

05.1-33 LOW-TEMPERATURE PHASE TRANSITION IN LiCsSO_4 .

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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 Pcmm 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 Pcmm 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 Pcmm abc	343 K B P2 ₁ /c ab2cβ	235 K B [†] ? ab2cβ		
$\text{Cs}_{.75}\text{Rb}_{.25}\text{LiSO}_4$	I Pcmm abc	255 K B P2 ₁ /c ab2cβ			
CsLiSO_4	I Pcmm 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 groups are oriented perpendicular to c-axis. The quenched high modification, I, reverts to III and Burkeite, B, after some time, figure 2.

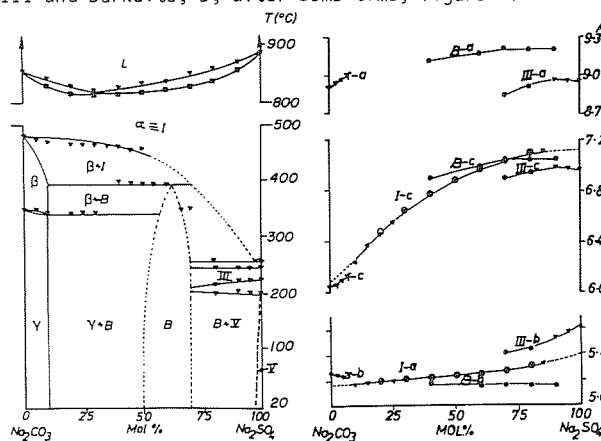


Fig. 1

Fig. 2

Single crystals of Na_2SO_4 III are grown by metastable nucleation from aqueous solutions at 50°C . This phase is orthorhombic with space group Cmcm and cell constants $a = 5.607\text{\AA}$, $b = 8.96\text{\AA}$, $c = 6.967\text{\AA}$, $Z = 4$. The structure is refined to $R = 4.5\%$. The structure consists of tetrahedral and octahedral framework. The thermal vibrations of most of the atoms are large along c -axis (Zeit. Krist. - in Press). Single crystals of this phase III (fig. 3a: Weissenberg Photograph 0-layer) on heating upto phase I and cooling, show oriented domains of phase III and phase II in the same crystals (fig. 3b: Weissenberg photograph 0-layer).

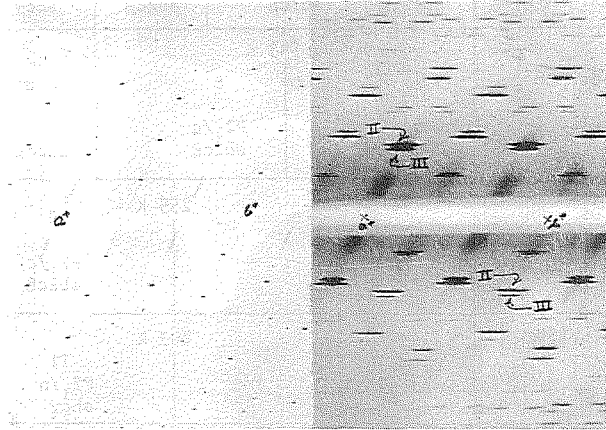


Fig. 3a

Fig. 3b

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05.1-36 ON THE LOW TEMPERATURE PHASE TRANSITION IN $(\text{NH}_4)_2\text{SO}_4$. By Y.A. Badr, G. Said, M. Mikhail and S. Awad, Faculty of Science, Cairo University, Cairo, Egypt.

An ultracryostat of type KT"90S" and multi-decameter (NF-Dekameter type WTW) provided with a special cell were used to determine the temperature dependence of the dielectric constant and dielectric loss over a wide range of frequencies of polycrystalline ammonium sulphate in the region of the low temperature phase transition. A sharp increase was observed in the values of ϵ' & ϵ'' at about -50°C . Besides, a dielectric dispersion was detected and it was found to be more pronounced in the higher temperature phase of $(\text{NH}_4)_2\text{SO}_4$. This dispersion was attributed to piezoelectric resonance (Badr, et al, Physica status solidi (a)53, K51(1979)).

The observed sudden increase in the values of the dielectric constant and dielectric loss below -50°C was inferred to the ferroelectric behaviour of phase II of $(\text{NH}_4)_2\text{SO}_4$. DTA studies showed that also a sharp peak at -50°C which indicated that the phase transition occurring in ammonium sulphate at -50°C was of the first order type. TMA thermograms showed that this transition was associated with a rapid increase in the expansion coefficient. Such increase in the lattice parameter might be attributed to the enhanced rotation of electric dipoles associated with the deformed SO_4^{2-} ions. The deformation of the SO_4^{2-} ions, in addition to their orientational motion, are thought to be responsible for the ferroelectric behaviour of $(\text{NH}_4)_2\text{SO}_4$ below -50°C .

05.1-37 CRYSTAL STRUCTURE CHANGES AND PRINCIPAL DEFECTS IN IRRADIATED CRYSTALS. By E.V. Kolontsova, A.E. Korneyev, V.P. Lutsenko. Moscow State University, Karpov Institute of Physics and Chemistry, Moscow, USSR.

Under the influence of radiation the crystals of Ca_2SiO_4 , CaAlO_3 , BaTiO_3 , PbZrO_3 , ZrO_2 , KNbO_3 , CsNO_3 and SiO_2 (quartz, cristobalite)

transform into the structural states, which are close to the high-temperature phases of unirradiated crystals. The investigation of radiation defects and comparison of crystal structure changes under the influence of irradiation and heating are important for the determination of such transformation mechanism.

By using X-ray diffuse scattering and X-ray crystal structure analysis it was shown that in neutron-irradiated quartz ($E \geq 0.5$ Mev;

$3 - 6 \times 10^{19} \text{ ncm}^{-2}$; $T_{\text{irrad}} \sim 100^\circ\text{C}$) structural

states intermediate between α and β -quartz are formed (E.V. Kolontsova, A.E. Korneyev, V.P. Lutsenko. Dokl. Akad. Nauk SSSR (1979), 247, 80). The dose dependences of these changes are qualitatively analogous to those in unirradiated crystals at about the α - β phase transition temperature. The investigation of diffuse X-ray scattering intensity (I_d) dependence of q (q -distance between reciprocal space point and the next nearest reciprocal lattice node)

showed, that I_d falls off like q^{-2} . $I_d \sim q^{-2}$

means (P.H. Dederichs. J. Phys. (1973), F3, 471), that isolated point defects are principal defects in neutron-irradiated quartz and therefore they are responsible for the new structural states.

The changes of diffraction pattern from single crystal and powder CsNO_3 during heating and X and γ -irradiation ($0.1 - 3.0 \times 10^{19} \text{ R}$; $E = 1.3$ Mev; $T_{\text{irrad}} \leq 40^\circ\text{C}$) were also studied.

Analysis of these experimental results allows to make a conclusion, that radiation-induced transformation of crystal structure is realized without forming of displacement spikes.

According to the analysis of our and literature data one can conclude that it is possible to consider isolated point defects concentration as an instability parameter under the influence of radiation for some compounds (such as α - SiO_2 , BaTiO_3 , CsNO_3 , and maybe

KNbO_3 , PbZrO_3).