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Note

DTA Measurements of Normal–Incommensurate Phase Transition in $(NH_4)_2ZnCl_4$ and K_2ZnCl_4 Crystals

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Differential thermal analysis (DTA) was applied to determine the changes in enthalpy and entropy of $(NH_4)_2ZnCl_4$ and K_2ZnCl_4 crystals at their phase transition from the orthorhombic normal phase to the incommensurate phase. The temperature of this transition, T_i, is 406 K for $(NH_4)_2ZnCl_4$ and 555 K for K_2ZnCl_4 and the entropy changes ($\Delta S/R$) are 0.053 and 0.035, respectively. The low value obtained for $\Delta S/R$ is characteristic of incommensurate phase transitions. The results were compared with the data reported for other crystals of the A_2BX_4 family. Thermal properties of the crystals of the A_2ZnCl_4 subgroup were found to the correlated with the length of A–Cl bonds.

KEY WORDS: differential thermal analysis (DTA); phase transition; incommensurability.

1. INTRODUCTION

The crystals of the family A_2BX_4 show an interesting sequence of phase transitions from the normal phase (N) to the incommensurate phase (I) and then to the ferroelectric phase (F). The normal phase has an orthorhombic symmetry with a space group Pnam and its prototype is a structure of β-K_2ZnCl_4. When the temperature is decreased to T_i, the crystals undergo the phase transition to the incommensurate phase. In this phase, the crystal lattice is modulated along the crystallographic direction $\mathbf{a}$ with the wave vector $q_x = (1-\delta)a_0^*/3$, where a_0^* is the vector of the reciprocal lattice of the normal phase. The incommensurability parameter

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δ takes a value of 0.02–0.04 at T_i and decreases with decreasing temperature. At the temperature T_C of the I → F phase transition, δ jumps down to zero. A characteristic feature of the compounds that belong to the subgroup A_2ZnCl_4 is a wide temperature range of the I phase, covering 150 K. The low-temperature phase F is commensurate and the elementary cell is tripled along the direction $\mathbf{a}$ ($q_x = a_0^*/3$). This is a ferroelectric phase of a symmetry $Pna2_1$ with the spontaneous polarization vector along the $\mathbf{c}$ direction. The above-described phase transitions have been the subject of extensive experimental and theoretical studies. Although the changes in many physical properties accompanying those transitions have been studied already, only a few papers have been devoted to thermal properties of those crystals. According to the thermodynamical theory, a jump change in the specific heat of the crystals should occur at both phase transitions, T_i and T_C [1, 2]. These predictions have been experimentally confirmed, by adiabatic calorimetry, only for K_2SeO_4 [3–6] and Rb_2ZnCl_4 [7–9] crystals. DTA investigations of $(NH_4)_2ZnCl_4$ and K_2ZnCl_4 revealed an anomaly related to the transition from the normal to the incommensurate phase. The temperature of this transition T_i was found to be 393 K [10] or 406 K [11, 12] for $(NH_4)_2ZnCl_4$ and 555 K for K_2ZnCl_4 crystals [8, 13, 14]. The changes in enthalpy and entropy accompanying this phase transition were not determined.

This paper is devoted to a detailed DTA investigation of $(NH_4)_2ZnCl_4$ and K_2ZnCl_4 crystals, in order to determine thermal effects occurring in them at T_i temperature.

2. RESULTS AND DISCUSSION

$(NH_4)_2ZnCl_4$ and K_2ZnCl_4 single crystals were grown by slow evaporation at a constant temperature 300 K from the aqueous solutions of

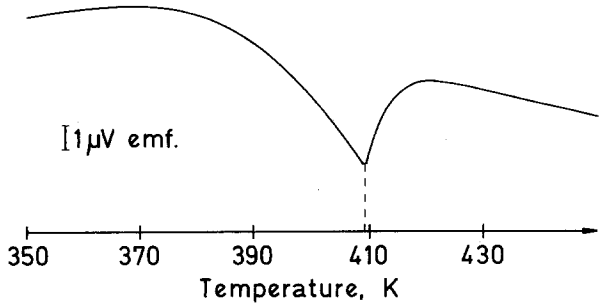

Fig. 1. $(NH_4)_2ZnCl_4$ thermogram near T_i. The rate of temperature change: 5 K · min^{-1}.

the appropriate halides at the ratio 2:1, with a slight excess of $ZnCl_4$. Purity of the substrates was of particular concern, since the physical properties of the incommensurate phase strongly depend on the presence of impurities [15]. Therefore the crystals were purified by triple recrystallization.

The studies were carried out on a computer-aided DTA apparatus, Type 606 made by UNIPAN (Poland). The mass of the samples studied varied from 50 to 80 mg. The rates of temperature changes were 2, 5, 10, and 20 $K \cdot min^{-1}$. The measurements were performed for three samples of each different monocrystal and repeated three times for each sample at each rate of temperature change. The temperature range of the studies was from room temperature to about 450 K for $(NH_4)_2ZnCl_4$ crystals and from room temperature to about 600 K for K_2ZnCl_4. Examples of the original thermograms obtained after computer smoothing are shown in Figs. 1 and 2. A clear anomaly was observed at T_i for both crystals, however, no changes were observed at T_C. Figure 3 presents K_2ZnCl_4 thermograms averaged over all series of measurements after baseline correction. The temperature T_i was determined by extrapolation of the dependence of the peak's temperatures on DTA thermograms on the rate of temperature changes to their zero rate. For $(NH_4)_2ZnCl_4$ the obtained T_i was (406.0 ± 0.5) K, and for K_2ZnCl_4 $T_i = (555.0 \pm 0.5)$ K. The observed change in the slope of the basic line in the thermogram around the phase transition (see Figs. 1 and 2) observed for both crystals suggests a jump change in the specific heat at T_i, analogously as in K_2SeO_4 [5, 6] and Rb_2ZnCl_4 [7].

On the grounds of the thermograms obtained, we could calculate the changes in enthalpy and entropy at the phase transition from the normal to the incommensurate phase. The results are presented in Table I. For the sake of comparison, Table I also includes the data obtained by other

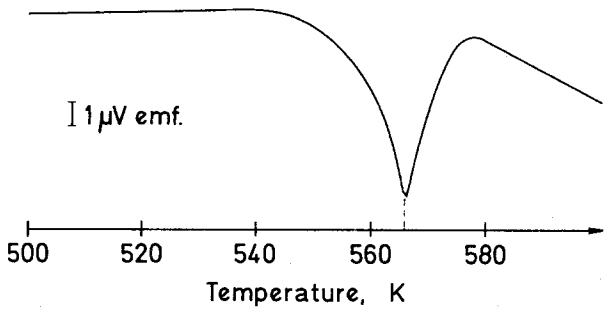

Fig. 2. K_2ZnCl_4 thermogram in the vicinity of T_i. The rate of temperature change: 10 $K \cdot min^{-1}$.

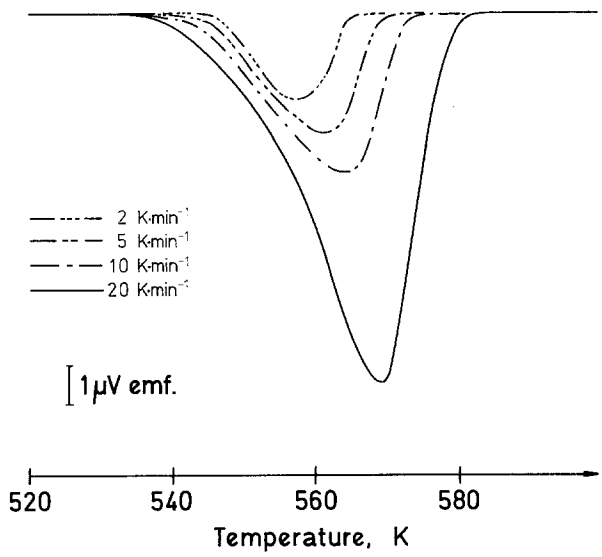

Fig. 3. The averaged thermograms for K_2ZnCl_4 after baseline correction. The rates of temperature change are given.

authors for other crystals of the A_2BX_4 family. The change in entropy at the considered phase transition is relatively small, which is characteristic of incommensurate phase transitions. For the subgroup A_2ZnCl_4 we observed an increase in $\Delta S/R$ at T_i with increasing length of the A–Cl bond (see Table I). These results indicate that A^+ ions placed inside the cavities made by BX_4 tetrahedrons influence the ordering of the tetrahedrons. Unfortunately, the results obtained in the DTA analysis are not sufficient to estimate the specific heat jump change because of the relatively large measurements errors. In the near-future we plan to carry out more accurate studies of the changes in specific heat of $(NH_4)_2ZnCl_4$ and K_2ZnCl_4 crystals by AC calorimetry.

Table I. Phase Transition Temperatures, Thermodynamic Functions, and Lengths of the A–Cl Bond for A_2BX_4-Group Crystals

	K_2SeO_4	Rb_2ZnCl_4	$(NH_4)_2ZnCl_4$	K_2ZnCl_4
T_i (K)	127.7	303.2	406	555
ΔH ($J \cdot mol^{-1}$)	110 ± 3 [5]	220 [10]	180 ± 20	160 ± 20
ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)	0.88 ± 0.03 [5]	0.66 [10]	0.44 ± 0.06	0.29 ± 0.05
$\Delta S/R$	0.106 [5]	0.079 [10]	0.053	0.035
A–Cl (Å)	—	3.53 [18]	3.374 [17]	3.273 [16]

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