

DIELECTRIC PROPERTIES OF $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ – $\text{NaNH}_4\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ MIXED CRYSTALS

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The mixed crystals of $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ – $\text{NaNH}_4\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ were grown and their properties were investigated. Dielectric and differential thermal analysis studies allowed us to construct the phase diagram of the system with molar fraction, x , of $\text{NaNH}_4\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ as a parameter. Nonlinear dependence of T_c versus composition was found.

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1. Introduction

Mixed crystals evoke an increasing interest according to their unusual properties. Special attention was paid to the $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ systems and its arsenate analogue in which the proton glass behaviour is observed [1–7]. Interesting structural effects were observed for the $\text{M}(\text{CN})_x\text{X}_{1-x}$ systems [8, 9] and for the mixed crystals of the general formula $[(\text{CH}_3)_4\text{N}]_2\text{ZnCl}_{4-x}\text{Br}_x$ [10].

Interesting features were also found for the RbHSeO_4 – NH_4HSeO_4 mixed crystals [11]. The NH_4HSeO_4 – NH_4HSO_4 mixed crystals in the concentration range $0.67 \leq x < 0.9$ exhibit some frustrated state [12].

In this paper we would like to report the dielectric properties of $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ – $\text{NaNH}_4\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ (abbreviation NAS and NASE) mixed crystals.

The NAS and NASE crystals are isomorphous. At room temperature they belong to the orthorhombic system, the space group $P2_12_12_1$, with the cell dimensions $a = 8.216 \text{ \AA}$, $b = 12.854 \text{ \AA}$, $c = 6.232 \text{ \AA}$ and $a = 8.405 \text{ \AA}$, $b = 13.137 \text{ \AA}$, $c = 6.287 \text{ \AA}$ for NAS and NASE crystal respectively. Their structure consists of chains of Na octahedra sharing one face with each other (the Na–Na distance is

3.15 Å for NAS and 3.163 Å for NAsE). The SO_4 tetrahedron is regular. The NH_4 ion coordinates seven oxygen atoms forming an irregular polyhedron. The two water molecules belong to the Na polyhedron and make additional hydrogen bridges between Na and NH_4 cations. The distances between oxygen atoms linked by hydrogen bridges are from 2.77 to 2.81 Å [13, 14].

2. Experimental

The mixed NAS–NAsE crystals were grown at 303 K by slow evaporation from water solutions with NAS/NAsE ratios 4:1, 3:2, 1:1, 2:3, 1:4. The net crystals of NAS and NAsE were also grown.

The composition of the crystals was determined on the basis of density measurements. The densities of net NAS and NAsE crystals equal 1.742 and 2.094 kg/dm^3 , respectively.

The dependence of the crystal composition on the concentration of the solution is shown in Fig. 1, where x is the molar fraction of NAsE. The static dielectric

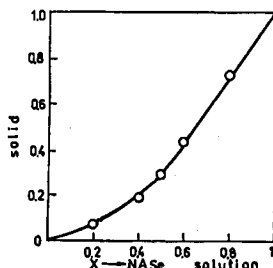


Fig. 1. Correlation between the composition of the solid state and the solution where x is the molar fraction of NAsE.

permittivity was measured at a frequency of 1 kHz using a Meratronic E 315a capacitance bridge.

The DTA (differential thermal analysis) measurements were performed by means of a Q-1500 D MOM type derivatograph.

The estimation of spontaneous polarization was performed by measurements of the pyroelectric effect by using an electrometer Unitra 219.

3. Results and discussion

For the NAS and NAsE crystals the dielectric anomaly is observed only along the c axis. The ferroelectric properties for NAS was discovered by Pepinsky et al. [15], while for NAsE by Aleksandrov et al. [16]. The temperature dependence of ϵ' for these crystals obtained by us is shown in Fig. 2a,b for NAS and NAsE respectively. The transition to ferroelectric phase is observed for NAsE at 172 K. Below T_c in the range of about 25 deg a high value of ϵ' is observed and then a drop in the permittivity is visible when the sample is cooled 25 deg below T_c .

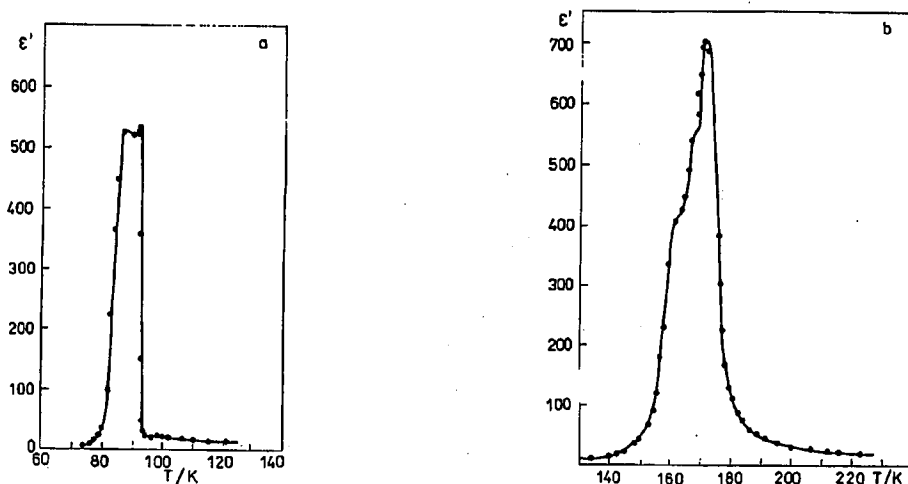


Fig. 2. Temperature dependence of ϵ' along the c axis for NAS (a) and NAsE (b).

The transition temperature for NAS is lower and equal to 92 K. Also for NAS a decrease in ϵ' was observed when the crystals were cooled 20–25 deg below the transition, the value of ϵ' in ferroelectric and paraelectric phases is almost the same. Both for NAS and NAsE the ϵ' value at T_c depends on the history of samples but for all of them the T_c value is almost the same. Such a behaviour is characteristic of these crystals and was confirmed especially for NAS crystal [17]. The results obtained from the linear electrooptical effect for NAsE [18] when compared with dielectric data indicate that the first anomaly at 172 K corresponds to the phase transition from paraelectric to ferroelectric phase and it is the second-order phase transition. The measurements of electrooptical effect under the polarizing field suggest that the second anomaly resemble the first-order phase transition.

The data obtained for this crystal indicate that the mechanism of the phase transition is still ambiguous [17–21], but it seems that the deformation of sulphate and selenate tetrahedra plays important role.

For the mixed crystals a similar dielectric behaviour is observed. The temperature dependence of the dielectric permittivity for chosen mixed crystals is presented in Fig. 3. In these crystals a decrease in the maximum ϵ' value should be pointed out. For all of them the range of enhanced permittivity is greater than for the net crystals. Simultaneously, the slope of permittivity versus temperature T_c becomes smaller.

The plots of ΔP versus temperature for mixed crystals are exemplified in Fig. 4a,b.

From these figures one can see that the temperature dependence of the spontaneous polarization, contrary to dielectric results, does not indicate any anomaly. Typical plots of ΔP were observed. This indicates that the second anomaly obtained in dielectric measurements is not connected with changes of spontaneous polarization.

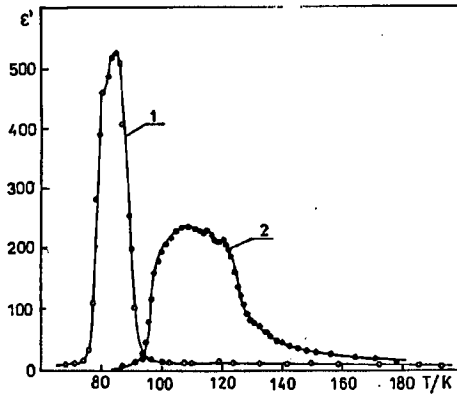


Fig. 3. Plots of ϵ' versus T for mixed crystals with $x = 0.075$ (1) and 0.74 (2).

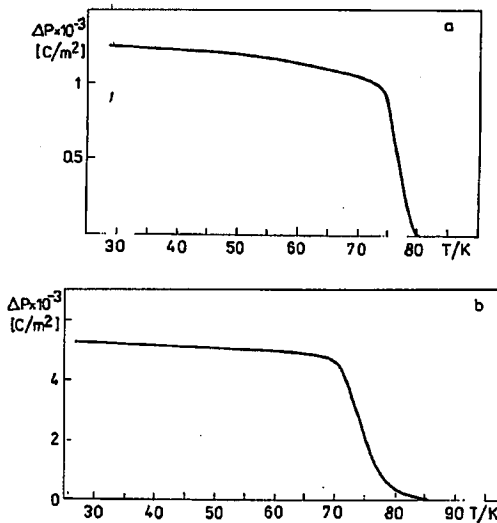


Fig. 4. ΔP plotted versus T for mixed crystals with $x = 0.18$ (a) and 0.43 (b).

On the basis of our results one can construct the phase diagram for the $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} - \text{NaNH}_4\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ system which is presented in Fig. 5. In this diagram the temperatures of dehydration obtained from DTA studies are also included. These temperatures are only slightly different for net and mixed crystals.

The effect of dehydration was also observed in dielectric measurements. Very high dielectric losses in this case have to be noticed. It is also worth noticing that during dehydration we do not observe the destroy of the samples.

Our studies show that in this system the relationship between the temper-

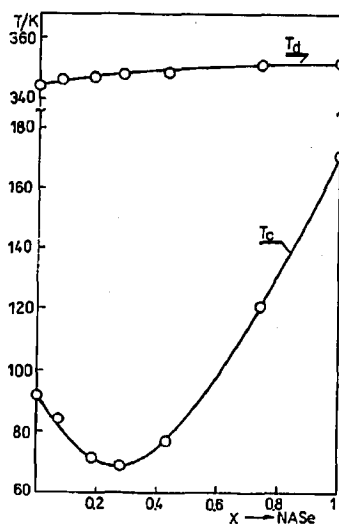


Fig. 5. Phase diagram for $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} - \text{NaNH}_4\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ crystals.

ature of transition to the ferroelectric phase and the concentration is nonlinear with negative deviation from linearity. For the mixed crystals of $0 < x < 0.3$ the value of T_c decreases below the transition temperature for NAS. The increase in T_c takes place for $x > 0.3$. Our diagram is very similar to that obtained for some alkali halide mixed crystal systems where the variation of melting point with composition has been examined [22]. It seems that relation between the transition temperature and the composition observed in our system may be explained according to Cahn [23] who assumed that the concentration of point defects and dislocations is greater in mixed than in pure crystals.

The substitution of SO_4 by SeO_4 ions makes a drastic changes in T_c to the concentration equal to 0.3. For the x value greater than 0.3 an increase in T_c is observed which suggests that from this concentration on the properties of mixed crystals become close to those of net NASe.

It is worth noticing that in our previous study an almost linear relation between T_c and the concentration of mixed [24] crystals was found.

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