Structural Study of Germanate Glasses by ^{119}Sn Mössbauer Spectroscopy

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Mössbauer study of potassium germanate glasses containing a small amount of Sn^{4+} has been performed to know the relationship between the abnormal composition dependence of physical properties, so-called germanate anomaly, and the local structural change of the glasses. Distinct increases in isomer shift and linewidth and a distinct decrease in quadrupole splitting are observed when the concentration of alkali oxide exceeds about 16 mol%. These changes are ascribed to the formation of nonbridging oxygen atoms in GeO_4 units. This is also supported by a drastic decrease in a parameter of intermolecular force constant obtained from the temperature dependence of Mössbauer absorption area. The composition dependence of the parameter is well consistent with that of glass transition temperature (T_g) of the same samples. Transformation of GeO_4 tetrahedra into GeO_6 octahedra is also confirmed by increases in the parameter of intermolecular force constant and in T_g in the alkali content region lower than 16 mol%. The role of Sn^{4+} is concluded to be a network modifier which is present at an interstitial site of three-dimensional network composed of GeO_4 and GeO_6 units.

Abnormal change in the physical properties of germanate glasses, so-called germanate anomaly, was first reported by Ivanov and Evstroviev.[1] They found maxima in the density- and refractive index-composition curves at the alkali oxide concentration of 10—15 mol%. Similar results were also obtained by Murthy and Ip,[2] and by Murthy and Scroggie[3] in germanate and aluminogermanate glasses, respectively. The germanate anomaly was also observed on viscosity[4] and glass transition temperature,[4,5] and in these physical properties-composition curves, the maxima were observed at the alkali contents of about 17[4] and 15—16[5] mol%, respectively. The decreases in viscosity and glass transition temperature at the alkali content region higher than the critical concentration (17 and 15—16 mol%) were tentatively attributed to the formation of nonbridging oxygen (NBO), because the decreases were thought to be due to the decrease in the cohesiveness of the glasses,[4] and to the depolymerization of the glass network.[5]

Structural study of germanate glasses was first carried out by Murthy and Kirby,[6] and a change in the coordination number of germanium(IV) from 4 to 6 was concluded from a red shift of IR absorption band due to Ge–O–Ge stretching vibration. Fraction of GeO_6 units was first estimated by Sakka *et al.*[7] based on the difference in the IR peak position of the Ge–O–Ge stretching vibration between hexagonal GeO_2 composed of GeO_4 units (875 cm^{-1}) and tetragonal GeO_2 composed of GeO_6 units (700 cm^{-1}). As the result, a maximum fraction of GeO_6 units (28%) was observed at a composition of about 15—20 mol% alkali oxide. The same idea as that in the IR study[7] was applied to X-ray diffraction study[8] and a maximum fraction of GeO_6 units (10—35%) was obtained at a composition region of 20—30 mol% alkali oxide. EXAFS study was also utilized by Sakka *et al.*[9] to know the fraction of GeO_6 units in germanate glasses, and a maximum was observed at an alkali oxide concentration of 15—16 mol%. Raman study by Verweij and Buster[10] revealed the presence of NBO in germanate glasses, in which stretching vibration band due to $Ge-O^-$ was observed at 850—880 cm^{-1}. The Raman study led to a conclusion that the fraction of GeO_6 units increases in the alkali content region ranging from 0 to 18 mol% and then decreases in the region from 18 to 33 mol% with the formation of NBO in GeO_4 units. Smets and Lommen[11] estimated the fraction of NBO in germanate and silicate glasses using X-ray photoelectron spectroscopy (XPS), and the formation of NBO was concluded to start at an alkali oxide concentration of 18 mol% in the case of germanate glasses.

Mössbauer spectroscopy of ^{57}Fe has been successfully used by the present authors for the structural studies of borate,[12–17] borosilicate,[18–19] phosphate,[20,21] and borophosphate[22] glasses to estimate the formation of NBO[12–14,18–22] and, furthermore, the fraction of NBO.[13,14,19] Mössbauer spectroscopy has also been used to examine the steric configuration of halide ions[15,16] in borate glasses as well as a chemical effect of $^{10}B(n,\alpha)^7Li$ nuclear reaction.[17] Kinetic study of the crystallization of borosilicate glasses has also been performed by means of Mössbauer spectroscopy.[23,24] Mössbauer spectroscopy of ^{119}Sn has been utilized to know the structures of borate[25–28] and silicate[25,29,30] glasses. The studies clarified that most Sn^{4+} species are present in octahedral environment and also that stannous ions in borate[27,28] and silicate[30] glasses play a role of network modifier when the SnO content is not so high. It is also noteworthy that the formation of NBO in borate glasses is observed in an alkali content region $\geq$20 mol%, which is consistent with our previous results[12–14,17] obtained from ^{57}Fe Mössbauer studies. These Mössbauer results are reproduced in a review article[31] by Müller-Warmuth and Eckert together with the NMR results of several kinds of glasses.

The present study was carried out to elucidate the local structure of germanate glasses, because most results on the structure and physical properties of the

glasses obtained so far are contradictory and also the germanate anomaly is assumed to be closely correlated with the presence of NBO.

Experimental

All glass samples, denoted by a formula $xK_2O\cdot(100-x)GeO_2\cdot 2SnO_2$, were prepared by fusing mixtures of weighed quantities of guaranteed reagent grade K_2CO_3, GeO_2, and SnO_2 at 1200 °C for 2h in an electric muffle furnace. The K_2O content, x, was changed from 10 to 30 at 5 intervals. Transparent and colorless glasses were prepared by quenching the melts in platinum crucibles with cold water. All the glass samples prepared in this way were confirmed to be amorphous by X-ray diffraction. Mössbauer measurements were performed by a constant acceleration method at various temperatures using a source of $Ca^{119m}SnO_3$. Barium stannate ($BaSnO_3$) was used as a reference for isomer shift. The velocity of spectrometer was calibrated with a metallic iron enriched with ^{57}Fe. All the Mössbauer spectra were fitted to Lorenzian lineshapes by computer calculations. DTA measurements of the glasses (10mg) were performed with a heating rate of 5 °Cmin^{-1} ranging from room temperature to 700 °C.

Results and Discussion

Mössbauer spectra for the germanate glasses containing tin proved to consist apparently of a single absorption peak, as shown in Fig. 1. The isomer shift suggests that tin is present as tetravalent ionic species (Sn^{4+}) with octahedral symmetry[32] because the value is close to, and also smaller than zero velocity. Each

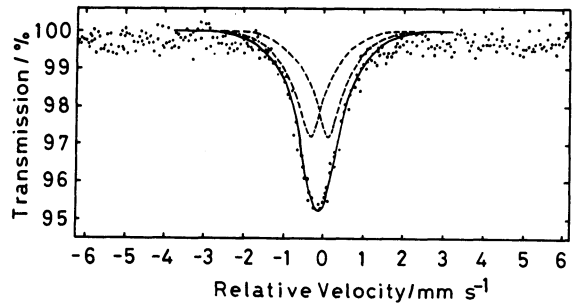

Fig. 1. Mössbauer spectrum of $10K_2O\cdot 90GeO_2\cdot 2SnO_2$ glass.

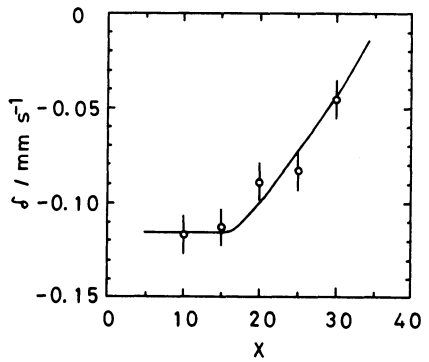

Fig. 2. Variation of the isomer shift of Sn^{4+} with K_2O content.

Mössbauer spectrum was analyzed into a kind of doublet, as shown by broken lines in Fig. 1, and also as a single peak shown by a solid line. The doublet analysis was performed because it was expected that some information on the electric field gradient at tin nucleus or symmetry around Sn^{4+}, if present, could be obtained from the quadrupole splitting. The change in the isomer shift of the Sn^{4+} absorption peak is shown in Fig. 2 as a function of the K_2O content. (Each isomer shift value plotted in Fig. 2 is also consistent with the corresponding value obtained from a single peak analysis, within the experimental error.) It is seen from Fig. 2 that the isomer shift of Sn^{4+} increases almost linearly in the alkali content region higher than $x=$ 16—17. The increase in the isomer shift means the increased s-electron density at tin nucleus.[32] This is consistent with our previous results obtained in the case of borate[12] and borosilicate[18] glasses containing iron, where a continuous decrease in the isomer shift of Fe^{3+} was attributed to an increased s-electron density at the iron nucleus owing to the formation of NBO. (The decrease in the isomer shifts of Fe^{2+} and Fe^{3+} corresponds to the increase in the s-electron density at the iron nucleus because the radius of iron nucleus at the excited state is smaller than that at the ground state). The increase in the isomer shift of Sn^{4+}, *i.e.*, the increase in the s-electron density at tin nucleus, is then assumed to be related in anyway with the formation of NBO in germanate glasses. In the case of Sn^{4+} the increase in isomer shift is known to be related to the increase in covalency.[27,32] The increase in the covalency with the formation of NBO is also observed in the case of borate glasses[28,28] containing Sn^{2+}, although the apparent phenomenon is contrary to the present result. Mössbauer measurements at lower temperatures also gave a result similar to that shown in Fig. 2, and the individual isomer shift values slightly increased as a whole because of the reduced second order Doppler effect (*ca.* 0.04—0.05 mms^{-1} in the temperature range from 78 to 298K). The second order Doppler effect shifts the peak position in the direction of negative velocity, in proportion to the vibration frequency of solid or measuring temperature.[33] The increase in the isomer shift of Sn^{4+} shown in Fig. 2 is therefore concluded to be due not to the second order Doppler shift, but to the increased s-electron density at tin nucleus and the increased covalency in the chemical bond between tin and oxygen, as described above.

Change in the quadrupole splitting of Sn^{4+} is shown in Fig. 3. The quadrupole splitting decreases linearly with alkali oxide content in the alkali content region higher than $x\simeq 17$. This is compatible with the result of isomer shift shown in Fig. 2. The decrease in the quadrupole splitting of Sn^{4+} suggests the increase in the symmetry around tin nucleus because the contribution of valence electrons (q_{val}) to the electric field gradient is negligible in the case of Sn^{4+} with an electron configuration of $4d^{10}$. This is also the case for

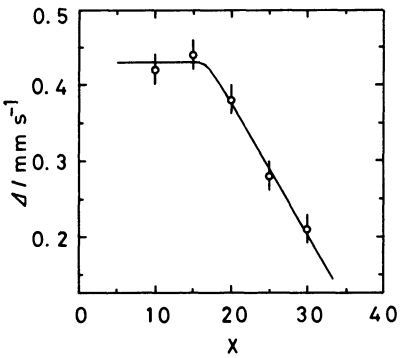

Fig. 3. Variation of the quadrupole splitting of Sn^{4+} with K_2O content.

Fe^{3+} with the $3d^5$ configuration, where a decrease in quadrupole splitting due to the formation of NBO has been observed in borate,[12] borosilicate,[18] phosphate,[20] and borophosphate[22] glasses. The continuous decrease in the quadrupole splitting shown in Fig. 3 is therefore ascribed to the increased symmetry around Sn^{4+} surrounded by six oxygen atoms, owing to the formation of NBO.

Change in the linewidth (FWHM) of the double peak is shown in Fig. 4. In general linewidths of absorption lines for amorphous materials are known to be greater than those for the corresponding crystalline materials. The linewidth ranges from 0.8 to 1.44 $mm\,s^{-1}$ in the case of Sn^{4+} in glasses.[25,26,29,34] The present result is also consistent with those results. The most remarkable feature of Fig. 4 is that the linewidth shows a drastic increase in the alkali content region higher than x=17—18, suggesting an increased irregularity of the steric configuration of glass forming atoms such as oxygen and germanium. This is a quite reverse phenomenon as compared with the earlier results of borate[12] or borosilicate[18] glasses containing Fe^{3+} ions where a continuous decrease in linewidth was observed with the formation of NBO. This will probably be explained by the difference in the structural roles of Fe^{3+} and Sn^{4+}, *i.e.*, the former ion plays a role of network former at the substitutional site of B and Si constituting BO_4 and SiO_4 tetrahedral units, respectively, and the latter is assumed to be present as a network modifier with octahedral symmetry at interstitial sites in a three-dimensional network composed of GeO_4 and GeO_6 units. In contrast with the well-studied role of iron in glasses, the role of tin has not been well understood and the results so far published are contradictory each other.[31] Dannheim *et al.*[30] suggested that both Sn^{4+} and Sn^{2+} in silicate glasses occupy the position of network modifier when the alkali concentration is not so high. This is consistent with the present result. In view of the distinct changes in the isomer shift (Fig. 2) and quadrupole splitting (Fig. 3), from which a formation of NBO could be deduced, the increase in the linewidth of Sn^{4+} is ascribed to the increased disorder brought about by the formation of NBO at the neighboring site of Sn^{4+}.

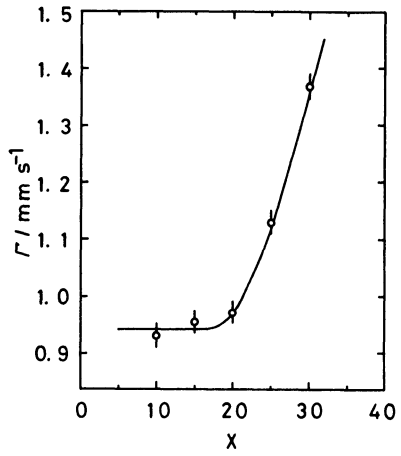

Fig. 4. Variation of the linewidth of Sn^{4+} with K_2O content.

Lattice dynamic study was then performed to confirm the conclusion obtained from the results of isomer shift, quadrupole splitting, and linewidth because it was expected that lattice vibration would be changed with the formation of NBO, *i.e.*, with the depolymerization of three-dimensional network. The correlation between the lattice vibration and the Mössbauer recoil-free fraction f has already been reported by using a Debye approximation.[32,33] In the high temperature limit

$$f = \exp(-6E_R T/k\theta^2), \tag{1}$$

where E_R and k are recoil energy and Boltzmann constant, respectively, and θ is the Debye temperature denoted as $k\theta = h\nu_{max}$ where h is Planck constant and ν_{max} is the maximum lattice vibration frequency. The correlation between E_R and Mössbauer transition energy E (23.9keV in the present study) is given by

$$E_R = E^2/2Mc^2, \tag{2}$$

where M is the mass of Mössbauer nucleus and c is the velocity of light. Combining the two equations, we obtain

$$f = \exp(-3E^2 T/Mc^2 k\theta^2). \tag{3}$$

Equation 3 is further modificated by differentiating the natural logarithm of f with T:

$$\theta^2 M = \frac{3E^2}{kc^2}\left(\frac{-\mathrm{d}\ln f}{\mathrm{d}T}\right)^{-1}. \tag{4}$$

Matsubara *et al.*[34] showed the proportionality of $\theta^2 M$ to the intermolecular force constant α and termed $\theta^2 M$ "parameter of intermolecular force constant." They also showed the relationship between $\theta^2 M$ and the degree of polymerization in a number of organotin compounds. As the result, the parameter was proved to be very useful for the determination of the degree of polymerization and molecular association. In the present study $\mathrm{d}\ln A/\mathrm{d}T$ was utilized instead of $\mathrm{d}\ln f/\mathrm{d}T$ because the latter can be approximated by the former

when a very thin sample is measured and the absorption area (A) is not saturated. In Fig. 5 the individual absorption areas are normalized by the area at 78K. It is seen from Fig. 5 that there is a linear relationship between $\ln A$ and T. Therefore θ^2M is obtained by dividing $3E^2/kc^2$, *i.e.*, 2.13×10^4 in the case of 23.9keV ^{119}Sn, with the slope of the individual straight line. The values of θ^2M are plotted in Fig. 6, together with the Debye temperature calculated by substituting the formula weight in M. Considering the Mössbauer and Raman study by Herber *et al.*,[35] where M is consistent with the molecular weight of organotin compound, the Debye temperatures shown in Fig. 6 are assumed to be rather reasonable ones. The values of θ^2M (All the values in the present paper must be multiplicated by a factor of 10^6) are reported to be about unity for monomer and to be 1.3 and 1.7 for one- and two- dimensional polymers, respectively.[34] It is also reported that the θ^2M values are 2.1 and 3.2 for two three-dimensional polymer compounds.[34] These are the values reported for the organotin compounds in which the chemical bonds between tin and the neighboring atoms are essentially covalent. The parameter (θ^2M) for ionic compound can also be obtained if the Debye temperature or the recoil-free fraction at different temperatures is known. The values of θ^2M calculated for the representative ionic compounds $BaSnO_3$[36] and SnO_2[37] are 22.4 and 8.9 (amorphous) —14.8 (crystalline), respectively, being larger than those for the covalent compounds. From the difference in the Debye temperature of SnO_2,[37] θ^2M is expected to be larger for the crystalline material than for the corresponding amorphous material. Comparing the magnitude of θ^2M obtained in the present study with those for the covalent and ionic compounds described above, the chemical bond between Sn^{4+} and oxygen seems to be essentially ionic. It is generally known that the chemical bonds between network modifier and the neighboring atoms, *i.e.*, oxygen in the case of oxide glasses, are essentially ionic. The present result therefore leads to a conclusion that the role of Sn^{4+} in germanate glasses is a network modifier which is present at an interstitial site of three-dimensional network composed of GeO_4 and GeO_6 units. It is expected that the intermolecular force for a Mössbauer nucleus at an interstitial site becomes less intense than that at a substitutional site. In fact, the θ^2M values obtained in the present study (6.2—8.7) are smaller than that for the amorphous SnO_2 (8.9). The role of Sn^{4+} in germanate glasses is therefore concluded to be similar to that of alkali metal ions like Na^+ and K^+.

Another important feature of Fig. 6 is the distinct composition dependence of θ^2M (and also θ) with a maximum at the K_2O concentration of about $x=16$. The increase in θ^2M with increasing alkali content of the germanate glasses is reasonably explained by an increase in the number of bridging oxygen atoms owing to the formation of GeO_6 units instead of GeO_4

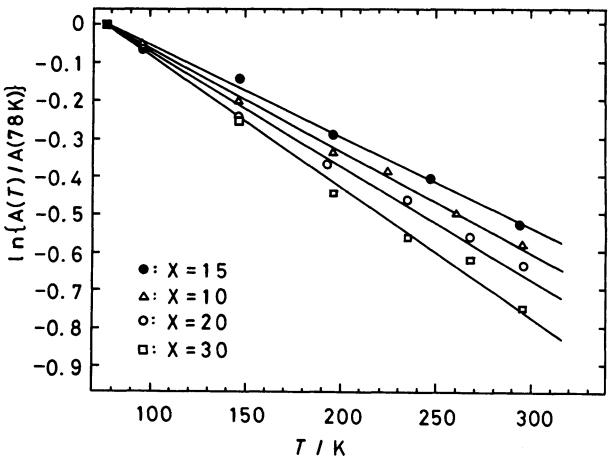

Fig. 5. Plots of the absorption area against temperature.

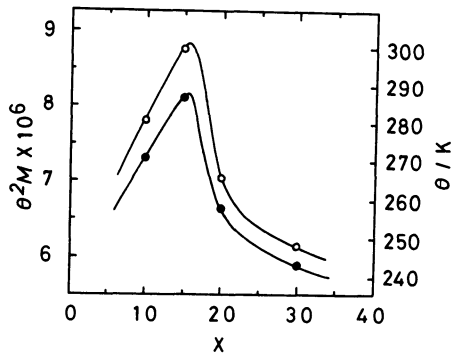

Fig. 6. Variations of the parameter of intermolecular force constant (○) and the Debye temperature (●) with K_2O content.

units. The decrease in θ^2M at the alkali content region higher than $x=16$ is well explained by the formation of NBO which is expected to bring about a drastic decrease in the intermolecular force because of the destruction of network structure. The structural change will result in some physical properties such as glass transition temperature (T_g) and viscosity. Figure 7 shows the result of DTA measurement, which is well consistent with the result of θ^2M. A maximum is observed at almost the same alkali concentration as does that in the θ^2M plot. It is interesting to note that the decrease in T_g is not so rapid as that of θ^2M at the higher alkali content region. This may be due to the different characteristics of the two methods, *i.e.*, T_g corresponds to the mean transition energy for the glass matrix, while θ^2M is closely concerned with the local vibrational energy in the neighborhood of ^{119}Sn. It is therefore, concluded that the parameter of intermolecular force constant, as well as the Mössbauer parameters like isomer shift and quadrupole splitting, is exceedingly sensitive to the structural change of glasses.

All the experimental results obtained in the present study are as follows. In potassium germanate glasses of which the alkali oxide contents are lower than about 16mol%, the increase of the alkali contents results in the increase in the fraction of GeO_6 units. In the alkali

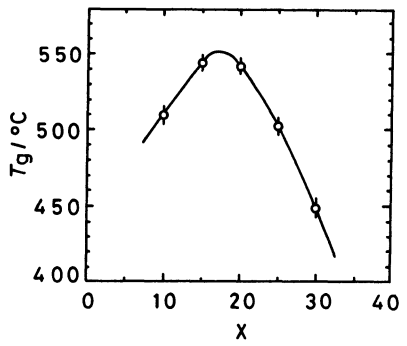

Fig. 7. Variation of the glass transition temperature with K_2O content.

content region higher than about 16mol% the increase in the alkali contents results in the formation of NBO in GeO_4 units in competition with the formation of GeO_6 units, and the former reaction will be predominant with increasing alkali contents. Stannic ion would be present at a site similar to that of K^+, *i.e.*, at an interstitial site in the network composed of GeO_4 and GeO_6 units, as a network modifier with octahedral symmetry.

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