Structural Study of Na_2O-TeO_2 Glasses by Mössbauer Spectroscopy and Differential Thermal Analysis

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(Received June 22, 1988)

A Mössbauer spectrum of xNa$_2$O·(95$-x$)TeO$_2$·5Fe$_2$O$_3$ glasses ($0 \leqq x \leqq 35$) consists of a paramagnetic quadrupole doublet peak with an isomer shift of 0.39 ± 0.01 mm s^{-1} with respect to metallic iron. Quadrupole splitting of the doublet peak changes gradually from 0.76 to 0.60 mm s^{-1} when Na_2O content is changed from 0 to 35 mol% at 5 mol% intervals. These results suggest that Fe^{3+} ions are present at substitutional sites of Te^{4+} ions constituting distorted TeO_4 trigonal bipyramids. Each of the distorted TeO_4 trigonal bipyramids has an oxygen vacancy and a lone electron pair at one of the equatorial sites. Decreased quadrupole splitting is ascribed to an increased symmetry of FeO_4 (and also TeO_4) trigonal bipyramids, due to a formation of nonbridging oxygen atoms followed by a gradual change of the glass matrix from a two-(β-TeO_2) or three-(α-TeO_2) dimensional network structure to a lower dimensional network structure. These structural changes are also deduced from a composition dependency of glass transition temperatures (T_g), which decrease continuously from 318 to 232 °C with increasing Na_2O content.

It is known that tellurite (TeO_2-based) glasses have some excellent physical properties such as low glass transition temperature (T_g), high refractive index, high dielectric constant, high thermal expansion coefficient, and high transmission in the IR region.[1–5] Structural study of tellurite glasses has been performed by several researchers by means of X-ray diffraction,[6–8] IR,[8–11] neutron diffraction,[12–16] and Mössbauer spectroscopy.[11,17–19] Local structure of TeO_2 glass was first studied by Brady,[6] who indicated that TeO_2 glass is composed of distorted TeO_6 octahedra. On the other hand, an X-ray diffraction study of V_2O_5–TeO_2 glasses performed by Dimitriev and Dimitrov[7] showed that coordination number of Te^{4+} ion changes from 4 to 3 when V_2O_5 is incorporated into TeO_2 matrix. An X-ray diffraction and IR absorption study of alkali tellurite glasses was performed by Dimitriev et al.,[8] who elucidated that alkali tellurite glasses are composed of TeO_4 groups. An IR study of binary alkali or alkaline earth tellurite glasses was performed by Mochida et al.,[9] who elucidated that these tellurite glasses have a layer structure composed of distorted TeO_4 trigonal bipyramids having a lone electron pair at one of the equatorial sites (in the xy plane). Each Te^{4+} ion has an oxygen vacancy at one of the equatorial sites.[9] The IR results obtained by Mochida et al.[9] were supported by Dimitriev et al.,[10] who showed that an introduction of MoO_3 into TeO_2 matrix results in a structural change from TeO_4 trigonal bipyramids to TeO_3 trigonal pyramids, similarly to the structural change of V_2O_5–TeO_2 glasses.[7] Neutron diffraction studies revealed that tellurite glasses are composed of distorted TeO_4 trigonal bipyramids.[12–16] Neov et al. proposed that tellurite glasses are composed of TeO_4 tetrahedra.[13] A neutron diffraction study performed by Neov et al.[14] revealed that TeO_4 trigonal bipyramids, constituting the glass matrix of tellurite glasses, gradually change into TeO_3 trigonal pyramids when P_2O_5 is incorporated into TeO_2 matrix. This structural change is similar to that of V_2O_5–TeO_2[7] and MoO_3–TeO_2[10] glasses described above. Structural change of V_2O_5–TeO_2 glasses was also observed by Johnson et al.[16] by using a neutron diffraction method. Mössbauer studies on the structure of tellurite glasses were performed by Binczycka et al.[17] and Bahgat et al.[11,18,19] Some of the Mössbauer studies[17,18] suggested that iron is present as octahedral Fe^{3+} ions in tellurite glasses, in spite that both the isomer shift (<0.40 mm s^{-1} with respect to metallic iron) and the quadrupole splitting (0.6—0.9 mm s^{-1}) indicated the coordination number smaller than 6. On the other hand, Mössbauer studies performed by Bahgat et al.[11,19] lead to a conclusion that Fe^{3+} ions are present at tetrahedral environments in strontium tellurite and several rare earth tellurite glasses. This conclusion[11,19] was drawn because the Mössbauer parameters of Fe^{3+} ions in these tellurite glasses were almost comparable to those of tetrahedral Fe^{3+} ions obtained for several oxide glasses. In Ref. 19, it was concluded that an increased SrO content results in an increased number of nonbridging oxygen atoms in FeO_4 and TeO_4 tetrahedra.

Present Mössbauer study of a series of Na_2O–TeO_2 glasses containing a small amount (5 mol%) of Fe_2O_3 was carried out in order to elucidate the short-range (local) and also middle- or long-range structures of tellurite glasses, e.g., a steric configuration around the iron (and also tellurium) atom and a structural change caused by alkali oxide (Na_2O) which was incorporated into TeO_2 matrix. DTA measurements of the Na_2O-TeO_2 glasses containing 5 mol% Fe_2O_3 were also performed in parallel, because glass transition temperature (T_g) is known to be sensitive to a change in the coordination number of network-forming atoms and to a formation of nonbridging oxygen,[20–24] chlorine,[25] and fluorine[26] atoms followed by a depolymerization of the network structure.

Experimental

A series of xNa$_2$O·(95$-x$)TeO$_2$·5Fe$_2$O$_3$ glasses were prepared by fusing individual mixtures (1 g) of commercially available Na$_2$CO$_3$, TeO$_2$, and Fe$_2$O$_3$, of guaranteed reagent grade. Each of the mixtures, in which x was changed at 5 intervals, was fused at 750 °C for 1 h in air by using an electric muffle furnace. After the fusion, each melt in a platinum crucible was immediately quenched with ice-cold water. Transparent and light brown glasses were obtained in a compositional region $0 \leqq x \leqq 35$. Mössbauer and DTA measurements were performed on pulverized tellurite glasses. Mössbauer measurements were performed by a constant acceleration method at room temperature, by using a proportional counter and a multichannel (1024-channel) analyzer. Cobalt-57 (10 mCi) diffused into a palladium foil was used as a Mössbauer source. As a standard material for the isomer shift, a piece of metallic iron foil enriched with iron-57 was used. The iron foil was also used for calibrating the velocity of Mössbauer spectrometer. Each Mössbauer spectrum was analyzed into a quadrupole doublet by a least-squares method. DTA measurements of tellurite glasses were performed in the temperature range between room temperature and 600 °C, with a heating rate of 5 °C min^{-1}. Powder of α-Al$_2$O$_3$ was used as a standard material in the DTA measurements.

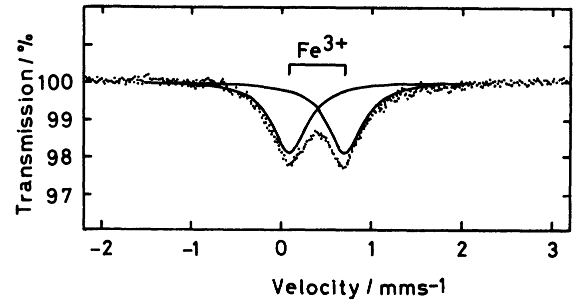

Fig. 1. Mössbauer spectrum of 20Na$_2$O·75TeO$_2$·5Fe$_2$O$_3$ glass measured at room temperature.

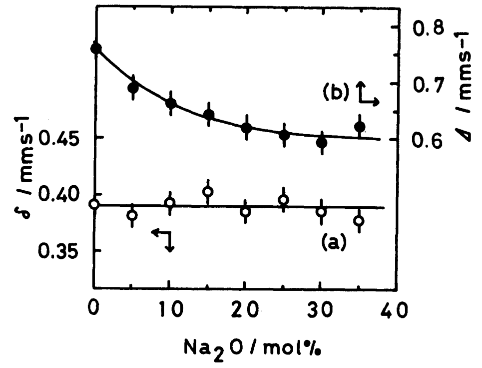

Fig. 2. Composition dependencies of (a) isomer shift (δ) and (b) quadrupole splitting (Δ) of Fe^{3+} ions in xNa$_2$O·(95$-x$)TeO$_2$·5Fe$_2$O$_3$ glasses.

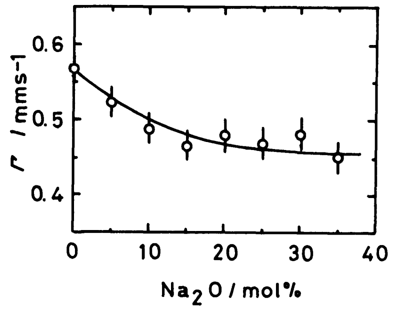

Fig. 3. Composition dependency of linewidth (Γ) of Fe^{3+} ions in xNa$_2$O·(95$-x$)TeO$_2$·5Fe$_2$O$_3$ glasses.

Results and Discussion

A Mössbauer spectrum of 20Na$_2$O·75TeO$_2$·5Fe$_2$O$_3$ glass is shown in Fig. 1, which indicates a characteristic doublet peak due to paramagnetic Fe^{3+} ions of high spin state.[27,28] Since the absorption is symmetric, each Mössbauer spectrum is analyzed into a quadrupole doublet peak having equal linewidth and equal intensity. All the Mössbauer parameters of Na$_2$O–TeO$_2$–Fe$_2$O$_3$ glasses are shown in Figs. 2 and 3. Figure 2a indicates that isomer shift is independent of the composition, showing a constant value of 0.39±0.01 mm s^{-1}. Comparing the present results with recent Mössbauer results of alkali borate,[25,29–32] alkali borosilicate,[32–34] and other glasses cited in review articles,[35–37] we can deduce that Fe^{3+} ions are four-fold coordinated in Na$_2$O–TeO$_2$ glasses, and that they are not octahedrally coordinated as in several phosphate glasses.[38–41] In the Mössbauer spectra of tetrahedrally coordinated Fe^{3+} ions, isomer shifts were located in a range of 0.22—0.38 mm s^{-1} with respect to metallic iron.[25,29–37] These experimental results obtained so far indicate that isomer shift of Fe^{3+} ions is less than 0.40 mm s^{-1} when they are four-fold coordinated. The experimental error of isomer shift is estimated to be ±0.01 mm s^{-1}. On the other hand, Mössbauer spectra of Fe^{3+} ions in several phosphate glasses[38–41] indicate that isomer shift is more than 0.42 mm s^{-1} when they are octahedrally coordinated with oxygen atoms. These results suggest that a boundary of isomer shift lies at about 0.40 mm s^{-1} for four-fold and six-fold coordinated Fe^{3+} ions with oxygen atoms.[42] Therefore, the isomer shift of 0.39±0.01 mm s^{-1} (Fig. 2a) will suggest four-fold coordinated Fe^{3+} ions (of high spin state). The relatively large isomer shift values (0.39±0.01 mm s^{-1}) suggest that s-electron density at iron nucleus is lower than that of tetrahedral Fe^{3+} ions observed in several oxide glasses.[25,29–37] Earlier Mössbauer results on tellurite glasses obtained by Binczycka et al.[17] and Bahgat et al.,[18] suggesting that Fe^{3+} ions are octahedrally present in tellurite glasses, are unlikely because the isomer shift values were less than 0.40 mm s^{-1} with respect to metallic iron. It should be noted that recent IR[9,10] and neutron diffraction[12–16] studies propose a presence of distorted

TeO_4 trigonal bipyramids having an oxygen vacancy and a lone electron pair at one of the equatorial sites. Taking into account these IR and neutron diffraction results,[9,10,12–16] we can tentatively conclude that the present Mössbauer results (isomer shift) suggest distorted FeO_4 trigonal bipyramids having an oxygen vacancy at one of the equatorial sites. Apart from Te^{4+} ions, Fe^{3+} ions will not have a lone electron pair at the equatorial sites. They will form sp^3d hybrid orbital, similarly to the Te^{4+} ions constituting TeO_4 trigonal bipyramids.

From the electronic point of view, the four-fold coordinated FeO_4 trigonal bipyramid having one oxygen vacancy is equivalent to an FeO_4 tetrahedron without oxygen vacancy. The almost constant and large isomer shift values located around 0.39 mm s^{-1} (Fig. 2a), irrespective of the composition, may be concerned with the oxygen vacancy at one of the equatorial sites in FeO_4 trigonal bipyramids. A part of negative charge on the Fe^{3+} ion will be attracted to the oxygen vacancy. As a result, 4s-electron density at the iron nucleus will be decreased. This will cause a relatively large isomer shift values. Also, the larger isomer shift values will be concerned with lower s-electron density in an sp^3d hybrid orbital, because a contribution of s-orbital to the sp^3d hybrid orbital is lower as compared with sp^3 hybrid orbital. The Fe^{3+} ions attached to oxygen vacancies will be less sensitive to a change of electron densities at iron nucleus. In several vanadate glasses,[20,21,42,43] a drastic change of glass matrix was observed from VO_5 tetragonal pyramids to VO_4 tetrahedra when alkali or alkaline earth oxide was incorporated into V_2O_5 matrix. This structural change corresponds to an orbital change in the V^{5+} or V^{4+} (and also Fe^{3+}) ions from sp^3d to sp^3 hybrid orbital. From the relatively large and constant isomer shift values (0.39 ± 0.01 mm s^{-1}) observed in tellurite glasses, we can deduce the presence of oxygen vacancies at neighboring sites of Fe^{3+} ions in FeO_4 trigonal bipyramids and also sp^3d hybrid orbital in the Fe^{3+} ions. This will be discussed later in connection with a formation of nonbridging oxygen atoms.

Continuous decrease in the quadrupole splitting shown in Fig. 2b suggests that a symmetry of FeO_4 (and also TeO_4) trigonal bipyramids increases with increasing Na_2O content. In the case of high-spin Fe^{3+} ions, an electric field gradient brought about by neighboring atoms (q_{lat}) primarily causes the quadrupole interaction. Similar decrease in the quadrupole splitting of Fe^{3+} ions was observed in several alkali borate[25,29–32] and alkali borosilicate[32–34] glasses, where the decrease was ascribed to a formation of nonbridging oxygen and chlorine atoms in BO_4, SiO_4, and BO_3Cl tetrahedra. Decrease in the quadrupole splitting of Fe^{3+} ions has also been observed in alkali vanadate[20,21,42] glasses, from which we could know a formation of nonbridging oxygen atoms in VO_4 tetrahedra and a depolymerization of the layer structure originally composed of VO_5 tetragonal pyramids. The experimental error of quadrupole splitting is estimated to be ±0.02 mm s^{-1}. Quadrupole splitting of Fe^{3+} ions octahedrally coordinated with oxygen atoms (e.g. 0.3—0.6 mm s^{-1}) is usually smaller than that of tetrahedrally coordinated Fe^{3+} ions (e.g. 0.6—0.9 mm s^{-1}), owing to a higher symmetry of the former. It should be noted that a change of middle- or long-range structure, as well as a change of short-range structure, is sometimes reflected in the quadrupole splitting of Fe^{3+} ions. Therefore, the continuous decrease in quadrupole splitting (Fig. 2b) is ascribed to a formation of nonbridging oxygen atoms in distorted FeO_4 (and also TeO_4) trigonal bipyramids having an oxygen vacancy at one of the equatorial sites. Furthermore, a lone electron pair will be present in the sp^3d hybrid orbital of Te^{4+} ion constituting a TeO_4 trigonal bipyramid. An introduction of alkali oxide (Na_2O) into TeO_2 matrix will result in a depolymerization of original α-TeO_2[10,13,14] or β-TeO_2[9,16] type structure, composed of distorted TeO_4 trigonal bipyramids having a lone electron pair at one of the equatorial sites. Comparing Fig. 2a with Fig. 2b, we can know that quadrupole splitting (Δ) is more sensitive to the structural change than isomer shift (δ). Similar phenomenon was observed in a crystallization study of several borate and borosilicate glasses.[32]

Figure 3 indicates that a formation of nonbridging oxygen atoms and a depolymerization of the glass matrix are reflected in the linewidth. It is generally known that linewidth of the absorption peak due to iron in glasses is greater than about 0.4 mm s^{-1}. This is a characteristic feature of the absorption for amorphous materials. Each linewidth shown in Fig. 3 is in a range of 0.46—0.57 mm s^{-1}. A continuous decrease in linewidth (Fig. 3) suggests that bond length and bond angle between Fe^{3+} (and also Te^{4+}) ions and neighboring oxygen atoms become more uniform when nonbridging oxygen atoms are formed in FeO_4 (and also TeO_4) trigonal bipyramids. Figure 3 demonstrates that linewidth decreases by adding Na_2O into TeO_2 matrix and becomes almost constant (about 0.46 mm s^{-1}) when Na_2O content is higher than about 20 mol%. This indicates that a distinct structural change occurs in tellurite glasses of low alkali oxide content. The composition dependency is in good agreement with that of quadrupole splitting described above.

Glass transition temperatures (T_g) of tellurite glasses obtained from DTA measurements are plotted in Fig. 4. Each DTA curve of Na_2O–TeO_2 glasses containing 5 mol% Fe_2O_3 shows a broad endothermic peak due to glass transition and exothermic peaks due to crystallization. Recent DTA studies on the structure of several glasses revealed that T_g is closely concerned with a change in the coordination number of network-

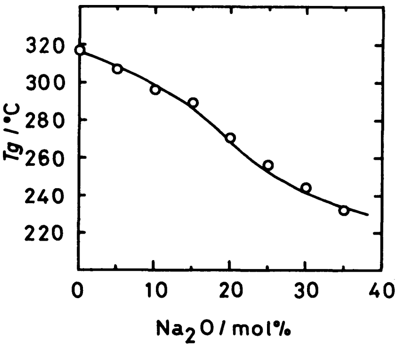

Fig. 4. Composition dependency of glass transition temperature (T_g) of xNaO·(95−x)TeO$_2$·5Fe$_2$O$_3$ glasses.

forming atoms and with a formation of nonbridging oxygen or halogen atoms.[20–26,42–44] The latter structural change causes a depolymerization of network structure. T_g shows a distinct increase/decrease with increasing/decreasing coordination number of network-forming atoms, because the coordination number is responsible for the degree of bridging in the glass matrix. Also, a formation of nonbridging oxygen atoms is deduced from a decrease in T_g.[20–24,42–44] Therefore, a continuous decrease in T_g ranging from 318 to 232 °C (Fig. 4) is ascribed to an increased fraction of less distorted TeO$_4$ and FeO$_4$ trigonal bipyramids having nonbridging oxygen atoms. At the same time, it is concluded that a middle- or long-range structural change occurs from the original three-dimensional network (α-TeO$_2$) structure or two-dimensional layer (β-TeO$_2$) structure to a lower dimensional network structure, i.e., one-dimensional chain structure. This structural change is similar to that of alkali vanadate (K_2O–V_2O_5,[20] Na_2O–V_2O_5,[21] and Li_2O–V_2O_5[42]) glasses. In alkali vanadate glasses,[20,21,42] a simultaneous decrease in T_g and quadrupole splitting (of the Fe^{3+} ions) was ascribed to a structural change from a two-dimensional layer structure composed of VO$_5$ tetragonal pyramids to a one-dimensional chain structure composed of VO$_4$ tetrahedra which have nonbridging oxygen atoms.

A simultaneous decrease in T_g and quadrupole splitting (of Fe^{3+} or Sn^{4+} ions) has been observed when nonbridging oxygen atoms are formed in GeO$_4$ and GaO$_4$ tetrahedra constituting alkali (K_2O-) germanate[24] and gallate[44] glasses, respectively. Concordant composition dependencies of T_g and quadrupole splitting, observed in several vanadate,[20,21,42,43] germanate,[24] gallate,[44] and tellurite glasses, suggest that a structural information obtained from Mössbauer measurements is representative of the whole glass matrix. Mössbauer atoms will be homogeneously distributed in the glass matrix either at the substitutional sites of the individual network-forming ions (e.g. V^{5+}, V^{4+}, Ga^{3+}, and Te^{4+}) or at the interstitial sites in the glass matrix (e.g. phosphate glasses), depending on the type of glass matrix. From the constant isomer shifts described above (Fig. 2a), it is speculated that nonbridging oxygen atoms will be preferentially formed at axial oxygen sites. The longer interatomic distance and resultant weaker covalent bond between Fe^{3+} (and also Te^{4+}) ions and oxygen atoms at axial sites will bring about little effect on the s-electron density and therefore on the isomer shift.

It is concluded that Fe^{3+} ions are present at substitutional sites of the Te^{4+} ions constituting TeO$_4$ trigonal bipyramids. Each of the TeO$_4$ trigonal bipyramids has an oxygen vacancy and a lone electron pair at one of the equatorial sites. An Fe^{3+} ion in the FeO$_4$ trigonal bipyramid does not have a lone electron pair. It is also concluded that an introduction of Na_2O into TeO$_2$ matrix results in a change of the glass matrix from an original three-dimensional network (α-TeO$_2$) or a two-dimensional layer (β-TeO$_2$) structure to a lower dimensional network structure, i.e., a chain structure composed of less distorted TeO$_4$ trigonal bipyramids which have nonbridging oxygen atoms.

The authors are grateful to Prof. Toshinobu Yoko of Kyoto University for his useful comments and discussion. One of the authors (TN) is indebted to Yoshida Science Foundation and Kazuchika Ohkura Memorial Foundation for a financial support.

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