Phase Separation of Phosphotellurite Glass Investigated by ^{57}Fe-Mössbauer Spectroscopy and DTA

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Synopsis. The isomer shifts (δ) of $x\mathrm{P_2O_5}\cdot(95-x)\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$ glasses (x=0—28), 0.38—0.39 mm s^{-1}, suggest that Fe^{3+} substitutes for Te^{4+} of TeO$_4$ trigonal bipyramids. The δ's of 0.42—0.43 mm s^{-1} obtained when $30\leqq x\leqq40$ indicate that Fe^{3+} (*Oh*) is present at interstitial sites of PO$_4$ tetrahedra in the phosphate-rich phase.

It is well known that tellurite glasses have high optical transparency in the IR region. They have attracted much attention as advanced materials showing optical non-linearity. Nishida et al. showed that the glass matrix of tellurite glasses is changed from the original layer structure to a pseudo-chain or three-dimensional structure, depending on the type of network modifier (NWM).[1,2] Structural studies of tellurite glasses were carried out by means of Mössbauer spectroscopy,[1-3] neutron diffraction,[4-6] and IR[7-9] techniques. Many of them showed that tellurite glasses comprise TeO$_4$ trigonal bipyramids having an oxygen vacancy at one of the equatorial sites. A drastic change in the IR transmittance was observed in $95\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$ glass by critical annealing performed above the crystallization temperature (T_c) of 352 °C.[10] It was discovered that the reduction rate of the IR transmittance can be used to investigate the mechanism of crystallization in $95\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$ glass when combined with the Johnson-Mehl-Avrami (JMA) equation.[10] This study was carried out in order to investigate the structural changes of phosphotellurite glasses, $x\mathrm{P_2O_5}\cdot(95-x)\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$, by ^{57}Fe-Mössbauer spectroscopy and DTA; it was conducted in order to evaluate the glass transition temperature (T_g), which is closely related to the structure.

Experimental

$x\mathrm{P_2O_5}\cdot(95-x)\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$ glasses were prepared by fusig individual mixtures (1 g) of commercially available NH$_4$H$_2$PO$_4$, TeO$_2$, and Fe$_2$O$_3$ of guaranteed reagent grade at 850 °C for 1 h in an electric muffle furnace. Each melt in a platinum crucible was quenched by immersing quickly the outer bottom of the crucible into ice-cold water. Transparent brown glasses were prepared when x was 0—40. ^{57}Fe-Mössbauer measurements of pulverized samples were performed by the conventional constant-acceleration method at room temperature. Ten mCi (3.7×10^8 Bq) of ^{57}Co(Pd) and a piece of iron foil were used as the Mössbauer source and reference for the isomer shift (δ), respectively. The Mössbauer spectrum was analyzed into one doublet peak by a least-squares method. DTA was conducted at a heating rate of 5 °C min^{-1} from room temperature to ca. 600 °C by using α-Al$_2$O$_3$ as a reference.

Results and Discussion

The Mössbauer spectra of $x\mathrm{P_2O_5}\cdot(95-x)\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$ glasses are illustrated in Fig. 1. These spectra are very similar to each other when x=0—28 (see x=0, 15, 25). They comprise a paramagnetic doublet peak with a larger quadrupole splitting (Δ) and a smaller δ. On the contrary, the spectra of glasses with x=35 and 40 have a smaller Δ and a larger δ. This is also the case for glass with x=30, suggesting that the structure of phosphotellurite glasses with x=30—40 is different from that of glasses with x=0—28.

Figure 2 shows the composition dependences of δ (upper) and Γ (FWHM, lower). The values of δ, 0.38—

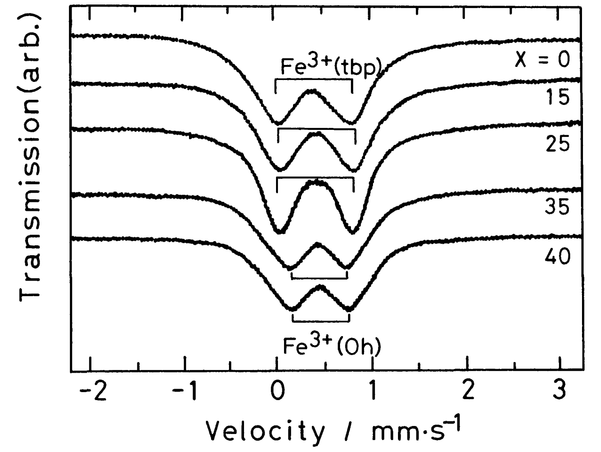

Fig. 1. Mössbauer spectra of $x\mathrm{P_2O_5}\cdot(95-x)\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$ glasses measured at room temperature. Fe^{3+}(*tbp*): trigonal bipyramidal Fe^{3+}, Fe^{3+}(*Oh*): octahedral Fe^{3+}.

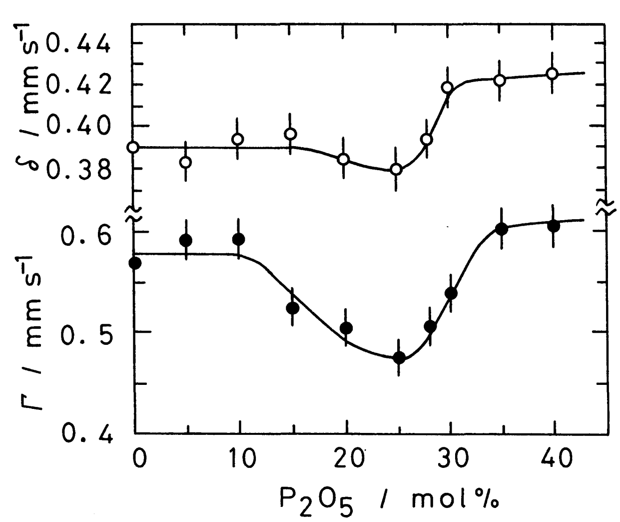

Fig. 2. δ (upper) and Γ (lower) of $x\mathrm{P_2O_5}\cdot(95-x)\mathrm{TeO_2}\cdot5\mathrm{Fe_2O_3}$ glasses.

0.39 (±0.01) mm s^{-1}, obtained for glasses with x=0—28 correspond to fourfold-coordinated Fe^{3+} (e.g. tetrahedral Fe^{3+}) which generally has a larger Δ.[1,2,11,12] Since Te^{4+}of TeO$_4$ trigonal bipyramids, having one oxygen vacancy, is fourfold coordinated with oxygen, it is considered that Fe^{3+} substitutes for Te^{4+} in phosphotellurite glasses with x=0—28. Such iron is indicated as Fe^{3+}(*tbp*) in Fig. 1. The δ of fourfold-coordinated Fe^{3+} becomes smaller by crystallization owing to a decrease in the Fe^{3+}–O bond length and an increase in the covalency: e.g., δ of 95TeO$_2$·5Fe$_2$O$_3$ glass decreases from 0.39 to 0.37 mm s^{-1} when annealed at 400 °C for 200 min. The values of δ, 0.42—0.43 (±0.01) mm s^{-1} obtained for glasses with x=30—40, correspond to octahedral Fe^{3+} species (Fe^{3+}(*Oh*)), as was observed for Fe^{3+} in several alkali phosphate glasses.[13] Octahedral Fe^{3+} generally has a smaller Δ (smaller electric field gradient, e^2qQ), reflecting a higher symmetry than that of fourfold-coordinated Fe^{3+}. The composition dependence of δ (Fig. 2) suggests that the coordination of Fe^{3+} varies from fourfold to sixfold when x exceeds 28. The decrease of Γ from 0.58 to 0.47 (±0.02) mm s^{-1}, observed when $0 \leqq x \leqq 25$ (Fig. 2, lower), indicates that the steric configuration of Te(Fe)O$_4$ trigonal bipyramids becomes more uniform owing to a "dilution effect" by PO$_4$ tetrahedra; PO$_4$ tetrahedra break the Te(Fe)–O–Te bonds and form a new bond with the resultant Te(Fe)–O– units. This change reaches a maximum when x=25; then, Γ increases with an increasing P$_2$O$_5$ content. The increase in δ from 0.38 to 0.43 mm s^{-1}, observed in glasses with x=28—40 (Fig. 2, upper), is in accord with the increase in Γ shown in Fig. 2 (lower). This suggests a drastic change of the structure in phosphotellurite glasses. It seems that Fe^{3+} prefers sixfold-coordinated (*Oh*) interstitial sites surrounded by PO$_4$ tetrahedra, as is in several phosphate glasses.[13] The change of the glass matrix is also reflected in a decrease in Δ from 0.76 to 0.61 (±0.02) mm s^{-1} observed when $x \geqq 25$ (Fig. 3), being consistent with the change from fourfold (Fe^{3+}(*tbp*)) to sixfold (Fe^{3+}(*Oh*)) coordination. The FeO$_6$ octahedra bond with the PO$_4$ tetrahedra by sharing the edges and corners with each other. These Mössbauer results indicate that an additional phosphate-rich phase is formed in phosphotellurite glasses with x=28—40.

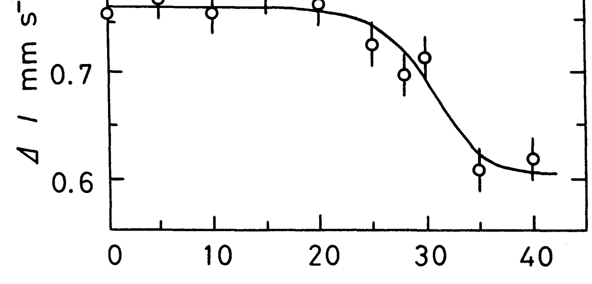

Fig. 3. Δ of xP$_2$O$_5$·(95−x)TeO$_2$·5Fe$_2$O$_3$ glasses.

The changes of the glass matrix are observed by DTA as shown in Fig. 4, in which T_g is indicated by the arrow. Figure 4 shows that T_g of the phosphotellurite glass phase increases with an increasing P$_2$O$_5$ content; i.e. 328→342→361→375→395→411 °C when x is changed from 0 to 25 at 5 intervals. In glasses with $x \geqq 28$, T_g increases in the following order: 420→431→455→478 °C. In addition to the T_g of the phosphotellurite phase, another T_g is observed when $x \geqq 28$; it decreases with an increasing P$_2$O$_5$ content in the following order: 225→223→215→213 °C when x is changed from 28 to 40 at 5 intervals. The additional T_g (225—213 °C) reflects the presence of a phosphate-rich phase. It was reported that several phosphate glasses have a T_g of less than 290 °C.[14] The composition dependence of T_g is illustrated in Fig. 5. T_g of the homogeneous phosphotellurite glass phase is indicated by the open circle. T_g of the phosphotellurite phase, coexisting with the phosphate-rich phase, is indicated by the semi-solid circle. It is seen from Fig. 5 that T_g increases drastically and two straight lines intersect each other when x=28. The solid circle indicates T_g of the phosphate-rich phase. It decreases gradually with an increasing P$_2$O$_5$ content. The experimental results shown in Figs. 4 and 5 indicate that phase separation takes place in phosphotellurite glasses with $x \geqq 28$. It is well known that P$_2$O$_5$, SiO$_2$, and B$_2$O$_3$ are representative network formers (NWF). The introduction of P$_2$O$_5$ into TeO$_2$ (intermediate oxide) causes phase separation with the phosphate-rich phase. The increase in T_g observed in the phosphotellurite phase reflects the change of the glass matrix from the original layer structure comprising Te(Fe)O$_4$ trigonal bipyramids to a three-dimensional network structure, as was observed in several magnesium and barium tellurite glasses.[2] A similar structural change was observed in phosphorus, magnesium, and barium vanadate

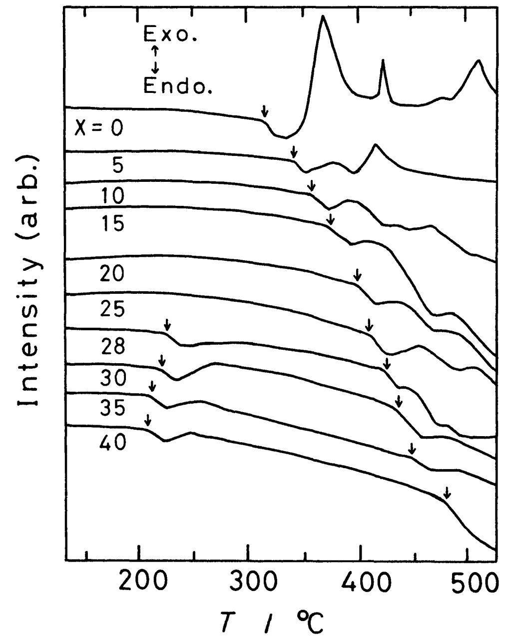

Fig. 4. DTA curves of xP$_2$O$_5$·(95−x)TeO$_2$·5Fe$_2$O$_3$ glasses. T_g is indicated by the arrow.

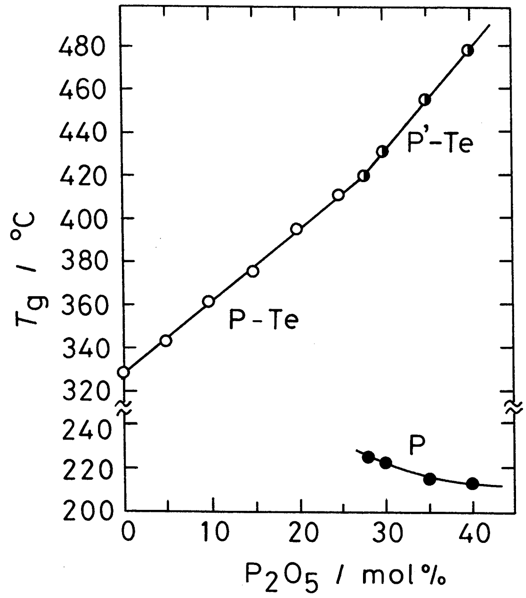

Fig. 5. T_g of xP$_2$O$_5$·(95−x)TeO$_2$·5Fe$_2$O$_3$ glasses. P–Te: phosphotellurite phase, P′–Te: phosphotellurite phase coexistent with phosphate-rich phase, P: phosphate-rich phase.

glasses.[11]

The phase separation observed in this study is consistent with the results of the neutron diffraction of a binary xP$_2$O$_5$·(100−x)TeO$_2$ system (x=8, 16, 20, 26) studied by Neov et al.[5] They suggested that the introduction of 26±5 mol% of P$_2$O$_5$ causes immiscibility, due to the formation of a microhomogeneous tellurite-rich domain and a microheterogeneous phosphate-rich domain. The consistent results obtained by the Mössbauer spectroscopy and the neutron diffraction suggest that 5 mol% of Fe$_2$O$_3$, incorporated into the binary P$_2$O$_5$–TeO$_2$ system as the Mössbauer probe, does not affect the intrinsic glass structure.

Following conclusions were obtained in this study:

1) The ^{57}Fe-Mössbauer spectroscopy is effective for investigating the phase separation of glasses.

2) A phase separation of xP$_2$O$_5$·(100−x)TeO$_2$ glasses occurs when $x \geqq 28$, and an additional phosphate-rich phase is formed. This conclusion is consistent with the results of a neutron diffraction study conducted by Neov et al.[5]

3) With the phase separation, Fe^{3+} changes its structural role from NWF, present at substitutional sites of Te^{4+}, to NWM present at the interstitial site of the PO$_4$ tetrahedra.

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