

High-Temperature Structural Phase Transition of K_2SO_4 and K_2SeO_4 Crystals Studied by X-Ray Diffraction¹

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High-temperature structural phase transitions in K_2SO_4 and K_2SeO_4 crystals have been studied by X-ray diffraction. Laue and precession photographs were taken with Mo radiation at several high temperatures. Results indicate that the symmetry of both crystals changes from the orthorhombic to the hexagonal system through structural phase transition. Possible space groups are $P6_3/mmc$, $P6_3mc$, or $P6_2c$ from extinction conditions in the high-temperature phases. The crystal structure of K_2SeO_4 is preliminarily assumed to be isostructural with K_2SO_4 in the high-temperature phase. Further studies of the crystal structure and the phase transitions of K_2SeO_4 are required. © 1994 Academic Press, Inc.

INTRODUCTION

Room-temperature crystals of potassium sulfate, K_2SO_4 , and potassium selenate, K_2SeO_4 , are known to crystallize in the orthorhombic space group $Pm\bar{c}n$ with unit cell $a_0 = 5.763(2) \text{ \AA}$, $b_0 = 10.071(4) \text{ \AA}$, $c_0 = 7.476(3) \text{ \AA}$, and $a_0 = 6.00 \text{ \AA}$, $b_0 = 10.47 \text{ \AA}$, $c_0 = 7.66 \text{ \AA}$, respectively (1, 2). Most crystals with the form A_2BX_4 are isostructural with the β -form of K_2SO_4 . The crystal transforms to the high-temperature α -form at $T = 587^\circ\text{C}$ for K_2SO_4 and at $T = 472^\circ\text{C}$ for K_2SeO_4 , as reported by Watanabe *et al.* (3) and Gattow (2), respectively. Different space groups have been proposed for the α - K_2SO_4 . Pannetier (4) proposed $P\bar{3}m1$ from the X-ray powder data analysis with $a_h = 5.788 \text{ \AA}$ and $c_h = 7.93 \text{ \AA}$ at 615°C . Eysel and Hahn (5) proposed $P6_3mc$ for the high-temperature form. From high-temperature Weissenberg measurements, Watanabe *et al.* concluded that the space group of α - K_2SO_4 is $P6_3mc$, but did not determine the structure (6). However, Shiozaki *et al.* (7) proposed that the space group is $P6_3/mmc$ from the twin-domain structure studies. This model is consistent with the high-temperature powder analysis by Van Den Berg and Tuinstra (8). Recently, Miyake *et al.* (9) and

Arnold *et al.* (10) determined the crystal structure of the high-temperature form of K_2SO_4 , based on the space group $P6_3/mmc$. On the other hand, the space group of high-temperature K_2SeO_4 is supposed to be the same as that of K_2SO_4 in many reports, but it has not yet been experimentally observed and reported. In this paper, we present the results of X-ray diffraction studies on the structural phase transitions of K_2SO_4 and K_2SeO_4 crystals above room temperature.

EXPERIMENTAL

Single crystals of K_2SO_4 and K_2SeO_4 were grown by slow evaporation from the aqueous solutions at room temperature. The compounds were purchased commercially from Merck and Wako. The K_2SO_4 crystals obtained were colorless and transparent in the form of long columns with the b_0 -axis along the long axis, while the a_0 -axis and c_0 -axis were along the diagonal of its nearly rectangular cross section. The crystal showed one single domain under the polarizing microscope. The crystals burst into pieces as they were heated to 500°C . It was reported that the explosion was due to the small amount of water remaining in crystals during the growth (10). Potassium sulfate crystals were then crystallized at a temperature above 40°C to minimize the content of water in crystals. On the other hand, the K_2SeO_4 crystals were usually crystallized in a colorless and transparent long triangular prism. The b_0 -axis was found along the long axis of the crystal and the c_0 -axis was along one edge of the triangular basal plane. X-ray Laue and precession photographs, with beams along the crystal axes of the samples, were then taken at several temperatures ranging from room temperature to 600°C , using Huber high-temperature attachments. The temperatures would vary within 1°C . Lattice parameters were measured from the zero-level precession photographs. For K_2SO_4 , the orthorhombic unit cell has $a_0 = 5.74(3) \text{ \AA}$, $b_0 = 10.03(5) \text{ \AA}$, and $c_0 = 7.46(4) \text{ \AA}$; for K_2SeO_4 , its unit cell has $a_0 = 5.93(3) \text{ \AA}$, $b_0 = 10.37(5) \text{ \AA}$, and $c_0 = 7.58(4) \text{ \AA}$. These values are in agreement with the previous results as reported by McGinnety (1) and

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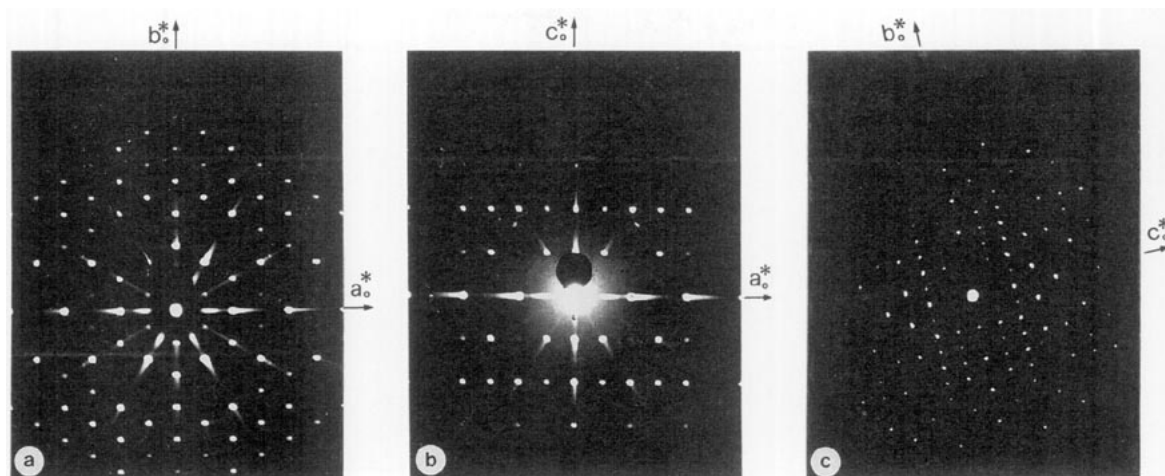


FIG. 1. The X-ray precession photographs of (a) $(hk0)$, (b) $(h0l)$, and (c) $(0kl)$ taken at room temperature for K_2SO_4 single crystals. The absent reflections are $h + k = 2n + 1$ in $(hk0)$ and $l = 2n + 1$ in $(h0l)$. The space group is $Pm\bar{c}n$.

Kalman *et al.* (11). The measured density using the floating method is 2.62 g cm^{-3} for K_2SO_4 and 3.01 g cm^{-3} for K_2SeO_4 .

RESULTS AND DISCUSSIONS

Precession photographs with the direction of the X-ray beam along a_0 , b_0 , and c_0 crystal axes of K_2SO_4 sample crystals were taken at room temperature. Figure 1 shows the three zero-level precession photographs taken with $MoK\alpha$ radiation. The reflection conditions were $(hk0)$ with $h + k = 2n$ and $(h0l)$ with $l = 2n$. It was confirmed that the space group of β -form K_2SO_4 is orthorhombic $Pm\bar{c}n$. It can be seen from Fig. 1a that the symmetry is pseudo-hexagonal along the c_0 -direction and the axial ratio $b_0/a_0 = 1.75$ is very close to $\sqrt{3}$. This is the reason that the high-temperature form of K_2SO_4 has been proposed to be hexagonal. Figure 2 shows the orientation precession photographs taken along the c_0 -axis of the crystal at room

temperature and at $T = 592^\circ\text{C}$. The symmetry of the crystal has changed obviously from mm to $6mm$.

Three high-temperature zero-level precession photographs taken at 592°C are shown in Fig. 3. From the photographs obtained, the unit cell of K_2SO_4 has $a_h = 5.90(4) \text{ \AA}$ and $c_h = 8.12(5) \text{ \AA}$. These values agree with the results of Miyake *et al.* (9) and Arnold *et al.* (10). The conditions for absences are $(00l)$ with $l = 2n + 1$ and (hhl) with $l = 2n + 1$, and the possible space groups are $P6_3/mmc$, $P6_2c$, or $P6_3mc$. This result rules out $P\bar{3}m1$. In the high-temperature phase, the c_h -axis of the hexagonal system was found along the c_0 -axis of the orthorhombic phase, and the a_h -axis was pointed along the a_0 -axis of the orthorhombic system.

Figures 4 and 5 show the zero-layer precession photographs of K_2SeO_4 crystals taken at room temperature and at $T = 480^\circ\text{C}$, respectively. The symmetry and the reflection conditions of K_2SeO_4 crystal are found to be the same as those of K_2SO_4 crystal at both temperatures. The cell

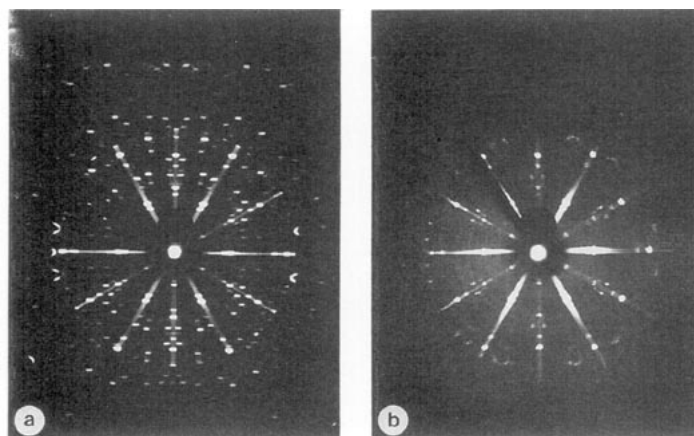


FIG. 2. The orientation precession photographs taken along the c -axis of the K_2SO_4 at (a) room temperature and (b) $T = 592^\circ\text{C}$. The symmetry of the diffraction has changed from mm to $6mm$ through the structural phase transition.

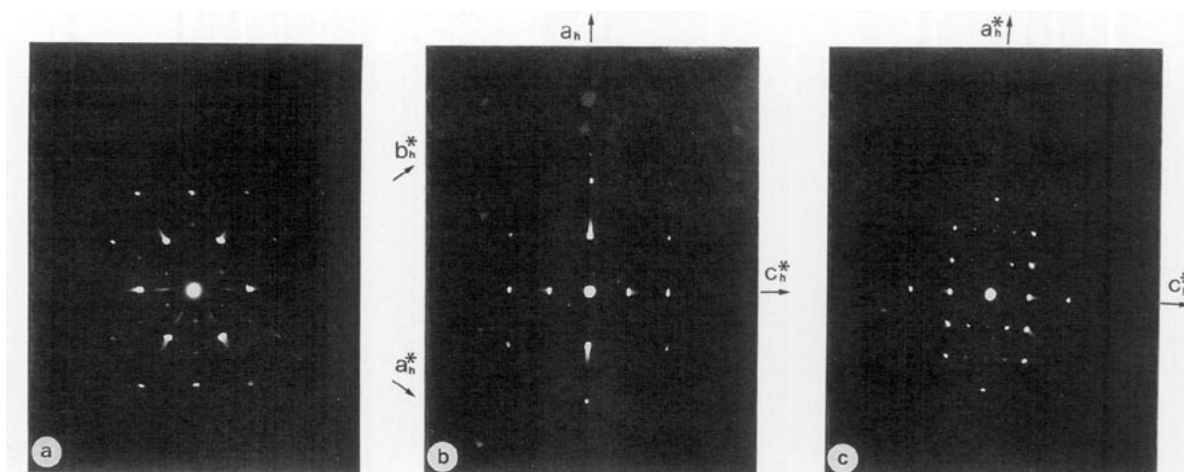


FIG. 3. The precession photographs of (a) $(hk0)$, (b) (hhl) , and (c) $(h0l)$ taken at $T = 592^\circ\text{C}$ for K_2SO_4 single crystals. The absent reflections are $l = 2n + 1$ in (b).

dimensions are $a_h = 6.05(5) \text{ \AA}$ and $c_h = 8.16(6) \text{ \AA}$ at $T = 480^\circ\text{C}$. The space group of the room-temperature phase of the K_2SeO_4 crystal is also $Pm\bar{c}n$, and the space groups of the high-temperature form are $P6_3/mmc$, $P6_2c$, or $P6_3mc$, the same as for K_2SO_4 . Figure 6 shows the projection of the atomic positions (as determined by McGinnety) of a $\beta\text{-K}_2\text{SO}_4$ unit cell onto a (001) plane. There are four molecules in a unit cell and they are symmetrically related to each other. Two mirror planes occur at $x = \frac{1}{4}$ and $\frac{3}{4}$. The potassium, sulfur (or selenium), and two oxygen atoms of SO_4 radicals (or SeO_4) are located in these symmetry planes. The other two oxygen atoms of SO_4 radicals (or SeO_4) were found on both sides of the mirror plane and are related by this mirror symmetry. Four oxygen atoms form nearly regular tetrahedra around each S or Se atom. As seen in the photographs presented, the diffraction patterns of both crystals changed drastically through the structural phase transition. The modification of the dif-

fraction intensity of each reflection is obviously due to the cooperative displacement of crystal atoms and/or the orientation of atom groups. For the K_2SO_4 crystal, two models have been proposed: that the SO_4 group atoms become dynamically randomly disordered with SO_4 tetrahedra orientationally pointing up and down along the c_h -axis in the apex model or that the atoms reorient one edge of the SO_4 tetrahedra along the c_h -axis in the edge model as they are compared with the room-temperature structure (9, 10). The space group was assumed to be $P6_3/mmc$ in both models from the best fit of the diffraction data (9, 10). The room-temperature cell constants for K_2SeO_4 are slightly larger than those for K_2SO_4 . The average bond lengths are 1.648 \AA for the selenate anion and 1.486 \AA for the sulfate anion (1, 11). The difference is large enough to cause different crystal fields in these two crystals. When the temperature is raised from room temperature, the

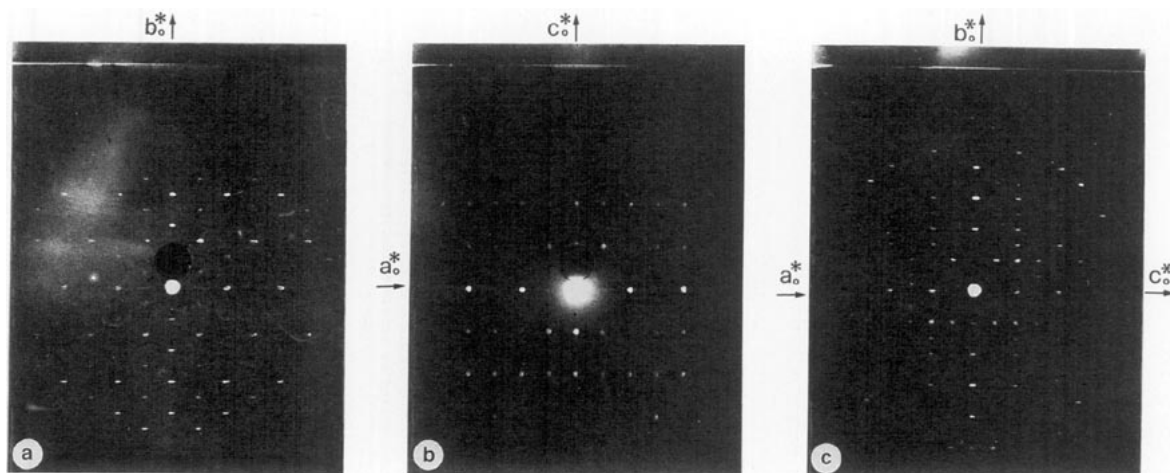


FIG. 4. The zero-level precession photographs of K_2SeO_4 crystals along three crystal axes: (a) $(hk0)$, (b) $(h0l)$, and (c) $(0kl)$ at room temperature. The space group is $Pm\bar{c}n$.

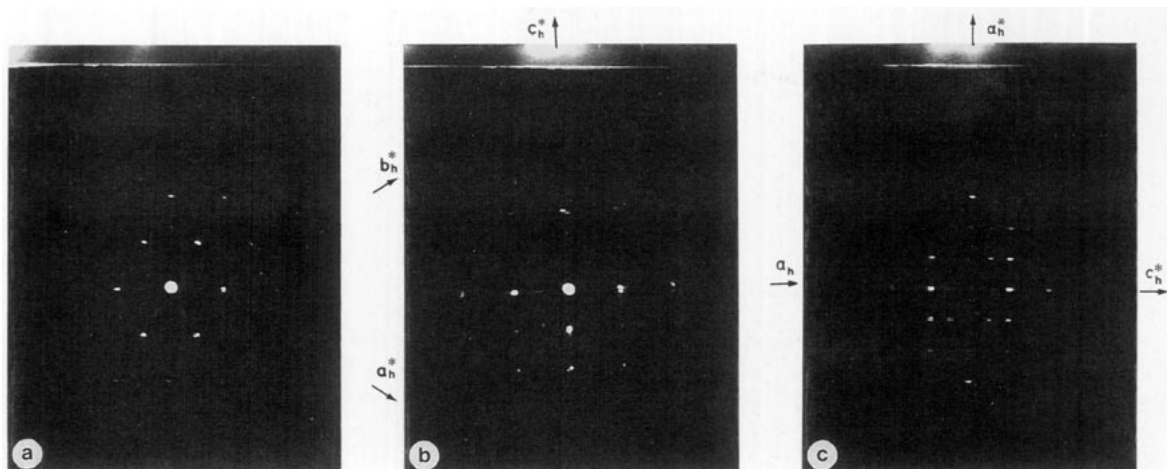


FIG. 5. The precession photographs of (a) $(hk0)$, (b) (hhl) , and (c) $(h0l)$ taken at $T = 480^\circ\text{C}$ for K_2SeO_4 crystals. The extinction conditions are the same as those of K_2SO_4 crystals. The space group in this phase is the same as that of K_2SO_4 .

cell dimensions increase. The increments in a_0 and in c_0 are 2.8 and 8.9%, respectively, for K_2SO_4 , and 2.0 and 7.7%, respectively, for K_2SeO_4 . The increment is found to be greater along the c_0 -axis than along the a_0 -axis for both kinds of crystals; hence the reorientation or the elongate distortion of SO_4 (or SeO_4) tetrahedra along the c_0 -axis might be expected. The changes in unit cell dimensions and consequence in bond lengths between atoms are also found to be larger in K_2SO_4 than those in K_2SeO_4 . Although the members of A_2BO_4 crystals are isostructural with β - K_2SO_4 at room temperature different members of the family still have remarkable differences in structural phase transitions (12). The different crystal fields in these crystals cause different phase transition mechanisms. For example, K_2SeO_4 , K_2ZnCl_4 , Rb_2ZnCl_4 , and Rb_2ZnBr_4 undergo a transition to an incommensurately modulated phase with the modulation wave vector \mathbf{q} close to the value of $\frac{1}{3}$ along the reciprocal c_0 -axis, while K_2SO_4 and Cs_2SeO_4 do not as the temperature is varied from room temperature (13–15). The modulated structure of K_2SeO_4 was found at a low temperature of 130°K, while the others were found at higher temperatures of 553, 303, and 347K, respectively (15). The modulation, which can be detected from the diffraction photographs as satellite reflections, is not

found in our high-temperature structural phase transition studies of K_2SO_4 and K_2SeO_4 . The similarity of X-ray intensity distributions in the diffraction patterns obtained from both crystals at high temperature shows that K_2SO_4 and K_2SeO_4 crystals are probably isostructural again in the high-temperature phase. Recently, it has also been proposed that the apex model is more likely from the molecular dynamics studies of the orientational distributions of Se–O bonds in K_2SeO_4 crystals (16), very similar to one of the models found in K_2SO_4 (9, 10). However, the experimental analysis is not available. The study in this report is a preliminary result; the correct space group and the structure of K_2SeO_4 crystals at high temperature can only be obtained through the more detailed analysis of X-ray diffraction data.

Both crystals have become optically turbid and disrupt easily in the high-temperature phase, and they do not return to their room-temperature phase as the temperature is lowered from high temperature. This is a rare case, especially that the crystals were found to be ferroelastic at room temperature (7), and most ferroelastic or ferroelectric crystals can return to their initial room-temperature phase after the structural phase transition cycle (17). The transition is also classified as group–subgroup related transition (17). In the present case the room-temperature-phase symmetry group, $Pm\bar{c}n$, is a subgroup of the high-temperature-phase symmetry group, $P6_3/mmc$. Exceptions are found in the martensite transition in which the group–subgroup transition condition is not fulfilled and the crystal reconstructs by a substantial change in the structure (18). The same property of the phase transition found in these two crystals suggests that the orientational disorder of SO_4 and SeO_4 groups in the high-temperature phase might be very drastic and similar. However, further studies of the high-temperature crystal structure and the transition mechanism in K_2SeO_4 are still required.

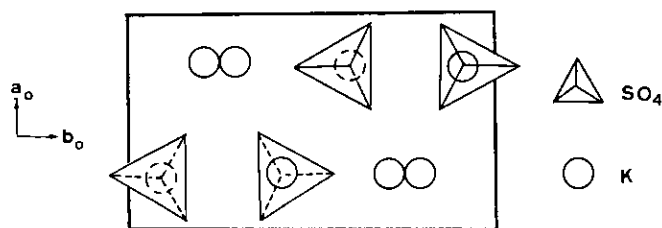


FIG. 6. Schematic drawing of the crystal structure of β - K_2SO_4 , as determined by McGinney, onto a (001) plane.

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