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STOICHIOMETRIC RATIO AND DOPING EFFECTS ON THE THERMAL PROPERTIES OF SODIUM POTASSIUM SULPHATE CRYSTALS

S. Abboudy, A. E. Hamed, M. E. Kassem and L. I. Abou-El-Nasr

PHYSICS DEPARTMENT, FACULTY OF SCIENCE, ALEXANDRIA UNIVERSITY,
ALEXANDRIA, EGYPT

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The influence of stoichiometric ratio on the phase transition of sodium potassium sulphate $(Na_xK_{1-x})_2SO_4$ crystals is investigated in the temperature range 300–500 K. The stoichiometric ratio x is chosen to be $x = 0.2$, 0.3, 0.4, 0.8 and 0.9. The study has been carried out by using differential scanning calorimetry, DSC technique. The value of the specific heat, C_p, at the transition temperature, T_c, increases as x is increased up to $x = 0.4$ and then decreases for higher values of x. The change in the specific heat, ΔC_p, is following a relation of the form $\Delta C_p\ \alpha(T-T_c/T_c)^{-\alpha}$ with $\alpha = 0.12$ which is in a fair agreement with the 3d Ising model. Insertion of Cu^{2+} ions into the lattice of $(Na_xK_{1-x})_2SO_4$ crystals leads to a multiple peak in the temperature dependence of C_p. The results are discussed from thermodynamical point of view.

Keywords: stoichiometric ratio, doping, phase transition

Introduction

Sodium potassium sulphate ($NaKSO_4$) crystals are known to have an orthorhombic symmetry at room temperature [1]. Measurements of both electrical and thermal properties of these systems have attracted the attention of many authors as they are suggested as potential electrolytes in application for SO_4^{2-} detectors [2, 3]. The effect of changing the stoichiometric ratio, x, on the phase transition of $(Na_xK_{1-x})_2SO_4$ is recommended as one of the important candidates for such a study. It is argued that the phase transition of some ferroelectric solid solutions becomes more diffusive as the concentration of one component is increased at the expense of the other one.

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The lack of information concerning the influence of foreign impurities upon the phase transition stimulates the study of the thermal properties of such systems. The introduction of foreign impurities into the lattice is thought to play an important role in anomalous behaviour of these systems.

In an early work, Kassem *et al.* [4] have studied the thermal properties of $NaKSO_4$ single crystal ($x = 0.5$). It has been suggested that under normal conditions, the pure $NaKSO_4$ crystal may exhibit a structural phase transition at about 453 K. Those authors argue that the transition is probably from orthorhombic symmetry with point group mmm to monoclinic symmetry with point group 2/m. The above study could be extended to embrace other stoichiometric ratios for this material.

The present study is also motivated by the work of El-Khatib *et al.* [5] and Kassem *et al.* [6] on $LiKSO_4$ and $LiRbSO_4$ crystals respectively. El-Khatib *et al.* have observed that a decrease in lithium content in $(Li_xK_{1-x})_2SO_4$ crystals leads to a disappearance of the first high temperature phase while the second one is shifted towards a lower temperature. On the other hand, the study performed by Kassem *et al.* revealed that the specific heat is increased as a result of impurity incorporation in $LiRbSO_4$ systems.

Experimental details

Single crystals of $(Na_xK_{1-x})_2SO_4$ were grown by the dynamical and slow evaporation method [4] at constant temperature of 315 K from aqueous solutions of different stoichiometric ratios of pure Na_2SO_4 and K_2SO_4. The stoichiometric ratio x was chosen to be $x = 0.2$, 0.3, 0.4, 0.8 and 0.9. Appropriate mass fraction of Cu^{2+} is introduced (as $CuSO_4 \cdot 5H_2O$) into the solution of some $(Na_xK_{1-x})_2SO_4$ crystals at percentages of 1, 5 and 10%.

Measurements of the specific heat, at constant pressure, C_p, of $(Na_xK_{1-x})_2SO_4$ crystals were carried out using a differential scanning calorimetry, DSC, in the temperature range of 300 up to 500 K. Data also were recorded for samples containing Cu^{2+} ions as dopants. The apparatus was calibrated with high purity indium ($T_M = 429.6$ K and $\Delta H = 28.5$ $J \cdot g^{-1}$). The heating rate during measurements was kept at 5 $deg \cdot min^{-1}$ and the sample weight was in the order of 20 mg.

Results and discussion

The temperature dependence of the specific heat, C_p, of the investigated $(Na_xK_{1-x})_2SO_4$ samples is demonstrated in Fig. 1. A phase transition occurs at a particular temperature depending weakly on the stoichiometric ratio x. The value of C_p at the transition temperature, T_c, is a function of x, it increases initially as x is increased and then decreased for higher values of x. Figure 2 shows such a dependence.

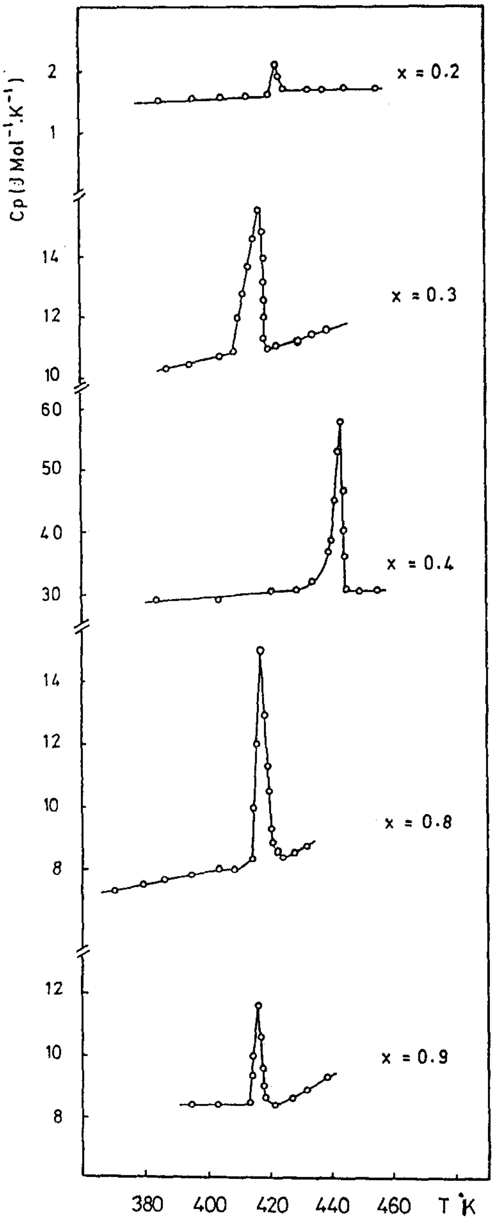

Fig. 1 Temperature dependence of the specific heat of the investigated $(Na_xK_{1-x})_2SO_4$ samples at different values of x

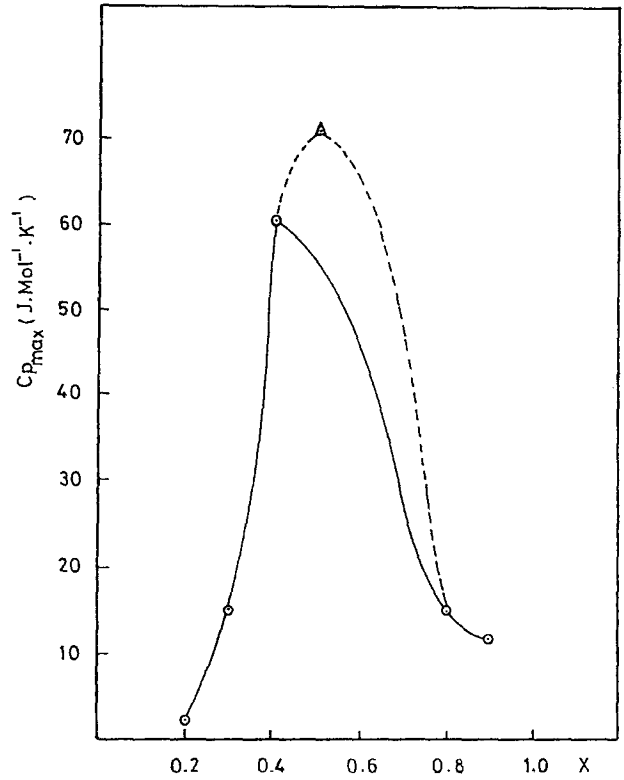

Fig. 2 The maximum value of C_p at the transition temperature as a function of the replacement parameter x. ⊙ Present measurements, △ Ref. [4].

At the transition temperature the ordered assembly of the ions becomes less ordered and the compound is said to undergo an order-disorder transformation. Since the radius of Na ion is less than that of K^+ the transition might be due to the migration of the interstitial Na^+ ions. In Fig. 3, a plot of the change in the enthalpy ΔH as well as the entropy ΔS *vs*. x is presented. One would observe that both ΔH and ΔS has a maximum at $x = 0.4$. The higher values of C_p, ΔH and ΔS at $x = 0.4$ relative to the other values suggest the existence of well defined compound as x approaches 0.5 [4].

The observed phase transition of $(Na_xK_{1-x})_2SO_4$ was found to be very sensitive to the replacement parameter x as reported from dc conductivity measurements [7].

It is a normal practice to describe the behaviour of the temperature dependence of the specific heat near a second order phase transition using the approach [8]:

$$\Delta C_p = Z\left(\frac{NU^2}{RT^2}\right)\exp\left(\frac{-U}{RT}\right) \tag{1}$$

where Z is the coordination number ($Z = 4$), N is the concentration of defects, U is the activation energy and R is the gas constant.

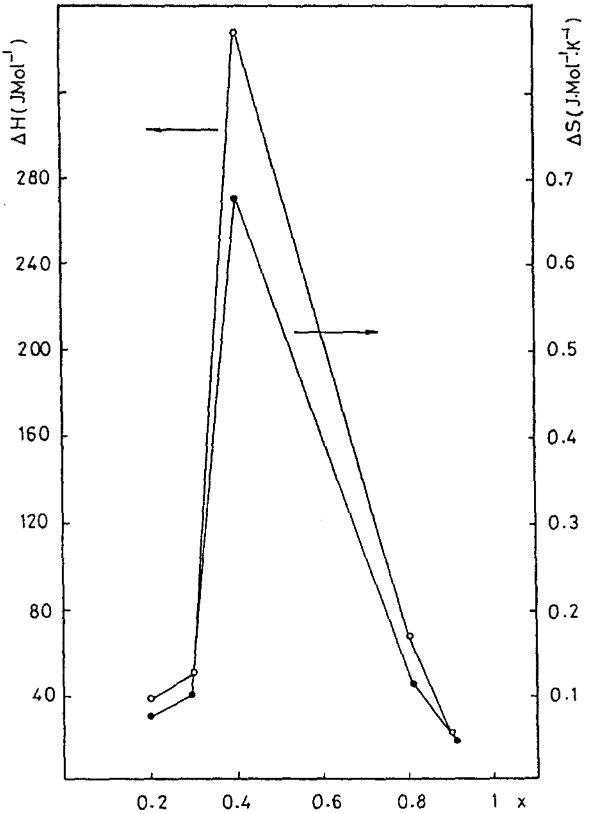

Fig. 3 The change in the enthalpy ΔH and entropy ΔS against x

In Fig. 4 we plot $\ln(\Delta C_pT^2)$ against $1/T$ at some selected values of the replacement parameter x. Fitting the experimental data to a straight line in the vicinity of the transition temperature (at $T<T_c$) leads to an estimation of the activation energy U. Values ranging from 2.8 to 4.4 eV were obtained for the activation energy. U increases slightly as x is increased. This might suggest that the transition in $(Na_xK_{1-x})_2SO_4$ crystals is due to rotation of Na^+ ions.

In an attempt to look at the critical behaviour of C_p around the transition region we have used the approximation:

$$\Delta C_p = A\tau^{-\alpha} \tag{2}$$

with A being a constant and $\tau = T - T_c/T_c$. The critical exponent α is calculated from Fig. 5 and is found to be 0.12±0.02. This value of α is in a fair agreement with the 3d Ising model [9].

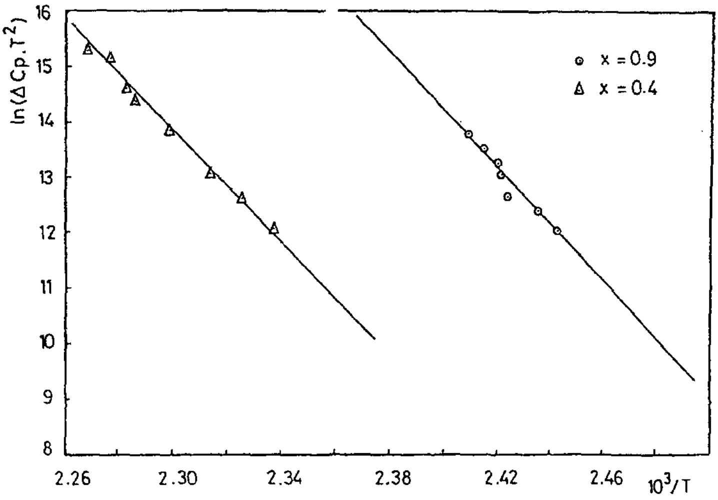

Fig. 4 ln(ΔC_pT^2) *vs.* $1/T$ at some selected values of x

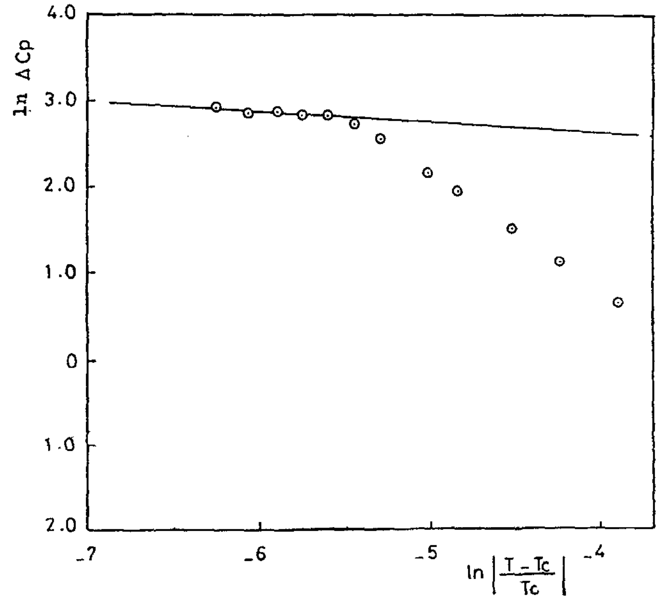

Fig. 5 The change in the specific heat ln ΔC_p plotted as a function of the parameter ln $|(T-T_c)|/T_c$ at $x=0.4$

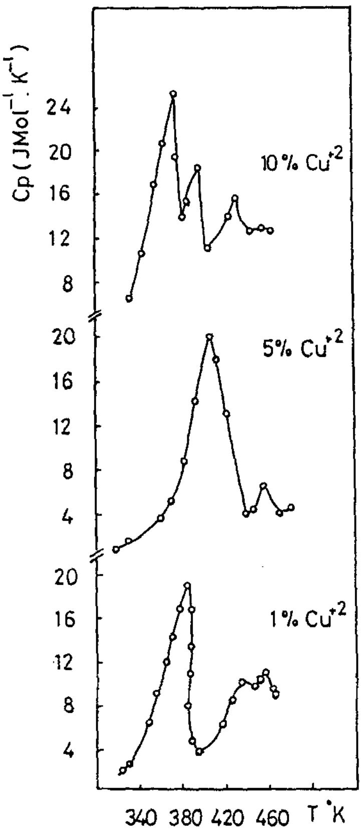

Fig. 6 Temperature dependence of the specific heat of $Na_{0.6}K_{1.4}SO_4$ crystal doped with Cu^{2+}

The insertion of Cu^{2+} ions of different concentrations into the solution during growth process of $Na_{0.6}K_{1.4}SO_4$ crystals has produced a considerable change in the specific heat at the transition temperature. In Fig. 6, a plot of C_p against T is given. Introduction of impurities into the crystal lattice can be regarded as an external perturbation and these impurities can partly or completely replace some of the atoms. Inspection of Fig. 6 reveals firstly that the value of C_p at the transition temperature is increased as the Cu^{2+} ion concentration is increased. The increase in C_p with Cu^{2+} concentration is probably due to the incorporation of these ions in the crystal lattice which may play an important role in the transformation process. Moreover, a multiple peak occurs in C_p *vs.* T curves. An inhomogeneous internal strain field generated by the presence of Cu^{2+} ions is a possible candidate to explain this behaviour [10].

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Zusammenfassung — Im Temperaturbereich 300-500 K wird der Einfluß der stöchiometrischen Verhältnisse auf die Phasenumwandlung von Natriumkaliumsulfatkristallen $(Na_xK_{1-x})_2SO_4$ untersucht. Dabei wurden für x die Werte 0.2, 0.3, 0.4, 0.8 und 0.9 gewählt. Die Untersuchung wurde mittels DSC durchgeführt. Der Wert für die spezifische Wärme C_p bei der Umwandlungstemperatur T_c steigt an, wenn x bis zu einem Wert von x=0.4 anwächst und sinkt für höhere Werte von x wieder ab. Die spezifische Wärme C_p ändert sich gemäß der Gleichung $C_p = (T-T_c/T_c)^{-}$ mit =0.12, was in guter Übereinstimmung mit dem 3D Ising Modell steht. Das Einbringen von Cu^{2+}-Ionen in das Gitter der $(Na_xK_{1-x})_2SO_4$-Kristalle führt zu einem Mehrfachpeak bei der Temperaturabhängigkeit von C_p. Die Ergebnisse wurden aus thermodynamischer Sicht diskutiert.