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Thermal Phase Transition of Potassium Sulfate, K_2SO_4

A High Temperature Polarizing Light Microscopic Study

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Abstract. The thermal phase transition of K_2SO_4 has been investigated by high temperature polarized light microscopy. K_2SO_4 undergoes a first-order transition at 587° C where the orthorhombic low temperature form (*Pmcn*) transforms into a hexagonal high temperature modification ($P6_3/mmc$).

Prior to the beginning of the phase transition, K_2SO_4 shows an anomalous optical behavior. The crystal apparently becomes optically uniaxial twice at 338° and 425° C, respectively, and truly optically uniaxial at 587° C.

The phase transition propagates through an intermediate temperature form, which is sandwiched between the low and the high temperature forms and moves in a definite direction, ⟨130⟩ (orthorhombic indices), in the vicinity of the phase transition. Passing through the phase transition point on cooling, dark belts crossing each other are observed which are a result of the transformation twins parallel to {110} and {130}.

Introduction

Two polymorphs of potassium sulphate, K_2SO_4, have been described by Bernard and Hocart (1961), Fischmeister (1962), and Eysel (1973). The low temperature form is orthorhombic (*Pmcn*) with lattice constants $a=5.76$, $b=10.07$ and $c=7.48$ Å at room temperature and its crystal structure was refined by McGinnety (1972). The high temperature form is hexagonal ($P6_3/mmc$) with the orthohexagonal lattice constants $a=5.84$, $b=10.12$ and $c=7.90$ Å at 600° C (Miyake and Iwai, unpublished data). The low temperature form transforms topotaxially to the high temperature form at 587°C. Miyake et al. (1977) concluded from discontinuities of the enthalpy and the cell volume that the phase transition is first-order. Prior to the beginning of the phase transition, potassium sulfate shows anomalous temperature dependence of its optical properties (Groth, 1905; Iwai et al., 1973). Recently, Shiozaki et al. (1977) reported the mechanism of mechanical twinning in potassium sulphate and potassium selenate from a ferroelastic point of view.

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In this study, the process of the thermal phase transition of potassium sulphate has been investigated by a continuous observation of optical properties using a high temperature polarizing microscope.

Experimental

The phase transition process of potassium sulfate was observed in the temperature range from 25° to 660° C under crossed polars using white light from a halogen lamp with a polarizing microscope (Nikon POH) equipped with a hot stage. The observation was carried out by orthoscopic and conoscopic methods.

Specimens used were recrystallized from a saturated aqueous solution of potassium sulfate in the temperature range from 60° to 80° C, resulting in single crystals elongated along the *a* axis. For the investigations, crystals free of twinning were cut into three kinds of lamellae about 0.2 mm thick perpendicular to the *a, b,* and *c* axes. The temperature was measured with a Pt-Pt/Rh 13% thermocouple and a controlled heating rate of 5° C/min was chosen.

The retardations of the crystals with increasing temperature were measured and occasionally checked with a Berek compensator. The birefringences were evaluated from the retardations and the thickness of the crystals, with a correction for the thermal expansions.

Results and Discussion

Figure 1 shows the temperature dependences of the birefringences along the *a, b,* and *c* axes, respectively. Prior to the phase transition, the birefringence along the *b* axis decreases with increasing temperature, becomes zero at 338° C,

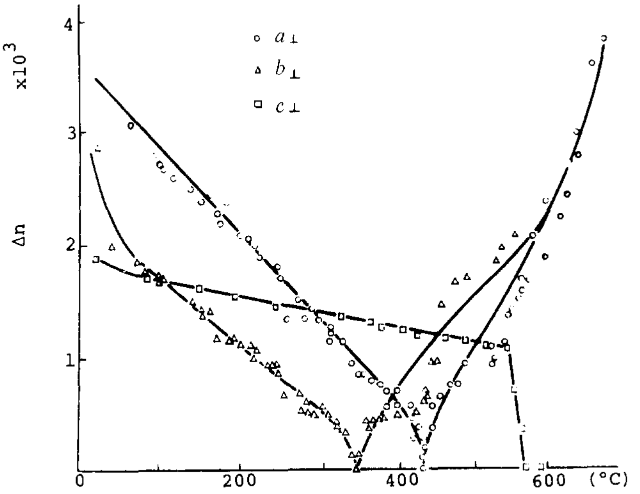

Fig. 1. Temperature dependences of birefringences of K_2SO_4. $a_\perp$, $b_\perp$ and $c_\perp$ denote those of crystal plates cut perpendicularly to the *a*, *b*, and *c* axes, respectively

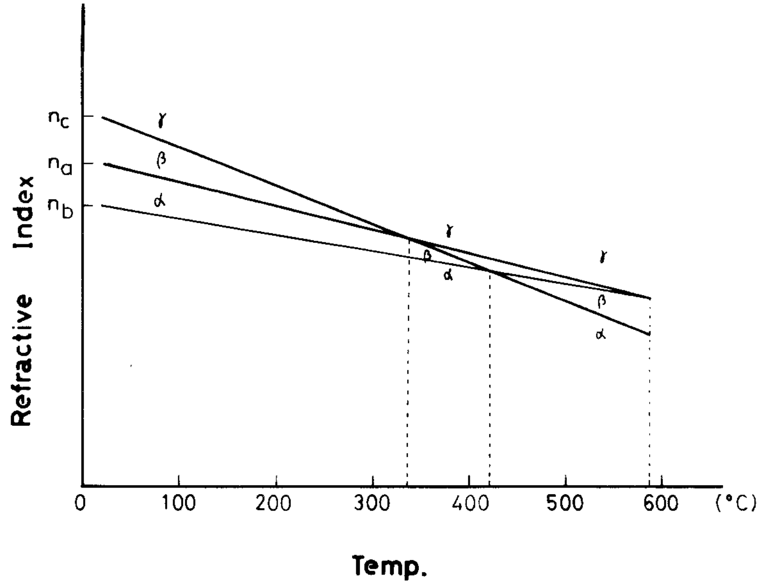

Fig. 2. Hypothetical temperature dependences of the principal refactive indices

and increases above this temperature. The crystal becomes apparentely optically uniaxial at 338° C, and the vibrational directions of the faster ray X' and the slower ray Z' change above 338° C. The temperature dependences of the optical properties are similar along the *a* and along the *b* axes. The birefringence decreases with increasing temperature and becomes zero at 425° C. Again the crystal becomes apparently optically uniaxial at 425° C, and X' is changed for Z' above 425° C. This anomalous optical behavior is probably related to the strong anisotropic thermal expansion along the *c* axis above about 300° C and the gradual increase of the specific heat above about 400° C (Iwai et al., 1973). The attainments of zero birefringences at 338° and 425° C are not a result of phase transitions since the changes of the birefringences are continuous. The birefringence along the *c* axis decreases continuously with increasing temperature and becomes zero at 587° C, exhibiting a large discontinuity which is ascribed to the phase transition. The crystal becomes truly optically uniaxial at 587° C when the orthorhombic phase transforms to a hexagonal one. Hypothetical temperature dependences of the principal refractive indices are shown in Fig. 2.

The optic axial angle 2Ω is calculated from the principal refractive indices using Eq. (1);

$$\sin \Omega = (\gamma/\beta)\cdot\sqrt{(\beta+\alpha)\,(\beta-\alpha)/(\gamma+\alpha)\,(\gamma-\alpha)}. \tag{1}$$

Where α, β, and γ are the minimum, intermediate, and maximum principal refractive indices, respectively. The acute optic axial angle $2V_z$ or $2V_x$ is represented by $2V_z = 2\Omega$ $(2\Omega < 90°)$ or $2V_x = 180 - 2\Omega$ $(2\Omega > 90°)$, respectively. Eq. (1) is simplified in order to evaluate the optic axial angle from values of the

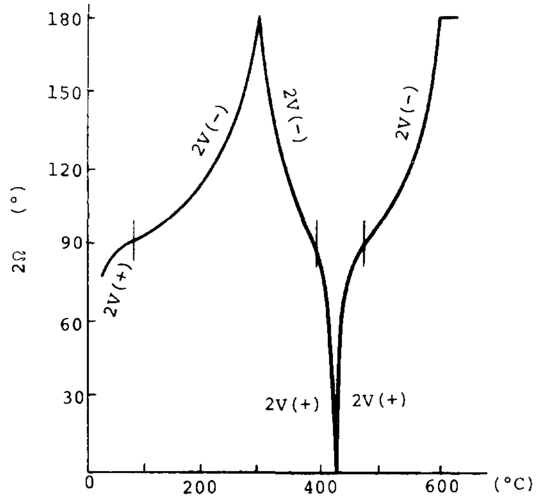

Fig. 3. Temperature dependence of the optic axial angle, 2Ω, of K_2SO_4

birefringences. Since in Eq. (1) for K_2SO_4 at room temperature

$$(\gamma/\beta)\cdot\sqrt{(\beta+\alpha)/(\gamma+\alpha)}\simeq 1.0, \tag{2}$$

Eq. (1) could be written approximately as Eq. (3) (Miyashiro and Kushiro, 1972);

$$\sin\Omega=\sqrt{(\beta-\alpha)/(\gamma-\alpha)}. \tag{3}$$

Figure 3 shows the temperature dependence of the optic axial angle calculated from the measurements of the birefringence using Eq. (3). Potassium sulfate is an optically biaxial crystal with $(+)2V_z=67°$ at room temperature and becomes an optically uniaxial negative crystal at 587° C. The optic axial angle increases continuously with increasing temperature up to 338° C, decreases up to 425° C, and increases again up to 587° C. The optical sign changes from positive to negative at about 100° C, then from negative to positive at about 380° C, and again from positive to negative at about 490° C, respectively. The optic axial angle becomes $(-)2V_x=0°$, $(+)2V_z=0°$ and $(-)2V_x=0°$ at the respective temperatures of 338°, 425°, and 587° C. The following optic elasticity axes were found;

$X\|b$, $Y\|a$ and $Z\|c$ (up to 338° C),

$X\|b$, $Y\|c$ and $Z\|a$ (from 338 to 425° C),

and

$X\|c$, $Y\|b$ and $Z\|a$ (from 425 to 587° C).

Figure 4 shows six conoscopic photographs viewed along the *b* axis at 325°, 330°, 336°, 338°, 342°, and 347° C, respectively, at diagonal positions. At 338° C, the crossing isogyres are observed on the photograph, indicating that the crystal becomes apparently optically uniaxial at this temperature.

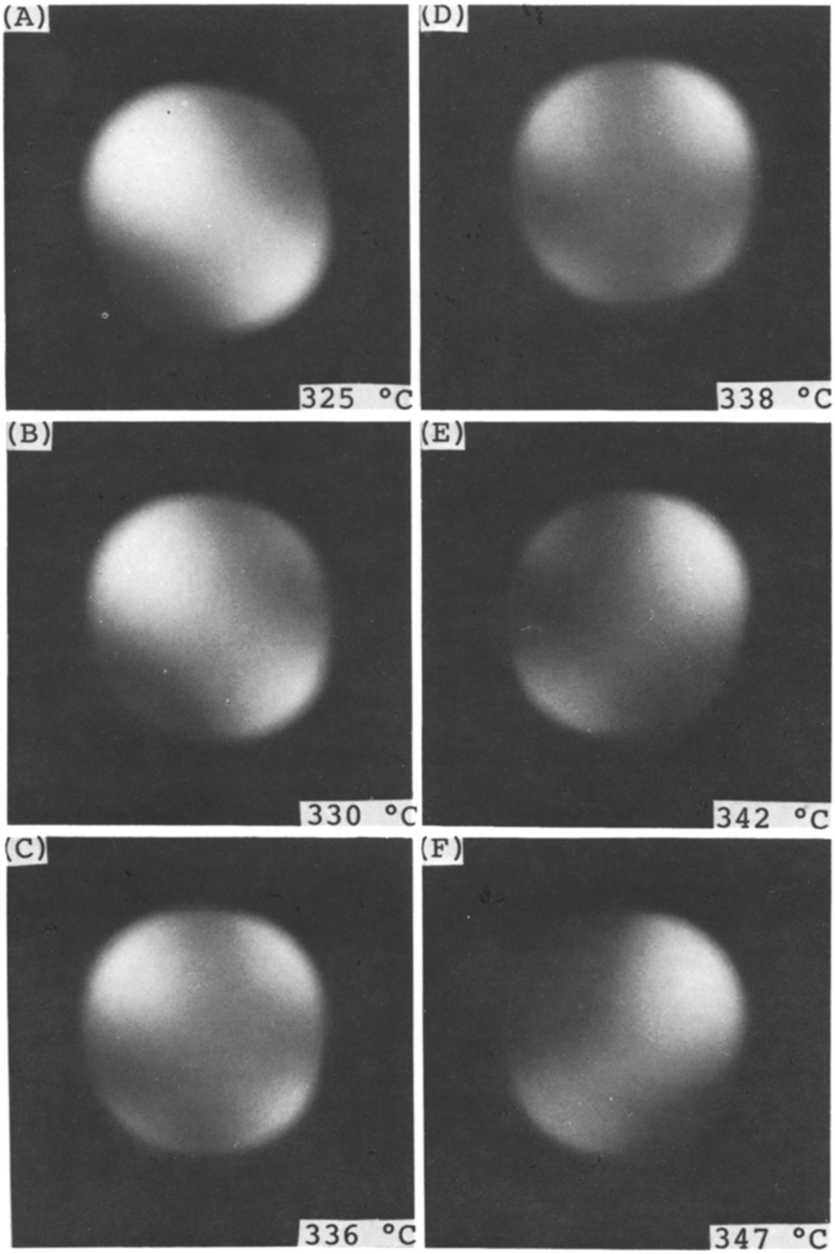

Fig. 4A–F. Conoscopic photographs viewed along the *b* axis at diagonal positions. **A–C**: $X \| b$, $Y \| a$ and $Z \| c$, **D**: $(-)2V_x = 0°$, **E** and **F**: $X \| b$, $Y \| c$ and $Z \| a$

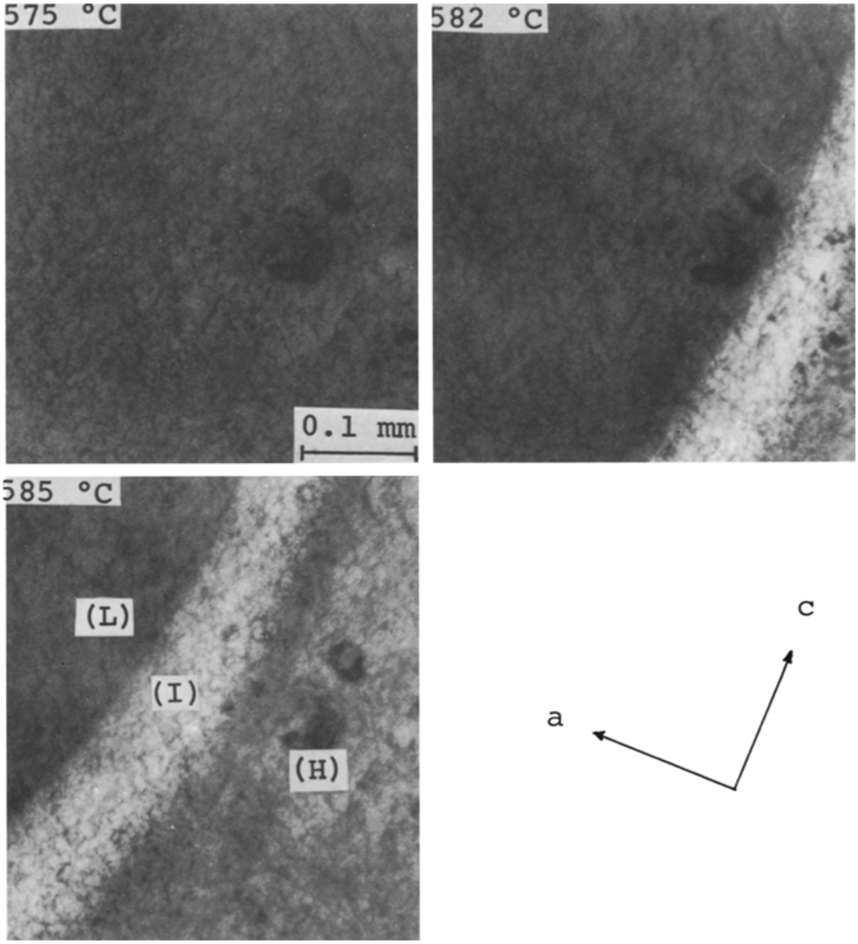

Fig. 5. Orthoscopic photographs viewed along the *b* axis at diagonal positions near the phase transition point. *L*: low temperature form; *I*: intermediate temperature form, and *H*: high temperature form

Figure 5 shows three photographs viewed along the *b* axis at 575, 582 and 585° C, respectively, at diagonal positions. Just below the phase transition point, at about 580° C, a zonal domain appears, and its retardation is different from those of the low and the high temperature forms. The zonal domain is considered an intermediate temperature form. The zonal domain moves in the ⟨100⟩[1]-direction with increasing temperature and is followed by the high temperature form. Viewed along the *a* axis, the intermediate temperature form moves in the ⟨010⟩ direction. Viewed along the *c* axis, the intermediate form is sandwiched between the low and the high temperature forms and moves in a definite direction, [130] or $[1\bar{3}0]$, just below the phase transition. Thus, the propagation of the

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[1] Orthorhombic = orthohexagonal indices are used

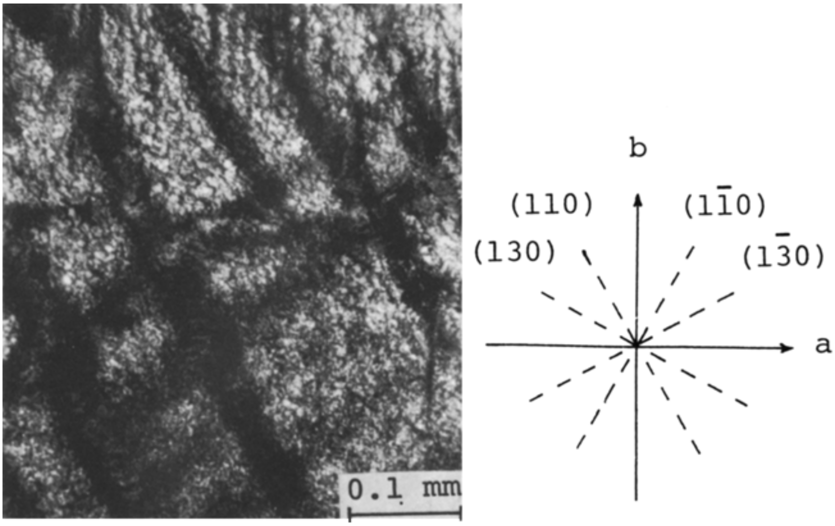

Fig. 6. Orthoscopic photograph of twins viewed along the *c* axis at 500° C on cooling, showing transformation twins

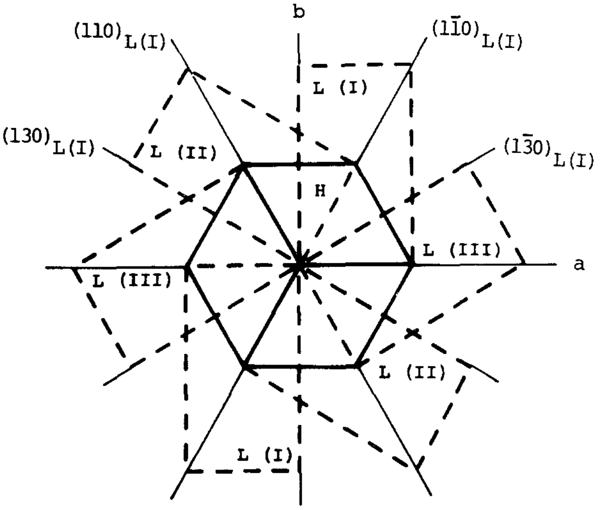

Fig. 7. Axial relationships of transformation twins projected along the *c* axis. *L(I)*, *L(II)*, and *L(III)*: twin individuals of the low temperature form, and *H*: high temperature form. $\{130\}_{L(I)}$ and $\{110\}_{L(I)}$: indices are based on *L(I)* twin individual

phase transition proceeds through an intermediate temperature form. The moving direction, [130] or [$1\bar{3}0$], is probably governed by a few defects in the crystal and/or a slight difference in the temperature distribution within the specimen. The duration of coexistence of the low, the intermediate and the high temperature forms ranges from about 580° to 587° C. This coexistence near the phase transition is compatible with a first-order transition.

Passing through the phase transition on cooling, dark belts crossing each other appear as a result of formation of transformation twins parallel to (110), ($1\bar{3}0$), ($1\bar{1}0$), and (130). (110) and ($1\bar{1}0$) are perpendicular to ($1\bar{3}0$) and (130), respectively. Figure 6 is a photograph of the twins viewed along the *c* axis at 500° C on cooling. The crystal is divided into three twin individuals rotated by the angle of nearly 60° with respect to each other. When the high temperature form transforms into the low temperature form, the twinning occurs in three different ways with one of the [100], [110], and [010] axes of the high temperature form becoming the *a* axis of the low temperature form. Figure 7 shows the axial relationships of the transformation twins. Above the phase transition point, the dark belts crossing each other disappear and the crystal becomes truly optically uniaxial on reheating as well as on heating. Below the transition point, the dark belts crossing each other appear on recooling. The twins are parallel to the same planes, {110} and {130}, as in the cooling process, but show different patterns.

Conclusions

1. Prior to the phase transition, orthorhombic potassium sulfate becomes apparently optically uniaxial twice at 338° and 425° C, respectively, and then becomes truly optically uniaxial at the transition point, 587° C. The optic axial angle increases continuously with increasing temperature up to 338° C, decreases up to 425° C, and increases again up to 587° C.

2. Coexistence of three forms, the low, the intermediate and the high temperature forms, was observed near the phase transition at 587° C. The phase transition propagates through the intermediate temperature form, which is sandwiched between the low and the high temperature forms and moves in a definite direction, ⟨130⟩.

3. Passing through the phase transition on cooling, transformation twins parallel to {110} and {130} occur.

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