Note

DTA Measurements of Normal–Incommensurate Phase Transition in (NH₄)₂ZnCl₄ and K₂ZnCl₄ Crystals

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Differential thermal analysis (DTA) was applied to determine the changes in enthalpy and entropy of (NH₄)₂ZnCl₄ and K₂ZnCl₄ crystals at their phase transition from the orthorhombic normal phase to the incommensurate phase. The temperature of this transition, Tᵢ, is 406 K for (NH₄)₂ZnCl₄ and 555 K for K₂ZnCl₄ and the entropy changes (∆S/R) are 0.053 and 0.035, respectively. The low value obtained for ∆S/R is characteristic of incommensurate phase transitions. The results were compared with the data reported for other crystals of the A₂BX₄ family. Thermal properties of the crystals of the A₂ZnCl₄ subgroup were found to be correlated with the length of A–Cl bonds.

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

1. INTRODUCTION

The crystals of the family A₂BX₄ 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-K₂ZnCl₄. When the temperature is decreased to Tᵢ, the crystals undergo the phase transition to the incommensurate phase. In this phase, the crystal lattice is modulated along the crystallographic direction a with the wave vector qₓ = (1 − δ)aₓ*/3, where aₓ* 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 $a$ ($q_x = a_0^*/3$). This is a ferroelectric phase of a symmetry Pna2$_1$ with the spontaneous polarization vector along the $c$ 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$^{-1}$. 