Thermal anomaly in sodium potassium sulphate crystals

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Thermal anomaly in sodium potassium sulphate crystals

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Résumé. — Les propriétés thermales du $NaKSO_4$ cristal, que l'on a fait croître à 315 K par la méthode d'évaporation lente, ont été étudiées dans l'intervalle de température entre 300 et 500 K en faisant des mesures de thermomécanique (TMA), de thermogravimétrie (TG), d'analyse thermale différentielle (DTA), et d'examen de calorimétrie différentielle (DSC). Les coefficients d'expansion thermale dans les trois directions cristallographiques fondamentales ont montré un comportement anormal près de 453 K. Aussi, près de cette température, des effets anisotropes ont été observés et pas de perte de poids n'a été détectée. Les mesures (DSC) de la chaleur spécifique à pression constante C_p, ont montré un accroissement faible et continu durant l'accroissement de température plus un sommet à 453 K.

Abstract. — The thermal properties of $NaKSO_4$ crystal, grown at 315 K by the slow evaporation method, were studied in the 300-500 K temperature range by performing Thermomechanical (TMA), Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) measurements. Thermal expansion coefficients for the three fundamental crystallographic directions showed anomalous behaviour around 453 K. Also, in this temperature range, anisotropic effects were observed and a weight loss was not detected. The DSC measurements of the specific heat at constant pressure C_p, showed a slight continuous increase with increasing temperature and a peak at 453 K.

1. Introduction.

The growing interest in the physical properties of double sulphate crystals is due to the fact that they show anomalous behaviour at transition points [1-5].

Sodium potassium sulphate is a member of the family of crystals having the general formula $M^IM^{II}BX_4$ (where M^I stands for Na or Li, M^{II} stands for K, Na, Rb, Cs, ammonium (NH_4) or hydrazine (N_2H_5) and BX_4 stands for SO_4^{--} or SeO_4^{--}).

It is known that $NaKSO_4$ crystals have orthorhombic symmetry at 300 K and belong to the mmm point group [6]. Moreover, pyroelectric and piezoelectric measurements on $NaKSO_4$ crystals show that they have a centre of symmetry. The lack of information concerning the thermal behaviour of $NaKSO_4$ stimulated the study for their physical properties.

2. Crystal preparation and experimental techniques.

Single crystals of sodium potassium sulphate $NaKSO_4$ were grown from an aqueous solution of equimolar mixture of Na_2SO_4 and K_2SO_4 by the slow evaporation method at 315 K. Purification of the crystals were achieved by slow recrystallization for five times. The crystals were cut along the three fundamental crystallographic axes using a wet thread saw and the samples prepared in the form of thin rectangular rods with the dimension of $3 \times 3 \times 20$ mm^3. The longest dimensions were oriented along the principal crystallographic directions [100], [010], [001].

The thermal behaviour of these crystals was studied in the temperature region between 300-500 K using the following techniques :

a) Thermomechanical analysis was performed with Heraeus TMA 500 dilatometer, fitted with a low temperature furnace. The sample temperature was monitored with Ni-Cr-Ni thermocouple inserted in a sample holder of the standard design. The linear thermal expansion coefficient was computed using the assumption that the quartz expansion coefficient was insignificant. The heating rate was 2 K/min.

b) Thermogravimetric measurements were performed with a Heraeus TGA 500 thermo-balance using a Pt-Rh-Pt temperature sensor. The 60 mg samples were placed in a platinum crucible. The

heating rate was 10 K/min. Dry nitrogen flowed over the samples at a rate of 15 ml/min and the chamber cooling water flow rate was 10 l/hour.

c) Differential thermal analysis DTA was performed with a Heraeus DTA 500 analyser using a Ni-Cr-Ni temperature sensor. The 45 mg sample was contained in a glass tube in the DTA cell. A heating rate of 5 K/min was used.

d) The specific heat was determined by differential scanning calorimetric measurements using the base line method [7]. Lidded pans, made of aluminium, were used to eliminate base line sloping. A Pt 100 thermocouple was used as a temperature sensor. A 43 mg sample was used and the heating rate was 5 K/min.

3. Results and discussion.

The thermal expansion coefficients were calculated from dilatometric measurements. The measurements were carried out when the temperature was increasing and once more when the temperature was decreasing and no hysterises phenomena were detected. Table I

Table I.

Temp. range	α_{11} K^{-1}	α_{22} K^{-1}	α_{33} K^{-1}
300-453 K	7.4×10^{-5}	7.0×10^{-5}	7.2×10^{-6}
453-460 K	-22.0×10^{-5}	-27.0×10^{-5}	-83.0×10^{-6}

shows the average values of the linear expansion coefficients α_{ii} in different temperature ranges. Figure 1 (a, b and c) revealed, for the first time, that $NaKSO_4$

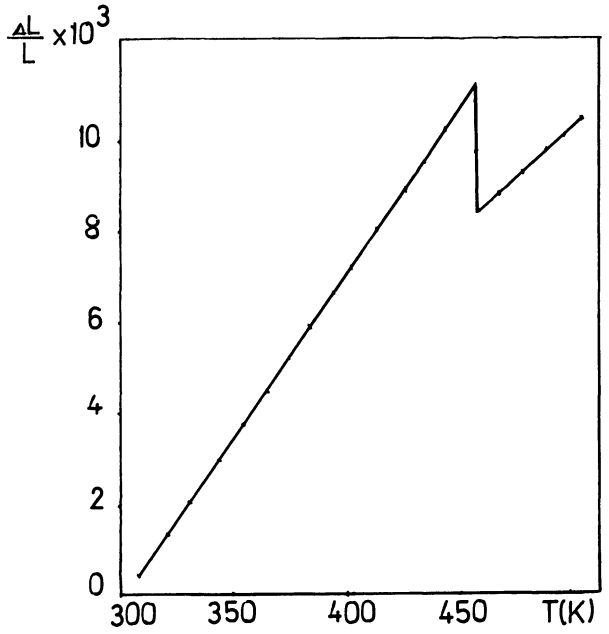

Fig. 1a. — Relative change of length measured along the *X*-axis of $NaKSO_4$ crystal with temperature.

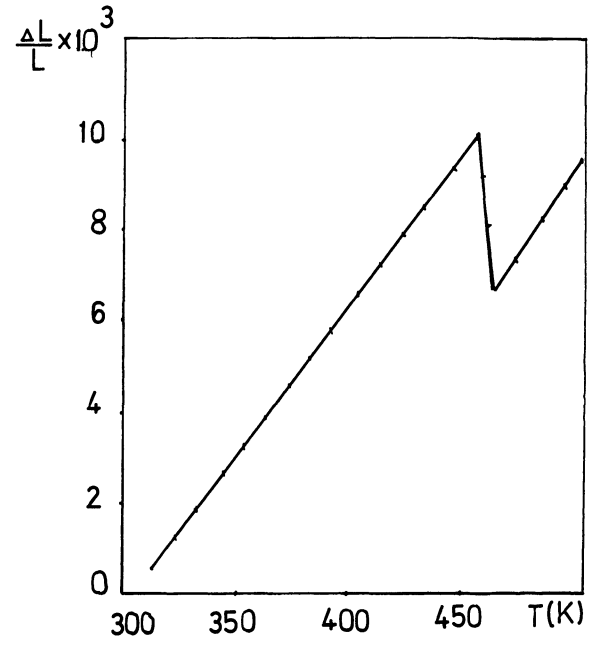

Fig. 1b. — Relative change of length measured along the *Y*-axis of $NaKSO_4$ crystal with temperature.

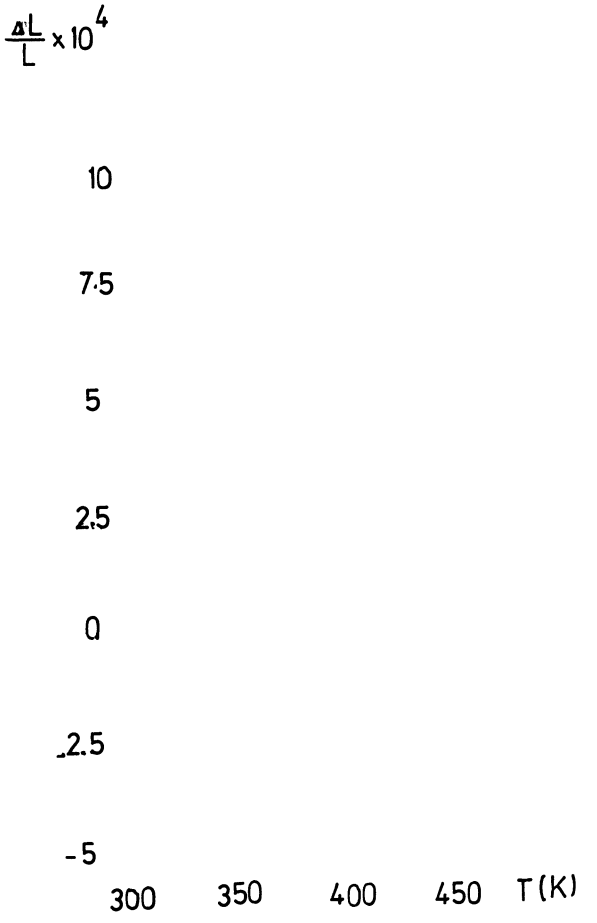

Fig. 1c. — Relative change of length measured along the *Z*-axis of $NaKSO_4$ crystal with temperature.

exhibits major thermal expansion anomalies in the immediate vicinity of the temperature 453 K. The thermal expansion is strongly anisotropic as shown by the large differences in contraction observed at temperatures above $T_c = 453$ K. The overall expansion is positive in the entire temperature region measured for the X- and Y-directions and is negative in parts of the 453-500 K phase transition region in the Z-direction. The expansion is linear with positive slope below 453 K, linear with a different negative slope between 453-460 K and linear with a different positive slope above 460 K. The sudden change in the thermal expansion coefficients may be due to a second order lambda transformation.

The DTA measurements showed transition peaks in the temperature region 453-470 K, as illustrated in figure 2a. The thermogravimetric curve, figure 2b, indicates that the sample did not lose weight in the entire temperature range of interest 300-500 K.

The DSC measurements of the specific heat at constant pressure C_p, figure 3, showed a pronounced maximum at $T_c = 453$ K. This may indicate that

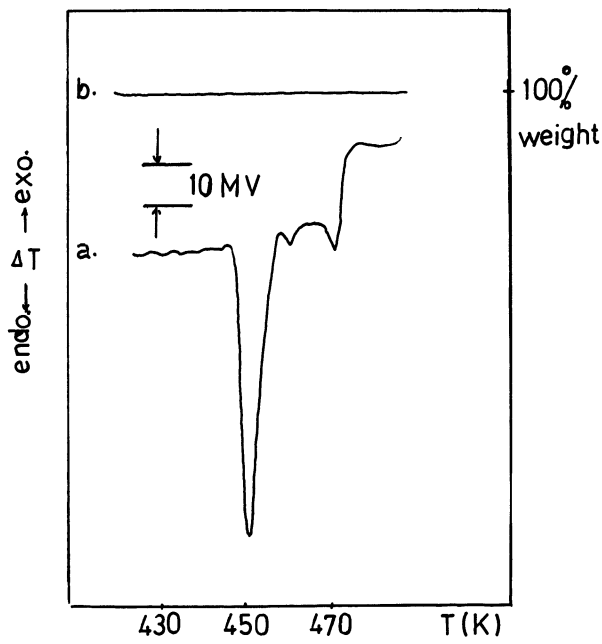

Fig. 2. — Thermal analysis curve for $NaKSO_4$ crystal. a) DTA curve; b) TG curve.

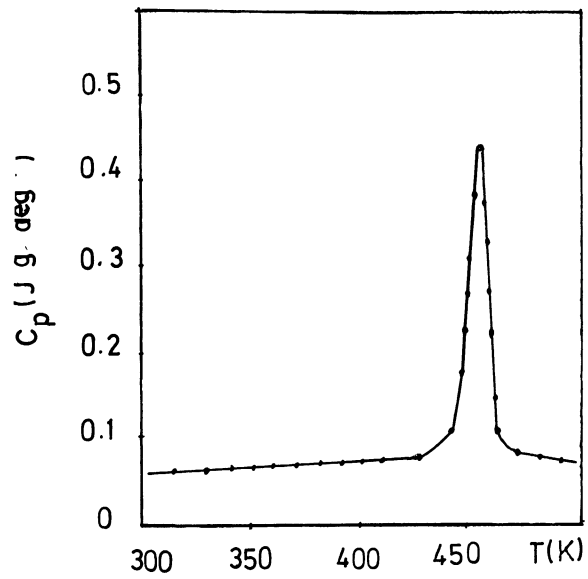

Fig. 3. — Temperature dependence of specific heat at constant pressure C_p for $NaKSO_4$ crystal.

the entropy change is continuous and therefore there is no latent heat. However, since specific heat peak was observed (anomalous specific heat) and have the shape given by figure 3, it could correspond to a second order lambda transition [8].

The anomalous behaviour of the thermal expansion coefficients, specific heat, and differential thermal analysis observed during the study of $NaKSO_4$ crystals through the temperature range 300-500 K suggests that the crystal may present a structural phase transition at $T_c = 453$ K. This transition is probably from orthorhombic symmetry with point group mmm to monoclinic symmetry with point group 2/m.

However, further and detailed investigation is still needed for such type of crystals to throw more light on its anomalous behaviour.

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