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A STUDY OF THE THERMAL ANALYSIS OF THE SOLID SOLUTION $(Ag_xK_{1-x})NO_3$

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Abstract

The effect of partial replacement of K^+ by Ag^+ in the mixed system of KNO_3 and $AgNO_3$ during a set of DSC heating cycles was studied by means of a modern computerized DSC system. Thermal analysis was performed in the vicinity of the phase transition II → I for pure KNO_3. The results revealed a large change in enthalpy and the phase transition temperature close to the morphotropic boundary $x=0.5$–0.6. At this boundary, the transformation enthalpy reached the maximum value of ~101 J g^{-1}. On the basis of the data obtained from this accurate thermal analysis work, a model is suggested for the energy barrier of rotation of the nitrate ion in the mixed nitrate system.

Keywords: $(Ag_xK_{1-x})NO_3$, DSC, IR, solid solution

Introduction

$AgNO_3$ and KNO_3 are two of the most important metallic nitrates, characterized by the presence of two different crystal structure phases, I and II, at normal pressure as the temperature is raised up to the melting point.

The crystal structure of $AgNO_3$ at room temperature and normal pressure is orthorhombic [1] and belongs to the class 222 and space group $P_{2,2,2}$ with $a=10.125$, $b=7.335$ and $c=6.992$ Å. This orthorhombic phase is a centrosymmetric structure which resembles neither the calcite nor the argonite structure. The high-temperature $AgNO_3$ modification is stable above 160°C. The space group is $R\bar{3}m$ with rhombohedral cell dimensions $a_{rh}=4.125$ Å, $\alpha=78.1°$ at 444 K and $z=1$ [2, 3]. This is a calcite-like structure, but is characterized by disorder of the anions around their three-fold axis. In a previous work [3], we studied the order – disorder phase transition of $AgNO_3$ by means of IR spectroscopy (400–4000 cm^{-1}) over a wide range of temperature (30–195°C).

KNO_3 undergoes a first-order phase transition from the ordered phase II (symmetry D_{2h}^{16}–P_{nma}) to the disordered phase I (symmetry D_{6h}^{3}–$R\bar{3}c$) at 135°C [4] (Fig. 1a).

We previously studied a series of mixed solid solutions, including metal and nonmetal nitrates, via their IR, electrical and thermal properties [5]. As an exten-

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sion to this work, it is thought that the partial substitution of K^+ by Ag^+ changes the characteristic thermal history of the order – disorder phase transition II→ I for KNO_3 according to the concentration of Ag^+. For such a study, a differential scanning calorimetry (DSC) system may be used. Through this thermal analysis, it is also desired to obtain the enthalpy phase diagram of mixed crystals of $AgNO_3$ and KNO_3 over a large temperature range covering the region of phases I and II at different Ag^+ concentrations. Such a study can reveal the effect of the NO_3^- environment (type, charge and concentration) on the kinetics of the phase transition.

Experimental

Mixed crystals of $AgNO_3$ and KNO_3 were prepared by the evaporation of mixtures containing given ratios of aqueous solutions of $AgNO_3$ and KNO_3 in a desiccator; these mixtures were kept at constant temperature for several days. The crystals produced were 2 mm×3 mm in cross-sectional area and 6 mm long. The DSC was carried out with a Shimadzu system DSC-50 for high-precision thermal analysis. All functions are incorporated into a single compact instrument, including detector, temperature, gas control and computer interface. The heating rate could be programmed in steps between 0.1 and 99.9°C min^{-1} within the temperature range from –150 to 400°C. The DSC-50 is a heat-flux type differential scanning calorimeter. The sample and reference material are simultaneously heated at a constant rate. The temperature difference between them is proportional to the difference in heat flow (from the furnace) between the two materials (Fig. 1). For the detection of these temperature differences, the pinwheel detector design provides more than enough sensitivity to analyse even the most difficult materials. The heat flow measuring range is from +0.01 mW to +100 mW (Fig. 2).

Results

Figure 3a shows the DSC curve of the pure KNO_3 sample, which clearly indicates the well-known endothermic phase transition of KNO_3 (II→I). The sudden and sharp change in the curve suggests a first-order reaction for this phase transfor-

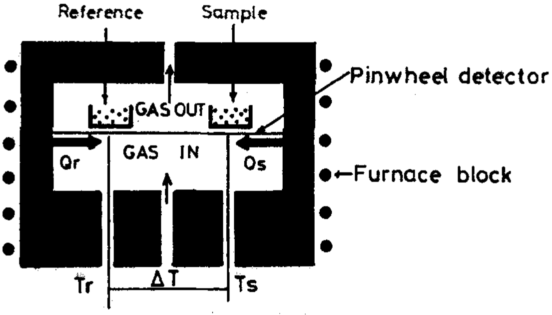

Fig. 1 DSC cell

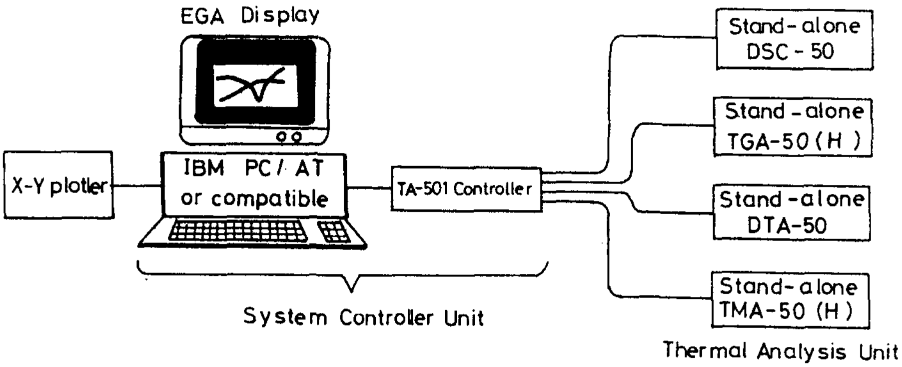

Fig. 2 Shimadzu Thermal Analysis Network system

mation, while the depth of the lowest point of the band is taken as a measure of the endothermicity and the rate of the transition. The energy required for such a transition is 31 J g^{-1} at 129.6°C. This confirms the result previously obtained by means of electrical measurements [4].

Figure 3b depicts the DSC curves of the solid solution $(Ag_{0.2}K_{0.8})NO_3$. A clear change can readily be observed. It can be seen that the sharp band of KNO_3 is now changed to a somewhat wider, split one, due to the presence of Ag^+. The phase transition point is increased by 3–4°C as compared with pure KNO_3. The sudden change character is still apparent in the presence of Ag^+.

Figure 4a shows the changes in the DSC curves of the solid solution of KNO_3 and $AgNO_3$ as the Ag^+ concentration x is increased to 0.4. The sudden change is now replaced by splitting and broadening before and after the sharp band. When the concentration of Ag^+ is increased to $x=0.6$, as shown in Fig. 4b, the broadening is much clearer, i.e. DSC is very sensitive to any partial replacement of K^+ ($r=1.33$ Å) by Ag^+ ($r=1.26$ Å). There was more scattering in the phase transition point values reported for mixed solid solutions than for pure samples.

Figure 5a shows the DSC curves obtained when the dilution reaches $x=0.8$. Here, the sharp endothermic band is characterized by its clear symmetry. The endothermic effect is observed over the whole composition range. When the Ag^+ concentration becomes predominant, at $x=0.9$, the DSC curve seems to be slightly different from that for pure $AgNO_3$ (Fig. 5b).

The transformation enthalpies ΔH of the solid solution system $(Ag_xK_{1-x})NO_3$ during the well-known order – disorder process are obtained with our computerized DSC system for each value of x (Table 1).

Figure 6a demonstrates that the solid solution requires its maximum transformation enthalpy ($\Delta H=101.1$ J g^{-1}) when the concentration of Ag^+ in the solid solution reaches 60%. The phase transition point T_i of the solid solution under test is found to be a very sensitive parameter for the dilution K^+ in the solid solution (Fig. 6b). Thermal analysis revealed an effect over the whole composition range and the order – disorder temperature shift.

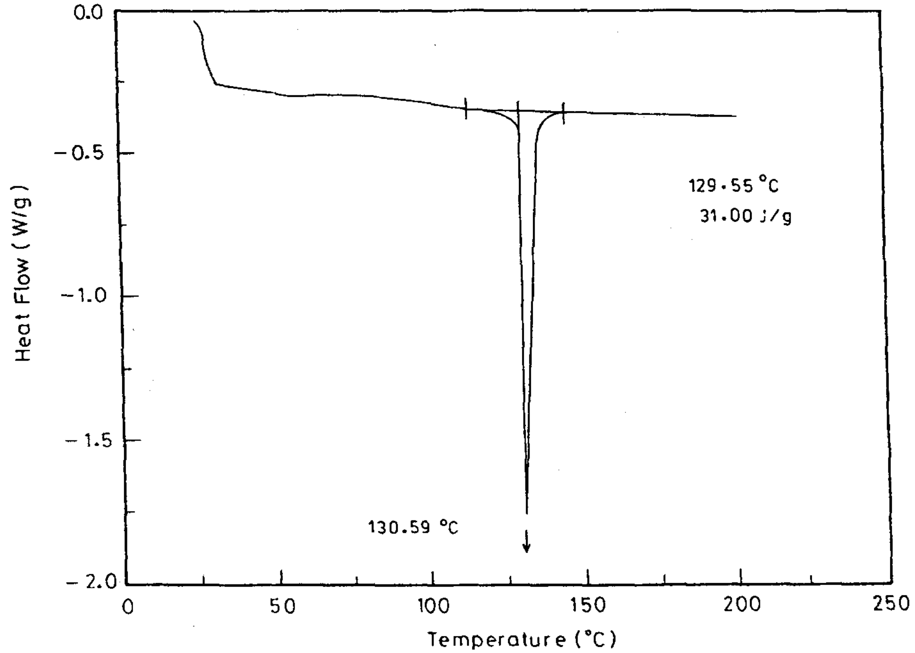

Fig. 3a DSC curve for KNO_3 sample

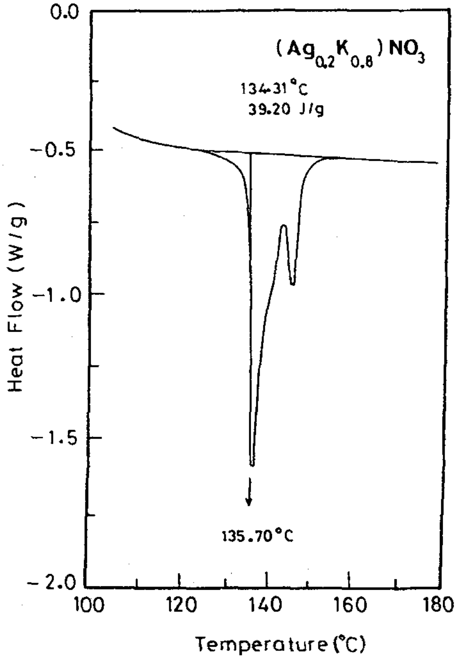

Fig. 3b DSC curves for the solid solution of $AgNO_3$ and KNO_3 for $x=0.2$

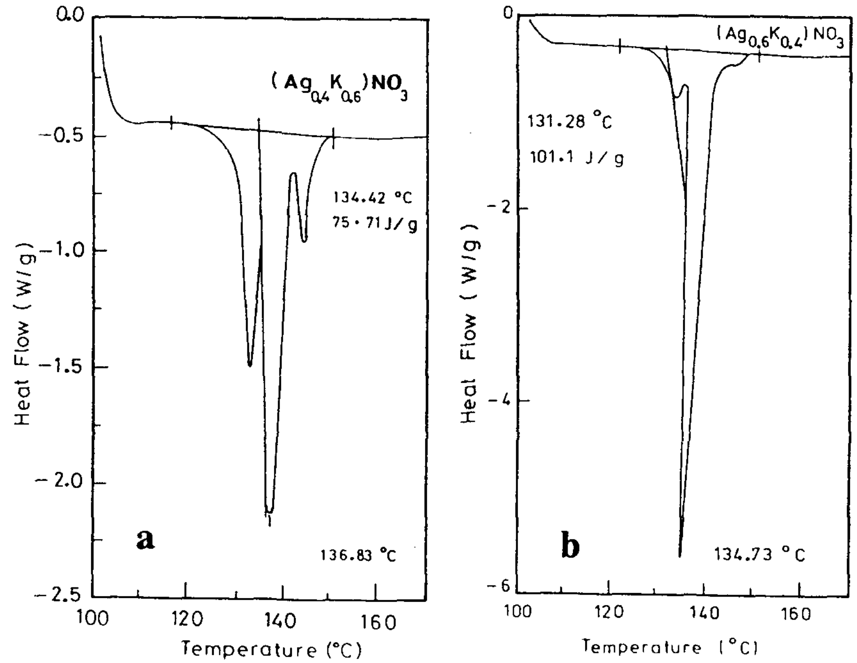

Fig. 4 DSC curves for the solid solution of $AgNO_3$ and KNO_3 for x=0.4 (a), DSC curves for the solid solution of $AgNO_3$ and KNO_3 for x=0.6 (b)

Discussion

Many investigations have previously been performed on the properties of univalent nitrates, particularly structure analysis, X-ray, IR and Raman spectroscopy and electrical measurements.

These measurements have shown that certain univalent nitrates experience a high-temperature phase transition. This transition has been explained as being associated with orientational disorder of the nitrate group. Such orientational disorder has been observed in other univalent nitrates [6]. However, its existence and the associated order – disorder phase transition are strikingly reflected in all the physical properties of these nitrates. Previous studies [6] indicated that the origin of the orientational disorder observed in KNO_3 and $AgNO_3$ and the resulting order – disorder phase transition might be related to the high symmetry of NO_3^- . Additionally, changes in the local field result from the disordered orientation of NO_3^-, i.e. rotation through an angle of 30° about the three-fold axis [6].

This means that disordering takes place through the NO_3^- rotating by an angle of 30° around the three-fold axis perpendicular to it. The two possible orientations are not strongly distinguishable in free energy and are separated by relatively low potential barriers [5], as shown in Figure [11]. However, this orientational disorder of NO_3^- is a normal characteristic of all nitrates.

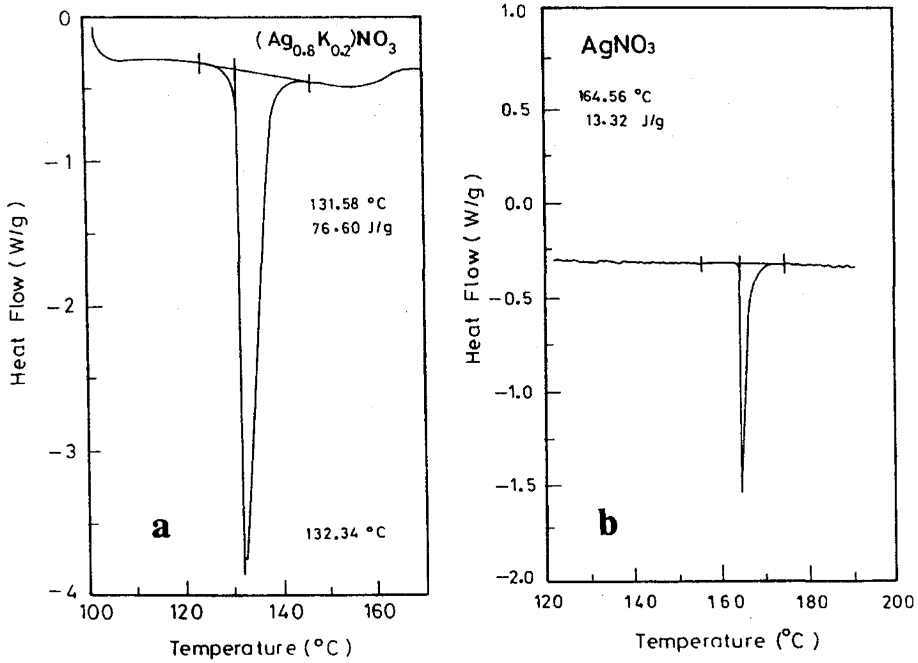

Fig. 5 DSC curves for the solid solution of $AgNO_3$ and KNO_3 for $x=0.8$ (a), DSC curves for the solid solution of $AgNO_3$ (b)

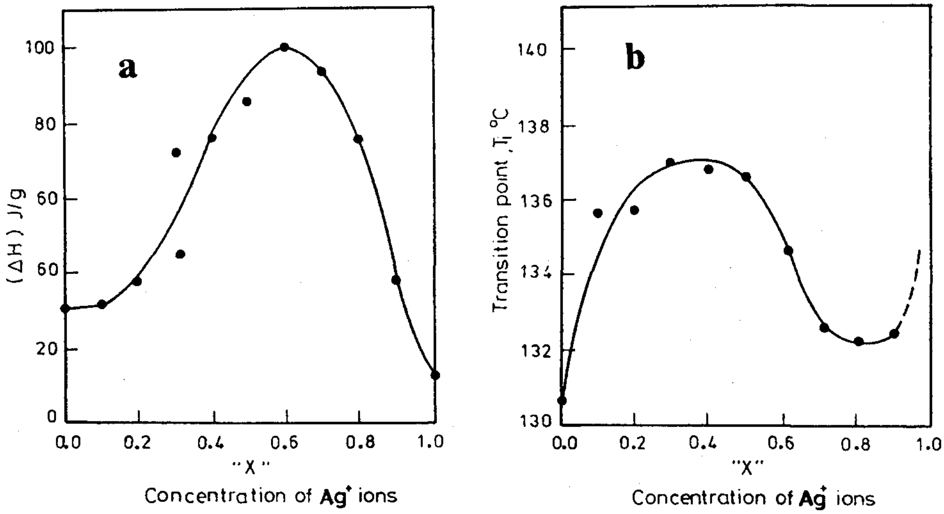

Fig. 6 Variation of heat of transformation ΔH with concentration of Ag^+ ions in the solid solution $(Ag_xK_{1-x})NO_3$ as calculated by computer (a), Phase diagram of the phase transition point T_i of the solid solution $(Ag_xK_{1-x})NO_3$ (b)

Table 1 Variation of transformation enthalpy and phase transition point with concentration of Ag^+

Solid solution	ΔH/J g^{-1}	T_i/°C
KNO_3	31.00	130.59
$(Ag_{0.1}K_{0.9})NO_3$	32.15	135.74
$(Ag_{0.2}K_{0.8})NO_3$	39.20	135.70
$(Ag_{0.3}K_{0.7})NO_3$	77.90	137.00
$(Ag_{0.4}K_{0.6})NO_3$	75.71	136.83
$(Ag_{0.5}K_{0.5})NO_3$	85.64	136.69
$(Ag_{0.6}K_{0.4})NO_3$	101.10	134.73
$(Ag_{0.7}K_{0.3})NO_3$	94.36	132.90
$(Ag_{0.8}K_{0.2})NO_3$	76.60	132.34
$(Ag_{0.9}K_{0.1})NO_3$	38.72	132.48
$AgNO_3$	13.32	164.87

ΔH=heat of transformation calculated by computer
T_i =transition temperature for the sample.

The results of the DSC measurements in the present work demonstrate that the partial replacement of K^+ by Ag^+ is associated with considerable change in the thermal characteristics of the order – disorder phase transition II → I in the mixed crystal system. The present results show that both the enthalpy and the phase transition point are sensitive functions of the composition. According to the statistical theories of the phase transition in a compressible Ising lattice model [7], mechanical instability and a first-order transition will occur whenever the specific heat exceeds a critical value depending on the compressibility of the disordered lattice [8, 9].

Very little can be stated about the variation in the transition order in the two phases II and I, but the characteristic behaviour of the DSC curves (sudden change) strongly indicates that this is a first-order transition whatever the value of x ($0<x\leq 5$). The regular shift observed in the behaviour of the transition point of the mixed crystal solid solution as x increases is quite interesting. The enthalpy (heat or energy of transformation) displayed a similar trend provided that the composition did not exceed the limit $0<x\leq 0.6$, which is most striking. Such behaviour seems to be intimately related to the unit cell and ionic radii of the cations. The radius difference between Ag^+ and K^+ is ~0.07 Å, which indicates that throughout this work K^+ is replaced regularly by the slightly smaller Ag^+. However, the detailed mechanism has not yet been consistently explained.

There are a number of reasons to believe that there is a mixed cation effect for the mixed nitrate system of Ag^+ and K^+. At a low concentration of added Ag^+, there is not much difference in the DSC curve as compared with that for pure KNO_3. However, the phase transition point (~131°C) is strongly affected by the partial replacement of K^+ by Ag^+. This behaviour can be explained by including the

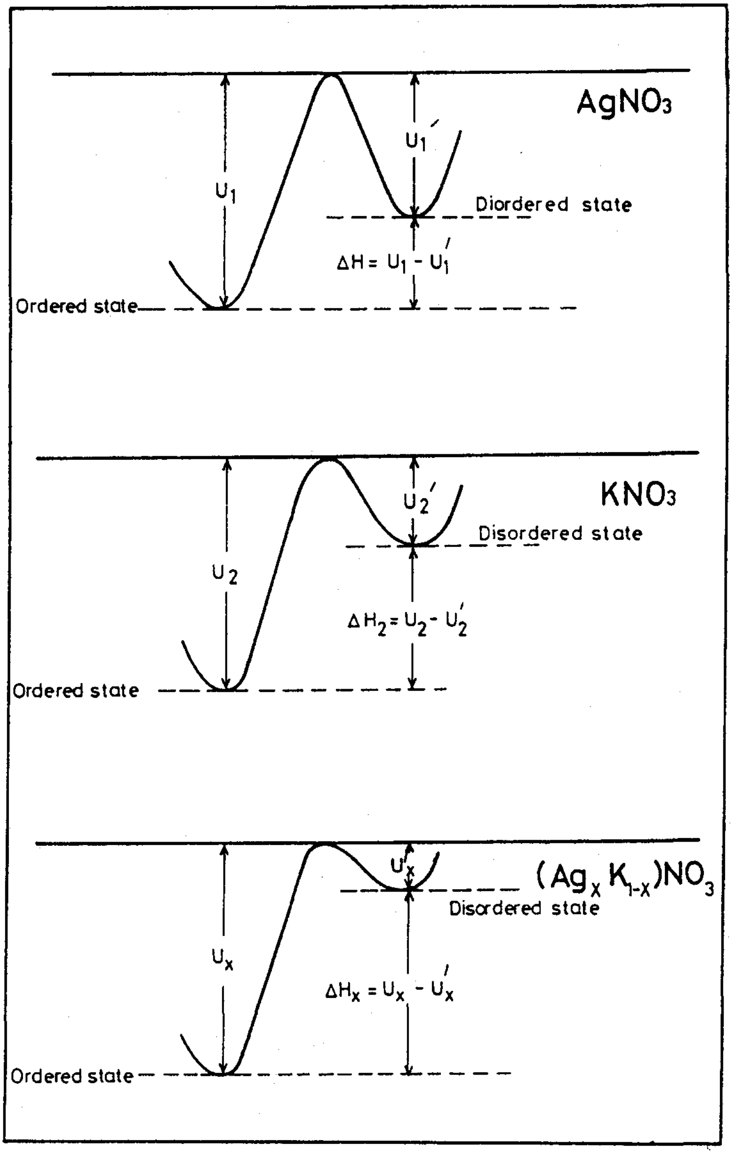

Fig. 7 Energy diagram showing the ordered and disordered positions of NO_3^- ions in $AgNO_3$, KNO_3 and the mixed solid solution $(Ag_xK_{1-x})NO_3$

effect of the added cation on the bonding. The substitution of K^+ by Ag^+ has two effects. The primary effect is the geometric dilution of the spin species, while the secondary effect involves the influence of the added cation on the frequencies of vibration for NO_3^- . The ionic size also plays an important role since the radius of the added ion is smaller than the original one. Lattice relaxation around the added cation causes NO_3^- to move towards the cation. Such a displacement effect weakens the bonds [10] due to the change in the interatomic distances. The partial replacement of one monovalent cation by a second leads to some sort of attractive interaction among the cations or, in the extreme, to the formation of associated catonic complexes [11, 12]. As the average distance between the cations increases, any intercationic interactions must become progressively weaker and any correlations among the interactions of the cations with the structure must vanish. A simplified model is proposed below for the energy barrier of rotation of the NO_3 group in the mixed crystal system $(Ag_xK_{1-x})NO_3$, as shown in Fig. 7. If U_1 and U_1' are the heights of the potential energy barrier of the ordered and disordered states in pure $AgNO_3$, the transformation energy or enthalpy ΔH is given by

$$\Delta H = U_1 - U_1'$$

According to our DSC measurement:
$\Delta H_1 = 13.3 \text{ J g}^{-1}$
For pure KNO_3, U_2 and U_2' are the heights of the potential energy barrier of the ordered and disordered states. Also,

$$\Delta H_2 = U_2 - U_2'$$

and here $\Delta H_2 = 31 \text{ J g}^{-1}$

For the mixed crystal system, U_x and U_x' are the energy barriers in the ordered and disordered states, respectively:

$$\Delta H_x = U_x - U_x'$$

ΔH_x is the enthalpy of the solid solution and it is found that it increases as x increases up to $x=0.6$. This means that the barrier height for the mixed system increases for $x \leq 0.6$ and a maximum value of $\Delta H = 101 \text{ J g}^{-1}$ is obtained. This value is in fact more than three times that for pure KNO_3.

References

1 M. Paulette, Acta Cryst., (B) 34 (1978) 1457.
2 F. Taylor, Acta Cryst., (B) 33 (1977) 311.
3 F. El-Kabbany, Y. Badr, S. Taha and M. Tosson, Ann. Physik, 5 (1989) 355.
4 F. El-Kabbany, W. Badawy and E. H. El-Khawas, J. Materials Sci., 23 (1988) 776.
5 F. El-Kabbany, S. Taha and M. Tosson, Ann, Physik, 5 (1989) 341.
6 Y. Badr and F. Karpov, Soviet Phys., Solid State, 15 (1974) 8.
7 C. W. Garland and R. Renard, J. Chem. Phys., 44 (1966) 112.
8 M. E. Fisher, Phys. Rev., 176 (1968) 257.
9 G. A. Baker and J. W. Essam, Phys. Rev. Lett., 24 (1970) 447.
10 C. Robert, Handbook of Chemistry and Physics, 2nd edition, 1982.
11 J. R. Hendrickson and R. J. Bray, Phys, Chem. Glasses, 13 (1972) 107.
12 I. Nakagawa and T. Shimanoueh, Spectrochim. Acta, 20 (1964) 429.