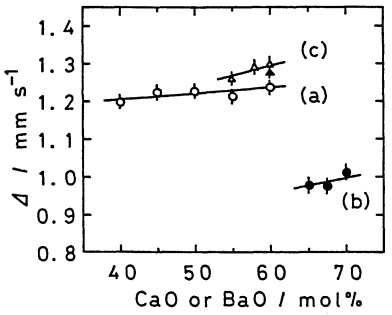

Fig. 3. The quadrupole splitting (Δ) of (a) xCaO·(90−x)Ga_2O_3·10Fe_2O_3, (b) xBaO·(90−x)Ga_2O_3·10Fe_2O_3, and c) xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses plotted against the CaO or BaO contents.

position dependencies of δ observed in the calcium gallate and calcium aluminate glasses suggest that these glasses have very similar local structures with each other.

Quadrupole splitting (Δ), corresponding to the difference in the energy level of nucleus (excited state) having a nuclear spin of 3/2, is expressed by

$$\Delta=(e^2qQ/2)\times(1+\eta^2/3)^{1/2}, \quad (1)$$

where eq and Q are the electric field gradient tensor ($=V_{zz}$) along the z-axis and the nuclear quadrupole moment, respectively.[28] The η is an asymmetry parameter of the electric field gradient ($(V_{xx}-V_{yy})/V_{zz}$).[28] The Δ will give us useful information on the local distortion of glasses, i.e., a deviation from the cubic symmetry. Figure 3 demonstrates the composition dependency of Δ for the calcium gallate, barium gallate, and calcium aluminate glasses. A solid triangle indicates the Δ of 60CaO·30Al_2O_3·10Fe_2O_3 glass (1.28 mm s^{-1}), which is identical with that of 60CaO·35Al_2O_3·5Fe_2O_3 glass (1.30 mm s^{-1}) within the experimental error of ±0.02 mm s^{-1}. In contrast to the gradual decrease observed for δ (Fig. 2), the Δ of xCaO·(90−x)Ga_2O_3·10Fe_2O_3 (Fig. 3a) and xBaO·(90−x)Ga_2O_3·10Fe_2O_3 (Fig. 3b) glasses has a discrete composition dependency. Figure 3a demonstrates that the Δ of calcium gallate glasses is much greater than that of barium gallate glasses (Fig. 3b). The Δ of Fe^{3+} ions, having a symmetric $3d^5$ electron configuration, evidently reflects the electric field gradient (eq) caused by the distortion of FeO_4 (GaO_4 and AlO_4) tetrahedra. Therefore, it is understood that the GaO_4 tetrahedra in the calcium gallate glasses are much more distorted than those in the barium gallate glasses. The Δ of xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses (Fig. 3c) is only a little larger than that of xCaO·(90−x)Ga_2O_3·10Fe_2O_3 glasses (Fig. 3a), indicating that the AlO_4 tetrahedra are a little more distorted than the GaO_4 tetrahedra. However, the almost comparable δ and Δ obtained for the calcium gallate and calcium aluminate glasses suggest that these glasses have very similar local and skeleton (three-dimensional network) structures with each other. On the other hand, the local distortion of barium gallate glasses (Fig. 3b) seems to be much less than that of the calcium gallate (Fig. 3a) and calcium aluminate (Fig. 3c) glasses. This can be explained by the difference in the ionic potential of Ba^{2+} ion (Z/r=14.8 nm^{-1}) which is smaller than that of Ca^{2+} ion (20.2 nm^{-1}). The ionic potential is obtained by using the ionic radii of 0.135 and 0.099 nm for Ba^{2+} and Ca^{2+}, respectively.[27] The Ba^{2+} ions having smaller Z/r will cause less distortion in the GaO_4 tetrahedra than the Ca^{2+} ions having larger Z/r. The increase in Δ observed with increasing CaO or BaO contents (Fig. 3a—3c) is ascribed to the relatively large ionic potential of the Ca^{2+} and Ba^{2+} ions compared with that of alkali metal ions. The Ca^{2+} and Ba^{2+} ions will easily attract the oxygen atoms constituting the GaO_4 and AlO_4 tetrahedra at the neighboring sites. By the way, the formation of NBO was observed in the form of a simultaneous decrease in δ and Δ in the case of potassium borate[24,25] and potassium borosilicate[26] glasses. The K^+ ion having a small Z/r (7.52 nm^{-1}) will produce a small distortion in the FeO_4, BO_4, and SiO_4 tetrahedra. In such a case a decrease in Δ will be observed when the NBO is formed, because the chemical interaction between the Fe^{3+} ions and NBO atoms is superior to that between the K^+ ions and oxygen atoms. This is also the case for the potassium gallate,[7] potassium tellurite,[16] and potassium vanadate[17,19] glasses. Large Δ values obtained for the gallate glasses may partly be related to the presence of so called "three-fold coordinated oxygen" atoms,[3-5] especially when the Ga_2O_3 content is high. The "three-fold coordinated oxygen" will cause a great distortion in the GaO_4 and FeO_4 tetrahedra.

The glass transition temperature (T_g) is illustrated in Fig. 4, which presents three straight lines with positive slopes. A solid triangle indicates the T_g of 60CaO·30Al_2O_3·10Fe_2O_3 glass, 761 °C, which is almost identical with that of 60CaO·35Al_2O_3·5Fe_2O_3 glass. It is noteworthy that Fig. 4 has a characteristic composition dependency similar to that of Fig. 3. The T_g of xCaO·(90−x)Ga_2O_3·10Fe_2O_3 glasses (702—

728 °C) is much higher than that of xBaO·(90−x)Ga_2O_3·10Fe_2O_3 glasses (580—583 °C). This is also explained in connection with the difference in the ionic potential (Z/r) of Ca^{2+} and Ba^{2+} ions. A strong chemical bond between the Ca^{2+} and oxygen will bring about much distorted GaO_4 tetrahedra, which will be reflected in the higher T_g of calcium gallate glasses. The local distortion of xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses, having the T_g of 750—773 °C and Δ of 1.26—1.30 mm s^{-1}, is the most noticeable among all the oxide and non-oxide glasses studied so far by this authors' group. In the study of gallate,[7] tellurite,[15,16] and vanadate[17-23] glasses, the T_g and Δ changed drastically when the glass matrix (skeleton) underwent a drastic structural change, depending on the ionic potential (Z/r) of the alkali or alkaline earth metal ions. These experimental results indicate that both the T_g and Δ have a close relationship with the Z/r of Ca^{2+} or Ba^{2+} ions, which play a role of network modifier (NWM) at the interstitial sites. Figure 5a presents the T_g-Δ plot for the gallate and aluminate glasses studied in this paper (indicated with open circles) and for the potassium gallate[7] and several tellurite[15,16] and vanadate[17-22] glasses studied recently. The latter results are illustrated with solid circles. Figure 5a indicates a linear relationship between the T_g and Δ: all the T_g values are increased in proportion to the Δ, i.e., to the distortion of network former (NWF)-oxygen polyhedra. The T_g (°C) and Δ (mm s^{-1}) can be expressed by the following equation,

$$T_g = a\Delta + b, \quad (2)$$

where "a" is 680 °C mm^{-1} s and "b" is −180 °C when the Fe^{3+} ions are present at substitutional sites of the NWF in the oxide glasses. Figure 5a demonstrates that most of the T_g values obey the "T_g-Δ rule" within the error of ±100 °C. It seems that the T_g is little related to the single bond energy of NWF-oxygen bond. According to the calculation made by Sun,[29] the bond energies are reported to be 3.9—4.9, 3.0, 3.9—5.2, 2.9, and 3.4—4.4 eV mol^{-1} for V-O, Te-O, B-O, Ga-O, and Al-O bonds, respectively. It is known that vanadate glasses have much lower T_g (165—337 °C[17-22]) than the gallate (580—728 °C) and aluminate (750—773 °C) glasses, although the V-O bond energy (3.9—4.9 eV) is higher than that of the Ga-O (2.9 eV) and Al-O (3.4—4.4) bonds. The T_g of R_2O-B_2O_3) glasses (R=Li, Na, K, Rb, Cs) has already been reported to be in the range of 332—482 °C,[30] and the T_gs of CaO-B_2O_3 and BaO-B_2O_3 glasses were reported to be 660—667 and 578—610 °C, respectively.[31] The T_g values are located between those of the gallate and tellurite glasses, although the single bond energy of B-O bond (3.9—5.2 eV) is much greater than that of the Ga-O (2.9 eV) and Te-O (3.0 eV) bonds. Nishida and Takashima reported that Δ of K_2O-B_2O_3 glasses containing 7 mol% Fe_2O_3 is in the range of 0.86—1.07 mm s^{-1}.[24] The Δ values are also located between those of the gallate and tellurite glasses illustrated in Fig. 5a, indicating that borate glasses obey the "T_g-Δ rule". (In the Mössbauer study of K_2O-B_2O_3-Fe_2O_3 glasses,[24] no DTA measurement was made.) The T_g and Δ of these glasses are increased in the following order:

vanadate<tellurite<borate<gallate<aluminate glasses.

On the other hand, the single bond energy is increased in the order:

gallate<tellurite<aluminate<vanadate<borate glasses.

In the light of these results, we can conclude that the T_g is primarily determined by the distortion of NWF-oxygen polyhedra and is little related to the single bond energy of the NWF-oxygen bond.

We have already elucidated that T_g has a close relationship with the structural changes such as a formation of NBO, a change of the coordination number of NWF, and a change of the dimension of skeleton structure.[7,14-26] It should be noted that these structural changes, at the same time, accompany

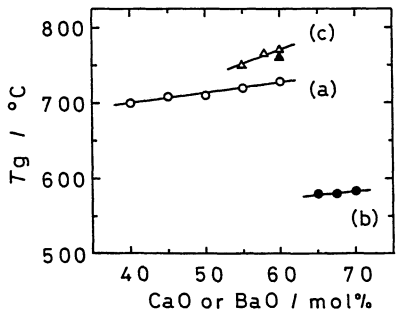

Fig. 4. The glass transition temperature (T_g) of (a) xCaO·(90−x)Ga_2O_3·10Fe_2O_3, (b) xBaO·(90−x)Ga_2O_3·10Fe_2O_3, and (c) xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses plotted against the CaO or BaO contents.

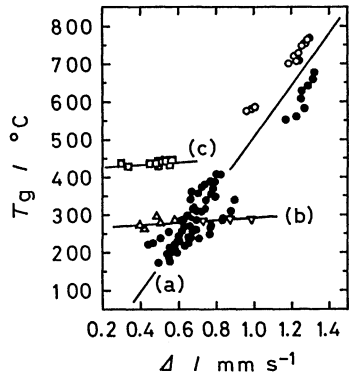

Fig. 5. (a): A T_g-Δ plot of xCaO·(90−x)Ga_2O_3·10Fe_2O_3, xBaO·(90−x)Ga_2O_3·10Fe_2O_3, and xCaO·(95−x)Al_2O_3·5Fe_2O_3 glasses (open circles). The T_g and Δ of other oxide glasses[7,15-22] are also illustrated with solid circles; (b): A T_g-Δ plot of phosphate[32] and fluorozirconate[33] glasses; (c); A T_g-Δ plot of sulfate glasses.[34]

the distortion of NWF-oxygen polyhedra. It is expected that the "T_g-Δ rule" is also applicable to the study of oxide glasses in which Fe^{3+} ions are present at interstitial sites of the glass matrix. In such a case, the T_g-Δ plot will give different "a" and "b" values because such Fe^{3+} ions have different local distortion and structure. This is shown in Fig. 5b, in the region $0.4\ mm\ s^{-1} \leqq \Delta < 0.6\ mm\ s^{-1}$, in which case the Fe^{3+} ions are present at the interstitial sites of K_2O-P_2O_5-Fe_2O_3 glasses composed of PO_4 tetrahedra.[32] Figure 5b indicates that T_g is proportional to the Δ, although "a" (35 °C mm^{-1} s) and "b" (260 °C) are quite different from those obtained for the several oxide glasses in which the Fe^{3+} ions are present at substitutional sites of the individual NWF. The much smaller "a" value indicates that T_g is a little affected by the local distortion of the NWM-oxygen polyhedra present at the interstitial sites.

It is considered that the T_g-Δ plot for non-oxide glasses will also give characteristic "a" and "b" values. Figure 5b (T_g plotted in the region $0.7\ mm\ s^{-1} < \Delta < 1.0\ mm\ s^{-1}$) and 5c are the results of BaF_2-ZrF_4-$FeF_2(FeF_3)$[33] and K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$[34] glasses studied by this authors' group. These glasses also have "a" value (35 °C mm^{-1} s) smaller than that of the oxide glasses ("a"=680 °C mm^{-1} s) in which the Fe^{3+} ions are present at substitutional sites of the individual NWF. It is already reported that the Fe^{3+} ions are present at the interstitial sites in these glasses.[33,34] The "b" values obtained for the BaF_2-ZrF_4-$FeF_2(FeF_3)$ and K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ glasses are 260 and 420 °C, respectively. As is shown in Fig. 5b, the "a" and "b" values obtained for the BaF_2-ZrF_4-$FeF_2(FeF_3)$ glasses are the same as those obtained for the K_2O-P_2O_5-Fe_2O_3 glasses. These findings indicate that "a" depends on whether the Fe^{3+} ions are present at the substitutional or interstitial sites, and that "b" depends on whether the glass matrix has a continuous network structure or not. The K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ glasses are composed of ionically packed SO_4 tetrahedra.[34] These experimental results suggest that the T_g-Δ plot is useful for determining whether the Mössbauer ions (Fe^{3+} in this paper) are present at the substitutional or interstitial sites.

On the basis of the experimental results obtained in this paper, it is considered that the highly optical (IR) transparency of the gallate (ca. 7 μm) and aluminate (ca. 6 μm) glasses has a close relationship with their noticeable local distortion shown in Fig. 5a and with a great number of NBO atoms. This is also the case for the tellurite glasses,[15,16] although they have less extent of distortion than the gallate and aluminate glasses. It seems that the relatively high IR transparency of the tellurite glasses (ca.5 μm) is ascribed to a large number of NBO atoms, because the local distortion of the tellurite glasses is comparable to that of the vanadate glasses (Fig. 5a). These results suggest that the noticeable local distortion and/or a large number of NBO atoms produce the highly optical (IR) transparency of the oxide glasses.

Conclusion

1) The Fe^{3+} ions are present at the substitutional sites of the Ga^{3+} and Al^{3+} ions (NWF) constituting the GaO_4 and AlO_4 tetrahedra, respectively.

2) Introduction of CaO or BaO into the Ga_2O_3 and Al_2O_3 matrix results in a formation of NBO in the GaO_4 and AlO_4 tetrahedra, respectively. At the same time, a little increased local distortion is brought about in the three-dimensional network structure.

3) The local distortion becomes more noticeable with an increasing ionic potential (Z/r) of the alkaline earth metal ions (Ca^{2+} and Ba^{2+}) present at the interstitial sites neighboring to the oxygen atoms.

4) The T_g of several oxide glasses is proportional to the distortion of NWF-oxygen polyhedra, being expressed by $T_g = a\Delta + b$, where "a" is 680 °C mm^{-1} s and "b" is −180 °C when the Fe^{3+} ions are present at the substitutional sites of the individual NWF. The "a" and "b" are 35 °C mm^{-1} s and 260 °C, respectively when the Fe^{3+} ions are present at the interstitial sites.

5) The highly optical (IR) transparency of the gallate and aluminate glasses is closely concerned with the noticeable local distortion and a large number of NBO atoms in the GaO_4 and AlO_4 tetrahedra.

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