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Dielectric Properties of $K_{1-x}(NH_4)_xH_2PO_4$ ($x = 0.095$) Crystal

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Temperature dependences of the dielectric permittivity were studied for the ferroelectric $K_{1-x}(NH_4)_xH_2PO_4$ mixed crystal. The experiments revealed presence of the beginning of the dipolar glass — embryos in the concentration of ammonium $x = 0.095$. Observations of the dielectric relaxations show much bigger effect domain mechanism than the one related to the growth of clusters of the dipolar glass.

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1. Introduction

The dipolar glass state can be realized in the mixed ferroelectric--antiferroelectric crystals of $K_{1-x}(NH_4)_xH_2PO_4$ (KADP). Dipolar glasses are related to the presence of random fields originating by nonequivalent replacement of the cations in the potassium sublattice. Random fields cause a glassy behavior of the dielectric properties in the KADP crystals.

In recent years, some measurements in the KADP crystals have been made [1–8]. The glass state of $K_{1-x}(NH_4)_xH_2PO_4$ occurs in the range of the concentration $0.25 < x < 0.65$ [1, 7, 8]. However, only few experiments were done on ferroelectric-side compounds around the boundary between the ferroelectric and the proton glass regime [3, 6–8]. This motivated us to continue our previous low temperature dielectric measurements [7, 8] on the KADP of a very small value of x, to look at the precursor of glass, the embryo of the proton glass.

2. Experimental method

The measurements were carried out for the crystal with the ammonium concentration $x = 0.095$. It was very important to determine the proper ammonium concentration x in the crystals. The relationship between the composition x in the crystal and the composition x in the aqueous solution is non-linear [1]. The concentrations x of KADP crystals were obtained by us from the X-ray measurements. Ono et al. [1] have shown linear relationship between the lattice tetragonal c axis and the composition x in the KADP crystal.

The small platelets were cut in two directions parallel and perpendicular to the tetragonal c-axis from a single crystal. The silver paste was used as electrodes.

The platelets were of the dimensions $1.1 \times 1.2 \times 0.25$ mm^3 for the KADP-c and $0.8 \times 1.3 \times 0.27$ mm^3 for the KADP-a. The measurements were performed in the helium flow cryostat enabling to decrease the temperature from 300 K down to 3.5 K with an error not greater than 0.1 K. The capacity of the sample was measured by HP 4275A bridge from 10 kHz to 1 MHz of the ac electric field. The magnitude of the ac measuring field was not higher than 5 V/cm.

3. Results

Figure 1 shows the temperature dependences of the electric permittivity $\varepsilon'(T)$ and $\varepsilon''(T)$ of the KADP $x = 0.095$ for the a and c axis, for the 20 kHz of the ac measurement electric field. The ferroelectric phase transition occurs at $T_\mathrm{c} = 106$ K for the c and a direction. This temperature is by 17 K lower than in the pure ferroelectric crystal of the KH_2PO_4. In the case of the c direction there is a second maximum $\varepsilon'(T)$ at $T = 67$ K of much bigger magnitude than at $T_\mathrm{c} = 106$ K and the ε'_c value in the temperature of 3.5 K remains about 103 (Fig. 1a). The anomaly at $T = 67$ K in the case of a direction is not so explicit but ε'_a is at the level of 93 in the lowest temperature in the experiment and does not decrease. The temperature dependence of the imaginary part of the electric permittivity ε''_a grows in the range of the temperature from $T = 65$ K to $T = 4$ K. The ε''_c value achieves maximum at the temperature of about $T = 45$ K and then decreases with the lowering of the temperature (Fig. 1b).

The data obtained for the temperature dependences of the complex electric permittivity along the crystallographic c-axis (Fig. 2) and a-axis (Fig. 3) for the different frequencies show the presence of the dielectric dispersion below the phase-transition temperature $T_\mathrm{c} = 106$ K.

In the dependence of $\varepsilon'_c(T)$ (Fig. 2a) below T_c the dispersion does not disappear up to the lowest temperature. It points to the presence of the other process, which coexists with the process of freezing of the domain wall-motions. This dispersion is due to the growth of the embryos of the proton glass phase. The maximum of the $\varepsilon''_c(T)$ moves into higher temperature with increasing frequency which is related to the domain wall response of the studied crystal (Fig. 2b).

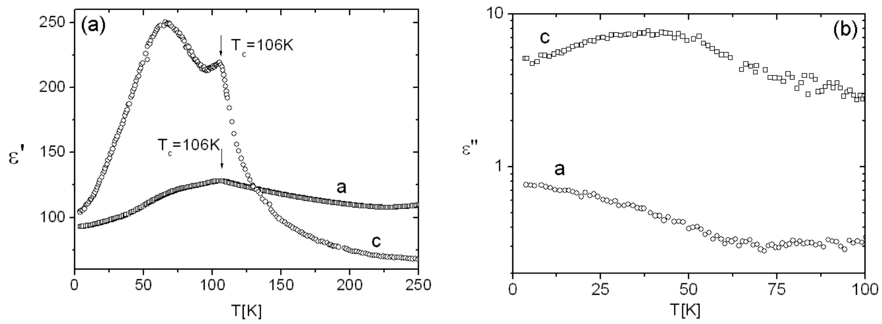

Fig. 1. The temperature dependence of the electric permittivity ε' (a) and of the imaginary part of the electric permittivity ε'' (b) of the KADP with $x = 0.095$ measured in the c and a crystallographic directions at the frequency of the ac measuring electric field 20 kHz.

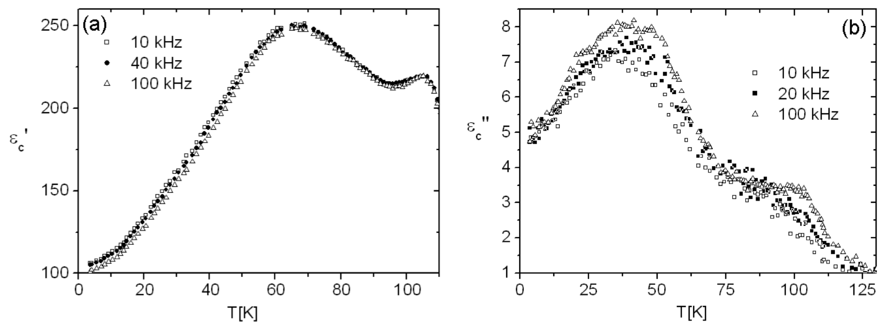

Fig. 2. The temperature dependence of the electric permittivity ε'_c (a) and of the imaginary part of the electric permittivity ε''_c (b) of the ferroelectric KADP with $x = 0.095$ for given values of the frequency.

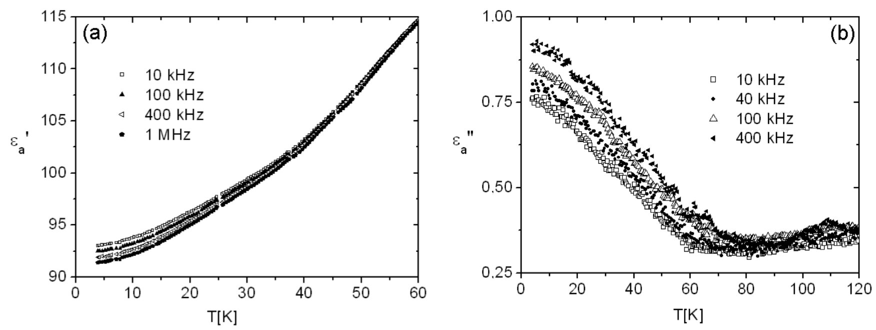

Fig. 3. The dispersion of the electric permittivity ε'_a (a) and of the imaginary part of the electric permittivity ε''_a (b) of the ferroelectric KADP with $x = 0.095$ for given values of the frequency.

4. Discussion and conclusions

Our study carried out on a sample $K_{1-x}(NH_4)_xH_2PO_4$ with $x = 0.095$ ammonium concentration revealed two coexisting dispersions in the measurements in the perpendicular crystallographic directions c and a below the temperature of the ferroelectric phase transition. By using dielectric technique, we have detected the precursor of the glass, the embryos of the glass clusters, in the mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystal. To obtain the freezing temperature T_g of the proton glass state in the crystal of this ammonium concentration, it will be necessary to do measurements in the lower temperatures. It turned out that the domain wall response is much stronger than the beginning of polar clusters formation along c. Measurements along c and a crystallographic directions enable to observe the coexistence of ferroelectric and proton glass state. There is a dispersion of the electric permittivity ε'_a and ε''_a (Fig. 3) related to the embryos of the glass clusters. This effect is stronger in a than in c direction. In this way, similarly as in our earlier paper [9] for the deuterated ferroelectric $Rb_{1-x}(ND_4)_xD_2AsO_4$ with $x = 0.04$, the second mechanism of the dielectric relaxation connected to the beginning of the "growth" of the glass state (embryos of the glass regime) detected in a crystallographic direction was not covered by the domain wall motion relaxation process. In the ferroelectric c direction we detected a large amplitude maximum of dielectric losses. Thus the "glass" relaxation cannot be well visible at low temperature in c direction.

References

[1] Y. Ono, T. Hikita, T. Ikeda, *J. Phys. Soc. Japan* **56**, 577 (1987).

[2] O.J. Kwon, J.J. Kim, *Phys. Rev. B* **48**, 6639 (1993).

[3] S.A. Gridnev, L.N. Korotkov, L.A. Shuvalov, R.M. Fedosyuk, *Ferroelectrics* **175**, 107 (1996).

[4] L.N. Korotkov, *Phys. Status Solidi B* **222**, R3 (2000).

[5] L.N. Korotkov, T.N. Korotkova, *Solid State Commun.* **115**, 453 (2000).

[6] L.N. Korotkov, L.A. Shuvalov, *Ferroelectrics* **285**, 67 (2003).

[7] Z. Trybuła, J. Kaszyński, *Ferroelectrics* **298**, 347 (2004).

[8] Z. Trybuła, J. Kaszyński, H. Małuszyńska, *Ferroelectrics*, in press.

[9] Z. Trybuła, J. Kaszyński, Sz. Łoś, S. Mielcarek, M. Trybuła, *Phys. Status Solidi B* **241**, 447 (2004).