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Phase diagram for $K_{(1-x)}(NH_4)_{(x)}H_2PO_4$ ($x = 0 - 0.15$) solid solutions embedded into magnetic glasses

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Effect of magnetic field application on phase transition in nanostructured solid solutions $(1-x)KH_2PO_4$ – $(x)(NH_4)H_2PO_4$ at $x = 0$, 0.05 and 0.15 has been studied by dielectric spectroscopy at $B = 0 - 10T$. 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 magnetostriction 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-nanoparticle" upon magnetic field application. The phase diagram for the bulk KH_2PO_4 (KDP) and $(NH_4)H_2PO_4$ (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 T_C. 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 T_C, as a function of ADP concentration on cooling and heating in comparison with the bulk KADP at the same $(NH_4)H_2PO_4$ concentrations. So the effect of ADP admixture on T_C 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 T_C 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 $10 \times 10 \times 0.5$ mm^3 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 SiO_2 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 $K\alpha$ 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 $\sim$ 40 nm.

3. Results and discussion

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

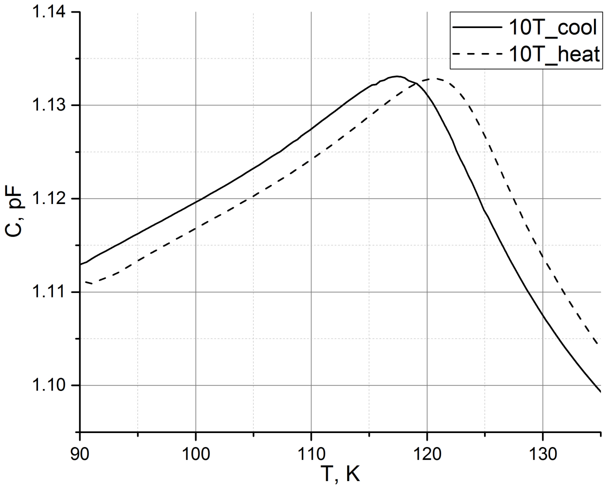


FIG. 1. Temperature dependence of capacity of NCM 0.95KDP – 0.05ADP on cooling and heating at magnetic field $B = 10T$

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) α_3 and magnetostriction. Indeed, on heating, both coefficients are positive, but on cooling, the α_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

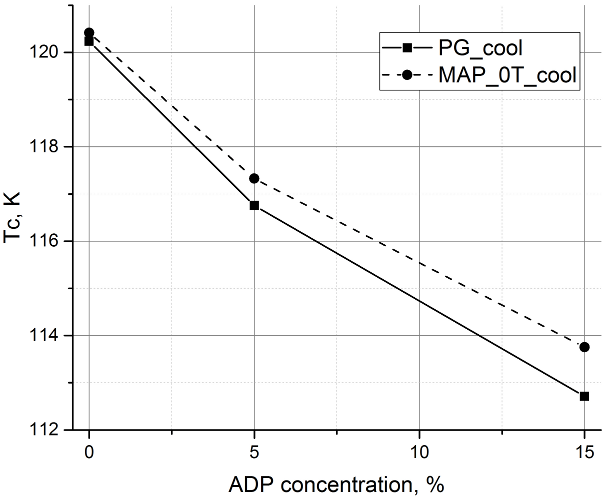
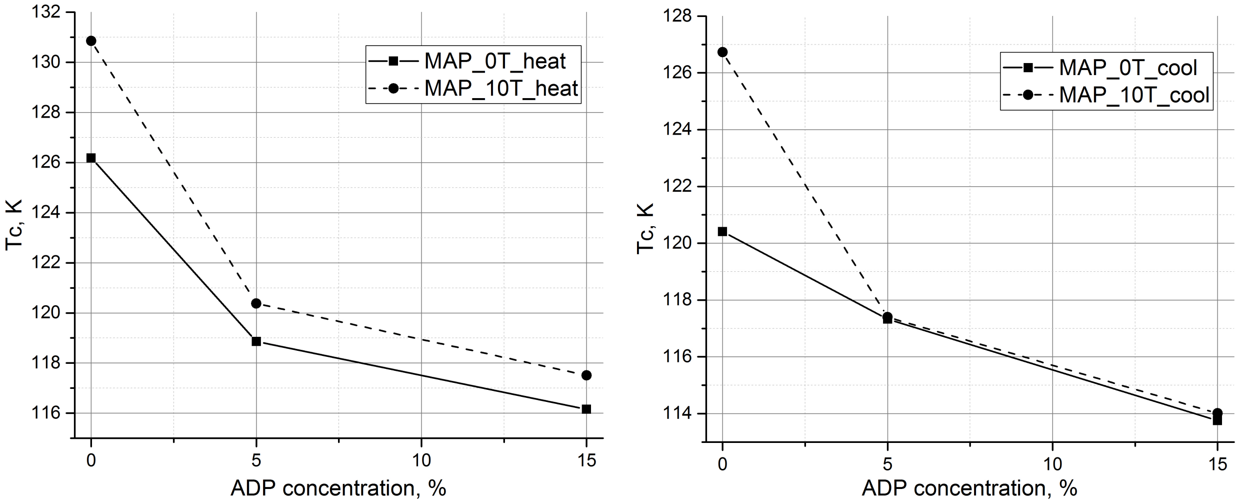


FIG. 2. Dependence of T_C as a function of ADP concentration for conventional PG [6] and magnetic MAP glasses on cooling without magnetic field



(a) (b)

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 ΔT_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 α_3 for the pure KDP. According to literature data [13] α_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 α_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 α_3 and the effects on interface become less pronounced. In summary, one can

TABLE 1. T_C values for NCM with embedded KADP solid solutions on base of PG and MAP glasses on cooling and heating and at applied magnetic fields

ADP concentration, %				**0**	**5**	**15**
Bulk samples [7–12]			T_C, K	~ 122	104.2	~ 73
Present work KDP-ADP nanoparticles	**Nonmagnetic glass**		$T_{C(cooling)}$, K	120.2 ± 0.1 [5]	116.7 ± 0.1	112.7 ± 0.1
			$T_{C(heating)}$, K	126.2 ± 0.1	119.8 ± 0.1	114.8 ± 0.1
			$\Delta T_C = T_{C(cooling)} - T_{C(heating)}$, K	6	3.1	2.1
	Magnetic glass	$B = 0$	$T_{C(cooling)}$, K	120.4 ± 0.1	117.3 ± 0.1	113.8 ± 0.1
			$T_{C(heating)}$, K	126.2 ± 0.1	118.9 ± 0.1	116.2 ± 0.1
			$\Delta T_C = T_{C(cooling)} - T_{C(heating)}$, K	5.8	1.6	2.4
		$B = 10$	$T_{C(cooling)}$, K	126.7 ± 0.1	117.4 ± 0.1	114.0 ± 0.1
			$T_{C(heating)}$, K	130.9 ± 0.1	120.4 ± 0.1	117.5 ± 0.1
			$\Delta T_C = T_{C(cooling)} - -T_{C(heating)}$, K	4.2	3.0	3.5

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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