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Correlation between the structure and glass transition temperature of potassium, magnesium and barium tellurite glasses

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The Mössbauer spectrum of tellurite glasses, containing 5 mol% Fe_2O_3 as a probe, consists of a paramagnetic quadrupole doublet with an isomer shift of $0.39 \pm 0.01\,\mathrm{mm\,sec^{-1}}$. This indicates that Fe^{3+} ions are present at substitutional sites of Te^{4+} ions constituting distorted TeO_4 trigonal bipyramids, each of which has one oxygen vacancy at an equatorial site. On increasing the K_2O content from 0 to 35 mol%, the quadrupole splitting (Δ) for potassium tellurite glasses decreases continuously from 0.76 to $0.44\,\mathrm{mm\,sec^{-1}}$. On the other hand, Δ for magnesium and barium tellurite glasses increases with increasing MgO and BaO content, respectively. When the alkali or alkaline earth oxide contents are the same as each other, Δ increases in proportion to the ionic potential (Z/r) of the alkali or alkaline earth metal ion. These results suggest that the glass matrices of alkali and alkaline earth tellurite glasses are continuously changed into a chain and a three-dimensional network structure, respectively. Differential thermal analysis studies reveal that there exists a linear relationship between the glass transition temperature T_g and the quadrupole splitting, indicating that T_g is primarily determined by the magnitude of the distortion of TeO_4 trigonal bipyramids. This relationship is also applicable to several oxide glasses.

1. Introduction

Tellurite (TeO_2-based) glasses have attracted much attention because of their excellent physical properties such as low glass transition temperature T_g, high refractive index, high dielectric constant, high thermal expansion coefficient and high optical transmission in the infrared (IR) region [1–5]. Brady [6] reported that TeO_2 glass is composed of distorted TeO_6 octahedra. Dimitriev and Dimitrov [7] showed that the coordination number of Te^{4+} in V_2O_5–TeO_2 glasses is changed from 4 to 3 by incorporating V_2O_5 into the TeO_2 matrix. Dimitriev *et al.* [8] also reported that alkali tellurite glasses are composed of TeO_4 groups by using X-ray diffraction and IR techniques. On the basis of IR measurements, Mochida *et al.* [9] elucidated that alkali and alkaline earth tellurite glasses have a layer structure composed of distorted TeO_4 trigonal bipyramids, each of which has a lone electron pair and an oxygen vacancy at an equatorial site. Dimitriev *et al.* [10] showed that introduction of MoO_3 into the TeO_2 matrix results in a structural change from TeO_4 trigonal bipyramids to TeO_3 trigonal pyramids. A neutron diffraction study performed by Neov *et al.* [11] also revealed that tellurite glasses are composed of TeO_4 trigonal bipyramids. Mössbauer studies of tellurite glasses performed by Binczycka *et al.* [12] and Bahgat *et al.* [13] suggested that iron is present as octahedral Fe^{3+} ions. Bahgat and co-workers [14, 15] suggested that tetrahedral Fe^{3+} ions are also present in strontium and rare-earth tellurite glasses. Mössbauer and differential thermal analysis (DTA) studies performed by Nishida *et al.* [16] revealed that the glass matrix of sodium tellurite glasses is gradually changed, with increasing Na_2O content, from the original two- or three-dimensional network structure to a chain structure having non-bridging oxygen (NBO).

The present Mössbauer study was performed in order to elucidate the local structure around Te^{4+} and Fe^{3+} ions and the skeleton structure of alkali and alkaline earth tellurite glasses containing a small amount (5 mol%) of Fe_2O_3 as a Mössbauer probe. DTA measurements were performed in order to determine the glass transition temperatures T_g, since it is known that T_g has a close relationship with the structural change of the glass matrix [16–27].

2. Experimental procedure

Potassium tellurite glasses denoted by $xK_2O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ were prepared by fusing individual mixtures (1 g) of commercially available K_2CO_3, TeO_2 and Fe_2O_3, of a guaranteed reagent grade, at 750° C for 1 to 2 h. After fusion in air, each melt in a platinum crucible was immediately quenched with ice-cold water. Transparent and light-brown glasses were obtained in the compositional region $0 \leqslant x \leqslant 35$.

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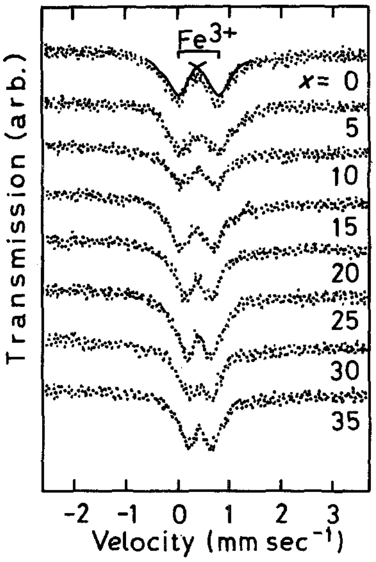

Figure 1 Mössbauer spectra of $x K_2O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ glasses measured at room temperature.

Magnesium and barium tellurite glasses were respectively prepared from MgO and BaO of a guaranteed reagent grade. Each mixture (1 g) composed of MgO or BaO, TeO_2 and Fe_2O_3 was melted at 750 to 850° C for 1 to 1.5 h. Glass formation was possible in the compositional ranges $0 \leqslant x \leqslant 25$ and $0 \leqslant x \leqslant 30$ for the magnesium and barium tellurite glasses, respectively. The composition of these glasses is denoted by $x R'O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$, where R' = Mg or Ba.

Mössbauer measurements were made on pulverized samples by a constant acceleration method at room temperature. ^{57}Co (10 mCi) diffused into a palladium foil was used as a Mössbauer source. As a reference of isomer shift, a piece of metallic iron foil enriched with ^{57}Fe was used, which was also used for calibrating the velocity scale of the spectrometer. Each Mössbauer spectrum was analysed into a quadrupole doublet peak having an equal line-width, using a least-squares method. DTA measurements on the tellurite glasses were made ranging from room temperature to 600° C at a heating rate of 5° C min^{-1}. α-Al_2O_3 powder was used as a standard in DTA measurements.

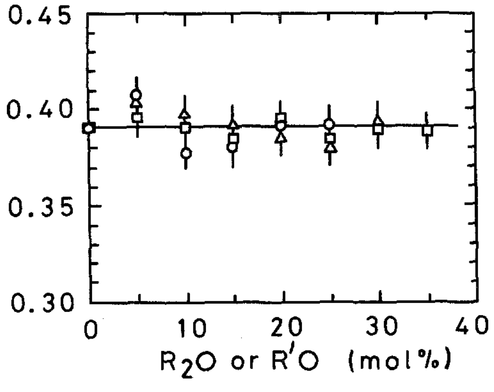

Figure 2 Isomer shift (δ) for (□) $x K_2O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$, (○) $x MgO \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ and (△) $x BaO \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ glasses plotted against the alkali or alkaline earth oxide content.

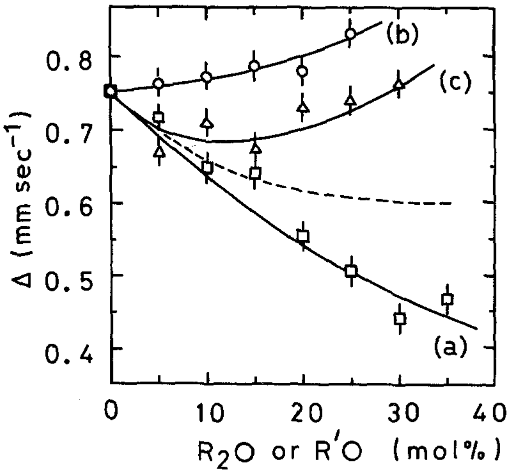

Figure 3 Composition dependence of quadrupole splitting (Δ) for (a) $x K_2O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$, (b) $x MgO \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ and (c) $x BaO \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ glasses; also for (- - -) $x Na_2O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ glasses from Nishida *et al.* [16].

3. Results and discussion

The composition dependence of the Mössbauer spectra for $x K_2O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ glasses is illustrated in Fig. 1, which shows a continuous decrease in the quadrupole splitting with increasing K_2O content. The Mössbauer spectra of $x MgO \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ and $x BaO \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ glasses are also composed of quadrupole doublet peaks similar to those shown in Fig. 1. In the magnesium and barium tellurite glasses, however, increasing MgO or BaO content causes an increase in the quadrupole splitting, as is shown in Fig. 3. All the isomer shift values obtained for the potassium, magnesium and barium tellurite glasses are shown in Fig. 2, which indicates that isomer shift is equal to or less than 0.40 mm sec^{-1} and is located around 0.39 ± 0.01 mm sec^{-1}. A very similar result has been obtained for sodium tellurite glasses, $x Na_2O \cdot (95 - x)TeO_2 \cdot 5Fe_2O_3$ by the authors' group [16].

These results suggest that most Fe^{3+} ions are present at substitutional sites of Te^{4+} ions, which constitute the matrix of tellurite glasses in the form of distorted TeO_4 trigonal bipyramids. Furthermore, each TeO_4 or FeO_4 trigonal bipyramid, having an sp^{3}d hybrid orbital, will have one oxygen vacancy at an equatorial site [9–11, 16]. Isomer shift values larger than those of the tetrahedral Fe^{3+} species will be concerned with the oxygen vacancy having electrically positive charge, and the 4s electrons of Fe^{3+} ions will be attracted to the oxygen vacancy. (The decrease in 4s-electron density at the iron nucleus is observed as an increased isomer shift). The larger isomer shift will also be concerned with a smaller contribution of s-orbital to the sp^{3}d hybrid orbital of FeO_4 trigonal bipyramids than the contribution to the sp^3 orbital of FeO_4 tetrahedra. The invariable isomer shift values (Fig. 2) indicate that Fe^{3+} ions attached to oxygen vacancies are less sensitive to the change of electron density at the iron nucleus. From the larger and invariable isomer shift values (0.39 ± 0.01 mm sec^{-1}) observed for alkali and alkaline earth tellurite glasses, we can deduce the presence of oxygen vacancies at neighbouring sites of Fe^{3+} and Te^{4+} ions constituting distorted FeO_4 and TeO_4 trigonal bipyramids, respectively.

The quadrupole splitting (Δ) corresponding to the Mössbauer transition between 1/2 and 3/2 states is expressed by

$$\Delta = \left(\frac{e^2qQ}{2}\right)\left(1 + \frac{\eta^2}{3}\right)^{1/2} \qquad (1)$$

where eq and Q are the electric field gradient tensor ($= V_{zz}$) along the z axis and the nuclear quadrupole moment, respectively [28]. e^2qQ is often called the "quadrupole coupling constant". An asymmetry parameter of the electric field gradient, $\eta = (V_{xx} - V_{yy})/V_{zz}$, is defined to be in the range $1 \geqslant \eta \geqslant 0$. It is also defined that the sum of the electric field gradient in every direction becomes zero, i.e. $V_{xx} + V_{yy} + V_{zz} = 0$, and that $|V_{zz}| \geqslant |V_{yy}| \geqslant | V_{xx}|$. The asymmetry parameter η becomes zero when the electric field gradient is axially symmetric ($V_{xx} = V_{yy}$). This is the case for a chain structure, in which the Te–O_{ax} bond is parallel to the z-axis. (O_{ax} indicates an oxygen atom present at an axial site of TeO_4 trigonal bipyramids [9–11].) η becomes unity when there is an extremely anisotropic chemical bond in the yz plane, where $V_{xx} = 0$ and $V_{yy} = -V_{zz}$. This is the case for a layer structure, where continuous Te–O_{eq} and Te–O_{ax} bonds are spreading two-dimensionally in the yz plane. (O_{eq} indicates an oxygen atom present at an equatorial site of TeO_4 trigonal bipyramids [9–11].) It is considered that η and e^2qQ give us useful information on the local skeleton structure of tellurite glasses and other oxide glasses, especially when the Mössbauer atoms are present at substitutional sites of network-forming atoms such as tellurium, vanadium, gallium and boron.

Curve (a) in Fig. 3 indicates the composition dependence of the quadrupole splitting (Δ) for $x K_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses. The drastic decrease in Δ, observed with increasing K_2O content, is similar to the result for $x Na_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses [16] shown by a dotted line in Fig. 3. It is considered that alkali-free $95 TeO_2 \cdot 5 Fe_2O_3$ glass has a layer structure, similarly to the case of β-TeO_2 [9, 16]. In such a case, Δ becomes $1.15 e^2qQ/2$ by substituting unity for the asymmetry parameter η in the Equation 1. When potassium tellurite glass has an axially symmetric chain structure, we can evaluate Δ to be $e^2qQ/2$. These results indicate that Δ will decrease from 0.76 to 0.66 mm sec^{-1} (87%) when the glass matrix of tellurite glasses is changed from a layer structure ($\eta = 1$) to a chain structure ($\eta = 0$) under the condition that e^2qQ is invariable. The value of Δ obtained for $x K_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses is decreased much more than this expection when the K_2O content exceeds 20 mol % (curve (a) in Fig. 3). On the other hand, Δ for $x Na_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses (dotted line in Fig. 3) is located around 0.60 mm sec^{-1} when the Na_2O content is 20 $\sim$ 30 mol %.

Comparing the composition dependence of Δ for potassium tellurite glasses with that for sodium tellurite glasses, we can understand that the smaller ionic potential ($Z/r = 7.52\,nm^{-1}$) of the K^+ ion is responsible for the pronounced decrease of Δ, which reflects a drastic change of the glass matrix. In the $x Na_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses, the slightly larger ionic potential ($10.5\,nm^{-1}$) of Na^+ ions will bring about an increased chemical bond strength between the Na^+ ions and oxygen atoms constituting the glass matrix. In such a case, larger e^2qQ and therefore larger Δ will be observed, because the distortion of TeO_4 and FeO_4 trigonal bipyramids in the $x Na_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses [16] is more remarkable than that in the $x K_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses. From the Δ values of 0.44 and 0.60 mm sec^{-1}, it is evaluated that e^2qQ for $x K_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glass ($x = 35$) is about 2/3 times that of $x Na_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glass ($x = 35$) when η is zero. The decrease in Δ observed both for $x Na_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ and $x K_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses is ascribed to a decreased degree of cross-linking and a depolymerization of the chain structure. This structural change will accompany the formation of NBO at an equatorial or axial site of distorted TeO_4 and FeO_4 trigonal bipyramids.

Curve (b) in Fig. 3 illustrates the composition dependence of Δ for $x MgO \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses, which shows a continuous increase with increasing MgO content. The value of Δ for $x BaO \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses also increases with increasing BaO content when it is higher than 15 mol % (curve (c) in Fig. 3). It is seen from Fig. 3 that Δ for $x MgO \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses is greater than that for $x BaO \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses at any composition. This is also explained by the ionic potential of Mg^{2+} ions ($Z/r = 30.8\,nm^{-1}$) which is much larger than that of Ba^{2+} ions ($Z/r = 14.8\,nm^{-1}$). A strong ionic bond between Mg^{2+} ion and oxygen atom will cause large e^2qQ and large distortion in the TeO_4 trigonal bipyramids, as discussed for $x Na_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses in comparison with $x K_2O \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses.

Curve (c) in Fig. 3 indicates that the distortion is not so prominent in $x BaO \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses, and that Δ shows a slight decrease when the BaO content is low. It seems that the local structure of barium tellurite glasses with lower BaO contents is similar to that of sodium tellurite glasses, probably because of the comparable Z/r values. (Z/r values are 14.8 and $10.5\,nm^{-1}$ for Ba^{2+} and Na^+ ions, respectively.) Since η is the maximum (unity) in the case of layer compounds, we cannot account for the increased Δ on the basis of the increase in η. Therefore, the increase in Δ is attributed to the increased e^2qQ due to the distortion of TeO_4 and FeO_4 trigonal bipyramids.

Incidentally, a similar composition dependence of Δ has been observed for alkali [17–20] and alkaline earth [19, 20] vanadate glasses. In the alkaline earth vanadate glasses, continuous increases in Δ were ascribed to a change of glass matrix from the original layer structure, composed of VO_5 tetragonal pyramids, to a three-dimensional network structure composed of VO_4 tetrahedra. These results on vanadate glasses suggest that the increase in Δ observed for $x MgO \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ and $x BaO \cdot (95 - x) TeO_2 \cdot 5 Fe_2O_3$ glasses reflects a change of glass matrix from

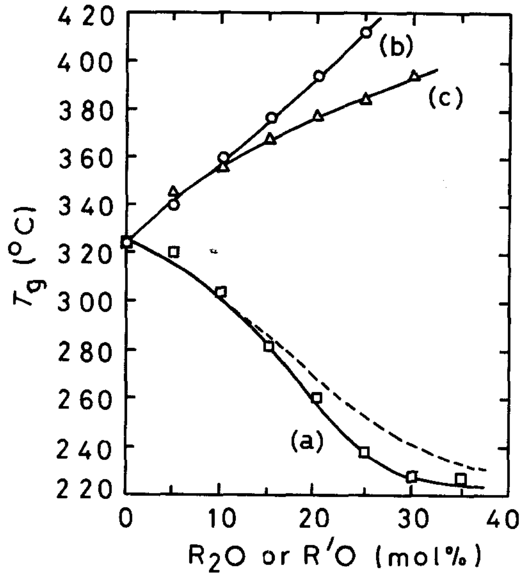

Figure 4 Composition dependences of glass transition temperature T_g of (a) $xK_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$, (b) $xMgO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ and (c) $xBaO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses; also (- - -) $xNa_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses [16].

the original layer structure to a three-dimensional network structure composed of highly distorted TeO_4 and FeO_4 trigonal bipyramids. The increase in e^2qQ, due to an increased electric field gradient tensor ($eq = V_{zz}$), is ascribed to a change of the glass matrix into a complicated three-dimensional network structure having a higher degree of cross-linking. It is speculated that alkaline earth oxide is preferentially present at interstitial sites between two layers located along the yz plane, attracting the layers to form a new bond in the x-axis direction.

The composition dependence of the glass transition temperature T_g is demonstrated in Fig. 4. The dotted line in Fig. 4 corresponds to the T_g of $xNa_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses [16]. The drastic decrease in T_g indicates that the glass matrix is changed into a chain structure. The T_g of $xK_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses shows a composition dependence similar to that of $xNa_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses. Fig. 4 indicates that T_g of $xNa_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses is higher than that of $xK_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses, similarly to the results for Δ shown in Fig. 3. In contrast to the alkali tellurite glasses, T_g of $xMgO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ (curve (b) in Fig. 4) and $xBaO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ (curve (c)) glasses increases drastically with increasing MgO or BaO content. The T_g of $xMgO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses is higher than that of $xBaO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses. A similar result has been observed for Δ (curves (b) and (c) in Fig. 3).

These experimental results indicate that both Δ and T_g have a correlation with the ionic potential (Z/r) of alkali and alkaline earth metal ions. This means that T_g is also affected by the distortion of TeO_4 and FeO_4 trigonal bipyramids, as discussed for Δ in connection with Z/r, e^2qQ and η. Mössbauer and DTA studies of several alkali [17–20], alkaline earth [19, 20], phosphorus [21] and silver [22] vanadate glasses revealed that structural change of the glass matrix (skeleton structure) is well reflected in both T_g and Δ. In these glasses, T_g changed drastically when the glass matrix underwent a change into a chain or a three-dimensional network structure. It is considered that this type of structural change is also the case for the tellurite glasses originally having a layer structure composed of distorted TeO_4 trigonal bipyramids.

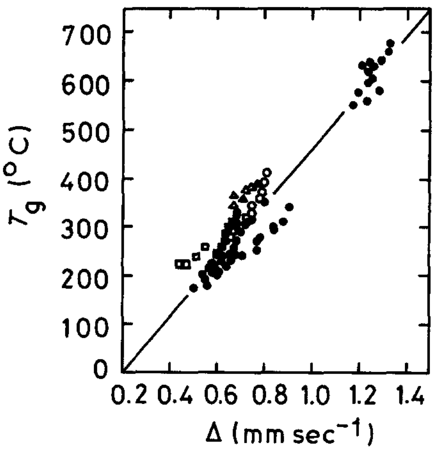

Figure 5 Correlation between T_g and Δ of $xK_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$, $xMgO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ and $xBaO \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses. Values for $xNa_2O \cdot (95-x)TeO_2 \cdot 5Fe_2O_3$ glasses [16] are also plotted together with those of several vanadate [17–22] and gallate [23, 24] glasses (see text for details).

The present Mössbauer and DTA study reveals that both Δ and T_g are closely concerned with the ionic potential (Z/r) of alkali and alkaline earth metal ions ionically bonded with oxygen atoms at the neighbouring sites. The larger is the Z/r value, the higher become both the distortion (Fig. 3) and T_g (Fig. 4). Fig. 5 illustrates the relationship between T_g and Δ for all the tellurite glasses studied in this paper, together with the results for sodium tellurite (indicated by solid squares [16]), several vanadate [17–22] and gallate [23, 24] glasses. In Fig. 5, solid circles plotted around 550 to 670° C (T_g) and 1.17 to 1.32 mm sec^{-1} (Δ) indicate the results for gallate glasses [23, 24]. Other solid circles plotted around 180 to 350° C (T_g) and 0.5 to 0.9 mm sec^{-1} (Δ) correspond to vanadate glasses [17–22].

Fig. 5 shows a good correlation between T_g and Δ for all the vanadate, tellurite and gallate glasses studied by the authors' group. The linear relationship shown in Fig. 5 indicates that T_g is primarily determined by the magnitude of distortion of network-former (NWF)–oxygen polyhedra, i.e. VO_4 and GaO_4 tetrahedra and TeO_4 trigonal bipyramids. It is noteworthy that this relationship is valid for several oxide glasses having different types of NWF. In the case of gallate glasses [23, 24], the large Δ values are ascribed to so-called "three-coordinated" oxygen atoms, which seem to produce highly distorted GaO_4 tetrahedra. According to the calculation made by Sun [29], single bond energies in the oxide glasses are 90 ~ 112, 68 and 67 kcal mol^{-1} for V–O, Te–O and Ga–O bonds, respectively. Fig. 5 demonstrates that T_g is inversely proportional to the bond energy, being increased in the order of vanadate, tellurite and gallate glasses.

We can therefore conclude that T_g has little relation to the chemical bond strength between the NWF and oxygen atoms. From the structural point of view, T_g

has a close relationship with a formation of NBO, a change of the coordination number of NWF and a change of dimensions of the glass matrix [16–27]. All these phenomena, at the same time, accompany an increase or decrease in the distortion of NWF–oxygen polyhedra. On the basis of the experimental results obtained in the simultaneous Mössbauer and DTA studies of the present tellurite and other oxide glasses [17–24], we can draw the conclusion that T_g for oxide glasses is primarily determined by the magnitude of the distortion of NWF–oxygen polyhedra.

4. Conclusions

1. Fe^{3+} ions are present at substitutional sites of the Te^{4+} ions constituting distorted TeO_4 trigonal bipyramids. Each TeO_4 trigonal bipyramid has an oxygen vacancy and a lone electron pair at an equatorial site.
2. Introduction of an alkali oxide (Na_2O or K_2O) into the TeO_2 matrix results in a change of the matrix from the original two-dimensional layer structure of β-TeO_2 type to a chain structure composed of less distorted TeO_4 trigonal bipyramids having non-bridging oxygen atoms.
3. Introduction of an alkaline earth oxide (MgO or BaO) into the TeO_2 matrix results in a change of the matrix into a three-dimensional network structure composed of highly distorted TeO_4 trigonal bipyramids.
4. The glass transition temperature T_g of tellurite glasses is in proportion to the distortion of TeO_4 trigonal bipyramids. The distortion becomes prominent with increasing ionic potential (Z/r) of the alkali or alkaline earth metal ion. This relationship is applicable to several oxide glasses.

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