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Ferroelectric Nanocomposites With Governed Interface on Base of Magnetic Porous Glasses

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***Abstract* — Two-phase (nonporous) magnetic alkali borosilicate glasses have been produced by induction melting. Their macroscopic properties and crystal structure have been studied and it is shown that in the silica skeleton there are the agglomerates of Fe_3O_4. These agglomerates are formed by monodomain nanoparticles of magnetite and demonstrate the superparamagnetic properties. After special thermal treatment (liquation process) and chemical etching the nanoporous matrices with random dendrite pore structure and magnetic properties have been produced. The channels (porous space) were filled by ferroelectric materials KH_2PO_4(KDP), KH_2PO_4+$(NH_4)H_2PO_4$ (KDP-ADP or KADP), and $NaNO_2$ and the effect of applied magnetic fields on phase transitions in these nanocomposite have been studied. It has also been established that a restricted geometry changed essentially the phase diagram of KADP.**

Keywords – magnetic glasses, nanocomposite materials, restricted geometry, interface, artificial multiferroics

I. Introduction

Mesoporous silica materials, especially alkali borosilicate glasses with magnetic properties, attract steadfast interest because of their unique physicochemical properties such as a low thermal expansion coefficient, perfect chemical and mechanical stability, a large and controllable porosity, a high surface area, tunable pore sizes and volumes, interesting optical and magnetodielectric characteristics [1–14]. The skeleton of these glasses is organized by rigid groups SiO2 and has an amorphous crystal structure. The pores form 3D dendrite random interconnected network, which is very suitable for deposition and incorporation of different guest molecules (substances) to produce multifunctional materials with unique capabilities and properties. The average pore diameter one can controllable change in a wide diapason from units to hundreds nanometers, the porous space achieves 40% from the total volume of glass sample. At present time these nanoporous matrices with magnetic properties use in medicine and in biology [2, 8-13], in magneto-optic devices [3,5,7], as different kinds of sensors [13] et cetera . It is important to note that in all the mentioned above cases the matrices themselves play a passive role providing conditions of a restricted geometry, and the magnetic nanoparticles synthesize into the pore space. However, one can realize another approach: to create the "active" porous media, which participates in modification of embedded material properties. Here the term "active" means that the magnetic properties become intrinsic feature of matrix itself. It is necessary to underline that these matrices can be used as a model object for creation of novel multifunctional materials, for example multiferroics with spatially separated coexisting magnetic and ferroelectric orderings and with a large interface between these subsystems. By acting on the interface (using temperature, external magnetic or electric fields, pressure and so on), we are able to govern the phase state of embedded substances, for example, due to elastic stresses. It should be note that this technology permits to produce artificial multiferroics possessing ferroelectric and magnetic properties at room temperature that is very attractive for application. The principle purpose of this contribution has been to study the properties of porous magnetic glasses and some nanocomposite materials (NCM) on base these matrices containing embedded ferroelectrics..

II. Samples and methods

For the first time the production of alkali borosilicate glasses with magnetic atoms into the matrix skeleton was realized in the paper [15] by melting in a platinum crucible with mechanical stirring. Their macroscopic properties and crystal structure have been studied [6,16]

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and we have proved the existence of magnetic properties of these glasses. Later we have developed a novel method of magnetic glass production – induction melting [17,18]. Magnetic properties of produced magnetic glasses were studied by SQUID. Crystal structure of produced porous magnetic glasses was studied by X-ray diffractometer (Supernova, Agilent Technologies) using $Cu_{K\alpha}$ line. The average pore diameter, which was determined by adsorption poroscopy, was about 54(5) nm (macroporous glasses – MAP). 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 (ILHMFLT, Wroclaw, Poland). The temperature dependences of the samples capacitances were measured from 40 – 200 K on cooling and heating at different applied magnetic fields. Temperatures of phase transitions were determined from a position of maximum in the capacity vs. temperature dependences. Temperature stability was better 0.1 K at measurements in ILHMFLT. The applied magnetic fields were varied from 0 to 10 T. The filling of MAP glasses by $NaNO_2$ was carried out from melt under vacuum. In a case of NCM MAP+$NaNO_2$ we have studied the temperature evolution of crystal structure of sodium nitrite on heating and cooling at the temperature interval RT- 460 K, i. e. below and above the ferroelectric phase transition (437 K in the bulk material), on the neutron diffractometer E9 (Helmholtz Zentrum Berlin, reactor BER II). The applied magnetic field was change from 0 till 2 T only due to some experimental restriction. Temperature stability was better 2 K.

III. Results and discussion

Magnetic macroporous glasses

The X-ray diffraction pattern of the empty MAP glass and the model spectrum for Fe_3O_4 are presented in Fig.1.

One can see that there are very good agreement between both parts, the additional peaks on the top part correspond to sample environment. The elastic peaks are essentially broaden due to size effect and using this information we have determined the characteristic size of Fe_3O_4 nanoparticles – 18 (3) nm. It means that in the matrix skeleton there are monodomain magnetite nanoparticles [19]. AFM and MSM data have shown that these nanoparticles have been self-organized in large agglomerates [20]. The additional evidence of presence of magnetite in the matrix have been obtained at studies of temperature evolution of magnetic properties of glasses at two regimes: Field Cooling (FC) at H= 100 Oe and Zero Field Heating after Field Cooling (ZFHaFC) – Fig 2. The anomaly at ~ 120 K corresponds to so-called Verwey transition existing in Fe_3O_4 only at this temperature. The difference between FC and ZFHaFC regimes testifies that Fe_3O_4 nanoparticles form a superparamagnetic system with very high irreversibility temperature (near 300 K).

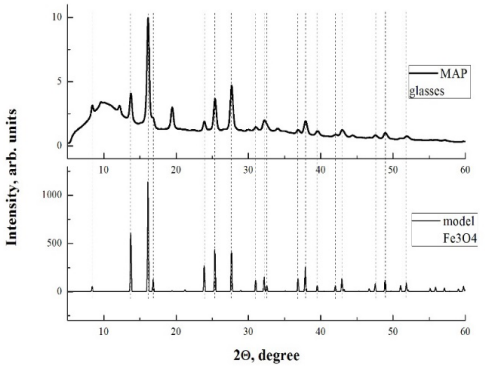

Fig. 1. Diffraction pattern for MAP glasses (top part) and model pattern for magnetite (bottom part) at RT. The vertical lines indicate the position of elastic peaks characterizing magnetite

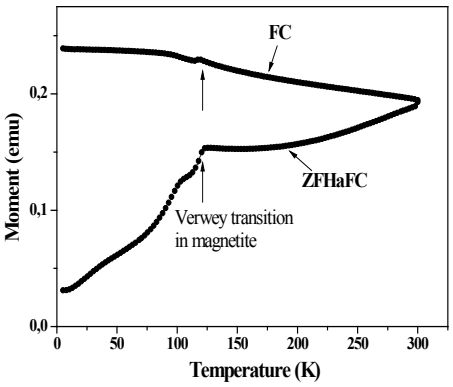

Fig. 2 Temperature dependence of magnetization of MAP glasses at FC and ZFHaFC regimes. Arrows point out the positions of Verwey transition in the bulk Fe_3O_4

Ferroelectric nanocomposites on base of MAP glasses

Initially we have characterized our samples with embedded KADP nanoparticles by X-ray diffraction. 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. From the broadening of elastic peaks 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. So the nanoparticle sizes coincide practically with average pore diameter in the MAP glasses. Further we have measured the temperature dependences of sample capacities on heating and cooling and have determined the temperatures (T_C) of ferroelectric phase transition. The obtained T_C values are presented in Table 1. As a reference sample we have used the conventional (nonmagnetic) alkali borosilicate glasses with average pore diameter 46(3) nm. The size of nanoparticles in this case was practically the same.

TABLE I

T_C FOR NCM KADP+MAP GLASS ON HEATING AND COOLING AS A FUNCTION OF APPLIED MAGNETIC FIELDLS

ADP concentration, %				0	5	15
Bulk samples [21, 22]			T_C, K	~ 122	104.2	-
Present work KDP-ADP nanoparticles	Nonmagnetic glass		$T_{C(cooling)}$, K	120.2±0.1	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	$T_{C(cooling)}$, 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	$T_{C(cooling)}$, 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

It is known that a small admixture of ADP leads to a drastic decreasing of the ferroelectric phase transition temperature T_C [21] (Fig.3), but as it is easy to see in a restricted geometry without an external magnetic field the T_C increases essentially at growth of ADP concentration in comparison with the bulk KADP solutions. Application of magnetic field increases (Table 1) T_C both during heating and cooling. It is necessary to note that the effect of ADP admixture on T_C in confinement becomes less pronounced than in the bulk KADP.

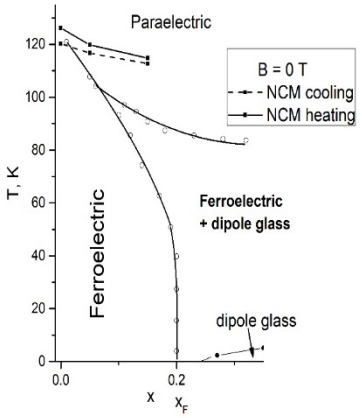

Fig. 3 Dependences of T_C in NCM KADP+MAP glasses on heating and cooling at B = 0 T

The observed shifts of T_C and the appearance of thermal hysteresis can be explained by the multidirectional influences of thermal compression (or expansion) plus positive magnetostriction of MAP glasses [23] on cooling and heating depending on magnetic field and temperature variation of thermal expansion coefficients for KADP or KDP [24]. On cooling the action of a part of these coefficients is compensated by positive magnetostriction. 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 ΔT between T_C on cooling and on heating. This fact points out that the appearance of additional tensile strains due to application of magnetic field effects really on T_C. The role of the form and tensile strains has been considered in the theoretical paper [25] for NCM on base of two types of porous glasses for $BaTiO_3$ and $PbTiO_3$ nanoparticles and it has been shown that the shift of T_C depends on an asymmetry of nanoparticle form and type of matrix.

The next sample was the magnetic MAP glasses with sodium nitrite embedded into the porous space. In this case we have studied the temperature evolution of crystal structure of this NCM by neutron elastic scattering

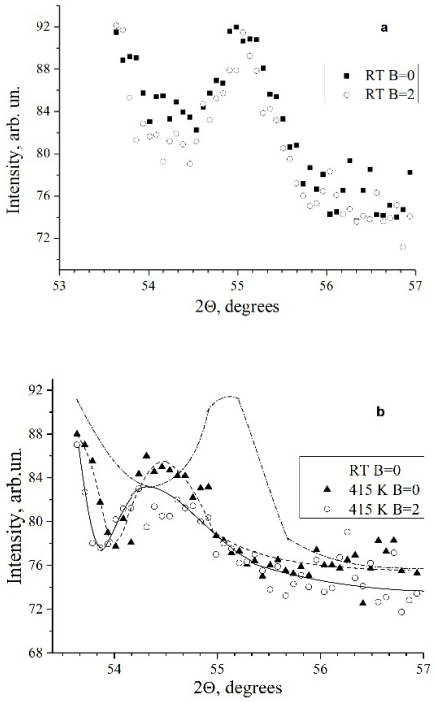

Fig. 4. Intensities of (022) Bragg peak in NCM MAP+NaNO2: (a) - at RT and at B = 0 and B=2 T, (b) – at 415 K and B = 0 and B = 2 T. The dash-dotted line in Fig.4b corresponds to the intensity of (022) peak at RT and B = 0 T.

Sodium nitrite belongs to the order-disorder ferroelectrics and undergoes the first order phase transition at $TC \approx 437$ K. At room temperature (RT) $NaNO_2$ has a body centered orthorhombic lattice (a = 3.57 Å, b = 5.578 Å, c = 5.39 Å) with two molecules per unit cell, and its space group is ***Im2m.*** In the low-temperature ferroelectric phase the spontaneous polarization points along the b-axis and appears due to a partial alignment of NO_2^-

groups along this axis, accompanied by the displacement of sodium ions. At high temperature (above T_C) a mirror plane perpendicular to the b-axis appears and the space group changes to ***Immm.*** The physical realization of the ferroelectric order parameter η in $NaNO_2$ is the difference between the occupations f_1 and f_2 of two crystallography equivalent positions of NO_2^- groups, i.e. $\eta=f_1-f_2$. As it has been shown in the paper [26], the intensity of diffraction peaks is proportional to

$$|F|^2 = F^2_{re} + \eta^2(T) \times F^2_{im} \qquad (1)$$

where F_{re} and F_{im} are the real and imaginary parts of the structure factor F, and η is the order parameter for the ferroelectric phase. In the case of NaNO2 there are two principal distinguishing groups of Bragg peaks. For example, for the (022) peak F_{re} is equal to 0.46 and F_{im} - 2.04 (for neutron scattering [27]). It means that in the equation (1) the value F^2_{re} becomes negligible in comparison with F^2_{im} and the total intensity of the (022) peak is practically proportional η^2.

The size of $NaNO_2$ nanoparticles in this NCM has been about 50(4) nm. In Figure 4a and 4b the temperature and field evolutions of (022) Bragg peak for NaNO2+MAP composite are presented. One can see that the application of magnetic field 2T suppresses the total intensity (the loss is about 30 %) in comparison with the measurement without field. At 430 K and at B = 2 T we have not observed this peak in diffraction pattern. Without magnetic field the phase transition takes place near 435 K [28]. This result means that the application magnetic field shifts the T_C to the lower temperature.

IV. Conclusion

The studies of crystal structure and magnetic properties of magnetic porous glasses produced by induction melting confirm the presence of magnetic agglomerates consisting of magnetite nanoparticles in the matrix skeleton. On base of magnetic MAP glasses the NCM with ferroelectrics KADP and $NaNO_2$ nanoparticles embedded into the pores have been prepared. It is shown that the restriction geometry leads to an essential increase of ferroelectric phase transition in nanostructured KADP. The measurements of dielectric response of nanocomposites KADP+MAP and temperature evolution of crystal structure of NCM $NaNO_2$+MAP in applied magnetic fields prove the possibility to govern by ferroelectric phase transition using magnetic field. It is shown that the interface "matrix-embedded material" plays the important role in modification of microscopic properties of nanocomposites. It open the way to the creation of multifunctional nanostructured materials with governed interface on base of porous magnetic glasses.

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