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Structural Study of Germanate Glasses Irradiated with γ-Rays and Thermal Neutrons

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^{119}Sn Mössbauer study of ^{60}Co-γ ray and thermal neutron irradiated potassium germanate glasses containing a small amount of SnO_2 has been performed to investigate the structural change of the glasses. The γ- and the thermal neutron-irradiation results in a disappearance of the distinct composition dependence of the Mössbauer parameters (quadrupole splitting and linewidth) observed before the irradiation. DTA measurement of the irradiated glasses also reveals drastic decreases in glass transition temperature (T_g) amounting to 20—120 °C and a simultaneous disappearance of the distinct composition dependence of T_g observed before the irradiation. This suggests a disruption of the chemical bond between germanium and oxygen atoms constituting GeO_6 units. On the other hand, Mössbauer measurement at lower temperatures reveals that a parameter of intermolecular force constant (θ^2M) obtained from the temperature dependence of the absorption area undergoes little change by the irradiations. This suggests that the irradiations bring about little changes in the ionic bond and the interatomic distance between tin and oxygen atoms, and that the irradiated germanate glasses can still be regarded as polymers from the lattice vibrational point of view.

Abnormal composition dependence of the physical properties of germanate glasses, *i.e.*, germanate anomaly has so far been found on density and refractive index,[1—3] viscosity,[4] and glass transition temperature (T_g).[4,5] Viscosity- and T_g-composition curves show maxima at the compositions of 17[4] and 15—16[5] mol% alkali oxides, respectively. The decrease in these physical properties in the higher alkali oxide content region was tentatively attributed to the formation of nonbridging oxygen (NBO) atoms, because it was expected that viscosity and T_g are well correlated with the cohesiveness and depolymerization of the glasses, respectively. The presence of NBO in germanate glasses was confirmed by Verweij and Buster[6] by means of Raman spectroscopy, and furthermore the fraction of NBO was obtained by Smets and Lommen[7] by means of X-ray photoelectron spectroscopy (XPS). In the Raman and XPS studies, the formation of NBO was concluded to start at an alkali oxide concentration of 18 mol%.

Mössbauer spectroscopy of ^{57}Fe has also been utilized for the structural studies of several kinds of glasses such as borate,[8—10] borosilicate,[11,12] phosphate,[13,14] and borophosphate[15] glasses. In ^{119}Sn Mössbauer study of germanate glasses[16] by the authors, the formation of NBO was concluded to start when the alkali oxide (K_2O) content is higher than about 16 mol%. The result was also supported by distinct composition dependences of T_g and parameter of intermolecular force constant (θ^2M) obtained from the temperature dependence of the Mössbauer absorption area. Structural studies of glasses by means of ^{119}Sn Mössbauer spectroscopy have also been performed on borate[17—20] and silicate[17,21,22] glasses, in which most Sn^{4+} species proved to be present in octahedral environment.

The present study was performed to elucidate the effects of γ- and thermal neutron-irradiation on germanate glasses by means of ^{119}Sn Mössbauer spectroscopy and DTA, because it was expected that the irradiation effects, if present, should depend upon the local structural change of the glasses based on the change in composition.

Experimental

Experimental procedures for the preparation of glass samples and for the Mössbauer and DTA measurements are already reported in our previous paper.[16] Gamma-ray irradiation of the germanate glasses denoted by $xK_2O\cdot(100-x)GeO_2\cdot 2SnO_2$ was performed in the ^{60}Co-γ ray irradiation facility of Kyushu University, with a dose rate of 5.9×10^5 R h^{-1} for 170 h at the ambient temperature (*ca.* 40 °C). Thermal neutron irradiation was carried out in the reactor of Atomic Energy Research Institute of Rikkyo University, with a flux of 5×10^{11} n cm^{-2} s^{-1} for 6 h at the ambient temperature. The γ-ray dose rate in the reactor is estimated to be 1×10^6 R h^{-1}. During the irradiation, each glass sample was kept in a sealed polyethylene bag filled with dry nitrogen gas, and the bag was placed in a glass tube or polyethylene capsule filled with dry nitrogen gas and silica gel to protect the sample from the atmospheric moisture.

Results and Discussion

Mössbauer spectra for the potassium germanate glasses irradiated with γ-rays of 10^8 R or thermal neutrons of 10^{16} n cm^{-2} consist apparently of a single absorption peak, which can be analyzed into a quadrupole doublet just like in the case of germanate glasses before the irradiation.[16] Change in the isomer shift of ^{119}Sn with K_2O content of the glasses is shown in Fig. 1, in which a broken line refers to the result obtained before the irradiation.[16] These isomer shift values correspond to the tetravalent ionic species (Sn^{4+}) with octahedral symmetry,[23] and the Sn^{4+} ion is considered to be present as a network modifier at an interstitial site of the network composed of GeO_4 and GeO_6 units.[16] It is seen from Fig. 1 that the isomer

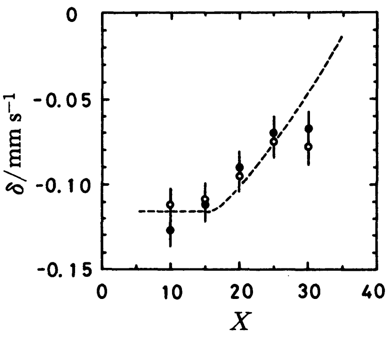

Fig. 1. Variation of the isomer shift of ^{119}Sn with K_2O content. (O): γ-Ray irrad., (●): thermal neutron irrad. The broken line refers to that of unirradiated glasses.

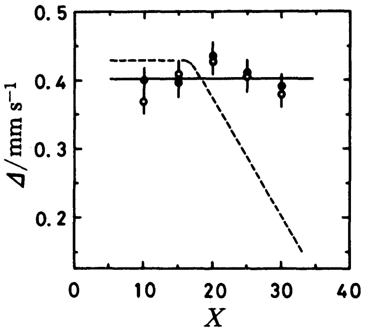

Fig. 2. Variation of the quadrupole splitting of Sn^{4+} with K_2O content. (O): γ-Ray irrad., (●): thermal neutron irrad. The broken line refers to that of unirradiated glasses.

shifts show little change by the γ- and the thermal neutron-irradiation, although only a small decrease is observed in the germanate glass with the alkali oxide content of $x=30$. The result shown in Fig. 1 is similar to the results of phosphate[14] and borophosphate[15] glasses in which both the isomer shift and quadrupole splitting show little change by the ^{60}Co-γ ray irradiations of 10^6 and 10^8 R. These results may be correlated with the structural role of Mössbauer nucleus, *i.e.*, both the iron (Fe^{2+} and Fe^{3+}) and tin (Sn^{4+}) play a role of network modifier which is present at an interstitial site of three-dimensional network in the case of phosphate,[13,14] borophosphate,[15] and germanate[16] glasses. On the other hand, the role of tin in borate and borosilicate glasses is reported to be a network former which is present at a substitutional site of tetrahedral boron or silicon atoms.[8,11] Irradiations of borate[9,24–26] and borosilicate[27] glasses with ^{60}Co-γ rays and thermal neutrons are reported to result in a decrease in isomer shift or an increase in the fraction of Fe^{2+} produced by the irradiation.

Change in the quadrupole splitting of Sn^{4+} in the germanate glasses irradiated with γ-rays and thermal neutrons is shown in Fig. 2, in which a broken line refers to the result obtained before the irradiation.[16] It is surprising that a drastic change in the quadrupole splitting observed before the irradiation disappears almost completely by the γ-ray (10^8 R) and thermal neutron (10^{16} n cm^{-2}) irradiations. This is very interesting and also quite different from the results of phosphate[14] and borophosphate[15] glasses in which little change in quadrupole splitting and linewidth was observed by ^{60}Co-γ ray irradiation. Irradiation of borate[9,24–26] and borosilicate[27] glasses with γ-rays or thermal neutrons is also reported to produce little change in the quadrupole splitting. The result of Fig. 2 therefore suggests that the irradiation brings about a structural change which has not been observed in the oxide glasses such as borate, borosilicate, and phosphate glasses. It is noteworthy that the quadrupole splitting values for the irradiated glasses are identical with those for the unirradiated germanate glasses with the alkali oxide content lower than 16 mol%. This means a disappearance of the structural role of NBO which has been concluded to be present only in GeO_4 units and causes an increase in the symmetry around Sn^{4+} ions.[16] Two possible explanations are given to the disappearance of the structural role of NBO in the irradiated glasses of which alkali oxide content is higher than 16 mol%, *i.e.*, one is a displacement of NBO from the neighboring site of Sn^{4+} to other site, and the other is a generation of a positive hole on an NBO atom. The former explanation, however, seems to be improbable because a displacement of NBO will bring about a change in the coordination number of tin (IV) and because such a change will be somewhat reflected in isomer shift. (Change in the coordination number of Sn^{4+} from 6 to 5 or 4 will result in an increase in the isomer shift of ^{119}Sn.) The latter explanation, *i.e.*, a generation of a positive hole on an electronegative NBO atom (—O^-) seems to be probable because the resultant oxygen atom is equivalent to a bridging oxygen from the electronical point of view. Therefore, the decreased symmetry around Sn^{4+} caused by the γ- and the thermal neutron-irradiaion is ascribed to a disappeared anionic character of NBO. This will result in a decreased Coulombic attraction between Sn^{4+} and NBO, and then a decrease in the symmetry around tin will be observed.

As is shown with a broken line in Fig. 3, a gradual and drastic increase in the linewidth (FWHM) has been observed for the unirradiated glasses with the alkali oxide content higher than 17 or 18 mol%. The increase in the linewidth has been attributed to the increased disorder brought about by NBO which is present at the neighboring site of Sn^{4+}.[19] It is obvious from Fig. 3 that γ- and thermal neutron-irradiation also results in a disappearance of the drastic increase in the linewidth caused by NBO. The disappearance of the drastic increase in the linewidth in the alkali oxide content region higher than 17—18 mol% is also concluded to be due to the disappeared structural role of NBO, because the magnitude of linewidth observed for the irradiated glasses is identical with that for the unirradiated glasses with the alkali oxide content lower than 17 mol%, just like the case of quadrupole splitting described above.

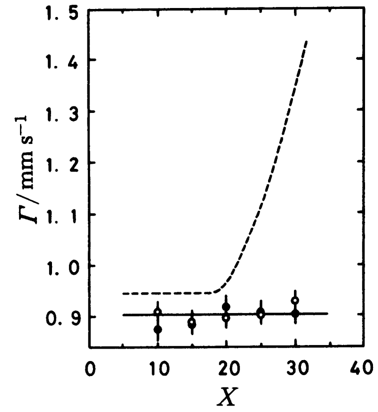

Fig. 3. Variation of the linewidth of Sn^{4+} with K_2O content.
(○): γ-Ray irrad., (●): thermal neutron irrad.
The broken line refers to that of unirradiated glasses.

The decrease in the linewidth is therefore explained by a rearrangement of oxygen atoms around Sn^{4+} as a result of the generation of a positive hole on an NBO atom, although no other experimental proof to support this idea has been obtained in the present study.

It is expected that some structural change, if present, will affect the physical properties such as T_g and viscosity. DTA measurement of the γ-ray irradiated germanate glasses was then carried out. This is shown in Fig. 4. It is noted that the irradiation gives rise to the decreases in T_g amounting to 20—120°C and a simultaneous disappearance of the distinct composition dependence of T_g observed before the irradiation. The composition dependence of T_g observed in the unirradiated glasses reflects, as described in our previous paper,[16] the formations of GeO_6 units and NBO in GeO_4 units in the alkali oxide content region lower than 16 mol% and in the range of 16—30 mol%, respectively. The decrease in the T_g brought about by the irradiation is ascribed to the disruption of the chemical bond between germanium and oxygen atoms constituting GeO_6 units, because the increase in T_g in the unirradiated glasses has been attributed to the formation of GeO_6 units.[16] This irradiation-effect seems not to affect the Mössbauer parameters such as isomer shift, quadrupole splitting, and linewidth, probably because the germanium or oxygen atoms in a GeO_6 unit of which chemical bond is disrupted by the irradiation are not present in the first or second coordination sphere of Mössbauer nucleus (^{119}Sn). (It is considered that a tin atom is interposed between two GeO_4 units to take an octahedral symmetry, and that a GeO_6 unit may be located at a site farther than the GeO_4 units.)

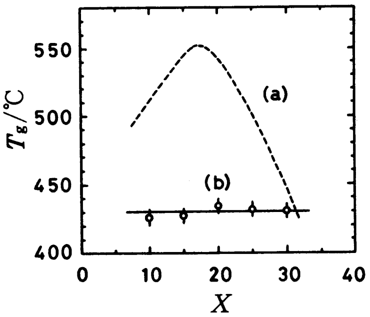

Fig. 4. Variation of the glass transition temperature (T_g) with K_2O content. (a): Unirrad., (b): γ-Ray irrad.

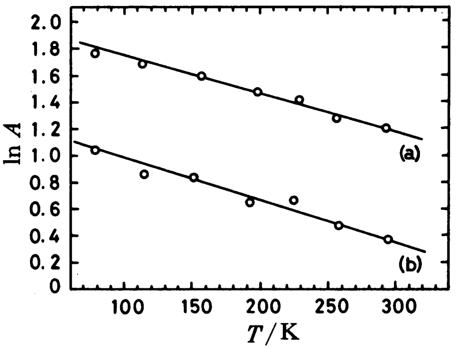

Fig. 5. Plots of the absorption area of $20K_2O\cdot80GeO_2\cdot2SnO_2$ glass against temperature. (a): γ-Ray irrad., (b): thermal neutron irrad.

Mössbauer measurements at lower temperatures were also carried out to elucidate the extent of the irradiation-induced disruption of the chemical bond between germanium and oxygen constituting GeO_6 units, because a parameter of intermolecular force constant (θ^2M) obtained from the temperature dependence of the Mössbauer absorption area is known to give much information on the degree of polymerization and molecular association.[16,28] In the θ^2M value, M is the mass of Mössbauer nucleus and θ indicates Debye temperature. The correlation between θ and the maximum lattice vibration frequency ν_{max} for overall the glass matrix is expressed as $k\theta=h\nu_{max}$ where k is Boltzmann constant and h is Planck constant. The θ^2M value can be correlated with the Mössbauer recoil-free fraction f by using a Debye approximation,[23,29] and is expressed as

$$\theta^2M = \frac{3E^2}{kc^2}\left(\frac{-\,\mathrm{d}\ln f}{\mathrm{d}T}\right)^{-1}, \qquad (1)$$

where E is Mössbauer transition energy and c is the velocity of light. Figure 5 shows the results of the Mössbauer measurements of $20K_2O\cdot80GeO_2\cdot2SnO_2$ glass at lower temperatures, in which natural logarithm of the absorption area (ln$A$) is plotted against measuring temperature T because ln$f$ can be approximated by ln$A$ when a very thin sample is used and the absorption is not saturated. It is seen from Fig. 5 that the absorption area for the thermal neutron irradiated germanate glass is more than one order smaller than that for the γ-ray irradiated glass. This means, as is generally known, that the thermal neutron irradiation results in a more drastic structural change in the network structure than the γ-ray irradiation. The decreased absorption area also suggests that the irradiations result in a disruption of the chemical bonds in the germanate glass, because the recoil-free fraction is closely concerned with the rigidity of the matrix in which Mössbauer nucleus is incorporated. The disruption of the chemical bonds caused by the irradiations, if present, may also affect the $\theta^2 M$ value for the germanate glass. These values being estimated from Eq. 1 by dividing the value of $3E^2/kc^2$, *i.e.*, 2.13×10^4 in the case of 23.9 keV ^{119}Sn, with the slope of the individual straight line are 7.3×10^6 and 6.7×10^6 for the γ-ray and the thermal neutron irradiated germanate glasses, respectively. It is noted that the $\theta^2 M$ value is 7.0×10^6 in the case of the $20K_2O\cdot80GeO_2\cdot2SnO_2$ glass before the irradiation.[16] Considering the magnitude of the error of $\theta^2 M$, *i.e.*, ±0.1—0.2, these results suggest that the γ- and the thermal neutron-irradiation results in little effect on the intermolecular force between two independent GeO_4 units which are connected with each other with the aid of a network modifier such as K^+ and Sn^{4+}. The irradiations are therefore concluded to bring about little change in the ionic bond between tin and the neighboring oxygen atoms constituting GeO_4 units, as is also concluded from the result of isomer shift shown in Fig. 1. The interatomic distance between tin and the neighboring oxygen atoms is also concluded to be unchanged, because the change in the isomer shift is reported to be closely correlated with the interatomic distance between Mössbauer atom and the neighboring atom.[30] This is well consistent with the unchanged $\theta^2 M$ values observed for the irradiated glasses, because $\theta^2 M$ value is also known to be closely affected by the degree of packing around Mössbauer nucleus besides the degree of polymerization. In the irradiated germanate glasses, recoil energy and the recoil momentum of Mössbauer γ-rays will therefore be transferred in almost the same way as do those in the unirradiated glasses. In other words, the irradiated germanate glasses studied in the present paper can still be regarded as polymers from the lattice vibrational point of view, although the chemical bond between germanium and oxygen constituting GeO_6 units is considered to be fairly disrupted.

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