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High temperature neutron diffraction study of $LiK_{1-x}Rb_xSO_4$ crystals

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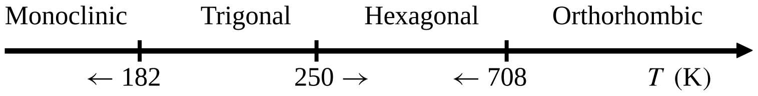
Abstract. $LiK_{1-x}Rb_xSO_4$ ($x \leqslant 0.50$) mixed crystals have been investigated by neutron powder thermodiffractometry. The temperature evolutions of the lattice parameters of the crystals $x = 0.10$, 0.20 and 0.50 are presented for the first time, in the temperature range 320 to 800 K. The main effects produced by the random substitution of the rubidium ions in the potassium sites are the variations of the critical temperatures and the smearing of the first order transitions presented by these compounds. A qualitative model based upon lattice parameter and steric repulsion changes is proposed to explain our results. The temperature variations of the c/a ratio show characteristic behaviours for each phase, being almost independent of the particular rubidium concentration.

1. Introduction

Very recently, we started a systematic study of $LiK_{1-x}Rb_xSO_4$ mixed crystals ($x \leqslant 0.50$), by means of different experimental techniques [1–4]. These studies revealed that the random distribution of rubidium atoms in the potassium sites introduces a local distortion of the structure, without destroying the long-range order. Moreover, it has been shown the similarities between the phase transition sequences of the mixed compounds and that of pure $LiKSO_4$ crystal. The readers interested in details concerning the different structures presented by this crystal can find good reviews in [5–10]. In the temperature region ranging from 50 to 800 K, this sequence can be summarized as below:



In this scheme, the temperatures are averaged over the values obtained for the pure system from different techniques and the arrows represent the directions of the transition temperature shifts due to Rb incorporation [3, 11].

At room temperature, the crystals with $x \leqslant 0.20$ present an average hexagonal symmetry like that of the pure system (space group $P6_3$). On cooling, they first transform into a trigonal structure ($P31c$) and, at still lower temperatures, into a monoclinic one (Cc), which is stable down to 50 K [1, 3]. In the case of the crystal with $x = 0.50$, we did not discern any structural

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phase transition below room temperature. Moreover, the room temperature phase presents, in this case, the average trigonal symmetry instead of the hexagonal one, i.e. the trigonal–hexagonal transition shifts to the high temperature region. In fact, this phase transition occurs at about 450 K, during the heating of this sample [3, 4].

At high temperatures, all crystals with $x \leqslant 0.50$ show a reconstructive phase transition to a high conductivity orthorhombic phase, whose average symmetry is probably $Pnma$ [2–4]. This transition displays very clearly an important feature of first order transitions in disordered crystals, namely, a highly diffuse or smeared character, denoting phase coexistence in large temperature intervals. Although less remarkable, the lower temperature phase transition of the mixed crystals become also diffuse. The main consequences of this kind of transition on the measured properties of our system are the rounding of the physical anomalies around the structural phase transition and the smoothing of any jumps or divergence therein.

As a whole, the phase diagram of the $LiK_{1-x}Rb_xSO_4$ system shows the stabilization of the trigonal phase, at the expense of the monoclinic and hexagonal ones. In addition, the hexagonal phase becomes less stable for increasing x (the hexagonal–orthorhombic transition shifts to lower temperatures). These variations lead to a progressive narrowing of the temperature region of hexagonal symmetry.

In order to understand the role of the rubidium ions in the different phase transitions of the $LiK_{1-x}Rb_xSO_4$ system, we realized a detailed analysis of high temperature neutron diffraction data, obtained for crystals with $x = 0$, 0.10, 0.20 and 0.50. The temperature variations of the lattice parameters, based upon unit cell expansion and steric repulsion increasing, allowed us to present a qualitative model, which displays the main characteristic features of the phase diagram of our system.

2. Experiment

$LiK_{1-x}Rb_xSO_4$ single crystals were grown by slow evaporation of aqueous solutions containing the salts Li_2SO_4:H_2O, K_2SO_4 and Rb_2SO_4 in molar ratios $x = 0$, 0.10, 0.20 and 0.50. The rubidium content in the crystals was verified by x-ray fluorescence analysis, which shows that the average concentrations correspond to the nominal ones. The samples with low Rb concentration ($x \leqslant 0.20$) grew in the form of hexagonal prisms, with typical dimensions of about $15 \times 10 \times 10$ mm^3. On the other hand, the sample morphology presented by the crystal $x = 0.50$ was of hexagonal-rod type, with relatively smaller dimensions. The optical quality of all samples was checked under microscope using polarized light along the c axis.

Neutron diffraction patterns of the mixed crystals were recorded on the DN5 diffractometer of the Siloé reactor at CEN—Grenoble. Powder samples were used because the corresponding results are insensitive to the presence of domains (present in the orthorhombic phase), which is not the case for single crystal techniques. Data were collected for a wavelength $\lambda = 1.339$ Å, in the angular range $2\theta = 10$ to 80°. The sample powders were heated in a conventional furnace, from 330 to 800 K. In the case of the $LiKSO_4$ pure crystal, the measurements were performed on the D1B diffractometer of the Institut Laue–Langevin, also in Grenoble. The data were obtained at a wavelength $\lambda = 2.524$ Å, in the angular range $2\theta = 5$ to 85°, between 600 and 800 K. In both cases, the heating/cooling rates used were 5 K min^{-1} and the diffractograms were recorded at 5 K steps. The peak profiles were analysed using the SIMPRO [12] program, assuming pseudo-Voigt line shapes.

3. Results

Neutron powder thermodiffractometry of LiK$_{1-x}$Rb$_x$SO$_4$ mixed crystals ($x \leqslant 0.50$) was performed above room temperature up to 800 K. The results show that the crystals $x = 0.10$ and $x = 0.20$ undergo only one structural transition, while the crystal $x = 0.50$ presents two phase transitions in the temperature interval above. Figure 1 illustrates the diffraction patterns corresponding to the three phases presented by the crystal $x = 0.50$, showing characteristic peak profiles for each phase. The symmetries of these phases are compatible with the trigonal $P31c$ (300 K), hexagonal $P6_3$ (550 K) and orthorhombic $Pnma$ (800 K) space groups. In the case of the crystals $x = 0.10$ and $x = 0.20$, the symmetries of the two observed phases are also compatible with the hexagonal and orthorhombic space groups above, with increasing temperature.

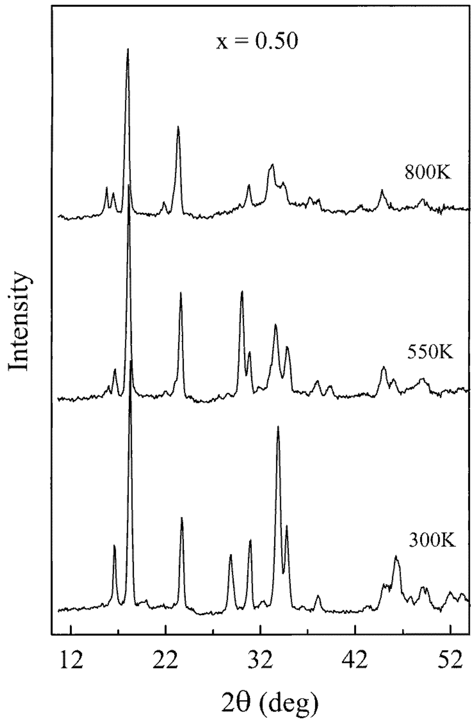

Figure 1. Neutron diffraction profiles of the mixed crystal with $x = 0.50$ for the trigonal (300 K), hexagonal (500 K) and orthorhombic (800 K) phases, on heating.

The temperature evolutions of the lattice parameters of the mixed crystals were obtained by the analysis of the diffraction patterns using the SIMPRO program. The hexagonal basis is used to present our results, in order to compare the lattice thermal behaviour of the different phases. Figure 2 shows the temperature dependence of the a lattice parameter for the crystals $x = 0.10$ (full diamonds), 0.20 (open circles) and 0.50 (full squares) during the heating processes. We remark first the monotonic increasing of this parameter with rubidium concentration. For the two crystals with $x = 0.10$ and 0.20, the a parameter increases continuously with the temperature into the hexagonal phase, showing a quite normal lattice expansion in this direction. For the crystal $x = 0.50$, the measurements show an anomaly at about 450 K, in the region of the trigonal–hexagonal transition. For higher temperatures, the hexagonal–orthorhombic transition is seen, for all crystals, by an important increasing of the a parameter and by the appearing of an elastic deformation, which can be easily represented by the doubling of this parameter. In the orthorhombic phase, both b_0 and $c_0/\sqrt{3}$ parameters are labelled as the a hexagonal (and trigonal) parameter in figure 2.

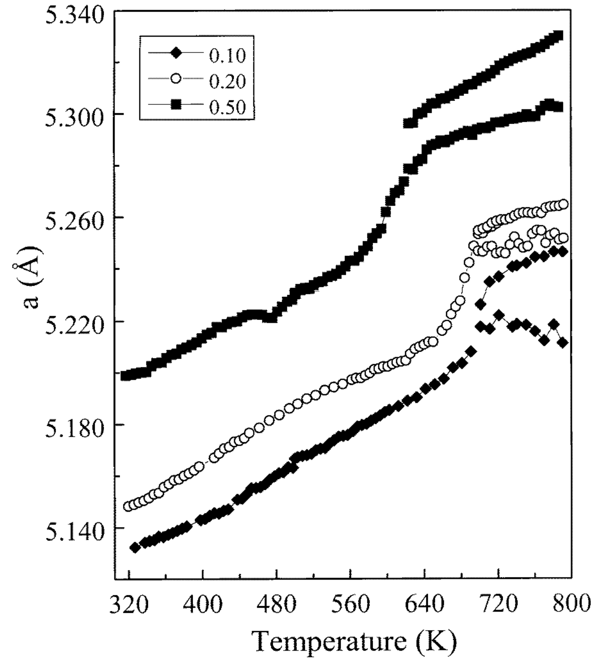

Figure 2. Temperature evolution of the a lattice parameter for the crystals with $x = 0.10$ (full diamonds), 0.20 (open circles) and 0.50 (full squares), on heating. The parameter accuracy was better than 0.002 Å.

The temperature dependence of the c lattice parameter for the same crystals, during the heating processes, is presented in figure 3. As in the preceding case, note the cell expansion with increasing Rb concentration. The crystals with $x = 0.10$ and $x = 0.20$ present initially a decreasing of the c parameter with the temperature, until ~440 K. Afterwards, they show a slight increase, which intensifies in the region of the hexagonal–orthorhombic phase transition. The initial contraction of the lattice in this direction must be still linked to the trigonal–hexagonal transition for both crystals. As we have mentioned before, this transition presents a smeared character, occurring in a temperature interval around a mean temperature value. In our recent work [3], these mean temperatures were found at about 280 and 310 K (on heating), for the crystals with $x = 0.10$ and 0.20 respectively, occurring relatively close to the initial temperatures studied here. On the other hand, we do not observe any anomaly in the a parameter, which seems to be insensitive to this transition, as in the case of $LiKSO_4$ [13]. For the crystal with $x = 0.50$, the c parameter decreases slightly with temperature, showing a strong linear expansion during its trigonal–hexagonal transition. The increasing of this parameter between 430 and 480 K is likely related to the smearing of this transition. In this region, the crystal acquires an average c value over the two possible values, which each have a different tendency to contract with temperature increasing (note the lattice contraction into

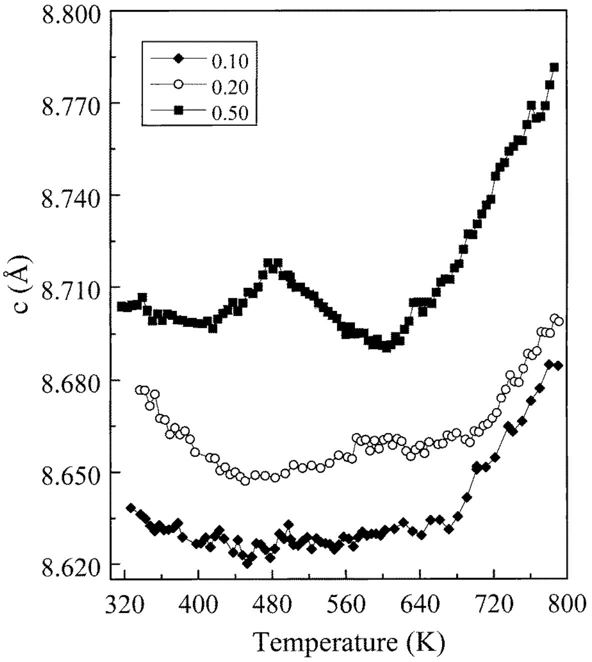

Figure 3. Temperature evolution of the c lattice parameter for the crystal with $x = 0.10$ (full diamonds), 0.20 (open circles) and 0.50 (full squares), on heating. The parameter accuracy was better than 0.003 Å.

the hexagonal phase above 490 K). For all crystal compositions, the hexagonal–orthorhombic transition is seen by a very strong thermal expansion of the c parameter, for higher temperatures.

The data presented above confirm the similarities between the phase transition sequence of pure and mixed compounds (we recall that the fitting procedure is related to the symmetries of the corresponding phases). In comparison with the pure crystal, we note the increasing of the trigonal–hexagonal transition temperatures, the lowering of the hexagonal–orthorhombic ones and the smearing of these transitions, with increasing Rb concentration.

4. Discussion

In order to discuss the structural transitions observed in our mixed system, we refer first to the corresponding structures of pure $LiKSO_4$. Its room temperature structure (hexagonal $P6_3$) can be described by an array of six-member rings of alternating SO_4 and LiO_4 tetrahedra. The tetrahedra form an ordered arrangement of the stuffed-trydimite type, in which the apices of two adjacent tetrahedra point in opposite directions. On cooling, the hexagonal–trigonal transition is driven by a reorientation of one of the sulphate groups in each unit cell (this tetrahedron turns by 60° around the c axis), accompanied by an increasing of the c parameter [13, 14]. In fact, this mechanism is induced by the contraction of the a parameter, which becomes too small to the hexagonal packing. Thus, the system assumes the trigonal symmetry, where the expanded unit cell allows the tetrahedra accommodation. In the mixed crystals, the larger rubidium ions occupy the potassium sites ($r_{Rb^+} = 1.48$ Å while $r_{K^+} = 1.33$ Å) increasing the steric repulsion, and competing with thermal expansion to define the stability of these

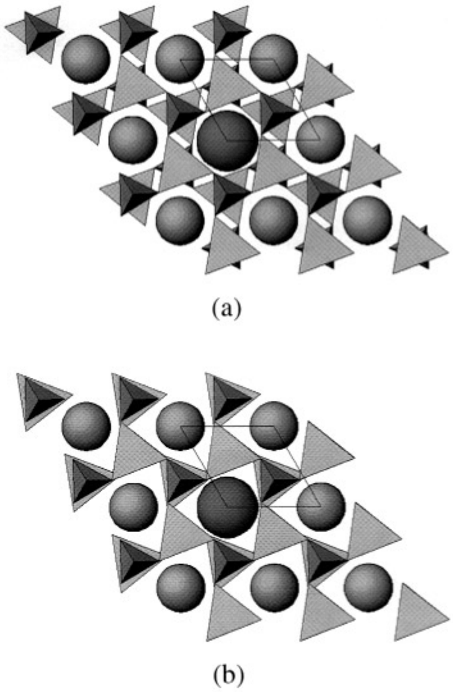

Figure 4. Projection of the (a) hexagonal and (b) trigonal structures of $LiKSO_4$ in the plane ab. Small and large tetrahedra represent SO_4 and LiO_4 groups, respectively. Spheres, whose radii are proportional to the ionic radii, represent K and Rb.

phases. This can be seen in figure 4, where we show the projection of the (a) hexagonal and (b) trigonal $LiKSO_4$ structures, in which SO_4 and LiO_4 groups are represented by small and large tetrahedra and K and one substitutional Rb ions by spheres, with radii proportional to the ionic radii. In these drawings, atomic coordinates and distances are given according to the crystallographic data of $LiKSO_4$ given in [16]. This figure shows clearly that the rubidium neighbourhood is more closely packed than that of the potassium (in the ab plane). This favours the trigonal phase, in which the cell assumes a larger volume. In order to stabilize the hexagonal phase, the system could achieve a relatively larger a parameter, which can occur only at higher temperatures, with Rb increasing.

Concerning the hexagonal–orthorhombic transition, we first analyse the atomic rearrangement accompanying the transition. With increasing temperature, there is a progressive increasing of the cell volume (mainly by the a parameter increase) and of the thermal agitation of the SO_4 tetrahedra. The phase transition occurs by the breakdown of the Li–O bonds associated with the reorientation of the SO_4 tetrahedra [17]. The rupture of the Li–O bonds leaves the Li ions free to move, giving rise to the high ionic mobility characteristic for this phase [9]. Since the rubidium ions also increases the a parameter, its presence favours the orthogonal phase, i.e., the necessary space for the tetrahedron reorientation is attained at lower temperatures, lowering the transition temperature.

Another important structural observation concerns the variation of the c/a ratio in the vicinity of the high temperature structural phase transition. It has been shown in several theoretical works that this ratio plays an important role in the stability of the many phases presented by $A'A''SO_4$ compounds, where A', A'' are alkali atoms [18, 19]. An analysis of the

c/a ratio is interesting because, after those models, the system behaviour is independent of the particular cations involved, depending rather on the interactions (pseudo-spin type) between the SO_4 tetrahedra. Thus, we present in figure 5 the temperature evolution of the c/a ratio for our mixed compounds, compared with that of the pure crystal. For the crystals $x \leqslant 0.20$, this ratio decreases until the transition to the orthorhombic phase, showing a jump at the critical region, followed by a linear increase into the orthorhombic phase. It is noteworthy that the thermal behaviour of this ratio, on both sides of the transition, is almost independent of the Rb concentration. In the case of the crystal $x = 0.50$, we observe a slightly different behaviour due to the stronger smearing character of this transition. Besides, we also observe an anomaly at the trigonal–hexagonal transition, depicted by a c/a increase between 400 and 480 K. We also remark that just above the trigonal–hexagonal transition, the c/a ratio for $x = 0.50$ matches the characteristic values of the hexagonal structures (the same as the other crystals). For higher temperatures, this ratio decreases quickly due to the rapid thermal expansion of the a parameter and to the proximity of the smeared transition to the orthogonal phase.

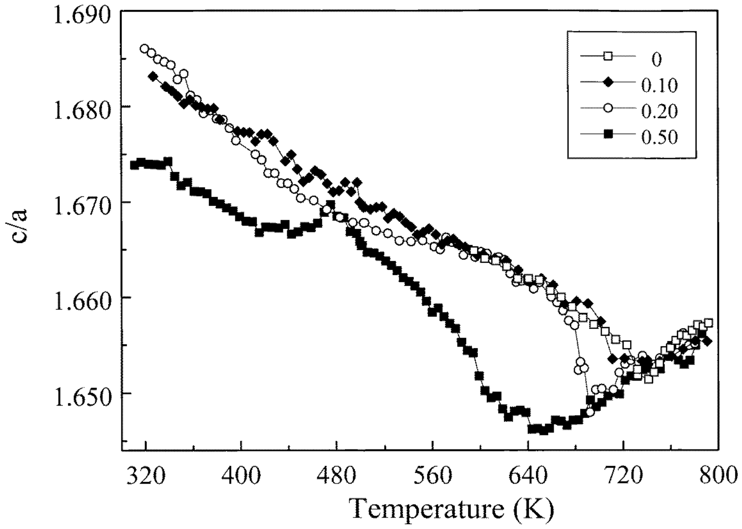

Figure 5. Temperature dependence of the ratio c/a for the crystals with $x = 0$, 0.10, 0.20 and 0.50, on heating. The error bars in the c/a ratio were typically 0.001.

In summary, figure 5 shows the existence of characteristic behaviours of the c/a ratio, as a function of the temperature, for the hexagonal and orthorhombic phases, irrespective of the Rb concentration. The results suggest $c/a = 1.655$, as a minimum value for the hexagonal phase stability, for the pure crystal.

5. Conclusions

Neutron powder thermodiffractometry of the system $LiK_{1-x}Rb_xSO_4$ ($x \leqslant 0.50$) was performed in the high temperature range 330 to 800 K. The temperature evolutions of the lattice parameters are presented for the crystals with $x = 0.10$, 0.20 and 0.50. Beside the regular lattice thermal expansions, the parameters show anomalous behaviours in the region of the two proposed structural phase transitions, namely the trigonal–hexagonal–orthorhombic sequence. The smearing of these reconstructive transitions is seen by the rounding of the

c parameter around the mean critical temperature and by the irregular behaviour of the a parameter before the trigonal–hexagonal transition. We have explained the variations of the critical temperatures produced by the random substitution of the rubidium ion. In comparison with the pure crystal, our results show a characteristic temperature behaviour of the c/a ratio, which is practically independent of rubidium concentration.

Acknowledgments

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