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Random Packing of Ions in the Ionic Glass xKNO$_3$·(100−x)Sr(NO$_3$)$_2$ (x=22—60) and the γ-Ray Induced Cleavage of K-ONO$_2$ Bonds

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Synopsis. The IR peak positions of the ν_3 (1386 cm^{-1}), ν_2 (814 cm^{-1}), and ν_4 (737 cm^{-1}) modes of NO$_3^-$ are constant in nitrate glasses. This is also the case for the Sr-ONO$_2$ (1439 cm^{-1}) and K-ONO$_2$ (1270 cm^{-1}) bonds. The latter peak is observed only in glasses in which the degeneracy is removed due to the lowered symmetry ($D_{3h}\rightarrow C_{2v}$).

It is generally known that "ionic glass" comprises randomly packed cations and anions. "Ionic glass" has no network formers (NWF: e.g. B^{3+}, Al^{3+}, and Si^{4+}), which constitute one-, two-, or three-dimensional network structures with covalent -O-NWF-O- bonds, depending on the chemical composition.[1—4] The absence of covalent -O-NWF-O- bonds produces interesting physical properties: e.g., high electrical conductivity and low glass transition temperature (T_g). Very little is known about the structure of nitrate glass.[1] This study was carried out in order to elucidate the local structure of binary nitrate glasses by means of FT-IR spectroscopy and DTA (differential thermal analysis). A DTA study was performed in order to estimate T_g, since it is closely related to the structure and the chemical composition.[2—4] Gamma-ray irradiation with a ^{60}Co source was carried out in order to elucidate the change in the structure, e.g., γ-ray induced crystallization as was observed in the IR-light transmitting gallate and tellurite glasses,[5] and the reduction of Fe^{3+} into Fe^{2+} observed in borate glasses.[6]

Experimental

The "ionic glass", xKNO$_3$·(100−x)Sr(NO$_3$)$_2$, was prepared by fusing a weighed amount of KNO$_3$ and Sr(NO$_3$)$_2$ of guaranteed reagent grade at 600 °C for 3 h in a dry nitrogen atmosphere. The melt was quenched with two copper plates at room temperature (RT). The chemical composition was determined with an atomic absorption/flame emission spectrometer (Shimadzu AA-625-11); the atomic absorption spectrometer was used for determining Sr^{2+} at 460.7 nm and the flame emission spectrometer was used for K$^+$ at 766.5 nm. Glass formation was possible when the KNO$_3$ content (x) was in the 22—60 mol% range. The IR spectra were recorded on an FT-IR spectrometer (JASCO FT/IR-5000) by the conventional KBr-disk method. DTA was conducted at a heating rate of 5 °C min^{-1} from RT to 300 °C with a reference of α-Al$_2$O$_3$. Gamma-ray irradiation with a ^{60}Co source was carried out at RT at a dose rate of 2.1×10^3 Gy h^{-1}.

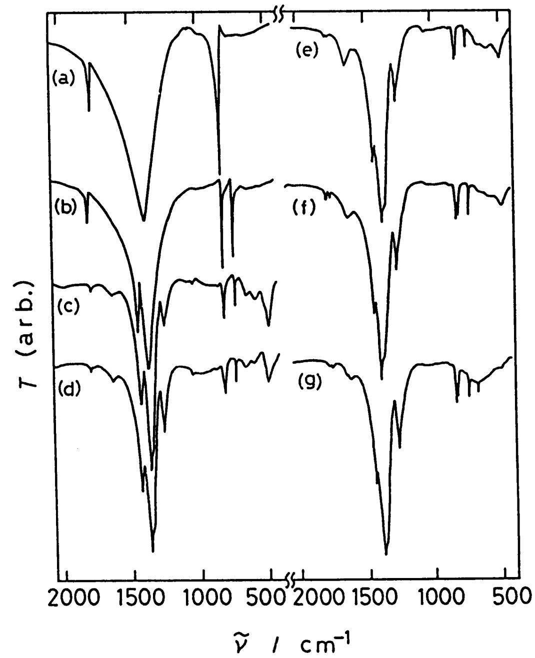

Fig. 1. FT-IR spectra of (a) crystalline KNO$_3$, (b) crystalline Sr(NO$_3$)$_2$, and (c)—(g) xKNO$_3$·(100−x) Sr(NO$_3$)$_2$ glasses; (c) x=22, (d) x=35, (e) x=43, (f) x=49, (g) x=60.

Results and Discussion

The IR spectra of xKNO$_3$·(100−x)Sr(NO$_3$)$_2$ glasses are illustrated in Fig. 1. The spectra of crystalline KNO$_3$ and Sr(NO$_3$)$_2$ are shown for comparison. The intense peak observed at 1386(±1) cm^{-1} in Figs. 1c—f is ascribed to the stretching vibration of a doubly degenerate vibration (ν_3 mode) of NO$_3^-$ ions.[7] The peak position of the ν_3 mode in the nitrate glasses is identical to that in crystalline KNO$_3$ (1386 cm^{-1}), as shown in Fig. 1a. (In the glass with the x of 60, the ν_3 mode was observed at 1383 cm^{-1} (Fig. 1g).) The corresponding mode was observed at 1373 cm^{-1} in crystalline Sr(NO$_3$)$_2$, as shown in Fig. 1b. The two peaks observed at 814 and 737 cm^{-1} in crystalline Sr(NO$_3$)$_2$ were, respectively, assigned to the out-of-plane bending (ν_2) and the O-N-O bending of a doubly degenerate vibration (ν_4) of NO$_3^-$ ions.[7] They were respectively observed at 814—816 and 737—739 cm^{-1} in nitrate glasses (Figs. 1c—g). The ν_4 mode was not observed in crystalline KNO$_3$ (Fig. 1a), probably because the doubly degenerate state of NO$_3^-$ ions was removed as a result of the lowered symmetry from D_{3h} to C_{2v}.[7] The broad peak due to the ν_3 mode reflects the lowered symmetry of the NO$_3^-$ ions. It can be seen from Fig. 1 that the peak positions of the stretching vibration (ν_3) and the bending vibrations (ν_2 and ν_4) are constant in nitrate glasses within an experimental error of ±1 cm^{-1}; the N-O bond length of NO$_3^-$ is constant in nitrate glasses, and is close to that in crystalline Sr(NO$_3$)$_2$. This is also the case for the weak peak observed at 1441—1439 cm^{-1}, which is ascribed to the N-O stretching vibration of the Sr-ONO$_2$ bonds;[8] it was observed in both crystalline Sr(NO$_3$)$_2$ and nitrate glasses. The peak can be observed because the doubly degenerate ν_3 mode is partially broken in crystalline Sr(NO$_3$)$_2$, due to the lowered symmetry.[8] Related to this, Bon et al.[9] have suggested that a phase transition of the order-disorder type occurs at 220—270 K in crystalline Sr(NO$_3$)$_2$ and that the Sr^{2+} ions can occupy sites other than the original lattice site; they can migrate at a temperature higher than the phase-transition temperature, producing a locally disordered phase. Figure 2b is consistent with the peak assignment, i.e. a decreasing fraction of the Sr-ONO$_2$ bonds is observed in the IR spectra with a decreasing Sr(NO$_3$)$_2$ (increasing KNO$_3$) content. The fraction was estimated from the peak intensity of Sr-ONO$_2$ normalized by the intensity of NO$_3^-$ (1386 cm^{-1}). Figures 1c—g indicate that the xKNO$_3\cdot(100-x)$Sr(NO$_3$)$_2$ glasses comprise randomly packed K$^+$, Sr^{2+}, and NO$_3^-$ and that the glasses should have very similar local structures.

An IR peak was observed at 1270—1272 cm^{-1} only in the glasses (Figs. 1c—g). This peak is ascribed to the N-O stretching vibration of singly bonded K-ONO$_2$, which is observed due to the removal of the degeneracy when the symmetry of NO$_3^-$ is lowered from D_{3h} to C_{2v}.[7] The chemical bond between K$^+$ and the oxygen of NO$_3^-$ in crystalline KNO$_3$ should be negligible due to the large interionic length between K$^+$ and NO$_3^-$ in the aragonite (CaCO$_3$)-type structure. Random packing of cations and anions produces new K-ONO$_2$ bonds in nitrate glasses, in which some K$^+$ ions have a single bond with the oxygen atoms in the NO$_3^-$ ions. The formation of new K-ONO$_2$ bonds is known from the IR-peak intensity of K-ONO$_2$ normalized by the intensity of the NO$_3^-$ (1386 cm^{-1}), as shown in Fig. 2a; the fraction of K-ONO$_2$ gradually increases with increasing KNO$_3$ content. Figure 2a is in contrast to Fig. 2b, which shows a decreasing IR-peak intensity of Sr-ONO$_2$ bonds.

Figure 3 shows the results of DTA, in which the intense endothermic peak observed at around 94—98 °C is due to the "glass transition." It is well known that structural relaxation occurs very frequently at around T_g. For example, a cleavage of the -O-NWF-O- bonds was observed in oxide glasses, followed by a rearrangement of the oxygen atoms.[10] On the contrary, migration of ions frequently occurs in "ionic glass". The endothermic peak observed at around 240 °C is due to melting. T_g is generally defined as being the temperature at which the tangent to the endothermic peak of the "glass transition" intersects with the base line of the DTA (or DSC) curve. They are estimated to be 75, 76, 77, 74, and 73 °C when the KNO$_3$ contents (x) are 22, 35, 43, 49, and 60 mol%, respectively. The almost constant T_g's, being in the range of 75 ± 2 °C, indicate that the structure is very similar to each other, as described above; same interionic distance between the cation (K$^+$ or Sr^{2+}) and anion (NO$_3^-$), same coordination number of the cations, and the same degree of random ionic packing. This is quite different from the results of oxide glasses in which T_g changes drastically depending on the composition and structure; a formation of nonbridging oxygen and a change in the skeleton structure were observed in several borate, vanadate, and tellurite glasses.[2-4]

The IR spectra of 49KNO$_3\cdot$51Sr(NO$_3$)$_2$ glass irradiated with ^{60}Co-γ rays (5×10^3—5×10^5 Gy) are similar to each other. The irradiation effect is reflected in the fraction of K-ONO$_2$ bonds observed in the IR spectra.

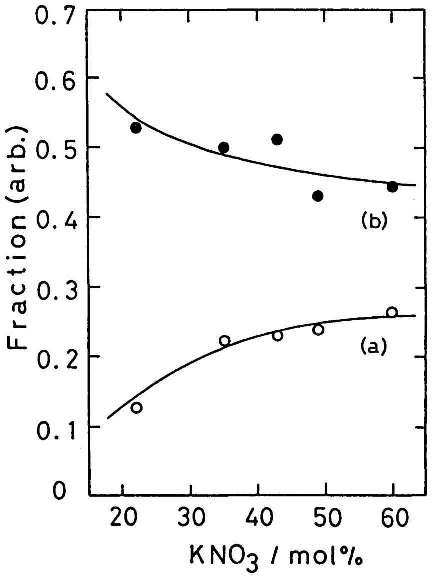

Fig. 2. Relative fraction of (a) K-ONO$_2$ (1270—1272 cm^{-1}) and (b) Sr-ONO$_2$ (1441—1439 cm^{-1}) bonds in the FT-IR spectra.

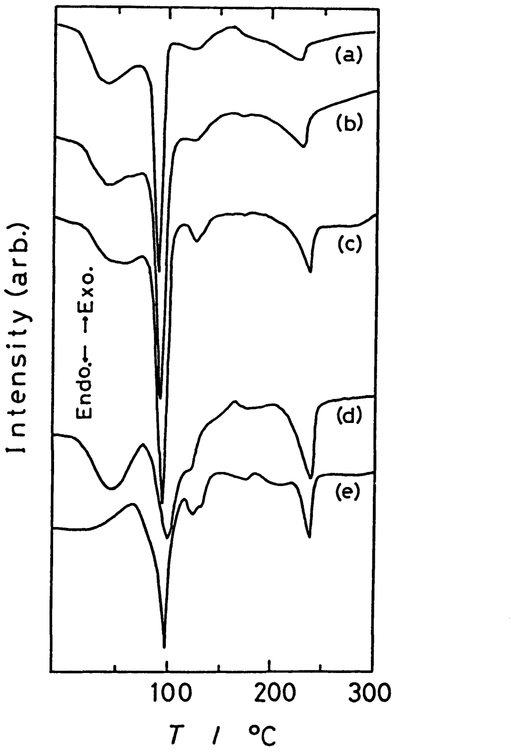

Fig. 3. DTA curves of xKNO$_3\cdot(100-x)$Sr(NO$_3$)$_2$ glasses; (a) x=22, (b) x=35, (c) x=43, (d) x=49, (e) x=60.

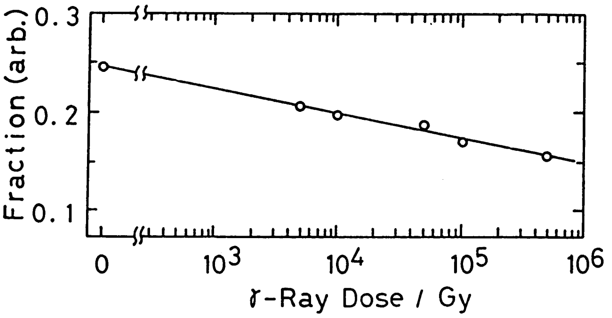

Fig. 4. Change of the relative fraction of the K-ONO$_2$ bonds in the IR spectra of 49KNO$_3$·51Sr(NO$_3$)$_2$ glass caused by γ-ray irradiation.

As shown in Fig. 4, the fraction of K-ONO$_2$ bonds (1270—1272 cm^{-1}) decreased linearly with the γ-ray dose. This indicates a cleavage of the K-ONO$_2$ bonds and a decreased degree of random packing (increased "ordering") of the K$^+$ and NO$_3^-$ ions. Regarding the structural change due to γ-ray irradiation, crystallization was observed in the IR-light transmitting gallate and tellurite glasses.[5]

The effect of γ-ray irradiation on 49KNO$_3$·51Sr(NO$_3$)$_2$ glass was also studied by DTA, in which T_g increased from 74 to 86—88 °C when the glass was irradiated with γ-rays of 5×10^3—5×10^5 Gy. The endothermic peak observed in the DTA curve of the irradiated glasses showed a distinct narrowing. A linear γ-ray irradiation effect was also observed in borate glasses; the Mössbauer spectra showed a linear reduction of Fe^{3+} into Fe^{2+},[6] although no crystallization was observed. Figure 4 suggests that the nitrate glass has a γ-ray memory effect, playing the role of a dosemeter.

Conclusion

1) The IR-peak positions of NO$_3^-$ (ν_2, ν_3, ν_4) are constant, irrespective of the composition (x=22—60). This indicates that the structure of NO$_3^-$, the interionic length, and the coordination number of ions remain unchanged in the glasses.

2) Constant T_g's (75±2 °C) were obtained in the DTA of the nitrate glasses, suggesting essentially the same structure comprising randomly packed K$^+$, Sr^{2+}, and NO$_3^-$.

3) The nitrate glasses have a new IR-peak due to the K-ONO$_2$ bonds, which are observed as the result of a lowered symmetry of NO$_3^-$ from D_{3h} to C_{2v}.

4) The nitrate glass undergoes "linear" crystallization upon γ-ray irradiation of 5×10^3—5×10^5 Gy.

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