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SPECIFIC HEAT AND PHASE TRANSITION OF $(Li_{1-x}K_x)_2SO_4$ SINGLE CRYSTALS

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A specific heat study of $(Li_{1-x}K_x)_2SO_4$ - LKS - mixed crystals has been made in a wide concentration range x covering the temperature range 300-800 K. The phase diagram was determined. It is shown that a variation of the Li^+:K^+ concentration changes the critical behaviour of the specific heat. The results are discussed in terms of scattering mechanisms of energy carriers.

Since the discovery of an incommensurate phase transition and the ferroelasticity in $LiKSO_4$ crystals [1-4], an increasing interest has arisen for this crystal as well as for other members of $M^IM^{II}BX_4$ family.

Lithium potassium sulphate crystals undergo two phase transitions above room temperature at about T_1 = 705 K [5] and T_2 = 950 K [6]. Below 708 K the crystal structure belongs to space group $P6_3$, above T_1 the crystal structure has orthorhombic symmetry with $Pc2_1n$ space group. The crystal structure of the high temperature phase above T_2 exhibits either the space group $P6_3mmc$ or that of $P6_3mc$.

The studies of thermal properties around the high temperature ferroelastic phase transition at T_1 = 705 K drew our attention [7, 8].

In the present paper, we report the thermal properties of the solid solutions $(Li_{1-x}K_x)_2SO_4$ with (x = 0.1, 0.15, ..., 0.5). The measurements were carried out in the vicinity of high temperature phase transition at T_1.

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Experimental

Single crystals of $(Li_{1-x}K_x)_2SO_4$ have been grown isothermally at 315 K by the dynamical method from aqueous solutions containing Li_2SO_4 and K_2SO_4 in the appropriate stiochiometric ratios.

The specific heat was measured in the temperature range 300-800 K using a Perkin-Elmer DSC7 differential scanning calorimeter. The melting points of indium and tin were used to calibrate the DSC in terms of temperature and heat of fusion. Sapphire was used as the standard reference [9-11] for the specific heat determination.

Results and discussions

The phase transition of some ferroelectric solid solutions becomes more and more diffusive when the concentration of one component is increased.

The results of specific heat C_p of $(Li_{1-x}K_x)_2SO_4$ for different values of x are presented in Fig. (1).

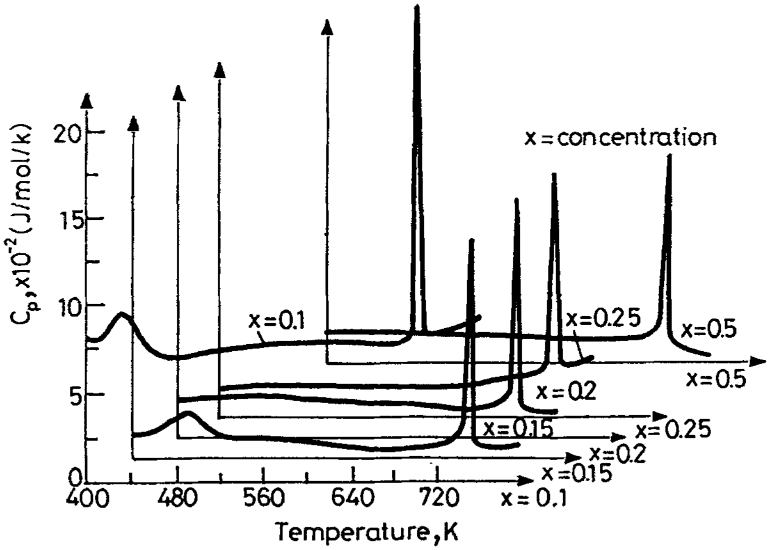

Fig. 1 Temperature dependence of the specific heat for $(Li_{1-x}K_x)_2SO_4$ crystals for different values of x

A clear anomaly in C_p appeared in the neighbourhood of T_1 and another less pronounced at 433.4 K and 451 K, for $x = 0.1$ and 0.15, respectively.

The results of C_p measurements support the previously published data [4, 12].

From Fig. (2) it is clear that the transition temperatures T_{c1} and T_{c2} are shifted towards higher temperatures as a result of increase of x.

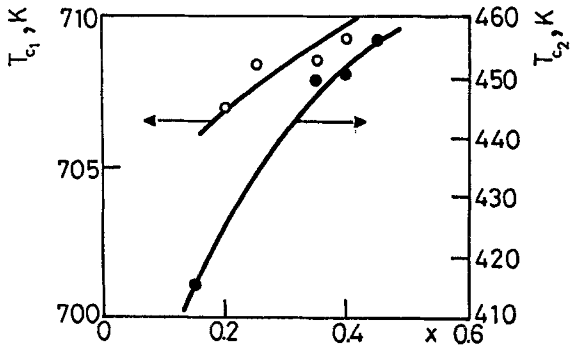

Fig. 2 Transition temperatures as a function of the concentration x in of $(Li_{1-x}K_x)_2SO_4$ crystals

At the transition temperature the arrangement of ions becomes less ordered and the compound is said to undergo an order-disorder transition.

Figure (3) presents the concentration dependence of the changes in entropy $\Delta S(T_c)$ and enthalpy $\Delta H(T_c)$ of $(Li_{1-x}K_x)_2SO_4$ at the transition temperature T_c.

The higher values of ΔH and ΔS for $x = 0.4$ (Fig. (3)) relative to the values of $LiKSO_4$ suggest the existence of well defined compounds, in good agreement with X-ray data.

The thermal properties of crystals of $(Li_{1-x}K_x)_2SO_4$ were found to be correlated with the concentration of the Li and K content.

Lithium potassium sulphate crystals exhibit a tridymite type structure, with alternating SO_4^{2-} and LiO_4^{2-} coordination tetrahedra.

In $LiKSO_4$ there are three different orientations of the tetrahedra with respect to the threefold axis.

Since the radius of the Li^+ ion is smaller than that of the K^+ ion, an effect of the Li ion concentration on the ordering of the SO_4^{2-} tetrahedra can be expected. This effect is evident from an entropy change at the phase transition.

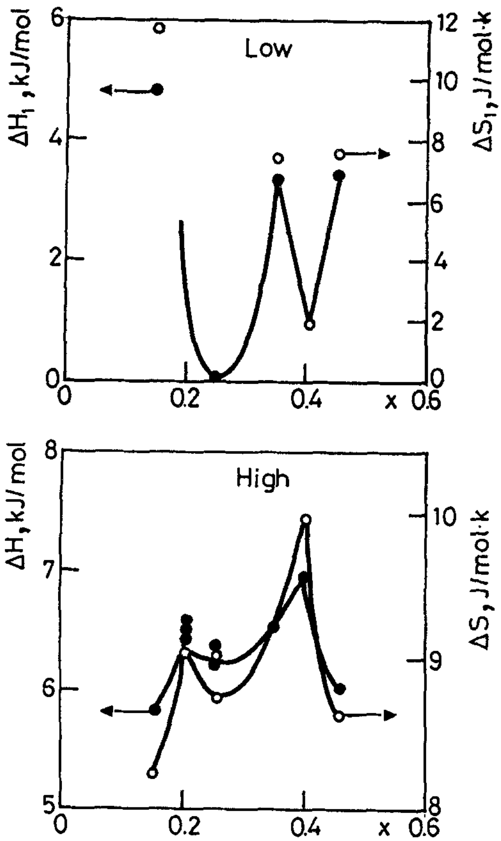

Fig. 3 The concentration dependence of the changes in entropy $\Delta S\,(T_c)$ and enthalpy $\Delta H\,(T_c)$ of $(Li_{1-x}K_x)_2SO_4$ crystals at transition temperatures T_c

Incommensurate phases are highly sensitive to the presence of defects [13]. Therefore the understanding of the properties of IC systems requires the study of the influence of defects. The behaviour of $C_p(T)$ for different stoichiometric ratios in the incommensurate phases of $(Li_{1-x}K_x)_2SO_4$ is more sensitive to the presence of defects.

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Zusammenfassung — Bei Temperaturen zwischen 300 und 800 K wurde für einen breiten Konzentrationsbereich für x die spezifische Wärme von $(Li_{1-x}K_x)_2SO_4$-Mischkristallen untersucht und das entsprechende Phasendiagramm erstellt. Es wurde gezeigt, daß eine Änderung des Verhältnisses Li^+:K^+ auch das kritische Verhalten der spezifischen Wärme verändert. Die Ergebnisse werden hinsichtlich von Sreuungsmechanismen der Energieträger diskutiert.