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A DSC study of $K_{1-x}(NH_4)_x$ SCN mixed crystals

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Abstract

The phase transitions in mixed crystals of the system $K_{1-x}(NH_4)_xSCN$ for a wide range of x values have been studied using differential scanning calorimetry (DSC). On the basis of the experimental data a phase diagram was constructed. The diagram contains two curves: (a) – the line of the order–disorder phase transition separating regions of the orthorhombic (phase II) phases, (b) – the line of coexistence of the monoclinic (phase III) and the orthorhombic one. The enthalpies of both transitions were determined. Careful investigations of the thermal hysteresis of the phase II–phase I transition showed no systematic dependence on the concentration. For most concentrations $\Delta_{\mathrm{hyst.}}T \approx 0$ and does not excite 0.8 K for any concentration. For pure ammonium thiocyanate the kinetics of the spontaneous transition of undercooled phase II into stable phase III has been investigated.

Keywords: Ammonium thiocyanate mixed crystals; Enthalpy; Phase diagram; Potassium thiocyanate; Thermal hysteresis

1. Introduction

The phase transition in pure potassium thiocyanate and ammonium thiocyanate has been studied by various methods [1–5]. High temperature order–disorder phase transition in both substance (at 413 K in KSCN and at 390 K in NH_4 SCN) is connected with disordering of the SCN^- ions. It is correlated with the structural change from orthorhombic phase II to the tetragonal phase I. A low temperature structural phase transition in ammonium thiocyanate $T \approx 360$ K is due to excitation of orientational degrees of freedom. The structure changes from monoclinic (phase III) to orthorhombic (phase II). The orientations of NH_4^+ ions are frozen in phase III. In phase II reorientation of these ions takes place. This transition does not, of course, exist in potassium thiocyanate. It was very interesting to investigate changes as the result of the partial substitution of NH_4^+ ions by K^+ ions and this is main aim of this work.

2. Experimental

All samples of the mixed crystals $K_{1-x}(NH_4)_xSCN$ with different x values were prepared from mixtures of methanol solutions with equal concentrations of the pure ammonium thiocyanate and potassium thiocyanate. Methanol was evaporated and the samples were dried in a furnace at ca. 60°C (333 K) for more than 10 h. The homogenous samples only, that is, those which gave singular peaks on the preliminary thermograms, were chosen for further investigations. Measurements were made for 13 samples with $x = 0.00$, 0.15, 0.34, 0.45, 0.60, 0.68, 0.75, 0.78, 0.80, 0.85, 0.90, 0.95, 1.00.

For all samples the enthalpy determinations were carried out using a Perkin–Elmer DSC-7 differential scanning calorimeter. The instrument was calibrated

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by means of the melting points and enthalpies of fusion of indium and zinc. Different scanning rates (heating and/or cooling) were used, typically 1, 2.5, 5 and 10 K min^{-1}.

3. Results and discussion

The DSC curves for the samples with high concentration of ammonium ions ($x \geq 0.75$) show two reversible phase transitions: (starting from low temperatures) phase III into phase II and then phase II into phase I. Typical thermograms both for heating and cooling are presented in Fig. 1. For the samples with lower concentrations ($x < 0.75$) only a single reversible phase transition, corresponding to the high temperature one in the previous cases, was registered. Unfortunately we could only make the measurements for temperatures above ambient and the phase III–phase II transition line could not be determined for a wider range of x values. From neutron diffraction experiments [7] it is known that at liquid helium temperatures the sample with $x = 0.75$ can exist both in the orthorhombic and in the monoclinic structure, depending on previous thermal treatment (i.e. cooling rate and annealing). For the construction of the phase diagram, the temperature of phase III–phase II transition was taken as the 'onset' temperature observed during heating at 5 K min^{-1} (calibration was also made for this scanning rate). At the temperatures of the phase II–phase I transitions we decided to choose the mean value of the 'peak' temperatures for heating and cooling, extrapolated to zero scanning rate. The phase diagram based on thus obtained transition temperatures is shown in Fig. 2. The solid curves represent a second order polynomial fit to the experimental points for the phase II–phase I transition and linear regression for the phase III–phase II transition.

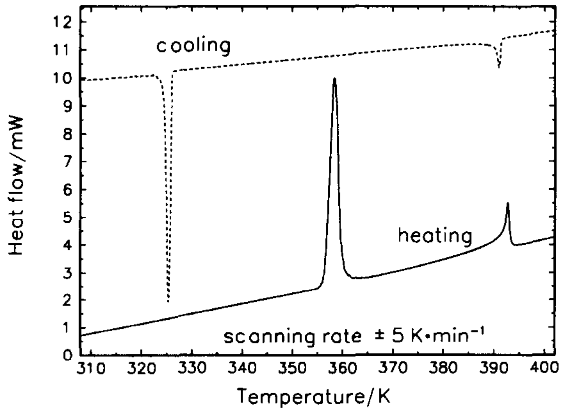

Fig. 1. Typical DSC curves for a sample with high concentration of NH_4^+ ions.

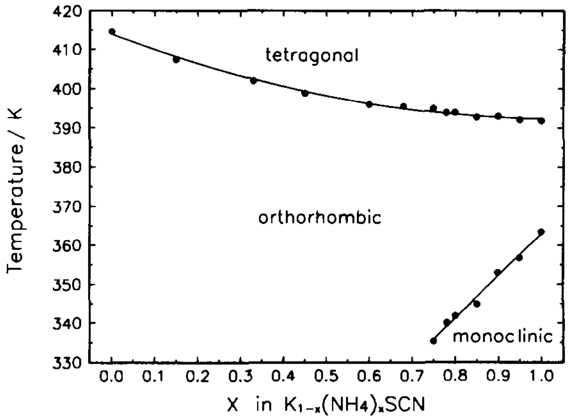

Fig. 2. Temperature-concentration phase diagram for $K_{(1-x)}(NH_4)_xSCN$ system.

Enthalpy determinations were made for both phase transitions by means of numerical integration of the peak areas observed at different heating rates. The results, as a function on concentration x, are graphically presented in Figs. 3 and 4 for the phase III–phase II and the phase II–phase I transitions respectively. In both cases second order polynomial fits to the experimental data are shown (solid lines) but they should be regarded as guides to the eye only. The errors of our enthalpy determinations (not shown in the figures) are

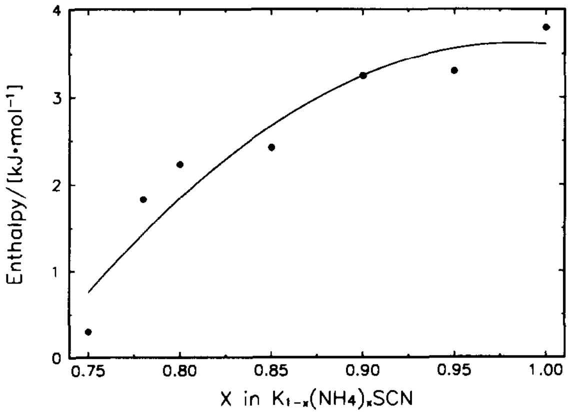

Fig. 3. Enthalpy of phase III–phase II transition vs. concentration.

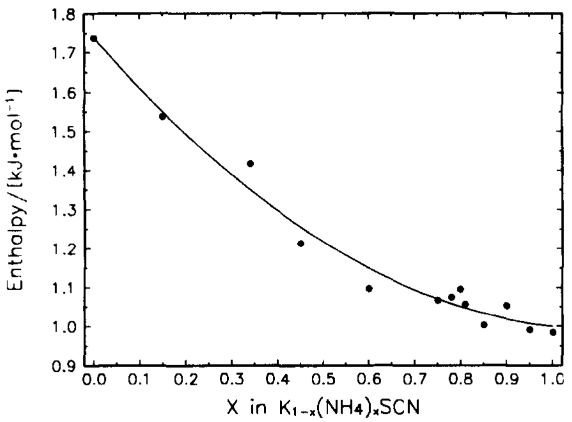

Fig. 4. Enthalpy of phase II–phase I transition vs. concentration.

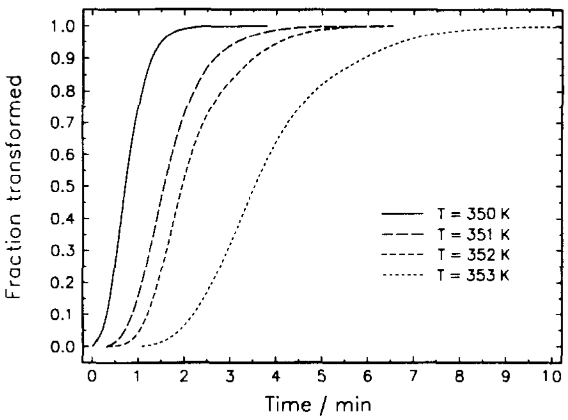

Fig. 5. Time dependence of the fraction transformed from undercooled phase II into phase III.

rather large, but for the low-temperature phase transition, it does not excite ca. 10%. In the case of the phase II–phase I transition they are much higher because the ranges of integration are not well defined (due to very long tails on the low temperature side).

Careful investigations of the thermal hysteresis of the phase II–phase I transition made for many different scanning rates showed no systematic dependence on the concentration. For most x values the 'peak' temperatures corresponding to zero scanning rate (obtained by extrapolation) calculated on the basis heating and cooling scans are equal. Thus these samples did not show hysteresis. The greatest difference (i.e hysteresis) amounted ca. 0.8 K and was observed for pure potassium thiocyanate. This result agrees well with an earlier paper [3]. We estimate that excess entropy change $\Delta_{trs}S \approx 4.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$ is more than two times higher than the average value $1.6\,\mathrm{J\,mol^{-1}\,K^{-1}}$ from Ref. [3] but smaller than $5.45\,\mathrm{J\,mol^{-1}\,K^{-1}}$ found by Sakiyama et al. [5] on the basis of adiabatic measurements. For NH_4 SCN we estimated entropy change equal to ca. 2.5 $\mathrm{J\,mol^{-1}\,K^{-1}}$ which is again almost two times greater than 1.3 $\mathrm{J\,mol^{-1}\,K^{-1}}$ known from literature data [6]. Disagreement between $\Delta_{trs}S$ obtained for KSCN and data of Sakiyama et al. is probably connected with some arbitrary chosen (in our experiment) linear background and difficult to define the range of the integration.

The phase transition from phase III to phase II showed a very big thermal hysteresis. Phase II can hence be undercooled very easily (several or more degrees). Even for very fast cooling (−200 K/min) we could, however, not obtain any glassy state. The rate of the spontaneous transition from the undercooled phase II to phase III, stable at this temperature range, increased drastically with decreasing temperature in the temperature range covered. This behavior is presented in Fig. 5. An attempt to use Avrami's equation for describing the observed kinetics failed. The shape of the observed curves (Fig. 5) is not adequate (complicated) to the predicted shape by that simple equation.

Acknowledgements

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