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Phase transitions in nanostructured $K_{1-x}(NH_4)_{(x)}H_2PO_4$ (x = 0 - 0.15) solid solutions

P. Yu. Vanina[1], A. A. Naberezhnov[2], O. A. Alekseeva[1], A. A. Sysoeva[2], D. P. Danilovich[3], V. I. Nizhankovskii[4]

[1]Peter the Great Saint Petersburg Polytechnic University, Polytechnicheskaya, 29, St. Petersburg, 195251, Russia

[2]Ioffe Institute, Polytechnicheskaya, 26, St. Petersburg, 194021, Russia

[3]Engineering center of St. Petersburg State Technological Institute, Moskovsky prospect, 26, St. Petersburg, 190013, Russia

[4]International Laboratory of High Magnetic Fields and Low Temperatures, Gajowicka, 95, Wroclaw, 53-421, Poland

p.yu.vanina@gmail.com, alex.nabereznov@mail.ioffe.ru, blackhole2010@yandex.ru, annasysoeva07@mail.ru, dmitrydanilovich@gmail.com, nizhan@ml.pan.wroc.pl

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Effect of ammonium dihydrogen phosphate admixture on phase transitions 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. The samples have been prepared by embedding of aqueous solutions into porous borosilicate glasses. The X-ray diffraction have shown that the crystal structure at room temperature corresponds to the bulk KDP and the average nanoparticle diameters are 49 (2) nm for the sample with 5 % of $(NH_4)H_2PO_4$ (ADP) and 46 (2) nm for the nanocomposites with 15 % of ADP. Dielectric response data analysis have revealed the shifts of the ferroelectric phase transition temperature as a function of $(NH_4)H_2PO_4$ concentration: at $x = 0$ ΔT_C is equal to ∼6 K, at $x = 0.05$ ΔT_C ∼3 K and at $x = 0.15$ ΔT_C ∼2 K.

Keywords: ferroelectrics, antiferroelectrics, phase transitions, nanocomposite materials.

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1. Introduction

Studies of size effect (or restricted geometry) in nanostructured systems with different topologies and dimensions in recent years have been significantly stimulated by the intensive development of nanotechnologies. The brightest example of similar systems is nanocomposite materials: polar dielectrics embedded into porous matrices that have a branched network (dendrite-like) through pores. The embedded materials form either a system of isolated particles or a complex dendritic structure, determined by the size and topology of the pores of the host matrix, surface tension, wettability, and so on. [1].

Nanocomposite materials (NCM) based on micro- and macroporous borosilicate glasses have been created at the Ioffe Institute. Pores in these glasses form a through dendritic three-dimensional system, the total porosity (depending on the average pore diameter) can reach 40–50 % of the sample volume. Previously, it has been shown that NCM based on conventional non-magnetic porous matrices containing embedded hydrogen-containing ferroelectrics KH_2PO_4 (KDP) and $(NH_4)H_2PO_4$ (ADP) in a confined geometry, demonstrate the dielectric response anomalies.

Despite the fact that KDP and ADP crystals belong to the same family and have a close chemical composition, at the same time, the baric effect in KDP is stronger than in ADP [2]. On the one hand, the increase of the dielectric constant at low frequencies and the growth of ferroelectric phase transition (PT) temperature have been clearly observed with a decrease in the average pore diameter for KDP [3]. Later, this growth in KDP and ADP nanoparticles has been explained assuming that tensile strains arising from heating due to the difference in the coefficients of thermal expansion for the embedded material and the matrix itself [4].

NCM based on macroporous glasses (PG) with average pore diameter from 20 nm to 60 nm (median value was 45(5) nm), containing embedded $(1-x)$KDP–(x)ADP mixture at $x = 0.05$ and 0.15 have been made for testing the possible phase transition temperature shift, depending on ADP admixture. NCM containing embedded pure KDP has been studied earlier in the paper [5].

2. Experimental part

The studies have been carried out on a capacitance bridge at 1 kHz in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland). The samples appear to be plates of macroporous glass with KDP-ADP (KADP) mixtures embedded into the pores from aqueous solution with triple recrystallization. The pore filling achieved 35 % for 5 % ADP sample and 38 % for 15 % ADP sample. The temperature dependences of the sample capacitances have been measured at temperatures ranging from 40–200 K, but in Figures for clearance, only the smaller diapasons in the vicinity of the phase transitions are shown. "Cooling-heating" cycles have been repeated twice for every sample during the experiment. The temperature stability was better than 0.1 K.

X-ray diffraction measurements have been performed at the Engineering Center of the St. Petersburg State Technological Institute (technical university) on the Rigaku Smartlab X-rays diffractometer in order to characterize the samples. We have used Cu K_α line, the wavelengths were 1.540593 Å for $K_{\alpha1}$ and 1.544414 Å for $K_{\alpha2}$ lines, respectively. The value of the intensity ratio in the doublet was equal to $I_{\alpha1}/I_{\alpha2} = 0.497$. X-ray diffraction experiments have been carried out at room temperature with germanium monochromator, the angular diffractometer resolution was of $\sim$0.05 °.

3. Results and discussion

On the first stage we have characterized all our samples using X-ray diffraction at room temperature (RT). In Fig. 1 the diffraction pattern for 0.95KDP+0.05ADP sample at RT and the results of fitting are presented.

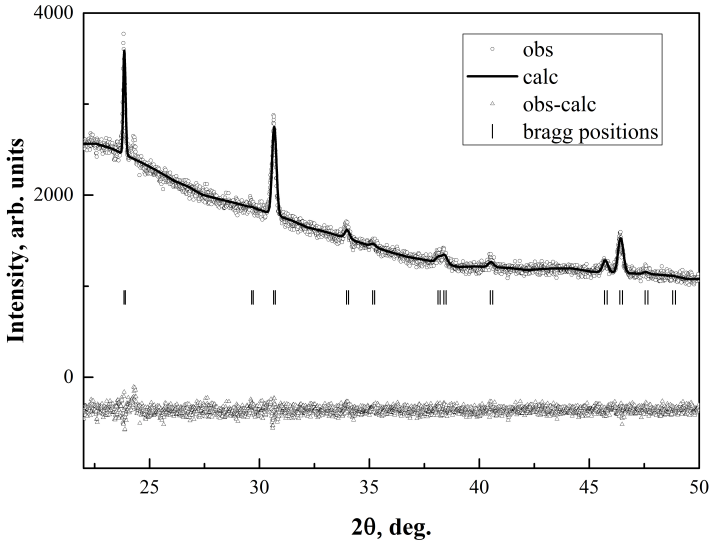

FIG. 1. X-ray diffraction pattern for 0.95KDP+0.05ADP sample at RT. Solid line ("calc") corresponds to profile analysis, open circles ("obs") – experimental data. Vertical bars – Bragg positions, the triangles in the bottom ("obs-calc") part is the difference between experimental data and fitting

The diffraction peak splitting observed in Fig. 1 occurs because of proximity of the $K_{\alpha1}$ and $K_{\alpha2}$ lines. Since the embedded materials are the solid solutions of KDP-ADP with a small admixture of ADP, the structures of these nanocomposites have to be close to the structure of KDP and according X-rays diffraction correspond to the spatial group **I-42d**, as well as the bulk KDP at RT, with the unit cell parameters $a = b = 7.459$ and $c = 6.994$ Å. It is also worth noting that the refined unit cell parameters are well correlated with the data obtained earlier for example by the authors [6]: $a = b = 7.448$ and $c = 6.977$ Å. From the broadening of elastic reflections we have estimated the average particle diameters: they are equal to 49 (2) nm for the sample with 5 % of ADP, 46 (2) nm for the sample with 15 % of ADP and 53(5) for NCM with a pure KDP.

Next, the temperature dependences of the capacities of the samples with 5 % and 15 % ADP mole admixture were measured (Fig. 2(b,c)) on cooling and heating. As a reference data, we have used our results related to the capacity of NCM on base of macroporous magnetic glasses with an average pore diameter of 50 nm filled by a pure KDP (Fig. 2(a)) [5].

From the $C(T)$ dependences on Fig. 2(a,b,c) it can be seen that the capacity maxima shift to the lower temperatures at increasing of the ADP admixture both on cooling and heating. It is necessary to note that there

are the temperature hysteresis (ΔT_C) between maximum $C(T)$ positions on cooling and on heating decreases with an increase in ADP concentration in the KADP mixture. The positions of maxima in $C(T)$ dependences and the values of ΔT_C for every sample coincide at repetition of "cooling-heating-cooling" cycles and depend only on the ADP concentration.

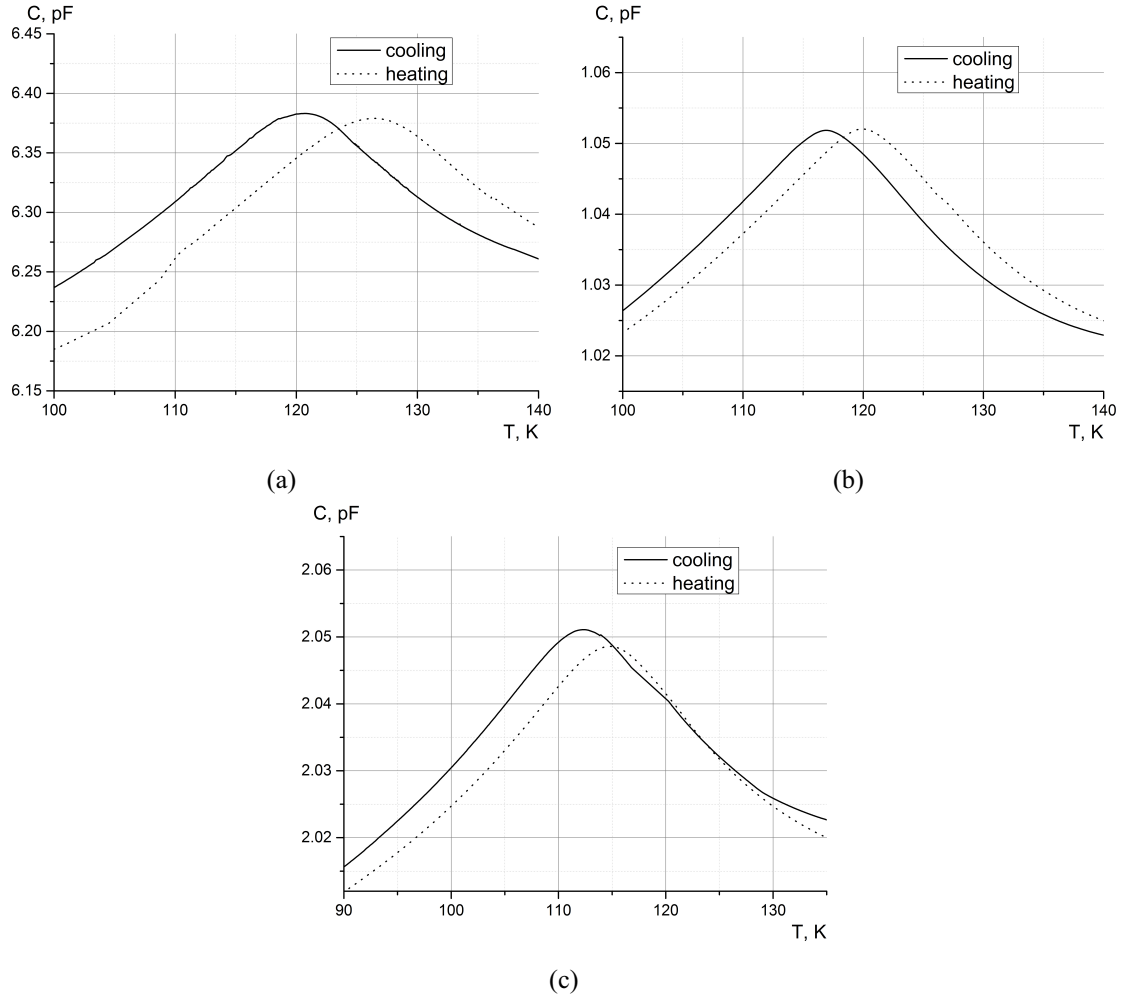

FIG. 2. The temperature dependences of the capacity for KADP samples with ADP concentrations 0 % (a) [5], 5 % (b) and 15 % (c) on cooling (solid lines) and heating (dotted lines)

The temperatures of ferroelectric phase transitions have been determined as the position of $C(T)$ maximum after fitting of temperature dependences of sample capacity in a vicinity of PT by the Lorentz function. The errors in determination of $C(T)$ maximum do not exceed 0.05 K.

For the bulk KADP the strong tendency of decreasing of T_C at increasing of APD concentration [9–11] exists, but the detail phase diagram stays ambiguous because the properties of bulk KADP essentially depend on preparation methods [12]. Concerning the thermal hysteresis value ΔT_C in the position of T_C on cooling and on heating, this factor remains unexplored until now.

Figure 3 shows the Curie temperatures T_C in KADP embedded into macroporous glasses as a function of ADP concentration. From these dependences, it is easy to see that the temperatures of phase transition on cooling and on heating shift gradually to lower temperatures, but these shifts are essentially smaller than in the bulk. Simultaneously the temperature hysteresis ΔT_C decreases with increased ADP concentration. The obtained results in comparison with literature data [6–11] for the bulk KADP are presented in Table 1.

4. Conclusion

We have studied the dielectric properties and crystal structure of $K_{(1-x)}(NH_4)_{(x)}H_2PO_4$ (KADP) nanoparticles at $x = 0 - 0.15$ prepared on basis of macroporous glasses by using aqueous solution impregnation. At RT the

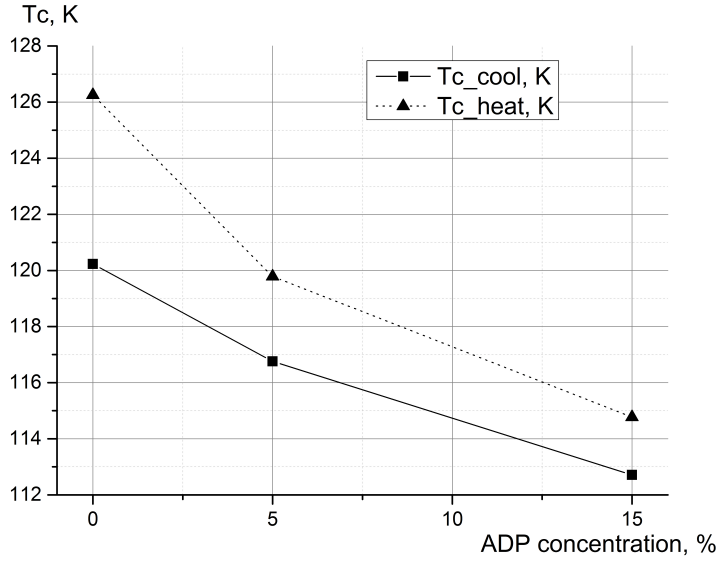

FIG. 3. The concentration dependences of the phase transition temperatures obtained on cooling and heating

TABLE 1. Temperatures of phase transitions in $K_{(1-x)}(NH_4)_{(x)}H_2PO_4$ solid solutions

	Bulk [6–11]	Present work KADP nanoparticles			
	T_C, K	$T_{C(cooling)}$, K	$T_{C(heating)}$, K	$\Delta T_C = T_{C(cooling)} - T_{C(heating)}$, K	Nanoparticle size, nm
$x = 0$	∼122	120.2±0.1 [5]	126.2±0.1	6	53±5
$x = 0.05$	104.2	116.7±0.1	119.8±0.1	3.1	49±2
$x = 0.15$		112.7±0.1	114.8±0.1	2.1	46±2
$x = 0.165$	64.5				

crystal structure of KADP embedded into the pores corresponds to the bulk structure. The average nanoparticle diameters are equal to ∼53(5) nm for the pure KDP nanoparticles, 49(2) nm for the sample with 5 % of ADP and 46(2) nm for 15 % of ADP. Analysis of dielectric response data has revealed the shifts of the ferroelectric phase transition temperature, T_C, as a function of ADP concentration on cooling and heating in comparison to the bulk KH_2PO_4 (KDP), but these shifts are essentially smaller than in the bulk KADP (relatively T_C in KDP) at adequate ADP concentrations. One can note that the increasing of ADP concentration in nanostructured KADP leads to decreasing $T_{C(cooling)}$, $T_{C(heating)}$ and ΔT_C. Most likely the increasing of T_C in NCM in comparison with the bulk materials can be associated with a presence of strains on the "host matrix–embedded materials" interface due to the discrepancy in thermal expansion coefficients.

Acknowledgments

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