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Thermal Properties and Radiation Damage in $NaNH_4XO_4 \cdot 2H_2O$ Single Crystals ($XO_4 = SO_4, SeO_4$)

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Differential thermal analysis (DTA) studies of $NaNH_4SO_4 \cdot 2H_2O$, $NaND_4SO_4 \cdot 2H_2O$, and $NaNH_4SeO_4 \cdot 2H_20$ single crystals were performed in the temperature range of the ferroelectric–paraelectric phase transition and of the dehydration process. The first-order phase transition at the Curie point was confirmed for $NaNH_4SO_4 \cdot 2H_2O$, whereas the transition in the isomorphous $NaNH_4SeO_4 \cdot 2H_2O$ at the Curie temperature was found to be similar to a contineous (second order) with considerable higher transition enthalpy. Dehydration process of the crystals studied was found to proceed in two stages, with maximum dehydration rates at ~355 and ~400 K. A linear decrease in thermal energy related to the long-range ordering in $NaNH_4SO_4 \cdot 2H_2O$ crystals was observed with the dose of γ-cobalt-60 irradiation and discussed with respect to the radiation induced decrease in spontaneous polarization.

KEY WORDS: dehydration enthalpy; ferroelectric–paraelectric phase transition; isotopic effect; radiation damage; transition enthalpy.

1. INTRODUCTION

Though the ferroelectric properties in $NaNH_4XO_4 \cdot 2H_2O$ crystals ($X = S$, Se) were discovered long ago [1, 2], their properties are not perfectly known. The phase transition in the crystals a few degrees below the Curie point ($T_c \simeq 101$ K in $NaNH_4SO_4 \cdot 2H_2O$ [3] and $T_c = 180$ K in $NaNH_4SeO_4 \cdot 2H_2O$ [4, 5]) and the origin of the spontaneous polarization [6] remain ambiguous as well. Sodium ammonium dihydrated sulfates

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and selenates were found to be isomorphous, with the c-orthorhombic axis being polar below T_c, and the space group $P2_12_12_1$ has been ascribed to the crystals at room temperature [3, 4]. The structure of $NaNH_4SO_4 \cdot 2H_2O$ has been solved by Corazza et al. [7] and found to consist of a three-dimensional network of coordination polyhedra of NH_4^+ ions linked together by hydrogen bonds with oxygens of near-regular SO_4 tetrahedra and chains of NaO_6 octahedra parallel to the c-axis filling the channels of the ammonium oxygen network. The two water molecules were found to belong to the Na polyhedron and form additional hydrogen bridges between sodium and NH_4 polyhedra.

There is, however, a difference in the character of the ferroelectric–paraelectric transition between the $NaNH_4SO_4 \cdot 2H_2O$ and $NaNH_4SeO_4 \cdot 2H_2O$ crystals: the selenates were found to exhibit a continuous (i.e., second-order) phase transition [5], whereas the transition of the sulfates was found to be of the first order [3, 8].

Thermal properties of $NaNH_4SO_4 \cdot 2H_2O$ crystals were studied by Osaka [8] by means of adiabatic calorimetry, and the λ-type anomaly, typical of the first-order phase transition, was observed. Osaka reported the value of transition enthalphy to amount to $\Delta H_{T_c} = 327\ \mathrm{J \cdot mol^{-1}}$, and the corresponding change in the entropy at the phase transition $\Delta S_{T_c} = 3.31\ \mathrm{J \cdot mol^{-1} \cdot deg^{-1}}$. The ΔH_{T_c} and ΔS_{T_c} involved latent heat $\Delta H_L = 234\ \mathrm{J \cdot mol^{-1}}$ and entropy $\Delta S_L = 2.34\ \mathrm{J \cdot mol^{-1} \cdot deg^{-1}}$.

The same method was used to study thermal properties of $NaNH_4SeO_4 \cdot 2H_2O$ by Aleksandrov and co-workers [9]. A maximum of the specific heat was observed at (179.36 ± 0.01)K, followed by a jump in specific heat $\Delta C_p = 37.4\ \mathrm{J \cdot mol^{-1} \cdot deg^{-1}}$ at a temperature of (180.00 ± 0.01)K. The authors reported the transition enthalpy to amount to $\Delta H_{T_c} = (670 \pm 21)\ \mathrm{J \cdot mol^{-1}}$, however, they did not detect latent heat when cooling through the phase change temperature.

It should be mentioned that no anomalies in C_p at temperatures a few degrees below T_c (where dielectric anomalies were found) were observed in either crystals. Gemin and O'Reilly [10] claimed, on the basis of their NMR data, that the transition at 101 K in $NaNH_4SO_4 \cdot 2H_2O$ is displacive in nature and accompanied by rather striking changes in the local electric field gradient at the sodium sites. They stated, moreover, that the transition a few degrees below T_c involves a much smaller lattice distortion. NMR studies of $NaNH_4SeO_4 \cdot 2H_2O$ showed that at T_c, a small deformation in the surroundings of Na ions appears, whereas 3 to 4 degrees below T_c, two nonequivalent positions of Na nuclei appear abruptly [11]. In the same temperature range two couples of structurally nonequivalent ND_4 groups were found to appear [6] in the deuterated crystal. The isotopic effect in the crystals was found to be rather small and an upward shift in T_c by

~1 K was reported in $NaNH_4SeO_4 \cdot 2H_2O$ deuterated by ~20% [6], whereas in $NaNH_4SO_4 \cdot 2H_2O$ crystals deuterated by ~50% a shift in T_c of ~2 K was reported [12].

The aim of the present paper was to verify the order of the ferroelectric–paraelectric phase transition in $NaNH_4SO_4 \cdot 2H_2O$, $NaND_4SO_4 \cdot 2D_2O$, and $NaNH_4SeO_4 \cdot 2H_2O$ crystals and to evaluate the enthalpy of dehydration process. Moreover, we studied the effect of radiation damage to $NaNH_4SO_4 \cdot 2H_2O$ crystals.

2. EXPERIMENTAL

$NaNH_4SO_4 \cdot 2H_2O$ single crystals (of a few centimeters in dimension) were grown by a dynamic method at constant temperature of 306 K from aqueous solution of $NaNH^4SO_4 \cdot 2H_2O$ purified by threefold recrystallization. Deuterated crystals $NaND_4SO_4 \cdot 2H_2O$ were obtained by fivefold crystallization (of purified $NaNH_4 \cdot 2H_2O$) from D_2O at room temperature. We observed that the sixth crystallization from D_2O does not change the Curie temperature any more, and that fact was taken as proof for almost-total substitution of protons by deuterium. $NaNH_4SeO_4 \cdot 2H_2O$ crystals a few millimeters in size were grown spontaneously at room temperature from an aqueous solution of threefold recrystallized salt.

Differential thermal analysis (DTA) studies were performed in the temperature range 80–500 K by means of computer-aided apparatus constructed at the Laboratory of Crystal Physics, Institute of Physics, A. Mickiewicz University, Poznań. The temperature difference between the sample studied and the reference sample was measured by a 50-junction Cu–constantan thermopile. Samples were kept in a thin-wall stainless-steel cruicible (~0.1 ml) placed together with temperature sensors in a stainless-steel holder. The measurements can be made under vacuum or a dry nitrogen gas atmosphere. The latter was used in our experiments. The holder was placed in a thermal bath, the temperature of which could be changed at a constant rate from 0.1 to 10 $K \cdot min^{-1}$ using a UNIPAN-680 temperature controller. The temperature difference DT and the temperature T were measured using digital V-544 Meratronik voltmeters and stored by an Armstrad microcomputer; 0.07 K temperature steps were stored at heating or cooling rates of a few degrees kelvin per minute. The apparatus enabled the measurements of single crystalline samples, as well as powdered and liquid samples. Temperature calibration of the apparatus was performed using the ICTA recommended standards: solid-state phase transition and melting point of cyclohexane, melting point of dichloroethane, solid-state transition on heating of KNO_3, and melting temperatures of In and Sn. The calibration measurements were used for obtaining the calibration constant of the apparatus needed for the assessment of the transition enthalpies. DTA studied with the use of a manganin microheater placed in a hole bored in a KCl single crystalline sample show that, within an error of 2 to 5%, the effect of the cruicibles on the calibration constant can be neglected in the whole temperature range. For studying the dehydration process we used also the thermogravimetry (TG) and differential thermogravimetry (DTG) of a Paulik–Paulik-type derivatograph working at a heating rate of 5 K · min^{-1}. Single crystalline $NaNH_4SO_4 \cdot 2H_2O$ samples were irradiated at room temperature in a γ-cobalt-60 source at a dose rate of 34 Gy · h^{-1}.

3. RESULTS

In Fig. 1 a DTA scan of a $NaNH_4SO_4 \cdot 2H_2O$ single-crystalline sample in the temperature range including the ferroelectric–paraelectric phase transition is presented. A DTA peak typical of the first-order phase transition is observed at $T_c = 99.6$ K and the scans were found to be reproducible on successive cooling and heating (below room temperature). Figure 2 shows the DTA scan of a $NaNH_4SeO_4 \cdot 2H_2O$ single-crystalline sample obtained on heating. The DTA peak at $T_c = 180$ K was found and followed by a jump due to the jump in the heat capacity observed at the second-order phase transition, for instance, in triglycine sulfate single crystals [13]. No thermal hysteresis is observed for $NaNH_4SeO_4 \cdot 2H_2O$ single crystals. By thermal hysteresis, we mean the difference in the phase transition temperature obtained on heating and on cooling, after correction for thermal lag. The absence of thermal hysteresis indicates that the transition does not have predominantly first-order characteristics.

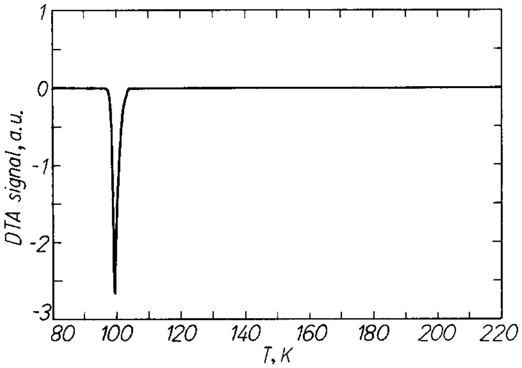

Fig. 1. DTA scan of a $NaNH_4SO_4 \cdot 2H_2O$ single crystal in the region of the ferroelectric–paraelectric phase transition; the heating rate amounted to 5 K · min^{-1}.

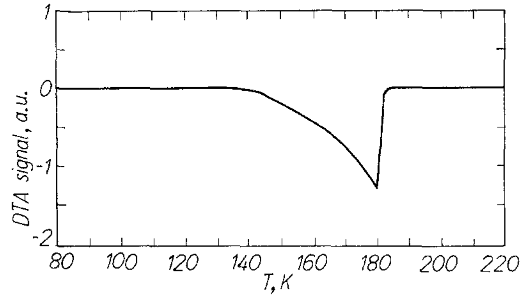

Fig. 2. DTA scan of a $NaNH_4SeO_4 \cdot 2H_2O$ single crystal in the region of the ferroelectric–paraelectric phase transition; the heating rate amounted to 5 K · min^{-1}.

The influence of deuterium substitution of protons in $NaNH_4SO_4 \cdot 2H_2O$ on the DTA scans is shown in Fig. 3. The character of the ferroelectric–paraelectric phase transition is found to be unchanged and deuteration results in a small upward shift in the Curie point, by ~4 K. The values of the transition enthalpies and the respective change in entropies are collected in Table I.

Our dielectric studies of $NaNH_4SO_4 \cdot 2H_2O$ crystals above room temperature have shown that the electric conductivity of the samples just after they have been cut from the bulk of the crystal is smaller by about two orders of magnitude than that of the samples stored at room

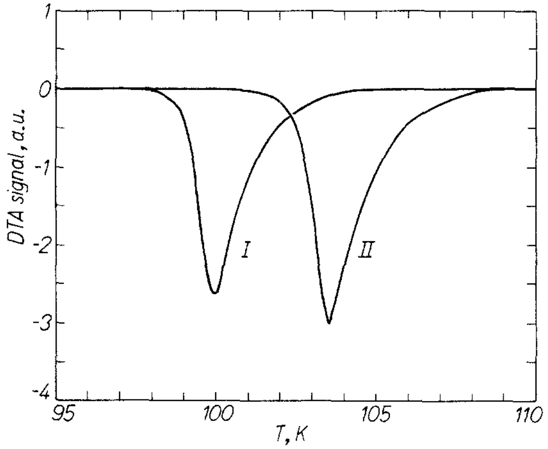

Fig. 3. DTA scans of $NaNH_4SO_4 \cdot 2H_2O$ (I) and $NaND_4SO_4 \cdot 2D_2O$ single crystals in the vicinity of the ferroelectric–paraelectric phase transition; the heating rate amounted to 5 K · min^{-1}.

Table I. Values of the Enthalpy ΔH of Ferroelectric–Paraelectric Phase Transition and the Respective Changes in the Entropy ΔS

Crystal	T_c (K)	ΔH ($J \cdot mol^{-1}$)	ΔS ($J \cdot mol^{-1} \cdot deg^{-1}$)
$NaNH_4SO_4 \cdot 2H_2O$	99.6	280 ± 35	2.8 ± 0.4
$NaND_4SO_4 \cdot 2D_2O$	103.6	362 ± 54	3.5 ± 0.5
$NaNH_4SeO_4 \cdot 2H_2O$	180.0	1290 ± 270	7.1 ± 1.5

temperature for 2 weeks. This fact led us to characterize the dehydration process in crystals of the $NaNH_4XO_4 \cdot 2H_2O$ family. Figure 4 shows the DTA, thermogravimetry (TG), and differential thermal gravimetry (DTG) of $NaNH_4SO_4 \cdot 2H_2O$ crystals. The dehydration process starts at about 320 K and proceeds in two steps: the first step of the process exhibits the maximum rate at $T_1 \sim 357$ K and the dehydration of the second water molecule reaches the maximum rate at $T_2 \simeq 401$ K. A similar dehydration

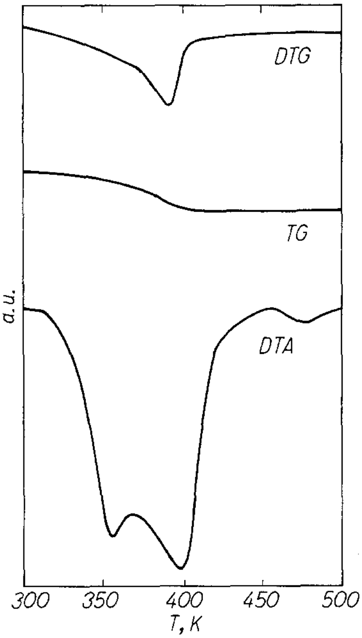

Fig. 4. DTA, thermogravimetry (TG), and differential thermogravimetry (DTG) scans of a $NaNH_4SO_4 \cdot 2H_2O$ single crystal in the temperature range of dehydration process; the heating rate amounted to 5 $K \cdot min^{-1}$.

Table II. Values of the Total Dehydration Enthalpy ΔH_{deh} and Temperatures T_1 and T_2 of Maximum Dehydration Rates

Crystal	ΔH_{deh} ($kJ \cdot mol^{-1}$)	T_1 (K)	T_2 (K)
$NaNH_4SO_4 \cdot 2H_2O$	228 ± 10	357	401
$NaND_4SO_4 \cdot 2D_2O$	290 ± 23	353	392
$NaNH_4SeO_4 \cdot 2H_2O$	260 ± 10	358	400

process was observed in $NaND_4SO_4 \cdot 2D_2O$ and $NaNH_4SeO_4 \cdot 2H_2O$ single crystals: the temperatures T_1 and T_2 of the maximum rate of dehydration and the total enthalpy of dehydration are shown in Table II. The dehydration enthalpies of the crystals studied and the temperatures T_1 and T_2 are very close.

We also studied the influence of defects introduced by γ-cobalt-60 irradiation on the thermal properties of $NaNH_4SO_4 \cdot 2H_2O$ single crystals in the temperature range including the ferroelectric–paraelectric phase transition. Ferroelectric ordering results in an excess of heat capacity over the lattice specific heat and we were interested in changes of thermal energy ΔH related to the ferroelectric ordering caused by lattice defects. The ΔH values of the samples irradiated with various doses of γ-radiation were determined from the DTA scans similar to that shown in Fig. 1 for a non-irradiated $NaNH_4SO_4 \cdot 2H_2O$. The dose dependence of the enthalpy related to the ferroelectric ordering, measured 2 weeks after termination of the irradiation, is shown in Fig. 5. A linear decrease in ΔH value is observed with an increase in the irradiation dose, with the value $d(\Delta H)/dD^*$ amounting to 1.1 %/kGy. It was found, however, that the ΔH

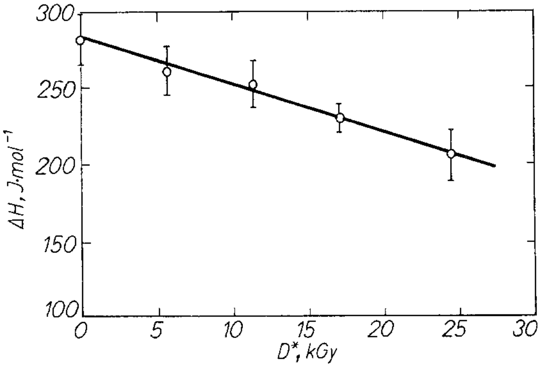

Fig. 5. The enthalpy of the ferroelectric–paraelectric phase transition of $NaNH_4SO_4 \cdot 2H_2O$ single crystals vs the dose of γ-cobalt-60 irradiation.

values were found to be dependent on time up to ~10 days after irradiation had been terminated. For instance, the ΔH value of the $NaNH_4SO_4 \cdot 2H_2O$ sample irradiated with the dose $D^* = 17.0$ kGy measured 36 h after the termination of the irradiation amounted to $\Delta H^* = (138 \pm 43)\,J \cdot mol^{-1}$, which is equal to ~50.7% of the ΔH value of the nonirradiated sample, whereas the ΔH^* value measured 2 weeks after terminating irradiation amounted to $(230 \pm 5)\,J \cdot mol^{-1}$, and the respective relative changes $(\Delta H^* - \Delta H)/\Delta H \simeq 17.9\%$.

4. CONCLUSIONS

Our studies of $NaNH_4SO_4 \cdot 2H_2O$ crystals confirm that the first order of the ferroelectric–paraelectric phase transition and enthalpy of the phase transition is in good agreement with that reported by Osaka [8]. The ferroelectric–paraelectric phase transition in $NaNH_4SeO_4 \cdot 2H_2O$ crystals was found by us to be in agreement with the temperature dependence of the spontaneous polarization $P_s^2 \sim T$ reported earlier [5]. Our transition enthalpy values were, however, higher than those reported by Aleksandrov and co-workers [9]. We consider the higher value of ΔH_{T_c} obtained by us to be connected with the better quality of our $NaNH_4SeO_4 \cdot 2H_2O$ samples (the crystals were purified by threefold recrystallization). It is a well-known fact that lattice imperfections cause a decrease in the transition enthalpy [13], as as for $NaNH_4SO_4 \cdot 2H_2O$ and $NaNH_4SeO_4 \cdot 2H_2O$ crystals—they dehydrate easily. For example, a much higher value of ΔH_{T_c} is reported by Osaka [8] for $NaNH_4SO_4 \cdot 2H_2O$ crystals of better quality than in the first work [14], where $\Delta H_{T_c} = (226 \pm 21)\ J \cdot mol^{-1}$ was reported.

The transition enthalpy and the respective change in transition entropy of deuterated crystals $NaND_4SO_4 \cdot 2D_2O$ are, within the experimental error, the same as those of nondeuterated crystals $NaNH_4SO_4 \cdot 2H_2O$—thus the deuteration has no influence on the ferroelectric–paraelectric phase transition. Only a small upward shift in the Curie temperature is observed. This corroborates the supposition that, similarly to $NaNH_4SeO_4 \cdot 2H_2O$ crystals [6], the NH_4 groups and the water molecules are not involed in the ferroelectric–paraelectric phase transition. The isotopic effect in the case where protons play the main role in appearing (or disappearing) the ferroelectric ordering, e.g., KH_2PO_4 single crystals, has been found to be considerable [15]; the upward shift in T_c has been observed to be of ~$90 \div 100$K.

The dehydration process of $NaNH_4SO_4 \cdot 2H_2O$, $NaND_4SO_4 \cdot 2D_2O$, and $NaNH_4SeO_4 \cdot 2H_2O$ single crystals is found to be similar and to proceed in two stages.

In general, the thermal energy ΔH of ferroelectric ordering is given by

$$\Delta H = \int_{T_1}^{T_c} [C_p(T) - C_p^D(T)]\, dT$$

where C_p denotes the specific heat of ferroelectric crystal, C_p^D the lattice specific heat, T_c the Curie temperature, and T_1 the temperature at which the ordering appears. In the case of proper ferroelectrics, for which the spontaneous polarization P_s is the order parameter of the phase transition, the thermodynamic potential ϕ can be written in the form

$$\phi = \phi_0 + \tfrac{1}{2}\alpha(T - T_0)P_s^2 + \tfrac{1}{4}\beta P_s^4 + \tfrac{1}{6}\gamma P_s^6 + \cdots$$

where ϕ_0 denotes the thermodynamic potential of the paraelectric phase [16]. Since to the first approximation the coefficients at higher powers of P_s can be taken as temperature independent, we obtain the difference in the entropy of the ferroelectric and the paraelectric phase,

$$\Delta S = S - S_0 = -\tfrac{1}{2}\alpha P_s^2$$

and the energy required to destroy the polarization of the crystal,

$$\Delta H = \tfrac{1}{2}\alpha T_c P_s^2$$

The $NaNH_4SO_4 \cdot 2H_2O$ single crystal, however, cannot be treated as a proper ferroelectric crystal since spontaneous deformation was found to appear below T_c [8]. Thus radiation-induced changes in ΔH observed by us cannot be simply related to the decrease in the spontaneous polarization. A radiation-induced decrease in ΔH was observed by Strukov et al. [13] in $(NH_2CH_2COOH)_3H_2SO_4$, a proper ferroelectric crystal, to be of ~0.3 %/kGy. Changes in ΔH found by us in $NaNH_4SO_4 \cdot 2H_2O$ due to radiation damage were about three times greater. This indicates that changes in spontaneous deformation are involved in the radiation-induced decrease in ΔH. The above-discussed values of $(\Delta H^* - \Delta H)/\Delta H$ for $NaNH_4SO_4 \cdot 2H_2O$ crystals were obtained at a steady-state condition, when the concentration of radiation-induced defects was stable. γ-cobalt-60 radiation damage to $NaNH_4SO_4 \cdot 2H_2O$ consists of the creation of point defects at all lattice sites (due to electron–nucleus interaction of Compton electrons of energy comparable to the energy of incident γ-radiation) and of free radicals. Recent ESR studies of γ-cobalt-60-irradiated $NaNH_4SO_4 \cdot 2H_2O$ [17] show the presence of NH_3^+ and SO_3^- radicals, and a decay of their concentration was observed. This result is in good agreement with our thermal studies of γ-irradiated $NaNH_4SO_4 \cdot 2H_2O$ performed for 36 h and 10 days after termination of irradiation. During this time we observed a recovery of radiation-induced changes in ΔH and the effect can be related to the decay of the free radicals. Thus the observed radiation-induced decrease in the enthalpy of long-range ordering in $NaNH_4SO_4 \cdot 2H_2O$ crystals is connected with the decrease in the concentration of ferroelectrically active dipoles (the spontaneous polarization) and vanishing of spontaneous deformation, caused mainly by the point defects and breaking of the chemical bonds in the crystal.

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