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Raman Scattering and Phase Transition of NH_4NO_3-KNO_3 Mixed Crystals

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NH_4NO_3–KNO_3 mixed crystals, $(NH_4)_xK_{1-x}NO_3$ (x=0.88, 0.75, and 0.61), are prepared by evaporation of aqueous solutions of ammonium nitrate and potassium nitrate. Polarized Raman spectra of single crystals of mixed crystals are observed at room temperature and are interpreted based on the NH_4NO_3(III) type D_{2h}^{16} structure. Raman spectra of powdered samples are examined at various temperatures and it is shown that the NH_4NO_3(IV) type phase which is a room-temperature phase of NH_4NO_3 is not realized in the mixed crystals. In $(NH_4)_{0.88}K_{0.12}NO_3$, NH_4NO_3(III) type is converted to NH_4NO_3(V) type around −120 °C. In the spectra of high-temperature phase of mixed crystals, only one broad band in the region 100 cm^{-1}—120 cm^{-1} is observed, which corresponds to KNO_3(I) or KNO_3(III) type structure.

In alkali nitrates, Rb and Cs salts, where the ionic radii of the cations are larger than that of K^+ ion, take the CsCl type structure at high temperatures as in NH_4NO_3, while Li and Na salts consisting of smaller cations take the distorted NaCl type structure. KNO_3 is ferroelectric in its phase III, which has not been known in other univalent nitrates. The ionic radius of NH_4^+ ion is slightly larger than that of K^+ ion, and the effect of the substitution of NH_4^+ ion for K^+ ion and the phase transition of NH_4NO_3–KNO_3 mixed crystals have been studied in relation to ferroelectricity.[1–4] It is considered that at high temperatures mixed crystals take the KNO_3(III) type structure, which is ferroelectric, as well as KNO_3(I) type, from the study on the temperature dependence of the lattice constant.[2,3] An X-ray crystallographic study showed that the room-temperature structure of mixed crystals is the NH_4NO_3(III) type.[5] As for the low-temperature structure no crystallographic study has been reported.

On these backgrounds we attempted spectroscopic studies on the phase transition of NH_4NO_3–KNO_3 mixed crystals. In the preceding paper we studied Raman scattering and phase transition of NH_4NO_3 and clarified a characteristic spectral feature for each phase.[6] In the present investigation Raman spectra of single crystals of NH_4NO_3–KNO_3 mixed crystals at room temperature are studied and the structural changes at high temperatures are examined spectroscopically. Furthermore an elaborate measurement of temperature dependence of Raman spectra at low temperatures is made to find whether an abrupt spectral change associated with the phase transition exists, since so far no study has been done as to the phase transition at low temperatures.

Another objective of this study is to make a definite vibrational assignment of NH_4NO_3(III) for which single crystal spectra could not be obtained, by using the results of NH_4NO_3–KNO_3 mixed crystals of NH_4NO_3(III) type structure.

Experimental

$(NH_4)_xK_{1-x}NO_3$ mixed crystals were prepared by evaporation of aqueous solutions of ammonium nitrate and potassium nitrate of appropriate molar ratio in a desiccator at room temperature. The initial crops in each solution which precipitate in microcrystalline form were removed from this solution and subsequently single crystals began to grow. Thus uniform solid solutions of NH_4NO_3 and KNO_3 were obtained. All these crystals grew as a long needle whose axis coincides with the b-axis of the NH_4NO_3(III) type crystal. It was confirmed from the X-ray powder diffraction measurement that these mixed crystals have the same structure as that of NH_4NO_3(III). The molar ratio of mixed crystals was determined by chemical analysis.

In the preparation of $(NH_4)_xK_{1-x}NO_3$ mixed crystals by evaporation of aqueous solutions, the molar ratio (x) of NH_4NO_3 amounts to the value in the range $0.96>x>0.60$ for the produced crystals. The mixed crystals with the x value in the range $0.60>x>0.04$ are not produced from aqueous solutions at room temperature. (It is reported that the crystal with $x<0.04$ is isomorphous with KNO_3 (II)[1,5]).

We prepared the following three kinds of mixed crystals:

Molar ratio of NH_4NO_3 in aqueous solution	Molar ratio of NH_4NO_3 in mixed crystal
0.9	0.88
0.8	0.75
0.7	0.61

Spectral measurements were performed in the procedure described in the preceding paper.[6]

Results and Discussion

Temperature Dependence of Raman Spectra of Polycrystalline Samples. Figure 1 shows the Raman spectra of powdered samples of $(NH_4)_xK_{1-x}NO_3$ mixed crystals (x=0.88, 0.75, and 0.61) at room temperature, compared with those of NH_4NO_3 at 32°C, which corresponds to the spectrum of NH_4NO_3(III) as discussed in the preceding paper.[6] The spectra of the above three kinds of mixed crystals are similar to that of NH_4NO_3(III), confirming the crystallographic conclusion that $(NH_4)_xK_{1-x}NO_3$ ($x>0.6$) at room temperature takes the NH_4NO_3(III) type structure with the space group D_{2h}^{16} ($z=4$).[5] Raman frequencies of $(NH_4)_{0.88}K_{0.12}NO_3$ at various temperatures in the process of cooling and heating from room temperature are shown in Fig. 2.

In the low-temperature spectra, a phase transition is found around −120 °C for $(NH_4)_{0.88}K_{0.12}NO_3$, while for the other two kinds of mixed crystals no sudden change in the spectra is found. Figure 3 shows the

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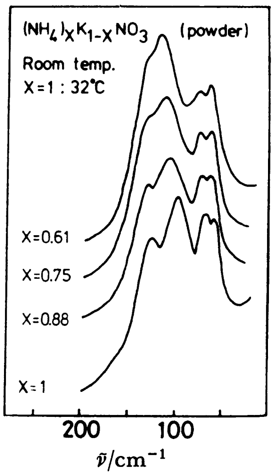

Fig. 1. Raman spectra of powdered samples of $(NH_4)_xK_{1-x}NO_3$ mixed crystals at room temperature. For NH_4NO_3 ($x=1$) the spectrum at 32 °C is given.

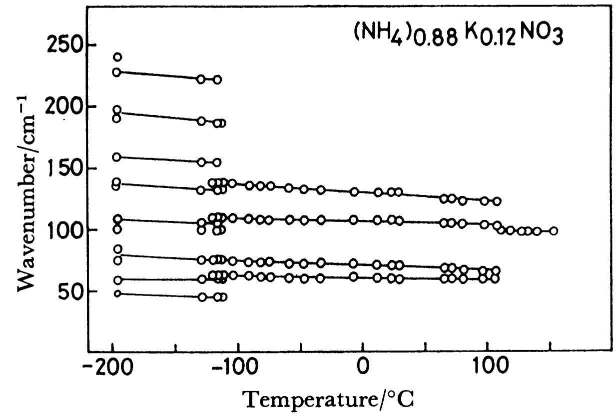

Fig. 2. Raman frequencies at various temperatures for $(NH_4)_{0.88}K_{0.12}NO_3$ mixed crystal.

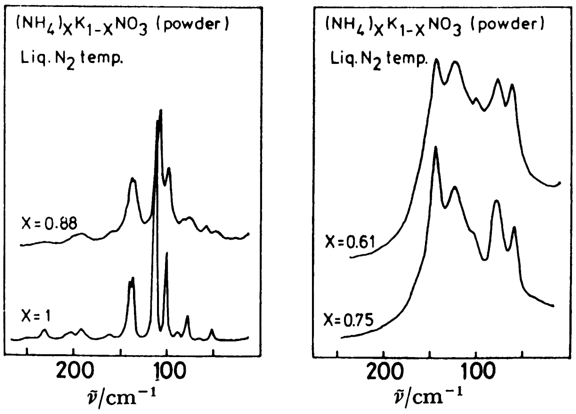

Fig. 3. Raman spectra of powdered samples of $(NH_4)_xK_{1-x}NO_3$ mixed crystals at liquid-N_2 temperature.

Raman spectra at liquid-N_2 temperature. From Fig. 3(a), it is shown that the low-temperature phase of $(NH_4)_{0.88}K_{0.12}NO_3$ takes the NH_4NO_3(V) type structure (low-temperature phase of NH_4NO_3). It should be noted that in this mixed crystal NH_4NO_3(III) type→ NH_4NO_3(V) type phase transition occurs without passing through NH_4NO_3(IV) type structure unlike NH_4NO_3 crystal. As seen in Fig. 3(b), for the mixed crystals with $x=0.75$ and $x=0.61$, the room-temperature structure of NH_4NO_3(III) type is still retained at liquid-N_2 temperature. However, it might be possible that a supercooling state is produced in these mixed crystals.

Next we see the spectra of high-temperature phase. It is generally accepted that the following phase transitions exist in the mixed crystals at high temperature:[3]

$$\mathrm{NH_4NO_3(III)\ type} \underset{75^\circ\mathrm{C}-115^\circ\mathrm{C}}{\overset{105^\circ\mathrm{C}-125^\circ\mathrm{C}}{\rightleftharpoons}}$$

$$\mathrm{KNO_3(III)\ type} \underset{\approx 120^\circ\mathrm{C}}{\overset{\approx 130^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{KNO_3(I)\ type}$$

The spectra of high-temperature phase are shown in Fig. 4. In the high-temperature spectra, only one broad band with the peak around 100 cm^{-1}—120 cm^{-1} is observed, which is assigned to the NO_3^- ion rotational lattice mode of C_{3v}^5 ($z=1$) or D_{3d}^5 ($z=1$) structure. KNO_3(I) type⇌KNO_3(III) type phase transition is not revealed in the spectra markedly.

Polarized Raman Spectra of Single Crystals. Figure 5 shows polarized Raman spectra of single crystals for $(NH_4)_xK_{1-x}NO_3$ mixed crystals at room-temperature in the low-frequency lattice vibration region. As the ratio of NH_4NO_3 decreases, the observed bands shift

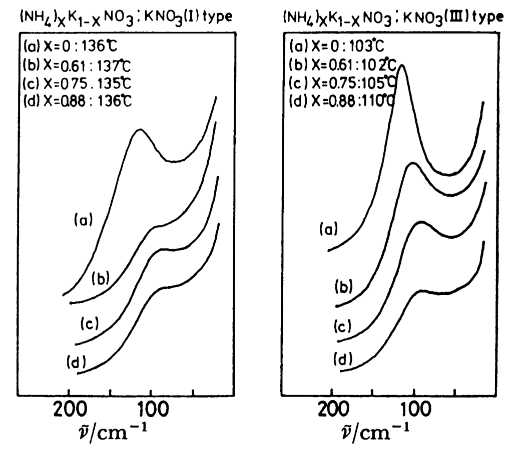

Fig. 4. Spectra of high-temperature phase of $(NH_4)_xK_{1-x}NO_3$ mixed crystals.

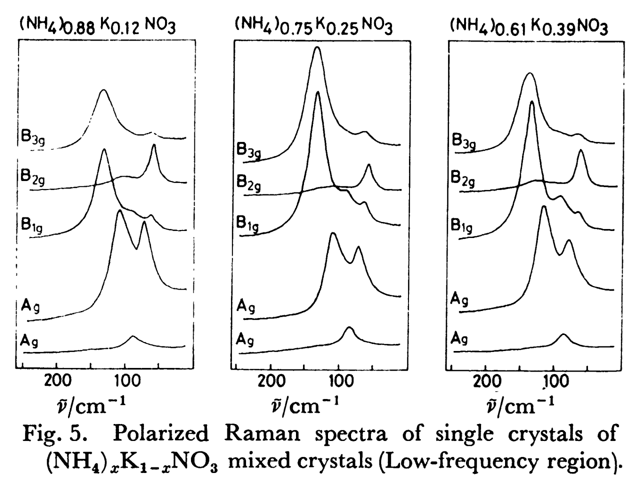

Fig. 5. Polarized Raman spectra of single crystals of $(NH_4)_xK_{1-x}NO_3$ mixed crystals (Low-frequency region).

TABLE 1. OBSERVED RAMAN FREQUENCIES IN cm^{-1} OF $(NH_4)_xK_{1-x}NO_3$[a)]

$x=1$[b)]	$x=0.88$	$x=0.75$	$x=0.61$	Assignment based on D_{2h}^{13}	
58	59	60	63	$(B_{2g})\ T_{ac}(NO_3^-)$	
	63	64	65	$(B_{1g})\ T_b\ (NO_3^-)$	
	65	66	65	$(B_{3g})\ T_b\ (NO_3^-)$	
68	71	73	76	$(A_g)\ T_{ac}(NO_3^-)$	
	88	88	88	$(A_g)\ T_{ac}(NO_3^-)$	
	93	93	93	$(B_{1g})\ T_b\ (NO_3^-)$	
100	105	109	115	$(A_g)\ R_b\ (NO_3^-)$	
128	131	133	135	$(B_{1g})\ R_a\ (NO_3^-)$	
	135	136	139	$(B_{3g})\ R_a\ (NO_3^-)$	
715	714	714	714	(B_{1g}, B_{3g})	ν_4
717	719	719	719	(A_g)	
	830	830	830	(A_g)	ν_2
1050	1048	1048	1048	(A_g)	ν_1
1320	1320	1325	1330	(B_{3g})	ν_3
	1330	1330	1335	(A_g)	
1355	1354	1356	1360	(B_{1g})	
	1360	1365	1373	(B_{2g})	
1410	1418	1422	1425	(A_g)	ν_4'

a) T and R denote translational and rotational lattice modes, respectively. ν_1—ν_4: internal modes of NO_3^- ion. ν_4': internal mode of NH_4^+ ion. b) Powdered sample at 32 °C.

to the higher frequency, which reflects the crystallographic result that the lattice constants become smaller. Table 1 summarizes the vibrational frequencies together with the mode assignments.

In NH_4NO_3(IV) crystal reported in the preceding paper, it was found that the lattice mode about a-axis of NO_3^- ion (R_a) is observed as a single band while that about b-axis (R_b) is accompanied by a band due to the translational lattice mode which is coupled with the rotational mode and strengthens its intensity. In the NH_4NO_3(III) type crystal a similar feature is seen, but somewhat in an approximate description. One of the oxygen atoms (O_I) in NO_3^- ion is located in the mirror plane in NH_4NO_3(III) crystal (refer to Fig. 1 of the preceding paper[6)]). Although NO_I is not exactly parallel to the a-axis of crystal, we designate approximately the rotational mode about the NO_I-axis, R_a, and that about the axis perpendicular to the NO_I-axis and in the NO_3^- plane, R_b. In the NH_4NO_3(III) type D_{2h}^{16} structure, R_a belongs to the B_{1g} and B_{3g} species and R_b to the A_g and B_{2g} species. As seen in Fig. 5, in the spectrum of the a scattering configuration (A_g), two strong bands are observed, while in the spectra of the ab (B_{1g}) and bc (B_{3g}) configurations one strong band is observed with a very weak band around 60 cm^{-1}. The spectral feature revealed in NH_4NO_3(IV) crystal and $(NH_4)_xK_{1-x}NO_3$ crystal of the NH_4NO_3(III) type, that the rotational lattice mode about a-axis is observed as a single band while that about b-axis coupled with the translational mode as two bands, is characteristic of the orthorhombic structure. In the crystals possessing C_3-axis perpendicular to NO_3^- plane, such as KNO_3(I), KNO_3(III), and $NaNO_3$(I) types, the rotational modes about a- and b-axes are degenerate and a single band corresponding to E_g species is observed, as seen in the high-temperature phase of mixed crystal.

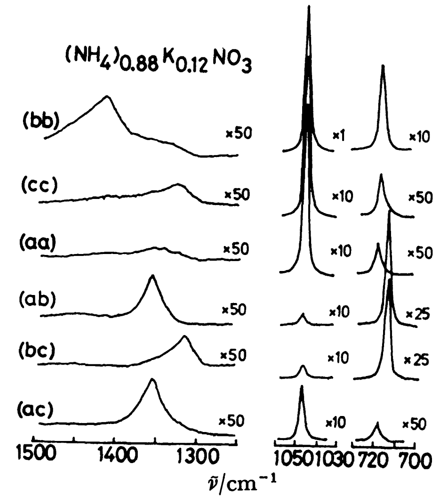

Fig. 6. Polarized Raman spectra of single crystals of $(NH_4)_{0.88}K_{0.12}NO_3$ mixed crystal (Internal vibration region).

Next we discuss briefly the polarized Raman spectra in the internal vibration region in Fig. 6. Based on the spectra of six kinds of scattering configurations, the observed bands are assigned straightforwardly to the symmetry species of D_{2h}^{16} factor group as shown in Table 1. The splitting of ν_3 (NO_3 asymmetric stretching mode) in mixed crystals is within ≈40 cm^{-1}, comparable with 35 cm^{-1} in NH_4NO_3(III), which indicates that in the NH_4NO_3(III) type structure no strong hydrogen bond is formed between NH_4^+ and NO_3^- ions unlike in the case of NH_4NO_3(IV) and NH_4NO_3(V) type structures.

To sum up, polarized Raman spectra of single crystals of mixed crystals at room temperature are interpreted based on the NH_4NO_3(III) type D_{2h}^{16} structure. In NH_4NO_3(III) itself single crystal spectra could not be obtained due to the crack of crystals at phase transition NH_4NO_3 IV→III. Therefore it is significant that a vibrational assignment of the spectra of powdered sample for NH_4NO_3(III) can be done on comparing with the single crystal spectra of mixed crystals at room temperature. The NH_4NO_3(IV) type phase which is a room-temperature phase of NH_4NO_3 is not realized in the mixed crystals. In some mixed crystals, the NH_4NO_3(III) type is converted directly to the NH_4NO_3(V) type around -120 °C, without passing through the NH_4NO_3(IV) type. At high temperatures, only one broad band in the region 100 cm^{-1}—120 cm^{-1} is observed, which corresponds to KNO_3(I) or KNO_3(III) type structure.

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