

CRYSTAL STRUCTURE OF $K_3Na(SeO_4)_2$ AT 340 K

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The crystal structure of tripotassium sodium diselenate, $K_3Na(SeO_4)_2$, at 340 K is studied by single-crystal X-ray diffraction. The space group symmetry (trigonal $P\bar{3}$) and structure parameters are determined. It is found that there exists the difference of the direction and the magnitude of the atomic displacement at the two phase transitions of 346 K and 334 K.

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1. Introduction

Tripotassium sodium diselenate, $K_3Na(SeO_4)_2$, crystal is a member of a family which can be described by chemical formula $A_3C(BX_4)_2$, where A, C = Na, K, Rb and $BX_4 = SO_4, SeO_4, CrO_4, MoO_4$ [1]. It undergoes several successive structural phase transitions above the room temperature: the melting point at 1170 K, two high-temperature phase transitions at 758 K and 730 K, and two low-temperature phase transitions at 346 K and 334 K [2, 3]. The low-temperature structural transitions are detected by a set of independent experiments. The former is accompanied by the anomalies as measured in differential thermal analysis (DTA) curves, thermal expansions, and dielectric constants. The structural phase transition at 334 K is deduced from the temperature dependence of the elastic constants [2-4]. Furthermore, it is determined from the studies of Brillouin shifts that the elastic constant c_{33} exhibits anomalous behavior at 346 K, and c_{44} has two minima at 334 K and 346 K [5]. It is shown that the sample crystal exhibits ferroelastic properties at room temperature. The ferroelastic character of the relevant transition is concluded from the observation of domain structure in the polarized light and the domains which are reorientable under the external force are clearly observed below 334 K [6]. Recently, the symmetry of the sample crystal in the intermediate phase (334-346 K) has been determined to be trigonal with the point group $\bar{3}$ in the Raman scattering measurements [7].

The crystal structure of $K_3Na(SeO_4)_2$ at 390 K has been determined to be trigonal $P\bar{3}m1$ with the lattice parameters: $a = 5.906(3)$ and $c = 7.552(1)$ Å, and there is one molecule in a unit cell. The crystal structure at 291 K was determined

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with the assumption that the observed X-ray intensities are overlapped by the reflections from the three domains. The determined structure at 291 K is monoclinic $C2/c$ and the cell parameters are $a = 10.162(2)$, $b = 5.867(1)$, $c = 15.021(2)$ Å and $\beta = 90.00(1)^\circ$. There are four molecules in a unit cell [8].

However, the structure of the sample crystal between 334 K and 346 K has not been reported yet. The purpose of this paper is to determine the crystal structure of $K_3Na(SeO_4)_2$ in this temperature range, and to discuss the details of its phase transitions.

2. Experimental

The sample crystal of $K_3Na(SeO_4)_2$ were grown at room temperature by slow evaporation from aqueous solutions containing K_2SeO_4 and Na_2SeO_4 in the molar ratio of 3:1. The obtained crystals are in the form of hexagonal c -plates. The X-ray measurement was carried out by using an Enraf-Nonius CAD-4 four-circle automatic diffractometer with an express software and graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The sample temperature was controlled by using heated N_2 gas with a low-temperature apparatus (FR558SH) of Enraf-Nonius, and the temperature fluctuations were kept within ± 0.5 K. The observed profiles of the X-ray reflection of the sample crystal at 340 K showed a single peak on the graphic display. Therefore, the sample crystal was considered to be mono-domain. Crystal data and the experimental conditions are listed in Table I. The inten-

TABLE I

Crystal data, data collection, and structure refinement.

Crystal data	
Compound	$K_3Na(SeO_4)_2$
Chemical formula weight	$M_r = 426.21$
Crystal system	Trigonal
Space group	$P\bar{3}$
Lattice constants	$a = 5.8725(5)$ Å $c = 7.5092(8)$ Å
Volume of unit cell	$V = 224.27(7)$ Å ³
Formula unit per cell	$Z = 1$
Density calculated from formula and cell	$D_x = 3.156$ g cm ⁻³
Number of reflections for cell measurement	25
θ range for cell measurement	$\theta = 21.0-24.7^\circ$
Linear absorption coefficient	$\mu = 96.13$ cm ⁻¹
Measurement of temperature	$T = 340.0 \pm 0.5$ K
Crystal shape	Hexagonal plate
Crystal color	Colorless
Sample shape	Sphere
Sample size in diameter	$2r = 0.028$ cm

TABLE I (cont.)

Data collection	
Data-collection method	$\omega/2\theta$ scans
Absorption correction type	Spherical
Number of reflections measured	3837
Number of independent reflections	1289
Maximum value of θ	$\theta_{\max} = 44.95^\circ$
Range of h , k and l for measured intensities	$h = -11 \rightarrow 11$ $k = -11 \rightarrow 11$ $l = -14 \rightarrow 0$
Number of standard reflections	3
Interval time	120 min
Intensity decay	-2.06%
Refinement	
Refinement on F	
R factor	$R = 0.0183$
wR factor	$wR = 0.0227$
Goodness of fit	$S = 0.554$
Number of reflections used in refinement	795
Criterion for reflections	$I > 3\sigma(I)$
Number of parameters refined	24
Equivalent reflections	$R_{\text{int}} = 0.057$
Weighting scheme	$w = 1/[\sigma^2(F) + (0.02F)^2 + 1.0]$
Maximum of shift/esd	$(\Delta/\sigma)_{\max} = 0.026$
Maximum of difference density	$\Delta\rho_{\max} = 0.615 \text{ e}\text{\AA}^{-3}$
Minimum of difference density	$\Delta\rho_{\min} = 0.0 \text{ e}\text{\AA}^{-3}$
Extinction coefficient	$0.85(1) \times 10^{-5}$

sity data were corrected for both Lorentz-polarization and absorption effects. The structure was refined by the full-matrix least-squares method using a MolEN crystallographic software package with a VAX4000 station, and all atoms were refined with anisotropic thermal parameters.

3. Results and discussion

Figure 1 shows the temperature dependence of the four measured intensities of X-ray reflections indexed with pseudohexagonal $K_3Na(SeO_4)_2$ on heating. The long measuring time is taken for $\omega/2\theta$ scan (2.06 degree/min). These four reflections have the strong intensity as chosen from all reflections with the l odd. It is found that the intensity of the four reflections decreases almost along the straight lines with increasing temperature but the slope of the line turns into the same at about 340 K. These four strong reflections and the other reflections with the l

odd disappeared at about 350 K. The obtained temperatures for the change of the slope and the disappearance of the chosen reflections are in good agreement with the phase transition temperatures as previously reported [2, 3].

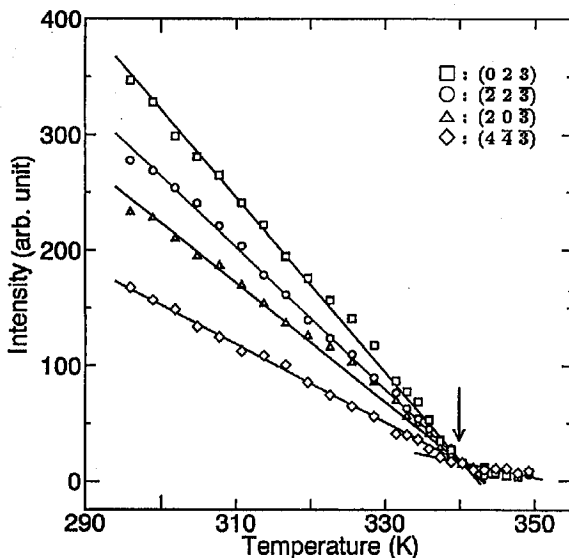


Fig. 1. Temperature dependence of four X-ray reflection intensities of pseudo-hexagonal $K_3Na(SeO_4)_2$ on heating. The change of the slope of the lines is indicated by an arrow.

The crystal structure of $K_3Na(SeO_4)_2$ at 340 K was analyzed by X-ray diffraction. The intensities of the all reflections with odd l as shown in Fig. 1 were very weak and were not detected by a usual method of the X-ray measurements. Then, the lattice parameter along the c -axis at 340 K was determined to be a half of that of the room-temperature phase. The observed systematic extinction of the X-ray reflection reveals that the possible space groups are $P\bar{3}m1$, $P3m1$, $P321$, $P\bar{3}1m$, $P31m$, $P312$, $P\bar{3}$, and $P3$. By the comparison of the equivalent reflections, it indicated that the Laue class of the sample crystal is $\bar{3}$. Then, the space group is considered to be $P\bar{3}$ or $P3$. This result is in agreement with the study from the Raman scattering [7]. In the preliminary structure analysis with an isotropic thermal parameter, the discrepancy factors (R factors) calculated for the above space groups are reduced to about 0.07. But the number of free parameters refined for $P3$ is about twice as many as that for $P\bar{3}$. Therefore, the space group $P3$ can be readily discarded with only a slightly better R factor, and the space group $P\bar{3}$ is chosen with the only possible. The final R factor was reduced to 0.0183.

Figure 2 shows the obtained crystal structure at 340 K. The positional parameters in fractions of a unit cell and the thermal parameters are listed in Table II. The bond lengths in Å and the bond angles in degree are given in Table III. Comparing the obtained fractions of the positional parameters of 340 K with those of 390 K, it is found that the O(2) atom deviates from the site symmetry of mirror

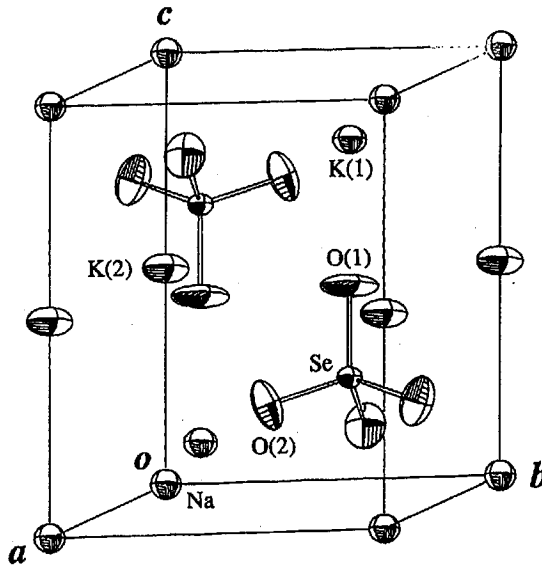


Fig. 2. Crystal structure of $K_3Na(SeO_4)_2$ at 340 K with 70%-probability-displacement ellipsoids.

TABLE II

Positional parameters in fractions of a unit cell and thermal parameters ($\times 10^{-4} \text{ \AA}^2$) at 340 K. The anisotropic thermal parameters are defined as $\exp[-2\pi^2(U_{11}a^*h^2 + U_{22}b^*k^2 + U_{33}c^*l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se	1/3	2/3	0.27407(3)	131.3(4)	131.3(4)	86.6(5)	65.7(2)	0	0
K(1)	1/3	2/3	0.82736(7)	227(1)	227(1)	156(1)	113(1)	0	0
K(2)	0	0	1/2	432(3)	432(3)	164(3)	216(2)	0	0
Na	0	0	0	187(3)	187(3)	172(5)	93(2)	0	0
O(1)	1/3	2/3	0.4884(3)	694(13)	694(13)	88(6)	347(7)	0	0
O(2)	0.1835(2)	0.3666(2)	0.1968(2)	300(4)	189(3)	461(6)	94(3)	-76(5)	-152(4)

plane (0.0007 along the a -direction and 0.0019 along the b -direction) in the phase at 340 K. It changes the space group symmetry from $P\bar{3}m1$ to $P\bar{3}$. The observed SeO_4 tetrahedra are slightly distorted from ideal tetrahedra in all three phases. The bond distances between the Se and O atoms are slightly decreasing with the increasing temperature.

Table IV shows the displacement of the atoms as the temperature changes from 390 K to 340 K and from 340 K to 291 K. It is found that all atoms shift to the negative direction of the a - and b -axes with the ratio about 1 : 2 as the temperature is lowered from 390 K to 340 K. That is, the displacement of the atoms is about 0.11 \AA along the negative direction of the b -axis. From 340 K to 291 K, the O(1) atom shifts to the positive directions of the a - and b -axes while the Se and O(2) atoms shift to the negative directions of the a - and b -axes with the even larger ratios. The displacements of the atoms from 340 K to 291 K are

TABLE III

Bond lengths in Å and bond angles in degrees at 340 K.

Bond lengths			
Se-O(1)	1.609(2)	Se-O(2)	1.632(1)
O(1)-O(1) ^a	3.3950(2)	O(1)-O(2) ^a	3.773(2)
O(1)-O(2)	2.668(2)	O(2)-O(2) ^b	2.643(2)
O(2)-O(2) ^c	3.230(2)	O(2)-O(2) ^d	3.495(2)
K(1)-O(1)	2.546(2)	K(1)-O(2) ^a	2.947(2)
K(1)-O(2) ^e	3.166(2)	K(2)-O(2)	2.943(1)
Na-O(2)	2.379(1)	Na-K(1) ^a	3.6299(2)
Bond angles			
O(1)-Se-O(2)	110.81(6)	O(2)-Se-O(2)	108.10(8)

^a $y, y-x, 1-z$; ^b $1-y, 1+x-y, z$;
^c $y-x, -x, z$; ^d $y, y-x, -z$; ^e $x, y, 1+z$

TABLE IV

Displacements (Å) of the atom positions (a) from 390 K to 340 K and (b) from 340 K to 291 K with the trigonal axis.

(a) From 390 K → 340 K			
Atoms	<i>x</i>	<i>y</i>	<i>z</i>
ΔSe	-0.0112	-0.0223	0.0008(5)
ΔK(1)	-0.0112	-0.0223	-0.010(1)
ΔK(2)	0	0	-0.0214
ΔO(1)	-0.0112	-0.0223	0.003(6)
ΔO(2) ^a	-0.013(2)	-0.023(2)	-0.006(4)
ΔO(2)	-0.010(2)	-0.023(3)	-0.006(4)
ΔO(2) ^b	-0.010(3)	-0.021(2)	-0.006(4)
(b) From 340 K → 291 K			
ΔSe	-0.0136(6)	-0.1682(2)	-0.0039(4)
ΔK(1)	0.015(1)	-0.1764(4)	-0.0102(5)
ΔK(2)	0	-0.1621(5)	0.00065
ΔO(1)	0.0475(8)	0.065(2)	-0.011(4)
ΔO(2)	-0.015(4)	-0.177(4)	-0.135(5)
ΔO(3)	-0.027(5)	-0.175(4)	0.153(5)
ΔO(4)	-0.023(6)	-0.121(4)	-0.027(8)

^a $y-x, -x, z$; ^b $-y, x-y, z$

significantly larger than those of the atoms from 390 K to 340 K. Therefore, it is found that there exists the difference of the direction and the magnitude of the atomic displacement in the structural phase transitions from 390 K to 340 K and from 340 K to 291 K.

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