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Specific heat of pure and doped $LiRbSO_4$ crystals

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Abstract

The specific heats C_p of pure and doped crystals of $LiRbSO_4$ were determined over the range 460–540 K. Impurity incorporation of Sm^{3+}, Dy^{3+} and V^{3+} generally increased C_p and an upward shift in the phase transition temperature T_c was also observed. The change in entropy and enthalpy was estimated for different dopants as well as dopant contents. The values of the critical exponent β in the relation $C_p \alpha (T - T_i)^\beta$ were found to lie between $-3/2$ ($T_i > T$) and $-5/2$ ($T > T_i$), which is in good agreement with the properties of the incommensurate phase.

INTRODUCTION

The influences of defects and impurities upon the phase transition in ferroelectrics have received significant attention lately. Recent theoretical interpretation shows that defects can produce drastic changes in the critical behaviour [1]. Theoreticians [2,3] have noticed that even small concentration of defects can increase the temperature width of the critical region and cause the anomalies at the phase transition to be rounded. The role of lattice defects has also been pointed out by experimentalists [4–9]. $LiRbSO_4$ crystals exhibit successive phase transitions above room temperature [10]. The commensurate structure appears as a result of some instability of the lattice mode with wavenumber which is not the zone centre or the zone boundary. As the temperature decreases, the free energy of the commensurate phase is lowered [11]. This leads to successive transitions from the normal to the incommensurate and, finally, to the commensurate phase.

$LiRbSO_4$ crystals possess pseudo hexagonal symmetry with space group $P112_1/n\text{-}C_{2h}^5$ at room temperature [12]. The lattice parameters are $a = 5.288$, $b = 9.105$, $c = 8.713$ Å and $\gamma = 90.12°$.

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The impurity contents of the different ferroelectric samples investigated up to now are different. It is not surprising that no correlation has been found for the excess term. Thus it seems necessary to elucidate, in much more detail, the influence of charged impurities such as Sm^{3+}, Dy^{3+} and V^{3+} in $LiRbSO_4$ crystals.

EXPERIMENTAL

Single crystals of $LiRbSO_4$ were grown from saturated aqueous solutions by dynamic and slow evaporation methods [13]. Impurities of V^{3+}, Sm^{3+} and Dy^{3+} were added to the growth solutions as sulphates. Doping with different concentrations was performed in three special crystallizing chambers designed to produce crystals under identical conditions [14]. Specific heat measurements were performed with a Perkin–Elmer differential scanning calorimeter Model DSC4. The instrument was calibrated with pure indium and single crystal sapphire. Sample weights ranged from 10–40 mg and all measurements were made at a constant heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

The introduction of charged impurities into ferroelectrics plays a specific part in the anomalous behaviour of physical quantities near the curie point [15,16]. The value of T_c is affected by the mass of ions, their charge, and the nature of interaction forces [17].

The temperature dependence of $C_p(T)$ was obtained for pure and doped crystals of $LiRbSO_4$. Dopants of Dy^{3+}, Sm^{3+} and V^{3+} in different concentration from 0.1 to 1 mol% were used. Figure 1 shows a typical example of

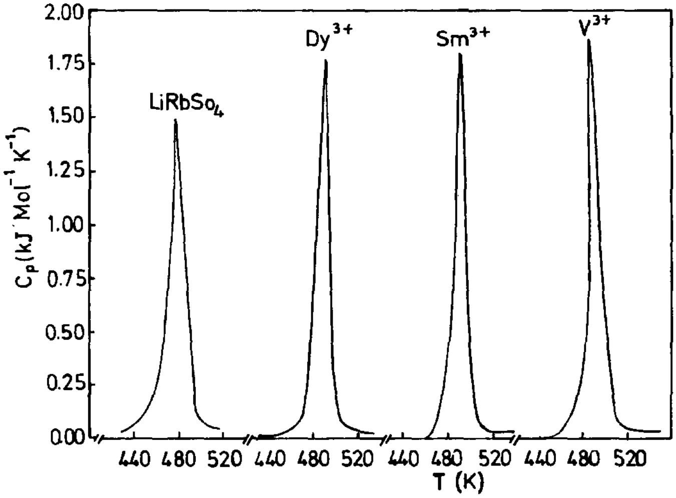
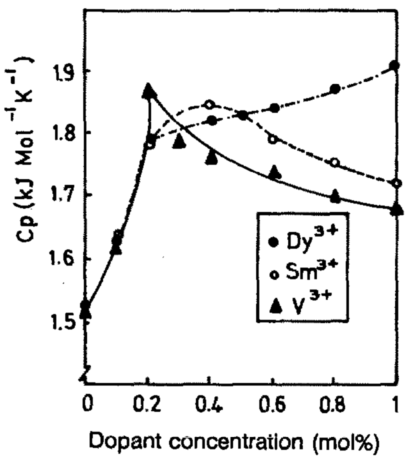


Fig. 1. Temperature dependence of specific heat for pure and doped crystals of $LiRbSO_4$ at 0.2 mol% concentration.



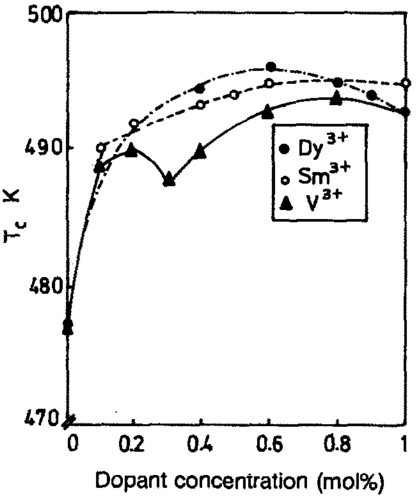


Fig. 2. C_p at maximum vs. the concentration of V^{3+}, Sm^{3+} and Dy^{3+}.

Fig. 3. T_c vs. the concentration of V^{3+}, Sm^{3+} and Dy^{3+}.

the observed behaviour for 0.2 mol% concentration. It is quite clear that the value of C_p at transition for doped crystals is greater than that for pure ones. Also, the transition temperature T_c is shifted to higher values for all the doped crystals. The dependence of the value of C_p at transition on the dopant concentration is shown in Fig. 2. A sharp increase in C_p with concentration is observed up to about 0.2 mol% for all the dopants. Subsequently, C_p decreases with concentration for V^{3+} and Sm^{3+} dopants. The behaviour of C_p with concentration for V^{3+} and Sm^{3+} dopants can be attributed to impurities and lattice imperfections in ferroelectric and coelastic crystals, which tend to build up local strain fields which interact with the order parameter [18]. For small concentrations, one can ignore the defect–defect interaction, but for higher concentrations of defects, consideration of the defect–defect interaction becomes essential, as it leads, among other effects, to a re-normalization of the chemical potential of defects.

The effect of rare earth doping (Sm^{3+}, Dy^{3+}) on the temperature dependence of C_p is quite different from that of V^{3+}, especially that of Dy^{3+}. The effect on C_p in solid solutions of $LiRbSO_4$ is less pronounced than that of V^{3+}. The values of C_p for Dy^{3+} dopants are generally higher than for Sm^{3+}. This difference probably results from the fact that substitution induces local lattice distortions around the impurities and a change in overall lattice constant [19]. Also, the insertion of Dy^{3+} into the $LiRbSO_4$ crystal probably replaces lithium in LiO_4 by a ratio less than that by Sm^{3+}. This means that the value of the ferroactive material decreases in crystals doped with Dy^{3+} rather than with Sm^{3+}.

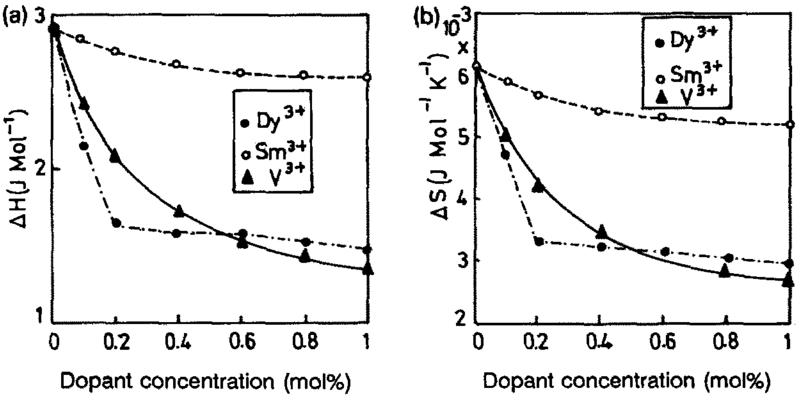


Fig. 4. The dependence of ΔH (a) and ΔS (b) on the concentration of V^{3+}, Sm^{3+} and Dy^{3+}.

Figure 3 shows the variation of the transition temperature T_c with concentration for different dopants. Again, a pronounced increase in T_c with concentration occurs up to 0.2 mol%. The T_c then increases slightly with concentration for Dy^{3+} and Sm^{3+} dopants. For V^{3+} dopant there is a dip at about 0.3 mol%, then T_c increases with concentration. This behaviour can be interpreted on the basis of differences between unstrained bond lengths and bond stiffness [20].

The changes in the thermodynamic functions in the phase transition region were calculated for different dopants and different concentrations. The regular part of the specific heat was separated by graphical extrapolation under the excess of specific heat peak. The variation of the enthalpy change ΔH and the entropy change ΔS with dopant concentration is shown in Figs. 4a and 4b respectively. For Dy^{3+} and V^{3+} dopants, both ΔH and ΔS decrease abruptly with concentration at the beginning, then more slightly, reaching a plateau. This behaviour indicates that the defect–defect interaction is dominant in the doped $LiRbSO_4$ crystals. On the other hand, for Sm^{3+} dopant the decrease in ΔH and ΔS with concentration is not as pronounced. There is no obvious effect on ΔH and ΔS upon increasing the concentration of Sm^{3+} above about 0.5 mol%. The decrease in the thermodynamic functions with induced defects from incorporating dopants is in agreement with that obtained from defects induced by γ-irradiation [21].

The contributions to the specific heat C_p in the IC phase could arise from the critical fluctuations, which have been examined by fitting C_p in the region of the IC phase at $T_i = 477$ K. The specific heat tail is given by

$$C_p = A(T - T_i)^{\beta} \qquad \text{for } T < T_i$$

$$C_p = A^*(T - T_i)^{\beta^*} \qquad \text{for } T > T_i$$

The critical exponents β and β^* were obtained for pure and doped $LiRbSO_4$ crystals using the same method as reported previously [21]. The obtained values were $\beta = -3/2$ and $\beta^* = -5/2$ for all samples. This means that doping $LiRbSO_4$ crystals with Dy^{3+}, Sm^{3+} or V^{3+} has no effect on the critical exponents. This is in accordance with the results obtained on the effect of γ-irradiation [21]. However, doping affects the values of the specific heat, the transition temperature and the thermodynamic functions of $LiRbSO_4$ crystals.

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