

## Study of $x$ -dependence of crystal structure of $RS_{1-x}-ARS_x$

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The mixed crystal structures of Rochelle salt and ammonium Rochelle salt,  $RS_{1-x}-ARS_x$ , are studied in the whole range of the mixed crystal system. The structures varies with  $x$ . The interatomic distances between potassium atoms and their neighbour oxygen atoms depend on the accommodation rate of  $NH_4$  ions. Among them the distance between K(1) and O(1) and that between K(2) and O(4) are kept constant, where hydrogen bonds occur locally by the replacement of potassium ions with ammonium ions. The thermal vibration of O(8) is anisotropically large in the direction of perpendicular to O(3)-O(8)-O(2) linkage in every mixed crystal. Displacement of O(8) atom between K(1) and K(2) are observed.

### I. INTRODUCTION

The mixed crystal system of Rochelle salt and ammonium Rochelle salt  $RS_{1-x}-ARS_x$  exhibits interesting and complex properties depending on the change of the content of RS, which reflect the change in the mechanism of the phase transition. RS and ARS are isomorphous crystal to each other, however the direction of the polar axis of RS is  $a$  and that of ARS is  $b$ . The phase diagram was given by Makita and Takagi, [1] who determined it by study of the dielectric behaviour of the mixed crystal system. According to the phase diagram the mixed crystal system is divided into four regions:  $0 \leq x \leq 0.025$  (region I),  $0.025 \leq x \leq 0.18$  (region II),  $0.18 \leq x \leq 0.90$  (region III) and  $0.90 \leq x \leq 1$  (region IV). In the mixed crystal system we have studied the ferroelectric atomic displacement in RS (region I), [2] the behaviour of the accommodation of  $NH_4$  ions, [3] the structural modification of ARS due to the replacement of  $NH_4$  ions with K ions (region IV), [4] and the temperature dependence of the crystal structure of  $RS_{1-x}-ARS_x$ ,  $x=0.28$ . [5] Calorimetric study of the mixed crystal system shows the transition entropy increases gradually with the increment of  $x$  in the region III, and it exhibits fairly large increment in the region IV. [6,7] Dielectric study in microwave region shows the elementary process of the dipole relaxation in RS is not the same as those in the mixed crystals of the region II and the region III. [8]

When we proceed into the clarification of the complex interactions among the dipoles in the mixed crystal system, the knowledge of the  $x$ -dependence of the crystal structure must be inevitably required.

Our studies on the behaviour of the accommodation of  $NH_4$  ions [3] and on the structural modification of ARS [2] show that there must be structural changes depending on  $x$ , that is, the increment of the accommodation of  $NH_4$  ions changes some bonds between atoms or molecules. To

study them crystallographically as the changes in nearest neighbour interactions among the mixed crystals is very interesting problem. Here we review the  $x$ -dependence of the crystal structures at room temperature and obtained characteristic features.

### II. CRYSTAL GROWTH AND DETERMINATION OF CRYSTAL STRUCTURE

$RS_{1-x}-ARS_x$  mixed crystals were grown by evaporation method in aqueous solutions at room temperature. Since the parameter  $x$  in the crystals is different from the mixing ratio of RS and ARS in aqueous solutions, [3] the parameter  $x$  was determined together with other crystallographic parameters in the process of the crystal structure analyses. Since RS has two K ion sites, the accommodations for the two sites are presented by two parameters  $\alpha$  and  $\beta$  and a relation  $\alpha + \beta = 2x$  holds. [3]

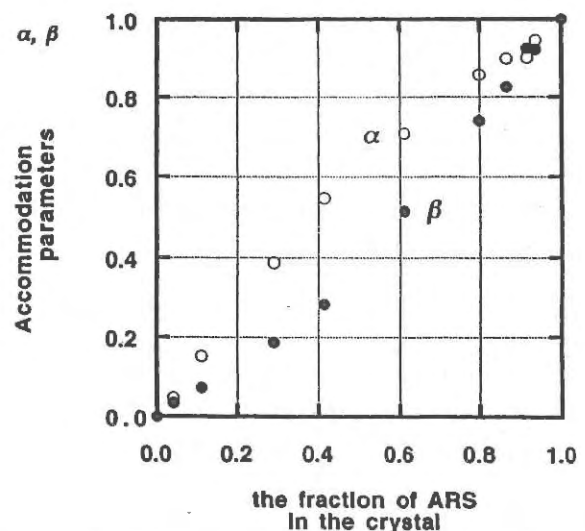


Fig. 1. Relation between accommodation parameter  $\alpha$  and  $\beta$  vs  $x$ .

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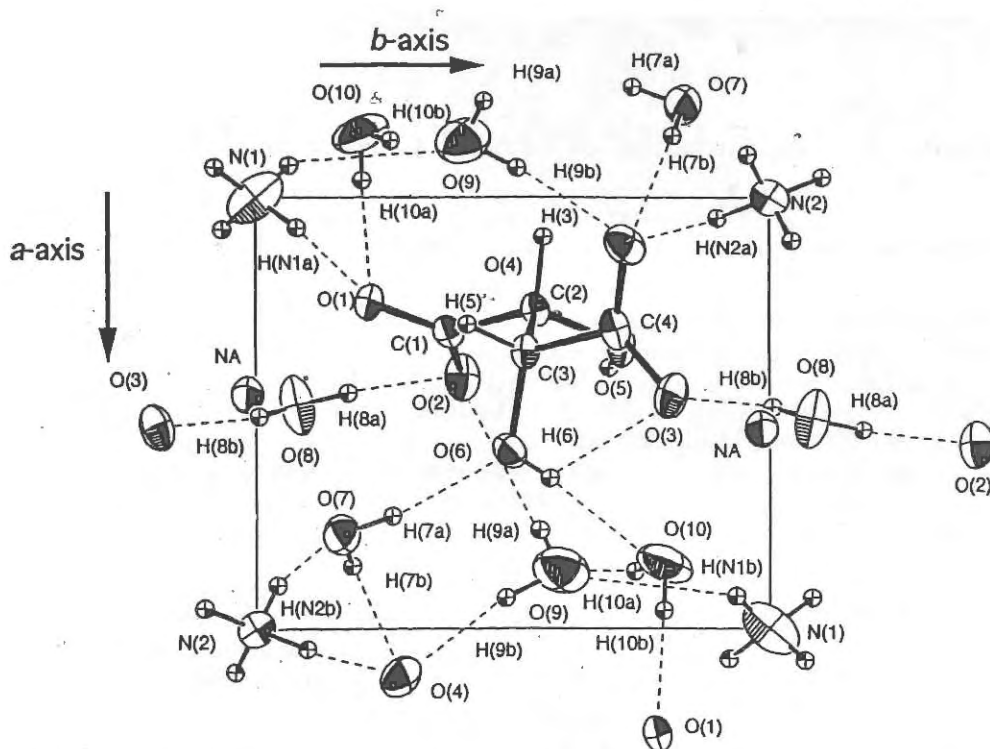


Fig. 2. Crystal structure of ARS at RT. Projection on (001) and a quarter of the unit cell is shown. Dashed lines stand

for hydrogen bonds.

The relation  $\alpha$  and  $\beta$  vs  $x$  thus obtained are shown in Fig. 1. It is confirmed also that the relation of the parameter  $x$  and the lattice constants  $a$ ,  $b$  and  $c$  has the good agreements with the relation presented as Vegard's law in the previous study. [3] Ten sample crystals having different parameter  $x$  were studied. All specimens were prepared in spheres of which diameters were between 0.25 and 0.5 mm, and they were sealed in glass capillary tubes for x-ray diffraction works. The used x-ray was Mo- $K\alpha$  monochromatized by a pyrolytic graphite. All the x-ray works were performed at room temperature (300 K).

The obtained crystallographic parameters for mixed crystal of  $x=0.10$  are shown in Table II, as an example of the crystal structure analyses. In this case,  $R$ -factor was 0.048 for 4350 reflections measured in the range  $5.0 \leq 2\theta \leq 80$ .

### III. REVIEW OF X-DEPENDENCE OF THE MIXED CRYSTALS

In the mixed crystals, there are planes perpendicular to  $b$ -axis composed of the cations  $Na^+$  and  $K^+$  (or  $NH_4^+$ ). The unit cell contains four kinds of water molecules  $H_2O(7)$ ,  $H_2O(8)$ ,  $H_2O(9)$  and  $H_2O(10)$ . The tartrate molecules are sandwiched between the cation planes. Three of them,  $H_2O(7)$ ,  $H_2O(9)$  and  $H_2O(10)$ , link the tartrate molecules along  $a$  and  $c$ . The rest water molecule  $H_2O(8)$  connects the tartrate molecules along  $b$ . These linkages are considered to be O-H...O hydrogen bonds. The hydrogen bonds in the unit cell are shown in

Table 1.  $x$ -dependence of direction cosines of the plane formed by the four carbon atoms in the tartrate molecule.

$x$	$\cos \alpha$	$\cos \beta$	$\cos \gamma$
0.10	0.823	0.454	-0.342
0.41	0.831	0.442	-0.337
0.61	0.839	0.434	-0.328
0.80	0.840	0.435	-0.323
0.86	0.841	0.434	-0.326
0.91	0.841	0.436	-0.321
0.93	0.841	0.435	-0.321
1.00	0.843	0.434	-0.318

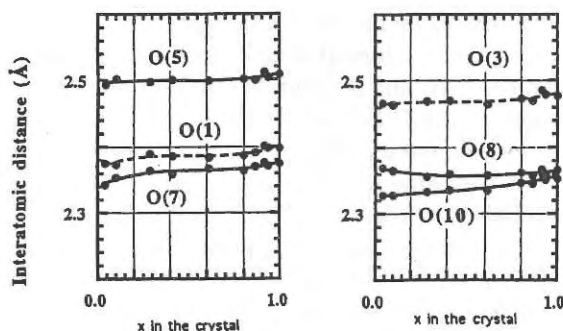


Fig. 3.  $x$ -dependence of the interatomic distances between Na and its neighbour oxygens

Fig. 2.

The carbon atoms in the tartrate molecule make a plane, and the planeness and the direction of the plane is kept unchanged practically in the mixed crystal system.

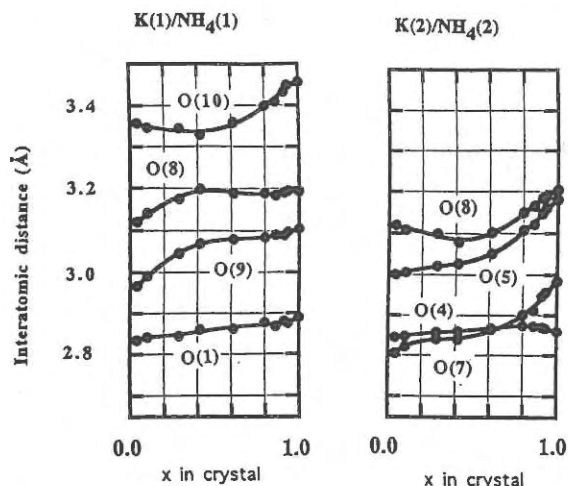


Fig. 4.  $x$ -dependence of the interatomic distances between potassium/ammonium ions and their neighbour oxygens

The direction cosines *vs*  $x$  are shown in Table I. Figure 3 shows changes of the interatomic distances between Na and its nearest neighbour oxygens. Figure 4 shows changes of the interatomic distances between independent K/NH<sub>4</sub> ions and their neighbour oxygens. Figure 5 shows changes in the interatomic distances between O(8) and the two kind of K/NH<sub>4</sub> ions.

#### IV. DISCUSSIONS

As shown in the previous study, [3] the lattice constants  $a$  and  $b$  obey Vegard's law and the lattice constant  $c$  remains constant. The fact suggests that the replacement by ions with larger ionic radius in the mixed crystals makes modification of the crystal structure as rearrangement of the constituent ions, molecules. It happens especially around the two K ion sites.

Table 2. Fractional positional parameters of non-hydrogen atoms and their thermal parameters, and those for hydrogens without thermal parameters of  $RS_{0.90}ARS_{0.10}$ .

atom	$x$	$y$	$z$	$U_{eq}(\text{\AA}^2 \times 10^4)$
Na	0.2313(1)	0.9931(1)	0.5230(2)	234(6)
KN(1)	0.0	0.0	0.0465(2)	539(11)
KN(2)	0.0	0.5	0.1590(1)	265(6)
C(1)	0.1542(2)	0.1879(2)	0.2845(4)	156(14)
C(2)	0.1246(2)	0.2731(2)	0.4245(4)	131(13)
C(3)	0.1782(2)	0.2642(2)	0.6440(4)	152(14)
C(4)	0.1535(3)	0.3518(2)	0.7784(4)	225(16)
O(1)	0.1197(1)	0.1090(1)	0.3519(3)	221(10)
O(2)	0.2088(2)	0.2029(1)	0.1178(3)	257(11)
O(3)	0.2339(2)	0.4062(1)	0.8124(3)	313(11)
O(4)	0.0546(2)	0.3627(1)	0.8435(3)	323(11)
O(5)	0.1634(2)	0.3571(1)	0.3250(3)	205(11)
O(6)	0.2957(2)	0.2478(2)	0.6287(4)	260(13)
O(7)	0.3955(2)	0.0824(2)	0.4817(4)	295(14)
O(8)	0.2449(2)	0.0411(2)	0.8852(3)	441(14)
O(9)	0.4374(3)	0.3005(2)	0.0366(5)	559(21)
O(10)	0.4249(2)	0.3986(2)	0.4160(5)	554(18)

(Continued).

atom	$x$	$y$	$z$
H(2)	0.036(2)	0.279(2)	0.441(3)
H(3)	0.145(2)	0.209(2)	0.727(4)
H(5)	0.191(2)	0.345(2)	0.217(4)
H(6)	0.322(3)	0.283(3)	0.606(7)
H(7a)	0.376(3)	0.120(2)	0.526(6)
H(7b)	0.442(3)	0.094(2)	0.367(5)
H(8a)	0.263(3)	0.006(2)	0.989(5)
H(8b)	0.244(3)	0.090(2)	0.949(5)
H(9a)	0.380(3)	0.278(3)	1.006(6)
H(9b)	0.460(3)	0.253(3)	0.074(6)
H(10a)	0.441(3)	0.372(2)	0.291(5)
H(10b)	0.487(3)	0.397(2)	0.476(4)
H(N1a)	0.106(20)	0.056(18)	0.208(43)
H(N1b)	0.447(22)	0.467(18)	-0.169(42)
H(N2a)	0.055(45)	0.366(34)	-0.131(73)
H(N2b)	0.383(36)	0.171(30)	0.864(81)

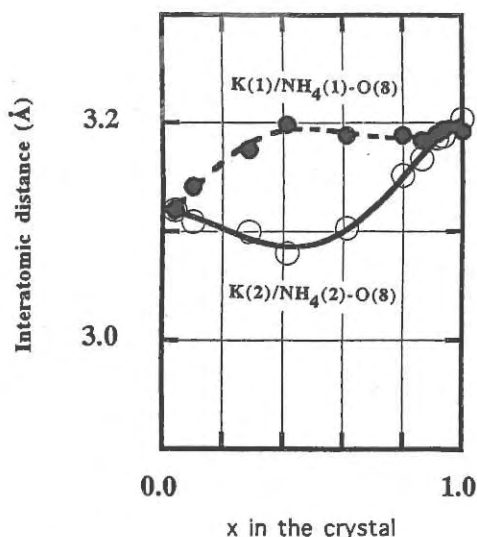


Fig. 5.  $x$ -dependence of the interatomic distances between two potassium/ammonium ions and O(8)

The interatomic distances between Na and its surrounding oxygens have no distinctive changes in the entire range of  $x$ . Interatomic distances around K/NH<sub>4</sub> ions make interesting changes. Among them, the effects on the interatomic distance between K(1)/NH<sub>4</sub>(1) and O(1) and that between K(2)/NH<sub>4</sub>(2) and O(4) are interesting. In RS, the cation K(1) is surrounded by oxygens O(1), O(8), O(9) and O(10), and the cation K(2) is surrounded by O(4), O(5), O(7) and O(8). The interatomic distances K(1)-O(1) and K(2)-O(4) are about 2.82 Å, and they are kept practically constant through the accommodation of NH<sub>4</sub> ions on the K ion sites. The interaction between K(1) and O(1) and that between K(2) and O(4) are replaced by N-H...O hydrogen bonds with the increment of the accommodation of NH<sub>4</sub> ions keeping their distances constant. It shows the interactions are very important

for the mixed crystal system.

Among the four water molecules, the behaviour of H<sub>2</sub>O(8) should be pointed. The feature of the large anisotropic thermal vibration of O(8) is common in the mixed crystals. The anisotropic direction is perpendicular to O(3)-O(8)-O(2) linkage; O(3) and O(8) are strongly connected by a hydrogen bond. As discussed in the study of the ferroelectric phase of RS, [2] the anisotropic thermal motion is not responsible to the ferroelectric state, although the change in the position of O(8) makes the collective ferroelectric movements of atoms corresponding to the appearance of the spontaneous polarization. The large anisotropic thermal motion is not explained at present. Changes in the interatomic distances between O(8) and the two K ions are distinctive. It is a future problem to study the relation between the changes in the interatomic distances and some physical properties or the mechanism of the phase transition in the mixed crystal system.

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