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THE THERMODYNAMIC BEHAVIOUR OF Sm^{3+}-DOPED $LiKSO_4$ CRYSTALS

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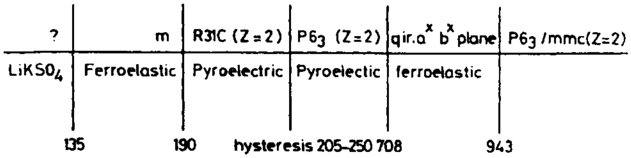
Abstract

The influence of the point defects introduced by means of Sm^{3+} on the thermal properties of $LiKSO_4$ crystals was studied in the vicinity of the high-temperature phase at 708 and 940 K. The temperature dependence of the specific heat was found to vary monotonously with the Sm^{3+} content, while the first transition temperature was unchanged. The change in the value of the specific heat was attributed to the correlation between the defect-defect interaction and the presence of internal local strain generated inside the crystal. The variation of the excess specific heat with the reduced temperature obeys the 3d Ising model.

Keywords: activation energy, crystals, high-temperature phase, $LiKSO_4$, specific heat

Introduction

In recent years there has been increasing interest in the applications of ferroelastic materials due to their successive phase transitions. It is well known that foreign ions present as defects in the crystal lattice enhance phonon scattering. A measure of this enhancement is provided by the change in the specific heat referred to the pure crystal [1]. Little information is available on the thermodynamic behaviour of either doped or distorted crystals [2–5].



$LiKSO_4$ crystals are known to undergo a variety of structural phase transitions (Scheme 1) over a long period, as well as incommensurate spatial modulations [6].

The aim of this work was to study the effects induced by the insertion of different contents of samarium into $LiKSO_4$ crystals, and the corresponding changes pro-

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duced in the thermodynamic properties in the vicinity of the high-temperature phase transitions.

Experimental

$LiKSO_4$ crystals were prepared by thoroughly mixing and grinding equimolar quantities of pure Li_2SO_4 and K_2SO_4 in an agate mortar. The powdered mixtures were melted in platinum crucibles and left to cool down to room temperature in an oven, then ground in an agate mortar. The prepared $LiKSO_4$ matrix was doped with different concentrations of Sm^{3+} in the range 0.2–2% by weight in solid solutions. The doped samples were mixed thoroughly to yield a uniform distribution, then heated to the melt at 950°C for 4 h. The samples were then left to cool to room temperature without control. Each batch was ground to 80–120 mesh. The contents of dopants were determined spectrophotometrically with a Pye Unicam Sp-1900 atomic absorbance.

The specific heat under constant pressure, C_p, was determined for all samples by a DSC technique, the Shimadzu DSC TA 30 thermal analyzer being used. The instrument was calibrated with a pure indium standard. Measurements were performed by applying the baseline method [7]. The heating rate was 20°C min^{-1} and the sample mass was 10 mg.

Results and discussion

Figure 1 displays the DSC traces of $LiKSO_4$ at different Sm^{3+} contents (0, 0.2, 0.5, 1 and 2%). There are two endothermic peaks, at T_1=708 and T_2=940 K. The first is a sharp peak, indicating a ferroelastic phase in pure $LiKSO_4$, which is in agreement with published data [8, 9]. Upon insertion of Sm^{3+} into $LiKSO_4$, the transition temperature does not change, while the peak height decreases at 0.2% Sm^{3+} but increases at 0.5%, then decreases again at 1 and 2% Sm^{3+} contents. This behavior can be explained on the basis that the insertion of impurities and other lattice imperfections into ferroelastic and coelastic crystals tends to build up a local strain field which interacts with the order parameter. For small defect concentrations, we can ignore the defect-defect interaction and find an approximation of lowest order [10]. However, for higher defect concentrations, the defect-defect interaction becomes essential, leading among others to a renormalization of the chemical potential of the defects. For sufficiently mobile defects, the phase transition may lead to exclusion and decoration of the microstructure. The memory effect and modifications of the phase diagram appear to be largely related to this effect. The second peak, at T_2=940 K, corresponds to a structural phase transition. It is clear from Fig. 1 that the transition temperature T_2 changes monotonously with the Sm^{3+} content. It is known that foreign ions present as crystal lattice defects enhance the phonon scattering of pure crystals [1].

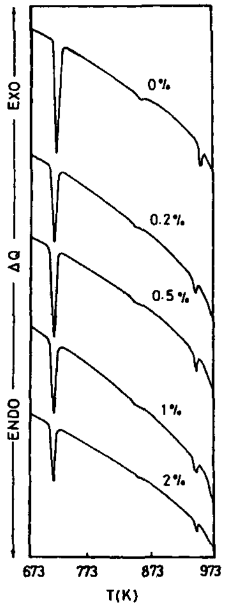

Fig. 1 DSC traces of $LiKSO_4$ at different Sm^{3+} contents

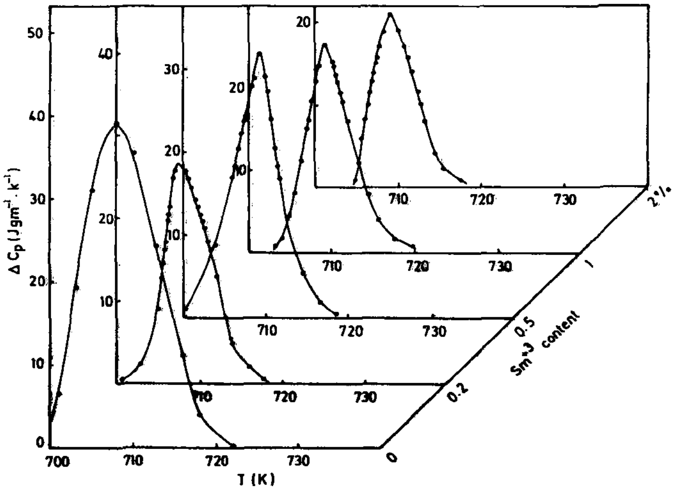

Fig. 2 Temperature dependence of the excess specific heat ΔC_p of $LiKSO_4$ crystals doped with different Sm^{3+} contents

The excess specific heat at transition temperature T_1 ($\Delta C_{p_{max}}$) decreases at 0.2% Sm^{3+}, then increases at 0.5% Sm^{3+} and decreases again at higher concentration, as seen in Fig. 2.

From the crystal structure data, it was concluded [11] that the motion of the SO_4^{2-} tetrahedra consisted of coupled rotational vibrations of the oxygens around the S atom. It was also concluded that the low-temperature phase transition to an intermediate phase is due to vibration of the SO_4^{2-} tetrahedra around the *a* axis resulting in a change in the relative orientation of SO_4^{2-} with respect to the LiO_4 tetrahedra [12]. The occurrence of the individual phase transitions may depend strongly on the actual structure of the crystal, i.e. on the type of defects and dislocations as well as on the thermal and mechanical history of the sample [13]. Thus, the observed changes in the behavior of $\Delta C_p(T)$ as a function of temperature for doped $LiKSO_4$ crystals are due to defects which may cause reorientation of the SO_4^{2-} tetrahedra. The vibration energy levels of the SO_4^{2-} in different crystalline environments are also of interest, because of the distortion from the perfect tetrahedral configuration in the free state. In solid solution, the only parameter acting is the cationic mass [14].

The behavior of the specific heat near the phase transitions can be described by employing an approach proposed earlier [15, 16]. In this approach, the temperature dependence of the excess specific heat (ΔC_p) near a continuous phase transition obeys an exponential law [17]:

$$\Delta C_p = Z(Nu^2/RT^2)\exp(-u/RT)$$

where N is the number of atoms displaced from equilibrium positions, u is the activation energy, R is the universal gas constant and Z is the coordination number. On plotting $\ln\Delta C_p T^2$ *vs.* $1/T$ for undoped and doped samples with different Sm^{3+} contents, straight lines are obtained with some deviation near the transition temperature. Table 1 shows the relative change in the activation energy (ordering energy), estimated from the straight lines, as a function of the Sm^{3+} content. From these data, it is noted that the activation energy has a minimum value at an Sm^{3+} content of 0.5%.

Table 1 The values of $\Delta C_{p_{max}}$, $(u-u_0/u_0)$, ΔH and ΔS for $LiKSO_4$ crystals at different Sm^{3+} contents

Sm^{3+} content / %	0.00	0.20	0.50	1.00	2.00
$\Delta C_{p_{max}}$ / J g^{-1} K^{-1}	39.06	27.29	31.92	25.19	20.80
$(u-u_0)/u_0$	0.00	2.46	0.84	1.16	2.00
ΔH / J g^{-1}	554.44	288.24	330.63	262.81	206.86
ΔS / J g^{-1} K^{-1}	0.78	0.41	0.47	0.37	0.29

The thermodynamic parameters of double sulphates are drastically affected by imperfections, even at low concentration, due to the creation of local strain. On increase of the Sm^{3+} impurity content, the interaction between the spontaneous strain and the spontaneous polarization [18] and also the enhancement of the phonon scattering result in an increasing relative change in the activation energy

$(u-u_0)/u_0$. This contribution to the specific heat could arise from critical fluctuations, which have been examined by fitting the specific heat ΔC_p according to the power law [19]:

$$\Delta C_p = A\tau^{-\beta}$$

where $\tau=(T-T_1)/T_1$ and β is the theoretical exponent. The relationship between $\ln\Delta C_p$ and $\ln\tau$ for a selected dopant concentration (0.2% Sm^{3+}) is shown in Fig. 3. The estimated values of β were found to be between 0.1 and 0.3 for both regions of temperature $T>T_1$ and $T<T_1$, which are the same as expected on use of the 3d Ising model [20].

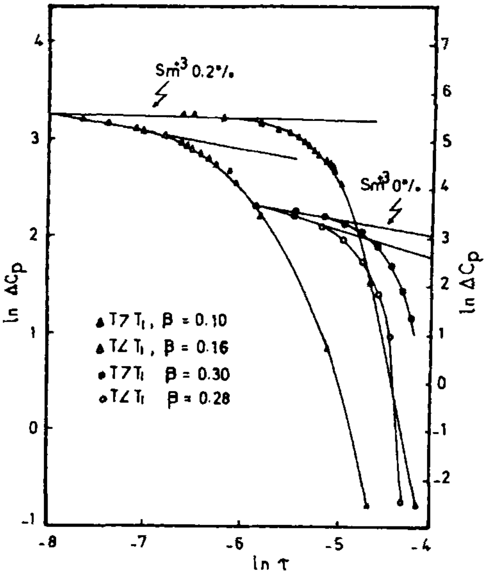

Fig. 3 Variation of ln ΔC_pT^2 with $\ln\tau$ for $LiKSO_4$ crystals and $LiKSO_4$ crystals doped with 0.2% Sm^{3+}

From DSC measurements, the transition peak area is directly proportional to the enthalpy change (ΔH) accompanying the transition [7].

For the peak observed at T_1=708 K, it is useful to integrate the area under the peak, thereby obtaining the heat of transition ΔH, from which the change in entropy at the transition (ΔS) can be obtained ($\Delta S=\Delta H/T_1$). The values ΔH and ΔS for the first transition, at T_1=708 K, estimated from Fig. 1 as a function of the Sm^{3+} content are shown in Table 1. It is clear that both ΔH and ΔS as behave as $\Delta C_{p_{max}}$ as a function of the Sm^{3+} contents (Fig. 2, Table 1).

From this investigation, it is concluded that the behavior of the specific heat $C_p(T)$ of LiKSO4 crystals is affected by the insertion of Sm^{3+}. This is apparent from the changes in $\Delta C_{p_{max}}$, the transition temperature T_2, the activation energy (u) and also ΔH and ΔS.

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