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THERMAL ANOMALY IN $LiKSO_4$ CRYSTALS IN THE TEMPERATURE RANGE 300–800 K

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Thermal analysis, DTA, TG, TMA and DSC were performed on $LiKSO_4$ in the temperature range 300 to 800 K, using a Heraeus TA 500 thermal analyser. The thermal expansion coefficients measured along the three fundamental crystallographic axes, together with the specific heat C_p, show anomalous behaviour around the phase transition temperature of these crystals at $T_c = 705$ K. Anisotropy in the thermal expansion coefficient as well as endothermic peaks around T_c were also observed, while no loss of weight was detected.

The temperature-dependence of the thermal conductivity of $LiKSO_4$ crystals has been estimated, using the temperature-variation of the thermal diffusivity.

Studies of the physical properties of lithium potassium sulphate ($LiKSO_4$) [1, 2] revealed that these crystals exhibit interesting behaviour in the low-temperature region as well as in the high-temperature one.

From the structural studies on $LiKSO_4$ crystals, it is well known that they possess hexagonal symmetry with polar point group 6 and space group $p6_3$ in the temperature range 300–700 K. The lattice parameters obtained from X-ray precision photography showed that the hexagonal unit cell of $LiKSO_4$ crystals has $a_0 = 5.15$ and $c_0 = 8.63$ Å [3]. According to Fischmeister and Roenquist [4], the phase transition in $LiKSO_4$ is not regarded as of continuous (or λ) type, though small changes in the lattice constant along both the *c* and *a* axes at the transition point were reported. Chung [5] reported that $LiKSO_4$ crystals show two different phase transition: the first is an orthorhombic one from 708 up to 940 K, while the second is a hexagonal one from 940 K up to the melting point. Measurements of the dielectric and thermal properties of $LiKSO_4$ crystals were first made by Ando [6] in the temperature range from 300 up to 800 K, and later by Delfino et al. [7] in the temperature range from 288 up to 580 K. Their results proved the existence of the paraelectric behaviour of $LiKSO_4$ crystals. Using a Fizeau interferometer, Sharma [8] observed anomalies in the thermal expansion coefficient of $LiKSO_4$ crystals at 178 and 695 K. However, the different interpretations given by the different authors on the basis of their studies pointed to the necessity of further systematic investigation of the thermal properties of $LiKSO_4$.

In the present work a Heraeus TA 500 instrument was used to study the temperature-variations of the linear thermal expansion coefficients as well as the specific heat at constant pressure for $LiKSO_4$ crystals in the temperature range from 300 up to 800 K.

Crystal preparation and experimental techniques

Single-crystals of $LiKSO_4$ were grown isothermally at 315 K by the dynamic method from an aqueous solution containing the initial salts in stoichiometric ratio. Rectangular crystal rods measuring $2 \times 2 \times 20$ mm^3 were cut out from the single-crystal in accordance with the directions previously proposed for $LiKSO_4$ crystal by Shiroishi et al. [9]. The longer axis of the sample is directed in the principal crystallographic directions (100), (010) and (001).

The thermal behaviour of these crystals was studied in the temperature region 300–800 K by applying the following techniques:

a) Thermomechanical analysis (TMA) was performed using a Heraeus TMA 500 dilatometer fitted with a low-temperature furnace. The sample temperature was monitored by means of NiCrNi thermocouple fitted in a sample holder of standard design. The linear expansion coefficient was calculated on the assumption that the quartz expansion coefficient has an insignificant effect on the produced values. The heating rate used was 2 degree/min.

b) The specific heat under constant pressure, C_p, was determined using a differential scanning calorimeter (DSC) technique, where a Heraeus DSC cell was connected to the Heraeus DTA 500 thermal analyser. Measurements were achieved by applying the base line method [10]. Lidded pans, made of aluminium, were used to eliminate the sloping of the base line. A Pt 100 thermocouple was used as a temperature sensor, while a heating rate of 2 degree/min was applied.

c) For differential thermal analysis, the sample was contained in a glass tube in the standard DTA cell connected to the DTA 500 analyser. The temperature sensor used was NiCrNi and the heating rate applied was 5 degree/min.

d) Thermogravimetric (TG) measurements were performed on a Heraeus TG 500 thermobalance with a Pt-Rh-Pt temperature sensor, and the heating rate used was 10 degree/min. Dry nitrogen was allowed to flow at a rate of 15 ml/min, while the flow rate of cooling water was 10 l/h.

Results and discussion

1. Thermal expansion

The data presented in Fig. 1A, B and C indicate that all lattice parameters *a, b* and *c* demonstrate a clear change in thermal expansion coefficient only at $T_c = 705$ K. Table 2 shows the average values of α in different temperature ranges. The overall expansion is positive in the whole temperature region for the *Y* direction, whereas it is negative in parts of the phase-transition region from 705 up to 750 K in the *X* and *Z* directions. The expansions were represented as straight lines interrupted by the contracted region at T_c (705–750 K). The straight lines were resumed with different slopes.

The linear thermal expansion coefficient of $LiKSO_4$ crystals measured along the three fundamental crystallographic axes *a*, *b* and *c* appeared to be anisotropic. Moreover, they show a temperature hysteresis of about 10 degrees, which is probably due to domain wall motion in the case of cooling and heating.

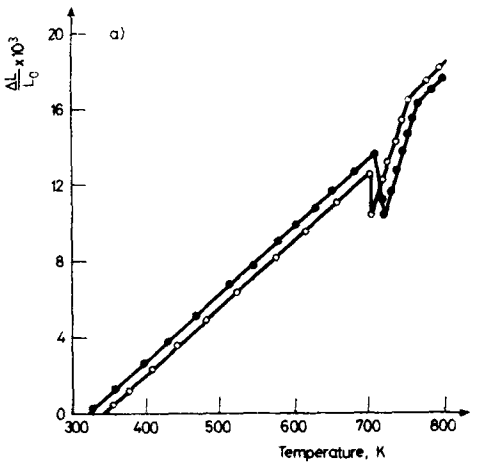

Fig. 1A The change of the thermal expansion coefficient of $LiKSO_4$ crystal with heating and cooling (along *X* direction). • heating, ○ cooling

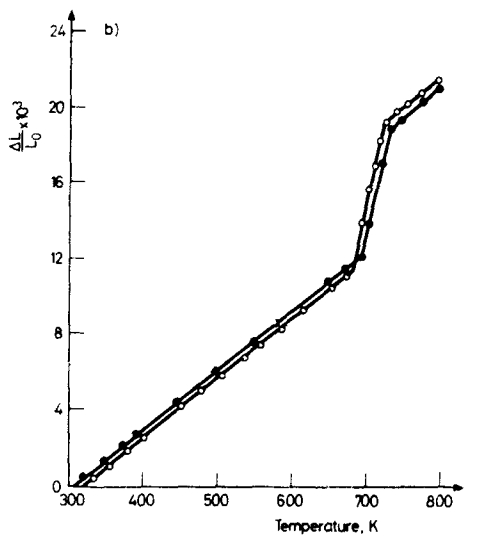

Fig. 1B The change of the thermal expansion coefficient of $LiKSO_4$ crystal with heating and cooling (along *Y* direction). • heating, ○ cooling

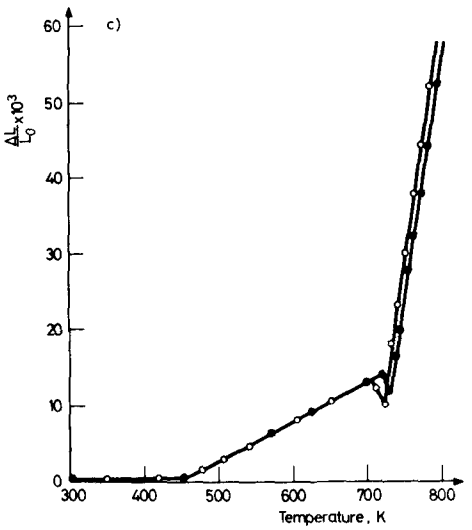

Fig. 1C The change of the thermal expansion coefficient of $LiKSO_4$ crystal with heating and cooling (along Z direction). • heating, ○ cooling

Table 1 Linear expansion coefficients along the different crystallographic axes through different temperature ranges

Temperature range K	$\alpha_{11}K^{-1}$	$\alpha_{22}K^{-1}$	$\alpha_{33}K^{-1}$
300–705	$1.5 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$5.6 \cdot 10^{-6}$
705–750	$-5.3 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$	$-1.5 \cdot 10^{-5}$
750–800	$1.16 \cdot 10^{-4}$	$2.8 \cdot 10^{-5}$	$5.4 \cdot 10^{-5}$

2. *Specific heat:* C_p

The results of specific heat measurements under constant pressure are shown in Fig. 2. Near the transition temperature $T_c = 705$ K there is a λ-type anomaly of the specific heat, typical of a phase transition of first order. The transition energy ΔQ was calculated by integrating the excess part of the C_p *vs.* T curve, and was found to be of the order of 25.83 JG^{-1}. Assuming the temperature-dependence of C_p to be as reported by Deffino et al. [7], it is interesting to note that agreement with our results can arise only when the following empirical formula is applied: C_p (J $mole^{-1}$ K^{-1}) = $= 2.54 + 0.1247\,T + 7.2 \cdot 10^{-6}\,T^2$.

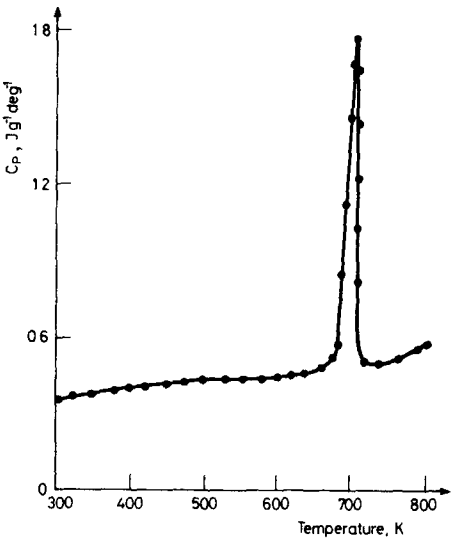

Fig. 2 The change of specific heat C_p of $LiKSO_4$ crystal with change of temperature

3. Differential thermal analysis and thermogravimetric measurements

The DTA measurements revealed a transition peak at $T_c = 705$ K, as shown in Fig. 3A, while no indication of weight loss was observed in the range of measurements. The thermogravimetric curve produced was a straight line and is represented in Fig. 3B.

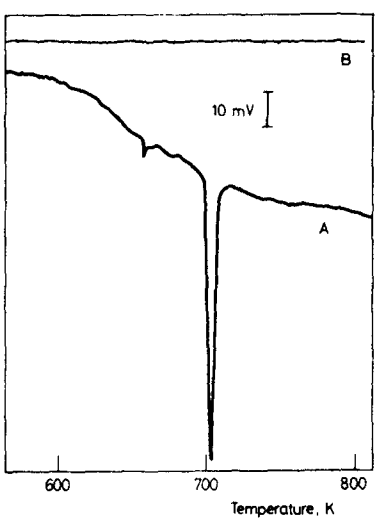

Fig. 3 Thermal analysis results of $LiKSO_4$ crystal. a) Differential thermal analysis, b) Thermogravimetry curve

4. Thermal conductivity

The temperature-dependence of the thermal conductivity K_{ii} of $LiKSO_4$ crystals was estimated using the temperature-variation of the thermal diffusivity h_{ii} [11] and the simple relation:

$$h_{ii} = \frac{k_{ii}}{C_p}$$

where ρ is the density of the crystal ($\rho = 2.39$ g/cm^3) and C_p its specific heat at constant pressure. The results obtained for the thermal conductivity are shown in Fig. 4. It is noted that the thermal conductivity also shows an anomalous temperature-dependence around the transition temperature, similarly as for the other thermal parameter.

It can be concluded that the anomalies observed in the thermal properties are due to the structural phase transition at $T_c = 705$ K.

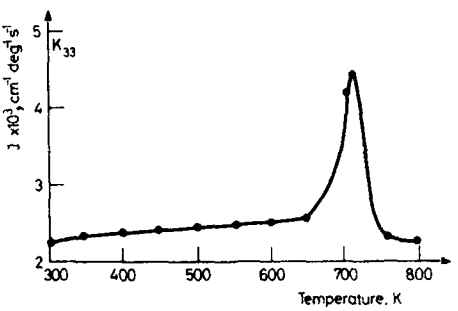

Fig. 4 Change of thermal conductivity of $LiKSO_4$ crystal with changing the temperature

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Zusammenfassung – $LiKSO_4$ wurde im Temperaturbereich von 300–800 K thermoanalytisch (DTA, TG, TMA und DSC) mit dem Thermoanalysator Heraeus TA 500 untersucht. Die thermische Ausdehnung, gemessen in Richtung der drei kristallographischen Hauptachsen, zeigt zusammen mit der spezifischen Wärme C_p ain anomales Verhalten in der Nähe der Phasenübergangstemperatur $T_c = 705$ K dieser Kristalle. Ebenfalls wurde eine Anisotrope in den thermischen Ausdehnungskoeffizienten und in den endothermen Peaks um T_c beobachtet, während kein Gewichtsverlust festgestellt wurde. Die Temperaturabhängigkeit der Wärmeleitfähigkeit von $LiKSO_4$-Kristallen wurde aus der thermischen Diffusion bestimmt.

Резюме – Используя термоанализатор типа Хераус ТА 500, проведен с кристаллами $LiKSO_4$ термический анализ, ДТА, ТГ, ТМА и ДСК в области температур 300–800 К. Коэффициенты термического расширения, измеренные по трем основым кристаллографическим осям, а также значения удельной теплоемкости показали аномальный характер около температуры фазового переходя этих кристаллов при $T_c = 705$ К. Около T_c проявлялась анизотропия коэффициента термического расширения, наряду с появлением эндотермических пиков. В тоже самое время потери веса не наблюдалось. Температурная зависимость удельной теплопроводности кристаллов $LiKSO_4$ была установлена, используя температурное изменение коэффициента термодиффузии.