Effect of magnetic field application on phase transition in nanostructured solid solutions (1 − x)KH2PO4 − x(NH4)H2PO4 at x = 0, 0.05 and 0.15 has been studied by dielectric spectroscopy at B = 0 − 10 T. The samples have been prepared by impregnation of magnetic porous glasses by KDP-ADP solid solutions. The average pore diameter in glasses was 50(5) nm. The temperatures of the ferroelectric phase transition have been determined, and the phase diagrams for these nanocomposite materials (NCM) on cooling and heating (including at magnetic field application) were constructed. The interface “matrix-nanoparticles” was shown to play the principal role in phase diagram formation.

**Keywords:** ferroelectrics, antiferroelectrics, phase diagram, nanocomposite materials, magnetic porous glasses.

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1. Introduction

It is known that a restricted geometry drastically modifies the macroscopic properties of nanostructured materials, especially when the correlation length of corresponding interaction becomes comparable with a characteristic size of nanoparticles. In the majority of nanocomposite materials (NCM), the host matrices play a passive role forming the conditions of restricted geometry only, except the interface “embedded material – matrix”. At the Ioffe Institute (in cooperation with Leibniz University of Hannover – LUH) we have developed a procedure for preparing porous alkali borosilicate glasses with magnetic properties [1, 2]. These glasses have positive linear and volume magnetostriiction coefficients [3] and can be named “active host matrix” as they can participate in modification of macroscopic properties of embedded materials due to the appearance of additional strains on the interface “matrix-nanoparticles” upon magnetic field application. The phase diagram for the bulk KH2PO4 (KDP) and (NH4)H2PO4 (ADP) solid solutions (KADP) are known [4, 5] and it is shown that a small admixture of ADP leads to a drastic decreasing of the ferroelectric phase transition temperature TC. In previous work [6] we studied the effect of restricted geometry on this phase transition for NCM based on conventional porous glasses (PG) with KADP at low ADP concentrations. It has been revealed that there are the shifts in the ferroelectric phase transition temperature, to higher temperature TC, as a function of ADP concentration on cooling and heating in comparison with the bulk KADP at the same (NH4)H2PO4 concentrations. So the effect of ADP admixture on TC in confinement becomes less pronounced than in the bulk KADP. The principal goal of the present work was to study the influence of applied magnetic fields on TC for NCM based on magnetic glasses with internal parameters similar to those of nonmagnetic alkali borosilicate glasses in the paper [6].

2. Experimental part

Magnetic glasses have been produced at LUH by induction melting process using convection and electromagnetic agitation [1, 2]. Rectangular plates of the size of 10 × 10 × 0.5 mm3 were cut out from the original glass. Porous glasses were obtained by two-stages etching of magnetic glass after phase separation procedure. These glasses contained about 87 % of SiO2 and about 6 % of magnetite into the matrix skeleton. The average pore diameter, which was determined by adsorption poroscopy, was about 50(5) nm (macroporous glasses – MAP). The total porosity of porous glasses was about 45 %. KDP-ADP (KADP) solid solutions were embedded into the pores from an aqueous solution with triple recrystallization. The pore filling achieved 35 % for the 5 % ADP sample and 38 % for the 15 % ADP sample. The dielectric response was studied using a capacitance bridge at 1 kHz in
the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland). The temperature
dependences of the samples’ capacitances were measured from 40 – 200 K, but in all figures (for visibility), only
the smaller diapasons in the vicinity of phase transitions are shown. “Cooling–heating” cycles were repeated twice
for every sample during the experiment. The temperature stability was better than 0.1 K. The applied magnetic
fields were varied from 0 – 10T. The nanoparticles’ crystal structures were studied using X-ray diffractometry
(Supernova, Agilent Technologies) using Cu Kα line (in SPbPU) and corresponded to structure of the bulk KDP-
ADP solid solutions at low ADP concentrations. The average size of nanoparticles, which was estimated from
broadening of elastic peaks, was ∼ 40 nm.

3. Results and discussion

The typical temperature dependence $C(T)$ of sample capacitance at magnetic field $B = 10$ T is presented in Fig. 1
for NCM 0.95KDP-0.05ADP on cooling and heating.

![Graph showing temperature dependence of capacity](image)

**Fig. 1.** Temperature dependence of capacity of NCM 0.95KDP – 0.05ADP on cooling and heating at magnetic field $B = 10T$

The principle feature of all dependences $C(T)$ is the presence of a shift in the maximum position on cooling
and heating. We have observed a similar hysteresis for NCM based on conventional PG [6] with embedded
KADP. Temperatures of ferroelectric phase transition ($T_C$) on cooling and heating have been determined from the
maximum positions for every sample, with an accuracy in the determination of $T_C$ of better than 0.1 K. In Fig. 2
the dependences of $T_C$ on cooling as a function of the ADP admixture are presented for PG and magnetic MAP
glasses.

It is easy to see that on cooling, the $T_C$ for MAP glasses decreases at higher ADP concentration, as for
PG-based NCM, but for MAP glasses, this curve follows a little bit higher. This may occur due to different
nanoparticle sizes in these glass types: in PG-type glasses the nanoparticle size was about 50 nm. Upon magnetic
field application, the behavior of $T_C$ as a function of ADP concentration changes essentially. Upon cooling,
(Fig. 3a) the shift of $T_C$ is practically independent of magnetic field.

On heating, we have observed the reliably identifiable difference in the $T_C$ values in magnetic field and without
it (Fig. 3b). It can be explained by multidirectional effects of glass volume thermal expansion (or compression
on cooling) $\alpha_3$ and magnetostriction. Indeed, on heating, both coefficients are positive, but on cooling, the $\alpha_3$
coefficient of KDP changes sign while the coefficient of volume magnetostriction remains positive. In this manner,
on cooling, both mechanisms compensate each other and the decrease of $T_C$ at higher ADP concentrations is an
internal feature of these solid solution nanoparticles. The final results for nonmagnetic and magnetic glasses are
presented for comparison in Table 1.

4. Conclusion

Introduction of ADP admixture into KDP nanoparticles leads to a decrease in the ferroelectric phase transition
temperature $T_C$ in NCM on base of magnetic MAP glasses, but this decrease is essentially smaller than in
the case of bulk solid solutions at the relevant concentrations. Application of an internal magnetic field does
not practically change $T_C$ on cooling. It is most likely that this effect relates to the multidirectional influences of
Phase diagram for $K_{(1-x)}(NH_4)_xH_2PO_4$ ($x = 0 - 0.15$) solid solutions embedded into magnetic glasses

![Diagram](image1.png)

**Fig. 2.** Dependence of $T_C$ as a function of ADP concentration for conventional PG [6] and magnetic MAP glasses on cooling without magnetic field.

![Diagram](image2.png)

**Fig. 3.** Dependences of $T_C$ as a function of ADP concentration for magnetic MAP glasses on cooling (a) and on heating (b) without magnetic field (black squares) and at magnetic field $B = 10T$ (black circles).

thermal compression and positive magnetostriction of MAP glasses at temperature decreasing: the both mechanisms compensate each other. On heating, they act in one direction and in this case $T_C$ becomes slightly higher. As a result, we have observed the temperature hysteresis between $T_C$ on cooling and on heating. It is worth noting that the effect of restricted geometry on $\Delta T_C$ in NCM on base of magnetic glasses for the pure KDP is larger than in NCM with embedded KADP solid solutions. The explanation is the temperature dependence of the volume expansion coefficient $\alpha_3$ for the pure KDP. According to literature data [13] $\alpha_3$ on heating from 90 to 130 K (in the vicinity of phase transition) decreases from $25 \cdot 10^{-6}$ to $(-)57 \cdot 10^{-6}$, i.e. this coefficient changes the sign and becomes a positive again above $\sim 126$ K only. In this manner, on heating, the properties of NCM is determined by competition on interface “host matrix – embedded material” of thermal compression of KDP itself and thermal expansion of glass, including the additional input due to positive magnetostriction. On cooling, the situation changes drastically: we have only one positive (magnetostriction) and two negative inputs (compression of KDP and glass). ADP has a positive and large ($\sim 45 \cdot 10^{-6}$ and more) coefficient $\alpha_3$ in the whole temperature interval, including a vicinity of the ferroelectric phase transition in KDP. It is logical to suppose that the admixture of ADP modifies the coefficient $\alpha_3$ and the effects on interface become less pronounced. In summary, one can
conclude that the phenomena on interface “host matrix- embedded KADP solution” play the principle role in the formation of the phase diagram for KADP in a restricted geometry.

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References


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