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DIFFUSE PHASE TRANSITION IN NON-STOICHIOMETRIC $LiRbSO_4$ CRYSTALS

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انتشار طور التحول في بللورات ذات نسب تكوين مختلفة من ثنائي كبريتات الليثوم والروبيديوم

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تم دراسة تأثير تغير نسبة كبريتات الليثوم على التحول البللوري لبللورات من النظام $(Rb_xLi_{1-x})_2SO_4$ حيث x تتراوح بين 0.1 - 0.7 وذلك باستخدام جهاز التحليل الحراري في مدى درجات الحرارة ٣٠٠ – ٦٠٠ درجة مطلقة . أظهرت التجارب المعملية وجود قمم متعددة في منحني التحليل الحراري التفاضلي للبلورات التي تحتوي على x = 0.1, 0.2 من الروبيديوم ، كما وجد أن قيمة الحرارة النوعية تحت ضغط ثابت تقل بينما درجة حرارة التحول الطوري تزداد مع زيادة كمية الروبيديوم كما لوحظ أن التغير في الحرارة النوعية مع درجة الحرارة يصبح أكثر إتساعاً وبصفة خاصة للبللورات التي بها كميات كبيرة من الروبيديوم . وهذه النتائج يمكن إعتبارها إعادة توزيع SO_4^{--} ، LiO_4^{--} داخل الهيكل البللوري .

Key Words: Phase transition, Stoichiometric ratio, $LiRbSO_4$.

ABSTRACT

The influence of changing the ratio of Li_2SO_4 on the structure transition of $(Rb_xLi_{1-x})_2SO_4$, LRS crystals, where x ranged from 0.1 to 0.7, was studied by thermal analysis techniques in the temperature range 300 - 600 K. Multiple peaks in the DTA traces were observed for crystals having x = 0.1 and x = 0.2. The values of C_p decreased while that of T_i increased with increasing Rb^+ content. The excess of the specific heat for LRS crystals showed a broadening in the temperature dependence especially for samples enriched with Rb^+. These results could be considered on the development of the ordering of SO_4^{--} and LiO_4^{--} and in their arrangement.

INTRODUCTION

Lithium Rubidium Sulphate, LRS, is known to exhibit an interesting sequence of structural phase transitions. The results of the experimental studies (Rao and Rao, 1966; Mashiyama, *et al*, 1979, Tanisaki, *et al*, 1980, Steurer *et al*, 1986, Farhi and Goudin, 1989), of such crystals are used to establish the sequence of phase transitions illustrated in an easy reference scheme as given in (Fig. 1).

The transition at T_i = 477 K is a second order transition, while that at 475 K is a first order one (Steurer *et al*, 1986). The alkali metal sulphate crystals show permanent phase transitions (Rao and Rao, 1966). Lithium sulphate transforms from a monoclinic to cubic structure at 863 K,(Farhi and Goudin, 1989), whereas rubidium sulphate shows transformation from the low temperature orthorhombic structure to the high temperature hexagonal structure at 913 K (Rao and Rao, 1986). The variation in transition temperature has been interpreted in terms of anion-

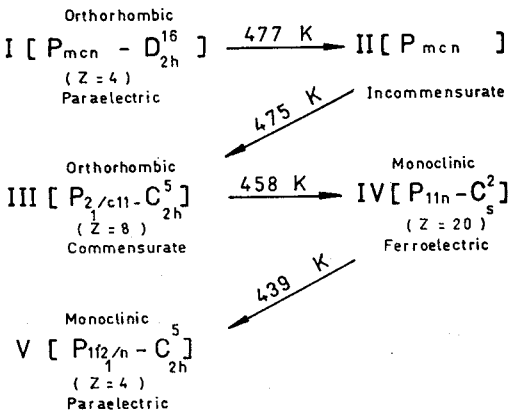

Fig. 1: Sequense of phase transitions in $LiRbSO_4$

cation polarization effect. It also depends on the Li-O, Rb-O bond length and the role of the rotation of SO_4 which determines the characteristics of the transition. Studies of the thermal properties of $LiRbSO_4$ in the vicinity of the incommensurate phase (T_i = 477 K) was previously studied(Dohata and Kawada, 1988; Kassem, *et al*, 1991, 1992). The aim of the present work is to investigate the thermal properties of the solid solution $(Rb_xLi_{1-x})_2SO_4$, where x = 0.1 - 0.7, in the temperature range 300 - 600 K.

EXPERIMENTAL PROCEDURE

Single crystals of $(Rb_xLi_{1-x})_2SO_4$ were grown at 308 K by the slow evaporation method (Kassem, *et al*, 1991). The content of Li and Rb in LRS was measured using atomic absorption spectroscopy (Pye Unicam Atomic Absorption). The thermal behaviour of LRS crystals was studied in the temperature range 300 - 600 K. The specific heat C_p was determined by the differential scanning calorimeter DSC technique, where a Shimadzu DSC TA30 thermal analyzer was used. Measurements were made by applying the base line method (Danniels, 1973). The sample weight ranged from 15 to 30 mg and the heating rate was 5 K/min.

RESULTS AND DISCUSSION

Differential thermal analysis was sued to differentiate between different stoichiometric $(Rb_xLi_{1-x})_2SO_4$ crystals by monitoring the endothermic peak of the incommensurate phase, T_i = 477 K previously reported (Mashiyama, *et al*, 1979, Steurer, 1986) for the transition $P2_1$ / C11-C^5_{2h} P_{mcn} — D^{16}_{2h}. (Fig. 2) shows a set of

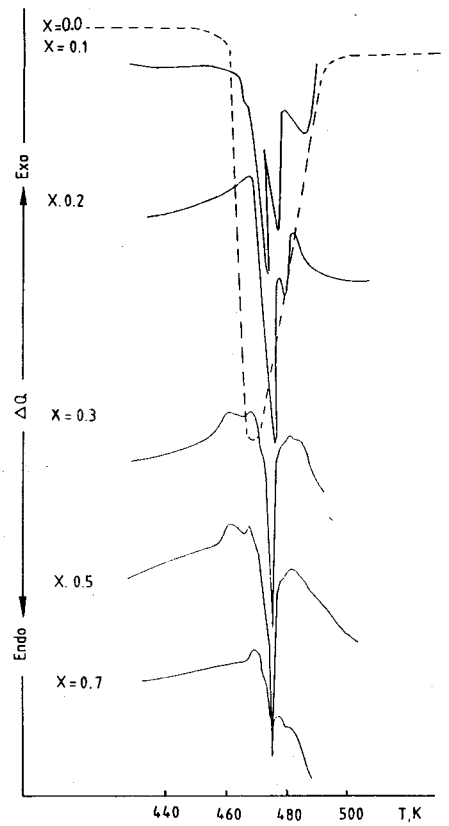

Fig. 2: DTA curves for $(Rb_xLi_{1-x})_2SO_4$ crystals

DTA curves for $(Rb_xLi_{1-x})_2SO_4$ crystals where x = 0.1, ---, 0.7. It is clear from the figure that the DTA behaviour depends on content of Rb. The most interesting curves are those of x = 0.1 and 0.2 where multiple peaks occur. This phenomenon of multiple peaks occurance might be due to handling, polishing or growing technique. It might also be due to phase change. Since the occurrence of multiple peaks in the DTA curves is reproducible, then, it is believed to be due to inherent phase transitions.

(Fig. 3) shows the temperature dependence of C_p for different stoichiometric ratios having x = 0.1, 0.2 and 0.5 as examples.

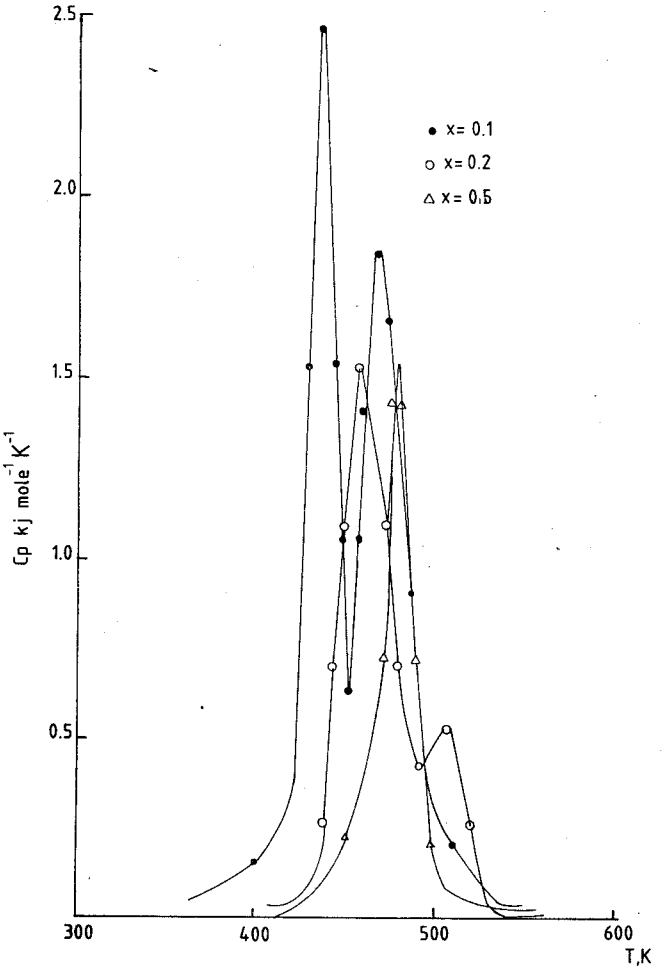

Fig. 3: Temperature dependence of C_p for $(Rb_xLi_{1-x})_2SO_4$ crystals

The appearance of multiple peacks is obvious for x equals 0.1 and 0.2. The dependence of the specific heat on the rubidium content is shown in (Fig. 4). The specific heat C_p decreases sharply with increasing Rb content till x = 0.2, then increases slightly till about x = 0.5; thereafter it decreases rapidly. It is also observed from (Fig. 4) that the transition temperature of the incommensurate phase T_i increases with the increase of Rb content. The shift of the peak temperature is attributed to the diffusion which controls the first order phase transition, as a result of the fluctuation nature of the nucleation at the new phase (Gridnev and Postnikov, 1980). The rate of the phase transition is assumed to be controlled by the time of the nucleation of the new phase. The nuclei of the new phase have

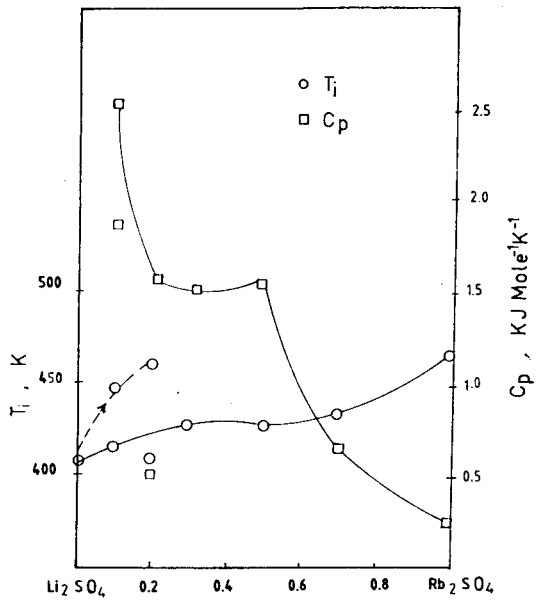

Fig. 4: Variation of C_p and T_i of $(Rb_xLi_{1-x})_2SO_4$ with Rb^+ content

different activation energies. It is expected that the thermodynamic forces, which decrease the nucleation activation energy of the new phase, play the main role in this process.

The enthalpy change $\triangle H$ which accompanies the transition is calculated for different stoichiometric samples of $(Rb_xLi_{1-x})_2SO_4$ and listed in (Table 1), together with the

Table 1

x	0.1	0.2	0.3	0.5	0.7	1.0
$\triangle H$ (kJ/Mole)	6.83	2.75	1.59	2.93	0.78	0.54
$\triangle S$ (J/Mole. K)	14.6	5.99	3.22	6.20	1.62	1.06

corresponding entropy change $\triangle S$. From (Table 1), $\triangle H$ and $\triangle S$ decrease with increasing Rb content till x = 0.3, then they increase for x = 0.5 and then decrease once again. From the above results, it is obvious that the heat capacity and hence the thermodynamic functions of $(Rb_xLi_{1-x})_2SO_4$ for x = 0.1 and 0.2 are quite different from that of other x values. Since the molecular arrangements and packing, as well as the crystal structure, control the thermal behaviour, it is then believed that the internal structure of $(Rb_xLi_{1-x})_2SO_4$ for x = 0.1 and 0.2 have different molecular arrangements and packing from the other ratios. This leads to the occurrence of successive phase transitions which are not observed in case of other stoichiometric ratios in the same temperature range. This is in good agreement with the results obtained from X-ray measurements (Kassem, 1992).

The excess of the specific heat of $(Rb_xLi_{1-x})_2SO_4$ is given by:

$$\triangle C_P = C_P \text{ (obs)} - 2 \times C_P (Rb_2 SO_4) - 2 (1\text{-}x)\, C_P (Li_2 SO_4).$$

Where C_p (obs) is the specific heat of the sample with x Rb content, C_p (Rb_2SO_4) is that of rubidium sulphate crystals and C_p (Li_2SO_4) is that of lithium sulphate crystals, all with the appropriate proportion of x. (Fig. 5) represents the variation $\triangle C_p$ with temperature for selected stoichiometric ratio of x = 0.3, 0.5 and 0.7. There is a broad excess specific heat with maximum value at 456, 457 and 458 K for x = 0.3, 0.5 and 0.7 respectively. For low content of Rb^+ (x = 0.3), a stepwise substitution of Li by Rb results in an increase of the temperature range of the disordered and the twofold phases; as well as in a reduction of the range of incommensurate and the sevenfold and fivefold commensurate (Kassem, 1992, Ganot *et al*, 1989). The substitution may work to supress the disordering of SO_4^- in $(Rb_xLi_{1-x})_2SO_4$ crystals.

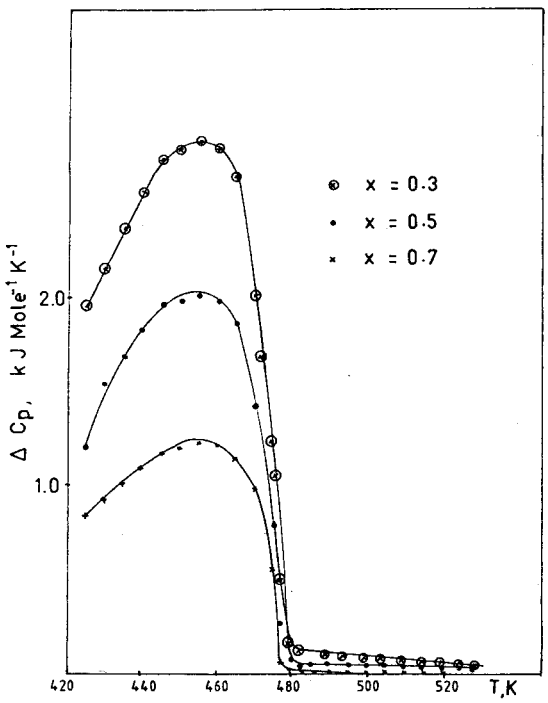

Fig. 5: Variation of $\triangle C_p$ with temperature for $(Rb_xLi_{1-x})_2SO_4$ crystals

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