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Mössbauer and DTA Studies of K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ Glasses

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A structural study of ternary sulfate glasses has been performed to elucidate the nature of the chemical bond and the local structure of these glasses. Mössbauer parameters (isomer shift and quadrupole splitting) show drastic decrease with an increase in the K_2SO_4 content. This is ascribed to the gradual change in the coordination number of iron (Fe^{3+}) from six (Oh) to four (Td) when the K_2SO_4 content is higher than about 60 mol%. Lattice dynamic information obtained from low-temperature Mössbauer measurements suggests that the chemical bond between the iron and the neighboring oxygen is essentially ionic. All the Mössbauer results for the ternary sulfate glasses suggest that the Fe^{3+} ions are present at the vacant sites (voids) of the pseudospherical SO_4^{2-} ions which are considered to be randomly packed to constitute the ionic glasses. Glass transition temperature (T_g) of these sulfate glasses, obtained from DTA measurements, also shows a gradual decrease with increasing K_2SO_4 content. This result is very similar to the composition dependency of the Mössbauer parameters described above, and suggests that the ionic field strength of the sulfate glasses decreases with increasing K_2SO_4 content. These experimental results are ascribed to the increased intermolecular bond length between the pseudospherical SO_4^{2-} units.

Zinc sulfate-based glasses are considered to be constituted of randomly packed SO_4^{2-} ions which have essentially spherical geometry.[1-5] The feature of these glasses will lie in the essentially ionic nature of the chemical bond between the SO_4^{2-} ions and in the lack of so-called network structure. This is quite distinguishable from the case of ordinary oxide glasses such as silicate and borate glasses, in which each network-forming atom (Si and B) is covalently bonded with each other by oxygen atoms. As for the ionic salt glasses other than the $ZnSO_4$-based glasses, nitrate, nitrite, carbonate, formate, and acetate glasses are known to be present.[1] These ionic salt glasses seem to be very interesting and important materials from the scientific point of view, because their glass structure is quite different from the structure of ordinary oxide glasses, as described above. Coulombic interaction between cation (e.g., K^+ and Zn^{2+}) and anion (e.g., SO_4^{2-}) and a packing effect of them are therefore considered to be predominant factors for the preparation of the ionic salt glasses. Physical properties of some $ZnSO_4$-based glasses, such as density, refractive index, glass transition temperature, and heat capacity, have been studied by Rao et al.[2,3] They reported that the increase in the $ZnSO_4$ content results in gradual increases in density and refractive index of these glasses. A structural model for the K_2SO_4-$ZnSO_4$ glasses was proposed on the basis of the composition dependency of these physical properties.[2] A few structural studies of $ZnSO_4$-based glasses have been performed by means of X-ray diffraction[4] and ESR.[5,6] Coordination numbers of K^+, Na^+, and Zn^{2+} in the $ZnSO_4$-based glasses are known to be twelve, eight, and six, respectively.[2-4] An ESR study of binary K_2SO_4-$ZnSO_4$ glasses doped with Cu^{2+} or Mn^{2+} suggests that these transition metal ions occupy the octahedral sites, just as in the case of the Zn^{2+} ions surrounded by six oxygen atoms given by six SO_4^{2-} tetrahedra.[2]

The present Mössbauer and DTA (Differential Thermal Analysis) studies of the ternary K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ glasses were carried out in order to obtain the structural information such as the coordination number and the symmetry of metal ions and the nature of the chemical bond between the metal ions and the SO_4^{2-} ions. Mössbauer spectroscopy is well utilized for the structural study of several inorganic glasses[7-18] by the authors. Mössbauer study of some halide glasses, i.e., KCl-$ZnCl_2$[17] and BaF_2-ZrF_4,[18] revealed that these glasses are constituted of three-dimensional network of $ZnCl_4$ tetrahedra and of the one- or two-dimensional chain-like polymer of ZrF_6 octahedra, respectively. DTA measurements also give us some useful information on the structure of glasses. In general, the increase in the coordination number of network-forming atom is known to result in a gradual increase in the glass transition temperature (T_g).[15,19-23] For example, step-by-step structural changes of network formers from BO_3 to BO_4 units and from GeO_4 to GeO_6 units are well reflected in T_g in borate and germanate glasses, respectively. This is probably due to the increased degree of bridging in the glass skeleton. On the other hand, a decreased degree of bridging in the glass skeleton, brought about by the formation of nonbridging oxygen atom, is observed as a gradual decrease in T_g.[15,22,23] As for the T_g of the $ZnSO_4$-based glasses, a composition dependency has so far been observed only in a ternary K_2SO_4-Na_2SO_4-$ZnSO_4$ glass system,[3] in which an increase in T_g is ascribed to the increased coordination number of alkali metal ion caused by the substitution of K_2SO_4 for Na_2SO_4.

Experimental

A series of K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ glasses, in which $Fe_2(SO_4)_3$ content is lower than 12 mol%, were prepared by fusing the individual mixtures (1 g) of K_2SO_4, $ZnSO_4\cdot 7H_2O$, and $Fe_2(SO_4)_3$, of a guaranteed reagent grade, at 640—740 °C for 2—40 min using an electric muffle furnace. The anhydrous $Fe_2(SO_4)_3$ was prepared by heating the commercially available $Fe_2(SO_4)_3\cdot nH_2O$ at 235 °C for 6 h, because the simultaneous DTA and TG (Thermal Gravity) measurements of the hydrous iron(III) sulfate proved to be almost completely dehydrated when heated at 235 °C. Each melt in a platinum crucible was quenched with ice-cold water after the fusion. All the glass samples prepared in this way show transparent and brown color. Mössbauer measurements were performed by a constant acceleration method at various temperatures with a proportional counter and a 1024 channel-multichannel scaler. Cobalt-57 (10 mCi) diffused into a palladium foil was used as the Mössbauer source. As for the reference material of isomer shift, a metallic iron foil enriched with iron-57 was used. Calibration of the Mössbauer spectrometer was also performed using the iron foil. Every Mössbauer spectrum obtained from room-temperature measurement was analyzed into a quadrupole doublet, having the same width and intensity with each other, due to Fe^{3+} ions. On the other hand, each Mössbauer spectrum obtained at temperatures lower than room temperature was analyzed into two kinds of quadrupole doublets due to Fe^{3+} and Fe^{2+} ions. Mössbauer measurements were performed in such a condition that the thickness of the glass sample should be as thin as possible. Simultaneous DTA and TG measurements were performed for each glass sample of 20 mg with a heating rate of 5 °C min^{-1}. The DTA and TG measurements were performed over the range from room temperature to 700 °C, using Al_2O_3 powder as a standard material for the DTA measurement.

Results and Discussion

The glass-forming region for the ternary K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses prepared in the present study is shown with a solid line in Fig. 1, in which open circles indicate the formation of glass samples. Closed and half-closed circles in Fig. 1 indicate the formations of ceramics (devitrified) and glass-ceramics (partially devitrified), respectively. It is seen from Fig. 1 that the glass-forming region for the binary K_2SO_4–$ZnSO_4$ system is in the range of 35—65 mol%, which is approximately consistent with the already published results.[2–4,24–26] At the early stage of the present study, ternary glass system K_2SO_4–$ZnSO_4$–$FeSO_4$ was also tried to prepare with $FeSO_4\cdot 7H_2O$ or $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$. As the result, the latter reagent proved to be useful for the preparation. The ternary $ZnSO_4$-based glasses prepared with $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$, however, showed the absorption only due to Fe^{3+} ions in the Mössbauer spectra. This will be due to the oxidation reaction of Fe^{2+} to Fe^{3+} during the sample preparation, because all of the sample preparations was performed in the atmosphere. The glass-forming region for the ternary $ZnSO_4$-based glasses prepared with $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$ is shown by a dotted line in Fig. 1. Sample preparation for the ternary K_2SO_4–$ZnSO_4$–Fe_2O_3 system was also attempted in the present study, but no vitreous sample could be obtained.

A typical Mössbauer spectrum of the ternary K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glass system is shown in Fig. 2a. The spectrum indicates that the iron is present as a paramagnetic Fe^{3+} ion in these glasses. It is speculated from Fig. 2a that only a small amount of Fe^{2+} ions is also present in these glasses. (Note that a weak peak around 2 mm s^{-1} is a part of the quadrupole doublet due to Fe^{2+} ions and that the relative absorption intensity of the Fe^{2+} peak is comparable to the amplitude of the scattering of the points around the base line.) Each Mössbauer spectrum measured at room temperature is therefore analyzed into a quadrupole doublet only due to Fe^{3+} ions, as is shown by a solid line in Fig. 2a.

Mössbauer parameters for the ternary $ZnSO_4$-based glasses are summarized in Table 1, in which the Mössbauer parameters for the anhydrous $Fe_2(SO_4)_3$ used for the preparation of the glass samples are also

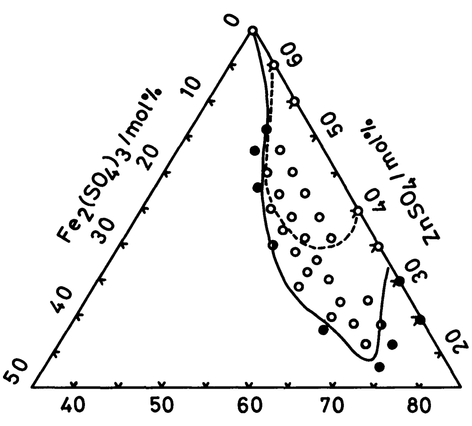

Fig. 1. Glass-forming region for the K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ system.

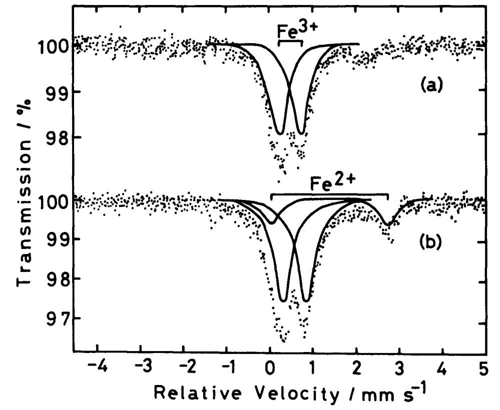

Fig. 2. Mössbauer spectra of $47K_2SO_4\cdot 45ZnSO_4\cdot 8Fe_2(SO_4)_3$ glass. (a): At room temperature (296 K), (b): at 78 K.

shown for comparison. Table 1 demonstrates that the isomer shift and the quadrupole splitting show drastic and gradual decreases when the K_2SO_4 content increases. On the other hand, linewidth shows a gradual increase with the increase in the K_2SO_4 content. The magnitude of the linewidth is larger than that of the ordinary crystalline compounds, which is usually smaller than ca. 0.4 mm s^{-1} in the case of ^{57}Fe-Mössbauer spectroscopy. (Compare to the linewidth of the anhydrous $Fe_2(SO_4)_3$ shown in Table 1.) The absorption peak with large linewidth is ascribed to the increased irregularities in the interatomic bond length and bond angle. Figure 3 shows the drastic decrease in the isomer shift with an increase in the K_2SO_4 content. The drastic change in the isomer shift corresponds to a gradual change in the coordination number of Fe^{3+} from six to four. The isomer shifts of Fe^{3+} with octahedral symmetry are known to be larger than ca. 0.4 mm s^{-1}.[7–14] On the other hand, the isomer shifts are usually smaller than ca. 0.4 mm s^{-1} in the case of tetrahedral Fe^{3+} ions.[7–14] In the several Mössbauer studies of oxide and halide glasses[7–18] performed until now by the authors, the coordination number of iron or tin has shown single values even if the composition changes. The change in the coordination number of iron from six to four shown in Fig. 3 is, therefore, considered to be a very rare case. It is speculated from Fig. 3 that the coordination number of iron is essentially six when the K_2SO_4 content is lower than about 60 mol% in the case of K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses containing 8 mol% $Fe_2(SO_4)_3$. In such glasses, Fe^{3+} ions are considered to be present at the substitutional sites of Zn^{2+} ions which are reported to be octahedrally surrounded by six oxygen atoms originating from six SO_4^{2-} tetrahedra.[2–6] On the other hand, the Fe^{3+} ions in the ternary K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses are speculated to occupy tetrahedral sites surrounded by four oxygen atoms when the K_2SO_4 content is higher than 60 mol%. The four oxygen atoms in these glasses will be provided by four SO_4^{2-} ions. Within the authors' knowledge, the four-fold coordinated metal ions are not observed in the $ZnSO_4$-based glasses until now, and most of the transition metal ions have been considered to occupy the octahedral sites at the substitutional sites of Zn^{2+} ions.[5,6] In the binary or ternary K_2SO_4–$ZnSO_4$ glasses, by the way, the increase in the K_2SO_4 content is known to result in decreases in density and ionic field strength of the glasses.[2–4] A decrease in the density seems to suggest the prolonged intermolecular distance between SO_4^{2-} ions. In such a condition, the interatomic distance between iron and the neighboring oxygen atom will also be prolonged, because every Fe^{3+} ion is considered to be present at the vacant sites (voids) surrounded by six or four SO_4^{2-} ions. The gradual increase in the interatomic distance between the iron and the oxygen will reduce the crystal field strength, and the coordination number of iron will gradually decrease from six to four with increasing K_2SO_4 content. The isomer shift of anhydrous $Fe_2(SO_4)_3$ used for the sample preparation (Table 1) is typical of the octahedral Fe^{3+} ion with high ionicity, and is in good agreement with the published data for the ionic crystals containing iron.[27,28]

The gradual change in the coordination number of iron from six to four seems to be correlated with the

Table 1. Mössbauer Parameters for K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ Glasses Measured at 296 K

Composition	δ[a)] mm s^{-1}	Δ[b)] mm s^{-1}	Γ[c)] mm s^{-1}
$47K_2SO_4 \cdot 45ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.45	0.57	0.44
$50K_2SO_4 \cdot 42ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.42	0.54	0.48
$53K_2SO_4 \cdot 39ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.41	0.51	0.43
$56K_2SO_4 \cdot 36ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.43	0.56	0.48
$59K_2SO_4 \cdot 33ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.39	0.49	0.45
$62K_2SO_4 \cdot 30ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.29	0.45	0.51
$65K_2SO_4 \cdot 27ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.32	0.49	0.55
$68K_2SO_4 \cdot 24ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.27	0.30	0.56
$71K_2SO_4 \cdot 21ZnSO_4 \cdot 8Fe_2(SO_4)_3$	0.25	0.33	0.53
$Fe_2(SO_4)_3$	0.48	0.24	0.37

a) Isomer shift. b) Quadrupole splitting. c) Linewidth.

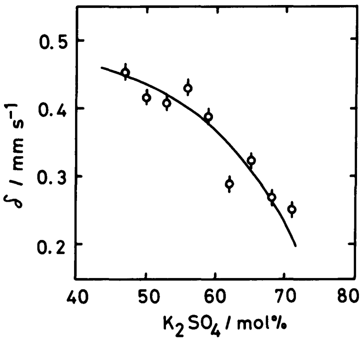

Fig. 3. Change in the isomer shift of Fe^{3+} with K_2SO_4 content of the K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses.

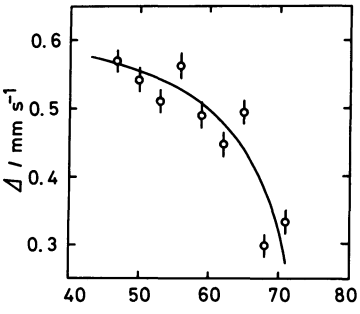

Fig. 4. Change in the quadrupole splitting of Fe^{3+} with K_2SO_4 content of the K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses.

composition dependency of the quadrupole splitting. This is shown in Fig. 4, from which it is seen that the quadrupole splitting decreases drastically with increasing K_2SO_4 content. Very small quadrupole splittings (0.30 and 0.33 mm s^{-1}) are observed when the K_2SO_4 content is close to 70 mol%; the quadrupole splittings are smaller than the linewidths of the corresponding absorptions, i.e., 0.56 and 0.53 mm s^{-1} in the cases of the glasses with the K_2SO_4 contents of 68 and 71 mol%, respectively. From the distinct decrease in the quadrupole splitting for the higher K_2SO_4-content glasses (Fig. 4), it is concluded that the symmetry around the Fe^{3+} ion increases with increasing K_2SO_4 content. (Each Fe^{3+} ion has a symmetric electron configuration of $3d^5$ in the outer-most orbital, and therefore only the electric field gradient caused by the neighboring atoms or ions, i.e., oxygen atoms in the present study, will be the primary origin of the quadrupole splitting.) The gradual decrease in the quadrupole splitting with increasing K_2SO_4 content therefore suggests that the symmetry around the Fe^{3+} ion is higher when surrounded by four SO_4^{2-} ions than when surrounded by six SO_4^{2-} ions. It is seen from Table 1 that the quadrupole splitting for the anhydrous $Fe_2(SO_4)_3$ is smaller than those for the ternary K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses. The very small quadrupole splitting for the Fe^{3+} ion is in agreement with the published data,[27,28] and reflects the nearly cubic symmetry. All the Mössbauer parameters for the anhydrous $Fe_2(SO_4)_3$ shown in Table 1 therefore suggest that the local environment of iron in the ternary K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses is quite different from that of iron in the anhydrous $Fe_2(SO_4)_3$ used for the preparation.

The composition dependency of the glass transition temperature (T_g), obtained from DTA measurements of the ternary K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses, is shown in Fig. 5. It is obvious from Fig. 5 that the T_g shows a distinct composition dependency similar to that of the isomer shift shown in Fig. 3. The gradual decrease in the T_g with an increase in the K_2SO_4 content suggests that the strength of the chemical bond between metal ions (K^+, Zn^{2+}, and Fe^{3+}) and SO_4^{2-} ions becomes weakened when the fraction of the K_2SO_4 content increases. This is ascribed to the increased intermolecular distance between SO_4^{2-} ions and to the increased interatomic distance between the metal ions and the SO_4^{2-} ions, as described above. The increased intermolecular and interatomic distances are assumed from the decrease in the density observed in the binary K_2SO_4–$ZnSO_4$ or ternary K_2SO_4–Na_2SO_4–$ZnSO_4$ glasses when the K_2SO_4 content increases.[2–4] (The interatomic distance between the sulfur atom and the four oxygen atoms constituting a pseudospherical SO_4^{2-} ion is considered not to be changed even if the composition is changed.)

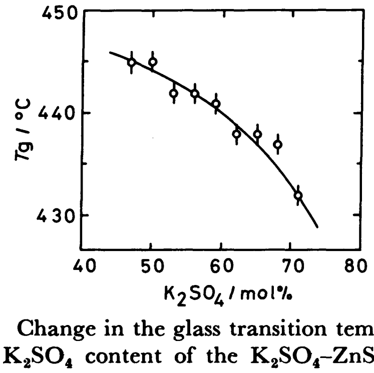

Fig. 5. Change in the glass transition temperature (T_g) with K_2SO_4 content of the K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses.

Mössbauer measurements of a ternary K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glass, at various temperatures lower than room temperature, were also performed to know the nature of the chemical bonds between metal ions and SO_4^{2-} ions and between two SO_4^{2-} ions. Measurements of Mössbauer spectra at low temperatures have already been performed on germanate[15,16] and BaF_2–ZrF_4–FeF_2[18] glasses, and some useful information on the intermolecular force constant has been obtained by the authors. The intermolecular force constant ($\theta^2 M$) is expressed by

$$\theta^2 M = 3E^2/kc^2(-\mathrm{d}\ln f/\mathrm{d}T)^{-1}, \tag{1}$$

where E and f are transition energy (14.4 keV in the case of ^{57}Fe-Mössbauer spectroscopy) and recoil-free fraction in the Mössbauer spectrum, respectively. In the Eq. 1, k and c are Boltzmann constant and the velocity of light, respectively. It is easily understood from Eq. 1 that the value of $\theta^2 M$, in which θ is so-called Debye temperature and M is the mass of Mössbauer nucleus, can be obtained by dividing $3E^2/kc^2$, i.e., 7.76×10^3 in the present study, with the slope of the straight line obtained in the $\ln f$ vs. temperature (T) plot. In the present study, an absorption area (A) is plotted instead of the recoil-free fraction f, because $\mathrm{d}\ln f/\mathrm{d}T$ can be approximated by $\mathrm{d}\ln A/\mathrm{d}T$ when a very thin sample is used.

Mössbauer spectrum of $47K_2SO_4 \cdot 45ZnSO_4 \cdot 8Fe_2(SO_4)_3$ glass at lower temperatures consists of two quadrupole doublets, as is also shown in Fig. 2b, due to Fe^{3+} and Fe^{2+} ions. At lower temperatures, the relative absorption area of the Fe^{2+} peak proved to be somewhat higher than that at room temperature. For example, the absorption area amounts to 17.5% at 78 K (Fig. 2b), showing a gradual decrease with increasing temperature. The formation of Fe^{2+} species is probably due to an electron transfer from a part of SO_4^{2-} ions, which are considered to be thermally decomposed into SO_2 and O_2 during the fusion, to the Fe^{3+} ions. All the Mössbauer parameters for the $47K_2SO_4 \cdot 45ZnSO_4 \cdot 8Fe_2(SO_4)_3$ glass, obtained at lower temperatures, are summarized in Table 2. It is obvious from Table 2 that the isomer shift and the quadrupole splitting of the Fe^{3+} absorptions show

Table 2. Mössbauer Parameters of $47K_2SO_4 \cdot 45ZnSO_4 \cdot 8Fe_2(SO_4)_3$ Glass Measured at Lower Temperatures

Temperature	Fe^{3+}			Fe^{2+}		
	δ[a)]	Δ[b)]	Γ[c)]	δ[a)]	Δ[b)]	Γ[c)]
K	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$
78	0.54	0.62	0.50	1.34	2.69	0.43
104	0.54	0.61	0.51	1.34	2.73	0.45
140	0.53	0.60	0.50	1.30	2.62	0.45
167	0.51	0.59	0.51	1.28	2.52	0.49
200	0.49	0.59	0.50	1.27	2.41	0.52
230	0.48	0.58	0.50	1.24	2.39	0.55
252	0.47	0.58	0.51	1.22	2.43	0.48
284	0.44	0.57	0.47	1.17	2.24	0.47

a) Isomer shift. b) Quadrupole splitting. c) Linewidth.

distinct decreases when the temperature increases. This is illustrated graphically in Fig. 6, from which it is seen that both Mössbauer parameters show linear relationships with temperature. These results indicate that no structural change, such as a phase transition observed in a BaF_2-ZrF_4-FeF_2 glass,[18)] occurs in the ternary K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ glass within the temperature region ranging from 78 to 284 K. In the case of the BaF_2-ZrF_4-FeF_2 glass,[18)] the corresponding plots of isomer shift and quadrupole splitting vs. temperature were found to be individually composed of two straight lines crossed with each other at the phase transition temperature of 225 K. Changes in the isomer shift and the quadrupole splitting of the Fe^{2+} absorptions are not graphically shown in the present study because they have large experimental errors. However, they also have a tendency to decrease almost linearly with increasing temperature.

Change in the absorption area with temperature is shown in Fig. 7, where the absorption area of Fe^{3+} plus Fe^{2+} (Fig. 7a) and that of only Fe^{3+} (Fig. 7b) are plotted separately. It is obvious from Fig. 7a and b that the absorption area shows a linear relationship with temperature. The linear correlationship between $\ln A$ and T suggests that a Debye model can be applied to the so-called lattice dynamic study of the K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ glass, and that no structural change occurs within the temperature range of 78 to 284 K. This is consistent with the results for the isomer shift and the quadrupole splitting described above. In Fig. 7, each absorption area is normalized by the absorption area at 78 K. From the slope of the straight line shown in Fig. 7a, θ^2M value proved to be 3.9×10^6. This is almost the same as the θ^2M value of 4.3×10^6 obtained from the corresponding plot of the absorption area of only Fe^{3+} ions (Fig. 7b). Anyhow, these values are larger than the representative values (1—3×10^6) reported for the monomer or polymer compounds[29)] of which chemical bond is known to be essentially covalent. The θ^2M value is known to reflect the degrees of bridging and packing as well as the nature of the chemical bonds of several crystalline and non-crystalline compounds.[15,16,18,29)] Considering the experimental results together with the structural model proposed for binary K_2SO_4-$ZnSO_4$ or ternary K_2SO_4-Na_2SO_4-$ZnSO_4$ glasses, that the glasses consist of random close packing of pseudospherical SO_4^{2-} ions,[2—4)] the θ^2M values obtained in the present study seem to reflect the essentially ionic nature of the chemical bonds between metal ions and SO_4^{2-} ions and between two SO_4^{2-} ions. It seems that the θ^2M values obtained for the $47K_2SO_4 \cdot 45ZnSO_4 \cdot 8Fe_2(SO_4)_3$ glass in the present study are a little smaller than those for the representative ionic compounds such as $BaSnO_3$ and SnO_2, of which θ^2M values are estimated to be 22.4×10^6 and 8.9×10^6, respectively.[15)] This is probably due to the difference in the degree of packing effect. ($BaSnO_3$ and SnO_2 are known to be rigid ionic crystals of perovskite- and rutile-type structures, respectively.) Mössbauer studies of several germanate glasses[15,16)] containing 2 mol% SnO_2 revealed that the θ^2M value has a close correlationship with the composition of glass, ranging from 6.2×10^6 to 8.7×10^6. In the germanate glasses,[15,16)] tin (IV) proved to be ionically present at the interstitial sites of the three-dimensional network composed of GeO_4 and GeO_6 units. In the case of $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass,[18)] the θ^2M value showed a drastic change from

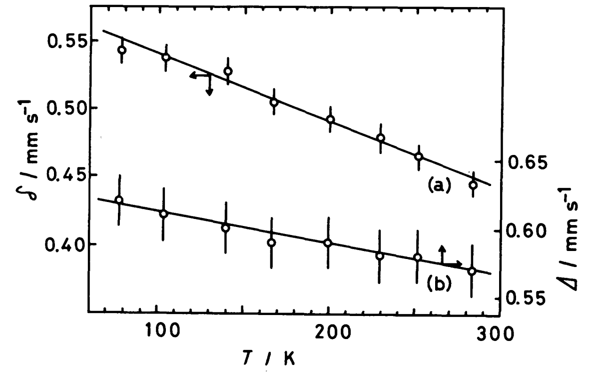

Fig. 6. Changes in the isomer shift(a) and quadrupole splitting(b) of Fe^{3+} in the $47K_2SO_4 \cdot 45ZnSO_4 \cdot 8Fe_2(SO_4)_3$ glass with temperature.

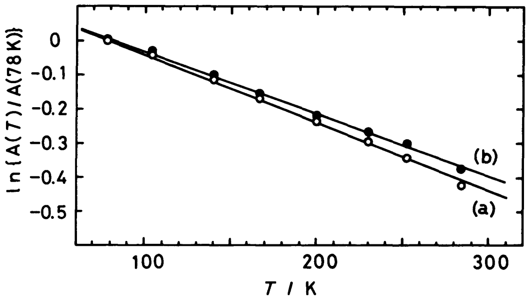

Fig. 7. Changes in the absorption area for the $47K_2SO_4 \cdot 45ZnSO_4 \cdot 8Fe_2(SO_4)_3$ glass with temperature. (a): Fe^{3+} plus Fe^{2+}, (b): only Fe^{3+}.

6.9×10^6 to 1.9×10^6 at the phase transition temperature described above. In the ZrF_4 -based glass,[18] iron(III) proved to be ionically present at the interstitial sites of one- or two-dimensional zigzag chains composed of ZrF_6 octahedra. Judging from all the experimental results discussed in the present paper, the chemical bonds between metal ions (K^+, Zn^{2+}, and Fe^{3+}) and SO_4^{2-} ions and between two SO_4^{2-} ions are concluded to be essentially ionic. The K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$ glasses are therefore concluded to be composed of random close packing of pseudospherical SO_4^{2-} ions. Potassium, zinc, and iron ions are considered to be ionically present at the vacant sites (voids) made by the pseudospherical SO_4^{2-} ions.

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