Phase transitions in Rb$_x$K$_{1-x}$LiSO$_4$ mixed crystals

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Structural phase transitions in Rb$_x$K$_{1-x}$LiSO$_4$ mixed crystals (with x varying from 0 to 1) have been studied from the melting point to liquid-nitrogen temperature. Calorimetric (DTA and DSM) data, birefringence and optical polarization measurements were used to construct the full phase ($T-x$) diagram. It has been established that crystals of most compositions ($x \leq 0.95$) grow in the hexagonal-trigonal KLiSO$_4$ structure. Replacement of K by the larger Rb atom results in a considerable increase of the region of existence of the $P31c$ phase and expulsion of the high-temperature hexagonal phase. © *1998 American Institute of Physics.* [S1063-7834(98)03507-2]

Tridymite-like crystalline compounds ALiSO$_4$ (A=Cs,Rb,K,NH$_4$) have a framework structure made up of alternating LiO$_4$ and SO$_4$ tetrahedra sharing vertices to form six-membered rings, inside which cation A is located. If this cation has a large ionic radius, the hexagonal symmetry of the rings can become distorted, as is the case with Cs and Rb. All the above-mentioned representatives of the family have totally different sequences of phase transitions (PT) setting in with decreasing temperature. The difference in symmetry of the phases is associated with different versions of ordering of the tetrahedral groups. KLiSO$_4$ (KLS) and RbLiSO$_4$ (RLS) feature very complex sequences of symmetry changes in phase transitions compared, say, to CsLiSO$_4$, which undergoes only one PT.

Although the properties of most of the above compounds are presently well known, there is still no answer to the question why it is RbLiSO$_4$ and KLiSO$_4$ that exhibit such a rich variety of phases and PTs compared to CsLiSO$_4$ and NH$_4$LiSO$_4$. Valuable information relevant to this problem can be obtained in a systematic study of solid solutions of these compounds.

Even small additions of Rb and Cs to pure RLS and KLS to form Rb$_x$Cs$_{1-x}$LiSO$_4$ mixed crystals with large cations[1,2] reduce strongly the temperatures of transition to the monoclinic phase $P112_1/n$, which eventually disappears. In the middle part of the phase diagram the $P2_1/c11$ phase with a negligible unit-cell monoclinic distortion becomes stable, which in pure RLS exists within a narrow interval of 475–458 K. The phase diagram of Rb$_x$(NH$_4$)$_{1-x}$LiSO$_4$ follows a similar pattern.[3] We believe, however, that studies of solid solutions of RbLiSO$_4$ and KLiSO$_4$, the crystals exhibiting the most complex phase-transition sequences, show the most promise.

The first of these crystals exhibits the following phases: 1—$Pmcn$, with $c=c_0$ above 477 K; 2—an incommensurate-commensurate ferroelectric phase sequence observed in the 477–475 K interval; 3—a monoclinic ferroelastic phase $P2_1/c11$ with $c=2c_0$ between 475 and 458 K; 4—$P11n$ phase with $c=5c_0$ between 458 and 439 K; and 5—

$P112_1/n$ with $c=c_0$ persists at lower temperatures.[4]

In KLS, the phase transition sequence is different: 1*—$P6_3mmc$ or $P6_3mc$ above 941 K; 2*—rhombic $Pc2_1n$, $Pbn2_1$, or $Pmcn$ (941–708 K); 3*—$P6_3$(708$-242\uparrow,\downarrow201$ K); 4*—$P31c$($242\uparrow,\downarrow201-178$ K), and 5*—Cc or $Cmc2_1$ below 178 K. Despite intense studies of this compound, there still remain many questions bearing on the symmetry of the phases, their number, and even the PT temperatures. The main reasons accounting for these difficulties are the complex twinning observed to occur in all phases and coexistence of different structures in some temperature regions.[5,6]

This work presents the results of a study of Rb$_x$K$_{1-x}$LiSO$_4$ solid solutions. We investigated their phase diagram ($T-x$) by the optical polarization technique on differently oriented plates and by measuring birefringence and thermal effects.

1. EXPERIMENTAL

The single-crystals to be used in the study were prepared by slow evaporation of the corresponding mixtures of aqueous KLS and RLS solutions at $T \approx 300$ K. The single crystals thus grown had the shape of hexahedral pellets for $x \leq 0.3$, hexahedral prisms for $x > 0.8$, and needles for intermediate values of x. The samples were subjected to quantitative characterization by x-ray fluorescence and atomic absorption analysis. The Rb:K ratio in the crystals differed, as a rule, from the one in the solution. The largest and best crystals obtained were those with a small x. The samples intended for optical microscope studies were cut perpendicular and parallel to the growth axis.

The region of the hexagonal-trigonal phase transition was investigated by the birefringence technique using a Berek compensator with an accuracy to within $\cong 10^{-5}$ on plates cut parallel to the growth axis. This method permitted us to use small samples and to choose single-domain regions. The existence of thermal anomalies was determined by means of a DSM-2M differential scanning microcalorimeter operating
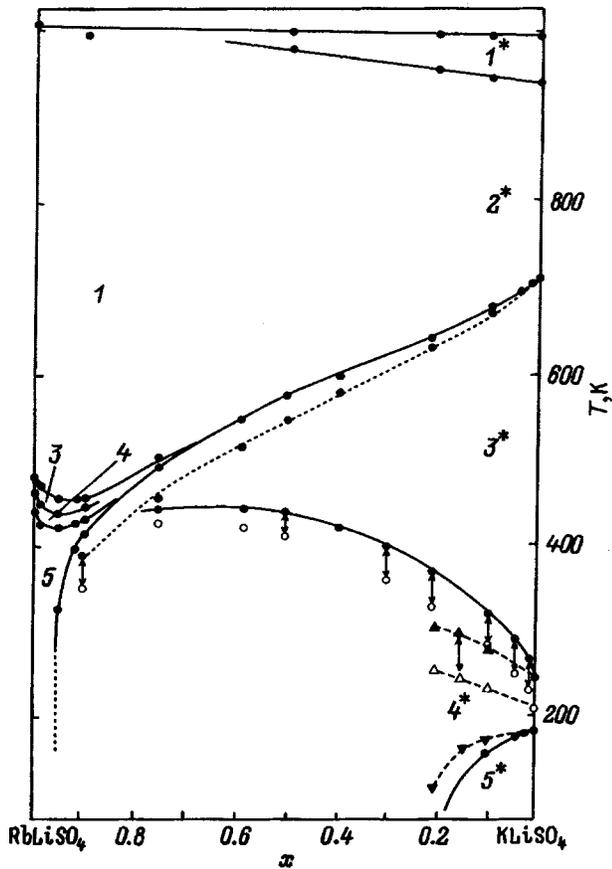
FIG. 1. Phase diagram of the $Rb_xK_{1-x}LiSO_4$ solid solutions. The triangles relate to Ref. 11.

FIG. 2. Thermal anomalies in crystals with different Rb content x: *1*—0.12, *2*—0.40, *3*—0.95, *4*—0.92, *5*—0.90.

within the temperature region of 150–750 K at temperature variation rates of 8 K/min, as well as differential thermal analysis (DTA) up to the melting point and above it.

Figure 1 shows the phase diagram of the $Rb_xK_{1-x}LiSO_4$ solid solutions obtained by us. Microscope studies using polarized light suggest the onset of optically uniaxial symmetry in the solid solution at room temperature up to $x \cong 0.95$. Heating changes it to rhombic, 2*, with characteristic 120° twins and straight extinctions. The temperature of this PT decreases from $\cong 700$ K to $\cong 400$ K with increasing x. This transformation has the features of a reentrant PT with explosive cracking of the sample and tailing of its temperature. This manifests itself in DSM measurements in the presence of one, two, or even three thermal-absorption peaks (curve *2* in Fig. 2). In Fig. 1 this region of coexistence of two phases is bounded by a dashed line from below and has the largest width for compositions with $x = 0.3 - 0.8$.

The compositions can be divided in two parts according to the change in enthalpy (ΔH) and entropy (ΔS), namely, compounds with low and high Rb content ($x = 0-0.5$ and $x = 0.9-1$, respectively) (see Table I). In the first case one or several anomalies corresponding to a clearly pronounced first-order PT between the 2* and 3* phases were observed. The change in enthalpy, 5200–6800 J/mol, is in a good agreement with data[7,8] obtained for pure KLS. The change in entropy, determined as $\Delta S = \Delta H/T$, varies, depending on x,
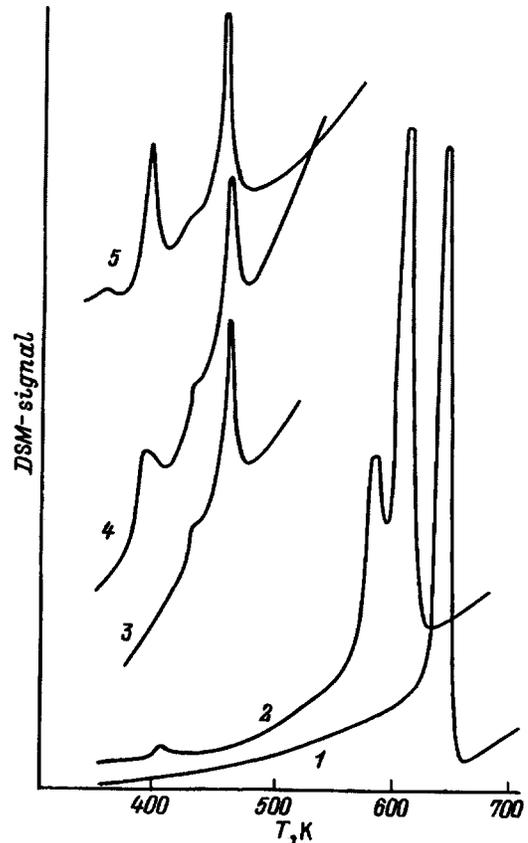
within the 8.7–9.7 J/mol·K interval, which is close to the value R ln 3 = 9.13 J/mol·K.

In the second case one detects several anomalies associated with different phase transitions. The anomalies are fairly close in temperature and rather diffuse, which makes their separation impossible. Estimation of ΔH and ΔS yields for the 1–3 PTs: $\Delta H_{1-3} = 1000-1300$ J/mol, and $\Delta S_{1-3} \cong 3-3.5$ J/mol·K. The change in the enthalpy and entropy in the 3-4-5 transitions was found to be 400–600 J/mol and 1–1.6 J/mol·K, respectively.

For the $x = 0.75$ compound, the total changes in enthalpy and entropy accumulated in several transitions from the rhombic to trigonal phase are $\Delta H = 3400$ J/mol and $\Delta S = 6.75$ J/mol·K.

TABLE I. Phase transition parameters derived from DSM measurements.

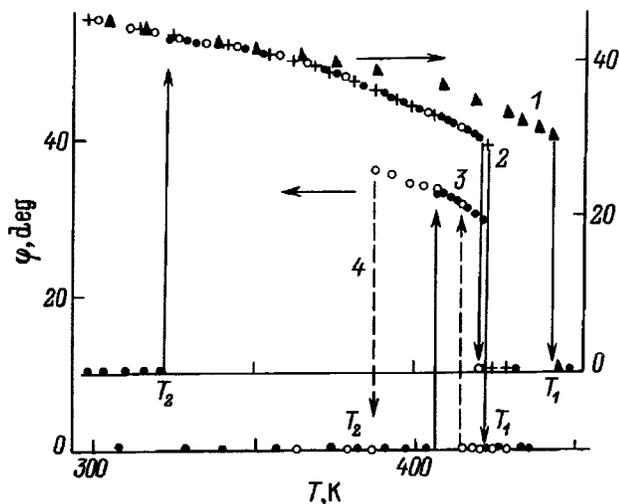| x	T, K	ΔH, J/mol	ΔS, J/mol·K
0.00	709	6193	8.73
0.014	703	6794	9.66
0.02	699	6088	8.78
0.043	697	6398	9.16
0.22	663; 635	6343	9.76
0.40	622; 595	5236	8.80
0.75	433–530	3400	6.75
0.90	457; 418; 385; 356	2000	4.6
0.92	453; 425; 380	1440	3.21
0.95	458; 428	1600	3.5

FIG. 3. Temperature dependence of the rotation angle of the optical indicatrix in the monoclinic phase of $Rb_xK_{1-x}LiSO_4$ ($P112_1/n$). *1*—$x=1.0$; *2*—$x=0.99$; *3*—$x=0.95$ ($\Delta T_1=2$ K, $\Delta T_2=\infty$); *4*—$x=0.90$ ($\Delta T_1=16$ K, $\Delta T_2=20$ K).

Small additions of K and Rb to the pure RLS and KLS reduce strongly the transition temperatures to the ferroelastic phases $5(P112_1/n)$ in RLS and $5^*(Cmc2_1)$ in KLS, so that for $x\leq0.95$ and $x\geq0.20$ these phases are no more observed in the solid solution. Figure 3 shows the temperature dependence of the rotation angle of the optical indicatrix about [001] in phase 5 for different compositions with respect to extinction in the rhombic $Pmcn$ phase. The $\varphi(T)$ dependence is the same for all compositions. Adding K to $RbLiSO_4$ does not affect the character of the PT, and only shifts its temperature. Remarkably, for some compositions the angle φ may exist within a narrow temperature interval bounded from below by an optically uniaxial phase. For instance, at $x=0.90$ the monoclinic phase 5 exists under heating in the interval 407–423 K, and under cooling, from 416 to 388 K. A $x=0.95$ crystal grows simultaneously in monoclinic phase 5 (extinguishing parts) and optically uniaxial phase (nonextinguishing, dark regions). When heated, such a sample starts to undergo total extinction at $T_0=323$ K at an angle $\varphi(T)$, while above $T_1=410$ K, $\varphi=0$. No PT was observed to occur under cooling at T_2, with the sample remaining monoclinic down to liquid nitrogen temperature. At a later time, however (after a few hours at room temperature), an optically uniaxial phase forms again in the crystal, and the above process can be repeated.

The boundary between the two optically uniaxial phases $P6_3$ and $P31c$ was studied by measuring the temperature dependence of birefringence. The results of these measurements are displayed in Fig. 4. The transition we are interested in exhibits a characteristic temperature hysteresis $\Delta n(T)\approx50$ K wide.[9] Adding Rb to KLS shifts this PT up and stabilizes the trigonal symmetry at room temperature. As x increases, the jump in birefringence δn and the temperature hysteresis ΔT decrease monotonically. For $x=0.00$, 0.043, 0.014 we have $\delta n=3\times10^{-3}$, $\Delta T\approx45$ K, and for $x=0.57$ and 0.74 we found $\delta n=2\times10^{-3}$ and $\Delta T\approx20$ K with an abrupt jump in birefringence. Note that the
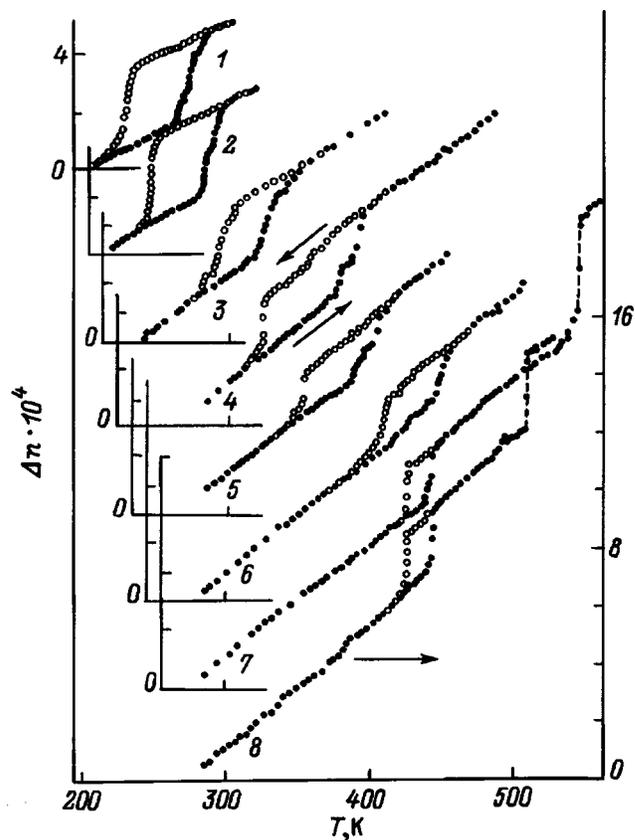

FIG. 4. Birefringence vs temperature in the vicinity of the hexagonal-trigonal phase transition in $Rb_xK_{1-x}LiSO_4$ (x): *1*—0.014, *2*—0.043, *3*—0.1, *4*—0.22, *5*—0.30, *6*—0.50, *7*—0.57, *8*—0.74.

hysteresis curve obtained for the compositions with $x=0.22$ and 0.10 has a larger extent. This is possibly due to the coexistence of phases characteristic of KLS,[1,2] or to the strong dependence of the transition temperature on x (Fig. 1).

2. DISCUSSION

We have studied the phase diagram $(T-x)$ of the $Rb_xK_{1-x}LiSO_4$ solid solutions from the liquid-nitrogen temperature to their melting point. Our studies permitted establishment of the corresponding phase boundaries (Fig. 1).

Addition of Rb ions to KLS increase the temperature of the uppermost structural PT from hexagonal (1^*) to rhombic (2^*) phase and displace it gradually to the melting point, so that for $x>0.5$ the two DTA anomalies accompanying these two processes can no longer be resolved. We were not able to find the boundary which would separate the regions where phases 1 (RLS) and 2^* (KLS) exist. For this reason we assume that phase 2^* (KLS) has the same symmetry as phase 1 (RLS), i.e. $Pmcn$. Besides, the data obtained suggest that $RbLiSO_4$ does not have a high-temperature hexagonal phase at all.

As the Rb content in the solid solution increases, the temperature of the 2^*-3^* reentrant transition decreases, and that of the 3^*-4^* transition, increases, so that most compositions have trigonal symmetry at room temperature. Thus the hexagonal-trigonal structure was found to be the most stable in these compounds.

The birefringence of the KLS crystal was widely studied by various authors (see, e.g., Refs. 9–11). It should be pointed out that all of them used the most sensitive relative methods, for example, the Sénarmont compensator. The Berek compensator employed in this work permits absolute measurement of the birefringence. It was found that both in KLS and in the solid solutions the room-temperature value $\Delta n \approx 4 \times 10^{-4}$ ($\lambda = 630$ nm) is small, and falls off to zero near 270 K. The birefringence becomes negative as the temperature is lowered still more. As seen from Fig. 4, the true temperature behavior of birefringence in KLS is different from its usual pattern.[9–11]

The compounds studied by us here have the so-called ''point of optical isotropy'' on the temperature scale, which depends both on x and on the light wavelength, because they are characterized by a large birefringence dispersion. The birefringence changes by $\delta n \approx 1 \times 10^{-3}$ from the red to green wavelength region. While in principle this offers a possibility of using these compounds in narrow-band optical filters, merohedral twinning poses an insurmountable obstacle on the way to implementing this idea.

Studies of the $Rb_x K_{1-x} LiSO_4$ solid solutions with $x = 0.10$, 0.15, 0.20, and 0.50 below room temperature were started in Ref. 11. It was shown[11] that a KLS crystal with added Rb undergoes the same PT as a pure one. Adding Rb shifts the trigonal-hexagonal transition toward higher temperatures, and the PT to the ferroelastic phase, toward lower temperatures. On the whole, our results are in accord with the conclusions of Ref. 11. Figure 1 shows, however, that the phase boundaries in our diagrams disagree markedly with those quoted in Ref. 11. We observed a stronger effect of substitution on the transition temperatures. The reasons for this lie possibly in different conditions of birefringence measurement. In our measurements, the sample was free, whereas in Ref. 11 it was subjected to uniaxial compression of 50 bars. Such compression is capable of shifting the temperature of the ferroelastic PT up by 7 K.[10] A similar effect

is observed also under hydrostatic compression.[12]

This explanation does not, however, apply to the PT between uniaxial phases. According to Ref. 12, this PT likewise shifts upward under pressure. Because the composition in different growth pyramids, in our opinion, can be different, we carried out atomic-absorption analysis of the samples after the measurements in order to avoid errors in determination of x.

To conclude, our data suggest that the hexagonal-trigonal structure of $KLiSO_4$ is more stable than $RbLiSO_4$ and occupies therefore most of the area bounded by the phase diagram (Fig. 1). Partial replacement of K by the larger cation Rb makes the structure more loose and favors stabilization of the $P31c$ symmetry with a larger unit cell volume.[5,6]

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