

05.1-33 LOW-TEMPERATURE PHASE TRANSITION IN LiCsSO_4 .

By P.E. Tomaszewski, A. Pietraszko and K. Łukasiewicz, Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

The alkali metal lithium sulphates, MeLiSO_4 , constitute an important group of materials with interesting ferroelectric and ferroelastic properties. Orthorhombic LiCsSO_4 has been observed to undergo a structural pure ferroelastic, typical second-order phase transition at 203 K. The ferroelastic behaviour similar to that observed in LiNH_4SO_4 and LiKSO_4 has been investigated in same detail. The monoclinic angle in the low-temperature phase has been interpreted as an order parameter. Its temperature variation in the range of two degrees below T_c agrees very well with predictions of Landau theory.

Lattice parameters have been determined as a function of the temperature in the range from 160 up to 550 K by using the Bond single-crystal diffractometer and copper radiation. The monoclinic strain has been measured by applying an attachment consisting of an additional silicon crystal which has converted our diffractometer into a two-crystal spectrometer. On basis of obtained results the thermal expansion and strain tensor have been calculated.

Optical inspection by means of a polarizing microscope with a special attachment applying a cold nitrogen flow indicates that in the monoclinic phase below 203 K the optical indicatrix rotates around the c-axis with decreasing temperature. The ferroelastic domains are clearly observable and their pattern changes with a lowering temperature in a very characteristic way contrary to that observed in LiNH_4SO_4 and LiKSO_4 .

Table 1

RbLiSO_4	I Pcmn abc	477 K A ¹ incomm. ab5cβ	475 K B P2 ₁ /c ab2cβ	458 K A incomm. ab5cβγ	438 K II P2 ₁ /n abcγ
$\text{Cs}_{.25}\text{Rb}_{.75}\text{LiSO}_4$	I Pcmn abc	453 K B P2 ₁ /c ab2cβ	388 K B [†] ? ab2cβ	377 K II P2 ₁ /n abcγ	
$\text{Cs}_{.5}\text{Rb}_{.5}\text{LiSO}_4$	I Pcmn abc	343 K B P2 ₁ /c ab2cβ	235 K B [†] ? ab2cβ		
$\text{Cs}_{.75}\text{Rb}_{.25}\text{LiSO}_4$	I Pcmn abc	255 K B P2 ₁ /c ab2cβ			
CsLiSO_4	I Pcmn abc	203 K II P2 ₁ /n abcγ			

05.1-34 THE PHASE TRANSITION AND THE DOMAIN STRUCTURE FOR MIXED CRYSTALS $\text{Cs}_x\text{Rb}_{1-x}\text{LiSO}_4$. By A. Pietraszko, Institute for Low Temperature and Structure Research, 50-950 Wrocław, Poland.

X-ray studies of CsLiSO_4 - RbLiSO_4 phase system have revealed successive structural phase transformations with ferroelastic and incommensurate phases. In our previous paper we presented the X-ray structure analysis of the RbLiSO_4 , $\text{Cs}_{0.5}\text{Rb}_{0.5}\text{LiSO}_4$ and CsLiSO_4 crystals. New results has been obtained using X-ray analysis and optical method at temperature range from 140 K to 600 K. It was found that for concentration of Cs ions above $x=0.4$, the intermediate monoclinic phase B existed at low temperature. For the phase B the ferroelastic structure along b axis was investigated. The observation of the monoclinic phase II under polarizing microscope showed ferroelastic domain structure along c axis below the transition point which at low temperature gradually disappeared. For small Cs concentration an additional intermediate ferroelectric - ferroelastic phases A and B[†] did appear. The domain structure of these phases is of typical mosaic pattern. Basing on the crystal structure analysis and the temperature dependence of domain structure the phase transitions for $\text{Cs}_x\text{Rb}_{1-x}\text{LiSO}_4$ mixed crystal have been discussed. The detected structural transformations are summarized in table 1.

05.1-35 UNLIMITED SOLUBILITY BETWEEN $\alpha\text{-Na}_2\text{CO}_3$ AND Na_2SO_4 I STRUCTURES. By B.N. Mehrotra, Institut für Kristallographie, Technische Hochschule Aachen, W. Germany.

The phase diagram of sodium carbonate and sodium sulphate has been investigated using X-ray and thermal methods, figure 1. The high temperature modifications $\alpha\text{-Na}_2\text{CO}_3$, and Na_2SO_4 I show complete solubility. Among low-temperature modifications Na_2SO_4 V, Fddd, does not form any solid solution, but $\gamma\text{-Na}_2\text{CO}_3$, C 2/m, form limited solid solution. A new compound Burkeite, B, is also formed at low temperature.

Unlimited solubility of high modifications is also confirmed by fusing the two compounds, and quenching at room temperature. The shortening of the c-axis is the evidence that CO_3^{2-} groups are oriented perpendicular to c-axis. The quenched high modification, I, reverts to III and Burkeite, B, after some time, figure 2.

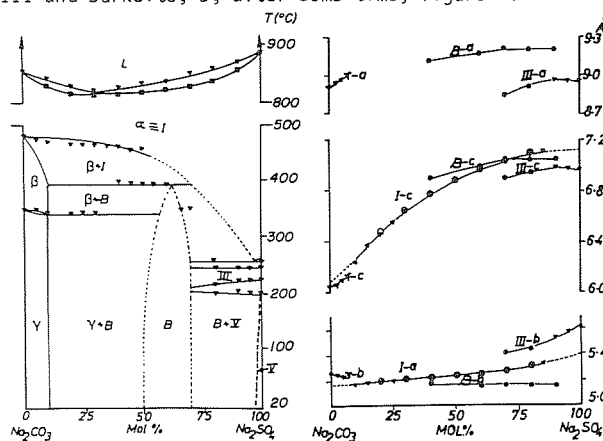


Fig. 1

Fig. 2