Properties and structure of magnetic alkali-borosilicate glasses prepared by induction melting

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Abstract. In this contribution we present the first results devoted to studies of structure, morphology and magnetic properties of magnetic alkali-borosilicate glasses prepared by induction melting. This procedure permits to fabricate a large amount of two-phase glasses with magnetic properties due to self-assembled magnetite (Fe_3O_4) nanoparticles and with branched dendrite-like structure of channels formed by a chemical unstable phase. After withdrawal of this phase we have obtained the porous matrices with two different average pore diameters: ~ 6 nm and ~60 nm. The empty pore spaces in these matrices were filled by ferroelectrics KH_2PO_4 from water solution. It is shown that application of external magnetic fields above B=1 T results in a linear growth of the ferroelectric phase transition temperature T_C on 6 K at B=10 T due to magnetostrictive properties of porous matrices.

1. Introduction

Mesoporous alkali borosilicate glasses with magnetic properties are very interesting materials for numerous applications because of its attractive physicochemical properties: a controllable average pore diameter, a low thermal expansion coefficient, a chemical and mechanical stability, a high specific surface area, dielectric and optic properties and so on [1-5]. These matrices use in medicine [6-8], in biology [9-11], in magnetooptic devices [4,5], as different kinds of sensors [10-13] et cetera [14-16]. Moreover they can be employed as a model object for creation of novel multifunctional materials (for example, multiferroics with spatially separated coexisting magnetic and ferroelectric orderings and a large interface) with characteristic sizes of nanoparticles embedded into the pores with controllable average diameter from units to tens nanometers [17,18]. Usually these matrices have been produced by the sol-gel approach [10, 11, 15] or by embedding magnetic nanoparticles into the pore of porous matrices [6, 14, 19, 20]. In all these cases the matrices play a passive role supported a restricted geometry, but there is another approach: to create the active porous media, which participates in modification of embedded material properties. Here the term “active” means that the ferroelectric (or magnetic) properties are intrinsic features of matrix itself. The first attempt to produce porous magnetic glasses (PMG) was made in the paper [17]. The technology of two-phase (nonporous) doped by hematite α-Fe_2O_3 and porous magnetic glasses was developed in Grebenshchikov Institute of Silicate Chemistry of the Russian Academy of Sciences (St. Petersburg, Russia) [21]. They have used the conventional method: melt of initial mixture in a platinum crucible with mechanical stirring. The principle disadvantages of this procedure are a small amount of glasses

(per one melt) and high costs (per cm^3) of commercial item. In the paper [22] we have proposed to use an induction melting for production of magnetic alkali-borosilicate glasses and the first results present in this contribution. In addition, we have prepared the nanocomposites with nanoparticles of ferroelectric KH_2PO_4 embedded into the pore of these glasses and have studied the effect of applied magnetic field on the temperature of ferroelectric phase transition in these composites.

2. Experimental Procedure and Results

2.1 Production and dielectric studies

To obtain the porous magnetic glasses suitable for preparation multifunctional nanocomposites it is necessary to solve the following sequences of intermediate problems:

1 - optimization the initial component mixture,

2 – selection of the preferable melting process parameter (temperature, rates of heating and cooling, thermal insulation, a generator power and frequency of electromagnetic field using at heating and melting),

3 - homogeneity of initial mixture stirring at melting due to convective and electromagnetic agitations,

4 – choice of liquation (phase separation) conditions providing a two-phase interconnected structure after liquation,

5 – developing of etching procedure for production of dendrite throughout pore system with controllable average pore size.

As a final stage it is necessary to produce nanocomposite materials (NCM) on base of these glasses and to study the possibility of handling by properties of embedded substances using applied external magnetic fields.

To solve the first problem, we have used the results presented in the paper [17] and our preliminary data concerning to melting of PMG [22]. We have chosen the initial mixture 60% SiO_2–15% B_2O_3–5% Na_2O–20% Fe_2O_3 and T_{melt}~1500 ºC. It permits us to compare the properties and structure of our glasses with PMG, described in [17].

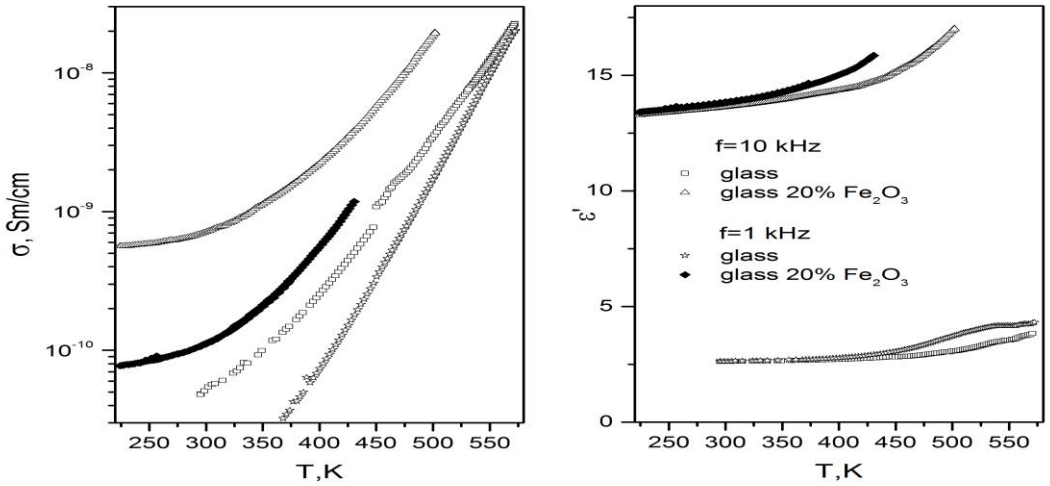

Figure 1 Temperature dependencies of conductivity (left) and dielectric glasses the conductivity permittivity (right) for conventional alkali borosilicate glasses and is more on order magnetic glasses with 20 % of hematite in the initial mixture at compared to frequencies 1 kHz and 10 kHz nonmagnetic glasses.

The principle difference between our method and a melting in platinum crucible consists in a heating process: we have used a heat transfer from an inductor via a carbon heater tube [22] to the melt as well as a heating due to application of high-frequency electromagnetic field. Indeed the preliminary measurements of dielectric properties and conductivity of produced two-phase (non-porous) magnetic glasses (figure 1) have shown that above 320 K the conductivity increases exponentially (as in the nonmagnetic glasses with very close initial mixture 7% Na_2O+ 23% B_2O_3, 70% SiO_2) with a growth of temperature as a result of appearance of ionic conductivity [23]. It is necessary to note that in a case of magnetic and grows essentially at increasing of frequency. The additional modelling of electromagnetic (EM) field distribution in our experimental geometry has shown that EM field in frequency diapason 1 -10 kHz penetrates well into the melt providing not only the melt heating but electromagnetic stirring also. Hereinafter in our experiments we have used this frequency interval. So the second peculiarity of this method is a possibility to use for heating and melting the heat transfer and electromagnetic heating simultaneously. Using this approach we have prepared 3 samples: S1 (T_{melt} ~ 1600 ºC), S2 (T_{melt} ~ 1500 ºC) and S3 (T_{melt} ~ 1400 ºC). After melting the ingots have been cooled down to 560 K and at this temperature we have carried out a liquation (phase separation) during 120 hours. The dielectric response in magnetic field has been studied using a capacitance bridge at 1 kHz in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland). The applied magnetic fields have been varied from 0 - 10T. The nanoparticles crystal structures has been studied using X-ray diffractometer (Supernova, Agilent Technologies) using Cu $_{K\alpha}$ line (in SPbPU). The dielectric properties of samples at B = 0 T we have studied at the frequencies 0.1 Hz - 10 MHz and the temperature diapason 293 -570 K using Novocontrol BDS80 dielectric spectrometer.

2.2 Morphology and structure of magnetic glasses

From the different parts of ingots the plates 10×10×0.5 mm have been cut and the morphology of these samples and element distributions have been studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

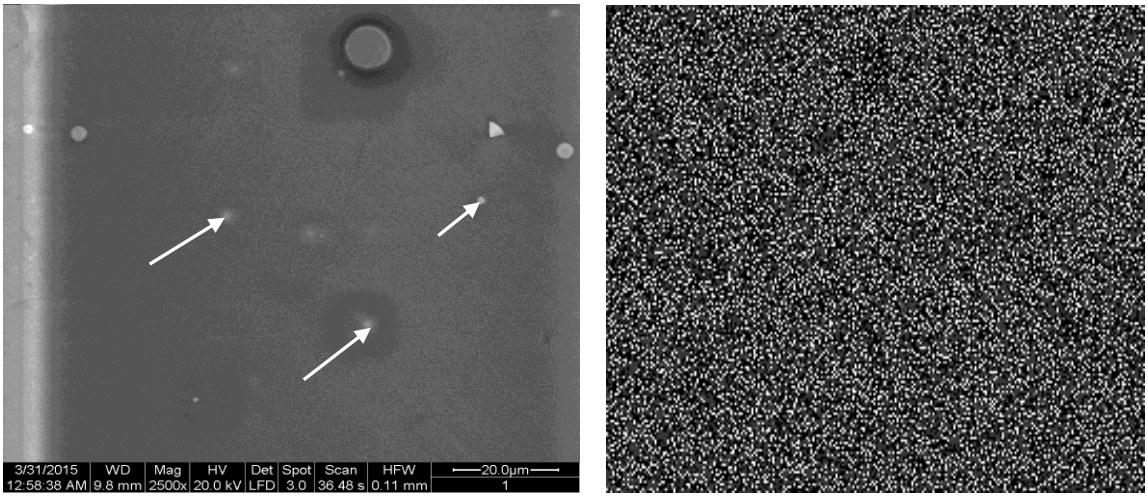

Figure 2 Total SEM image of S2 sample. Left – surface of S2, the white arrows mark the regions enriched by Fe. Right – carbon distribution in this region. The scale (20 μm) indicates in the right bottom part of S2 SEM image.

In figure 2 (left) SEM image of S2 sample surface is presented. The white arrows mark the positions of Fe-enriched agglomerates. The characteristic size of these agglomerates (~500 nm) is very closed

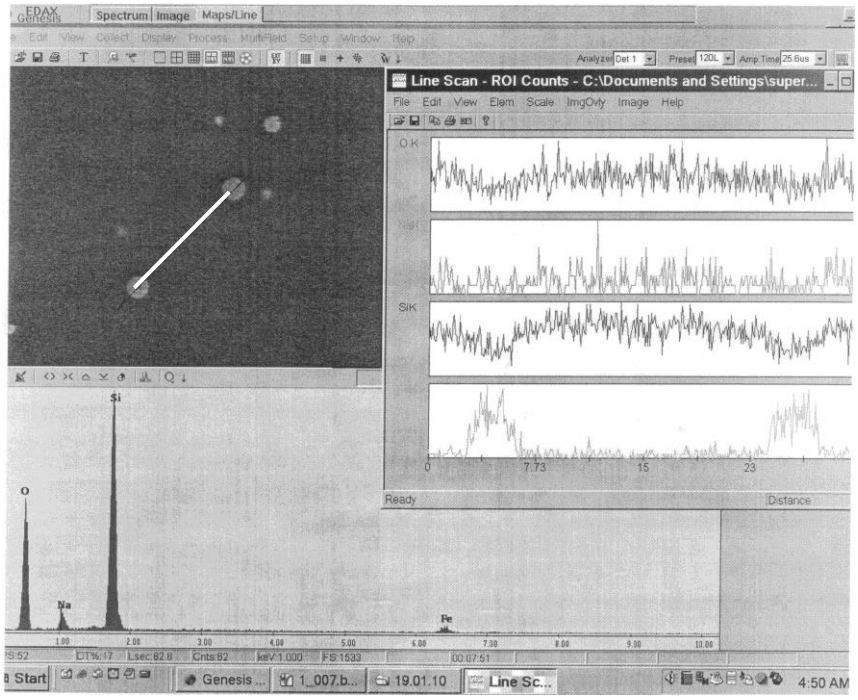

Figure 3 Distributions of elements along the white line connected two agglomerates. In the upper right corner (from top to bottom) – distribution of O, Na, Si and Fe in relative units (SEM data).

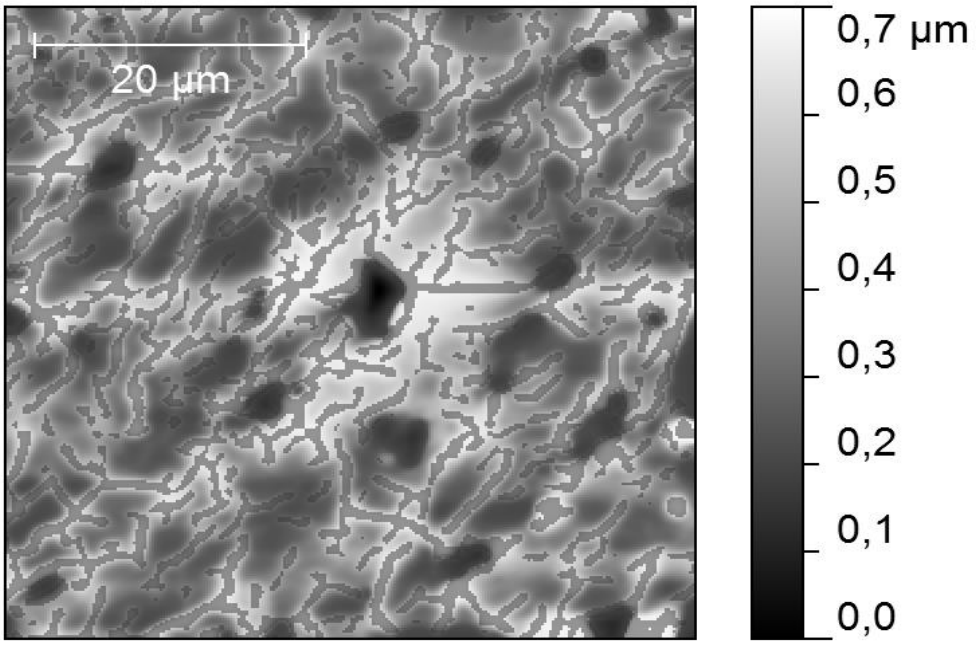

Figure 4 AFM image of S2 sample surface, branching interconnected grey lines correspond to a chemically unstable phase.

to the sizes of similar regions observed in the magnetic glasses [3] and prepared by melting in a platinum crucible. In the right part of figure 2 the distribution of carbon in this region is presented and it is easy to see that this distribution is practically uniform. The analogous pictures we have obtained for Na, Si and O. As it is mentioned above in our first experiments we melted the initial mixture in graphite crucible directly and a part of carbon dissolved in the melt near the crucible walls. So these atoms can be used as independent marker of melt homogeneity. It confirms our supposition concerning to a possibility to achieve the uniformity of melt due to convection and electromagnetic agitations. In figure 3 the distribution of elements along the line (white color) connected two aggregates enriched by iron atoms is presented. In insert on the wright upper corner of figure 3 one can see that the maximum of Fe concentration is observed precisely in the positions of agglomerates. The necessary condition for production of porous glasses is a formation of two-phase structure after liquation procedure. To check the morphology of surface and an appearance of two-phase structure we have used AFM. In figure 4 AFM image of S2 sample surface is presented. The branching dendrite-like interconnected structure corresponds to the chemically unstable phase and this phase can be removed after chemical one- or two-stage etching. In S2 sample this structure occupies approximately 30 % of the total sample surface. In S1 dendrite-like structure is practically absent, but in S3 it occupies not more 15 % of total surface. The scale on the right side – the height above the basic sample level. At the next step we have studied the crystal structure of samples S1, S2 and S3 by X-rays diffraction and have performed a comparison of S1, S2 and S3 structures with crystal structures of row iron oxides and Fe.

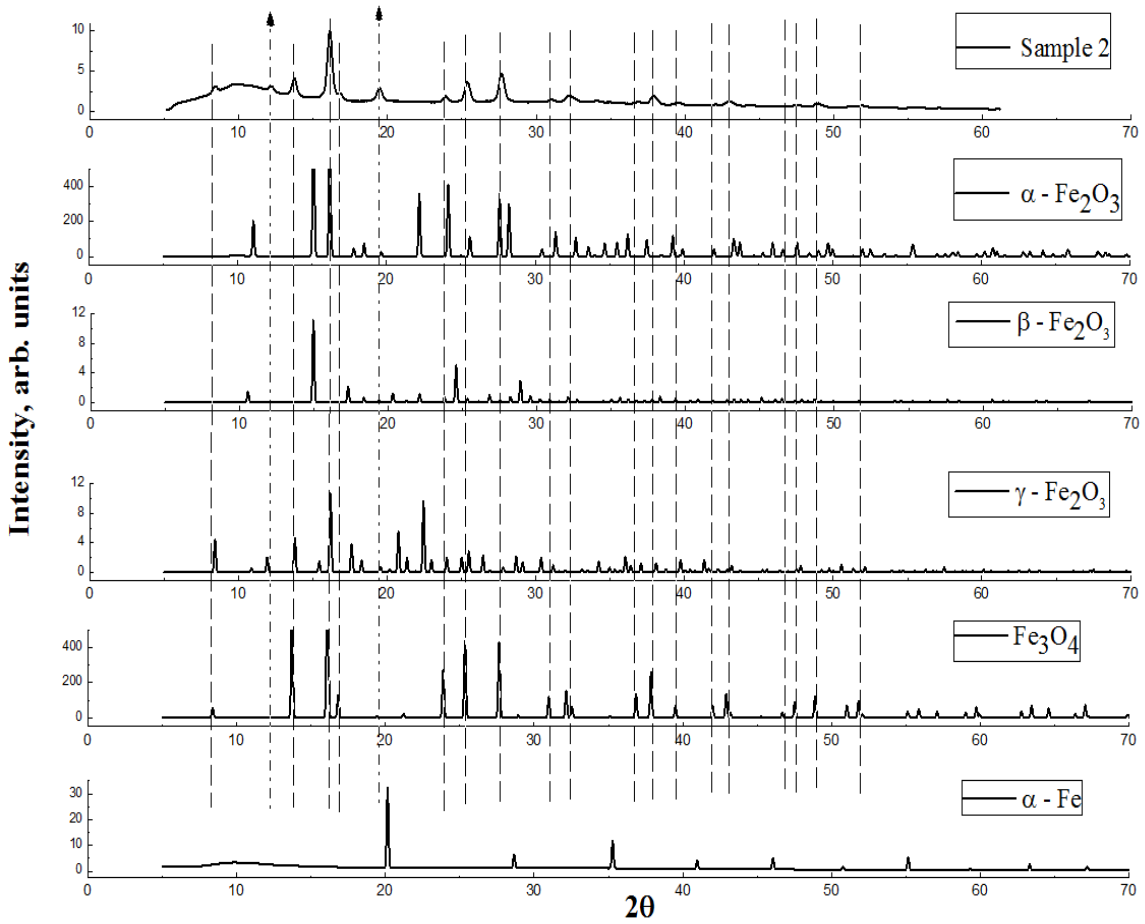

Figure 5 Diffraction pattern (upper picture) and phase analysis of S2 sample. Vertical lines corresponds to the principle elastic peaks for different iron oxides and Fe.

The best results was obtained for S2 sample (figure 5). The phase analysis showed that about 80% of initial α-Fe_2O_3 transferred in magnetite (Fe_3O_4). S1 sample (T_{melt} ~ 1600 ºC) was overheated and we did not observed the magnetite structure, but in S3 sample (T_{melt} ~ 1400 ºC) the input of hematite (α-Fe_2O_3) dominated. We should like to note that the average size of magnetite nanoparticles in S2 sample obtained from a broadening of elastic peaks (16±4 nm) is in a good agreement with the results presented in [17]. Thus, one can conclude that the more suitable sample for preparation of porous glasses is S2 sample.

2.3 Studies of NCM on base of magnetic porous glasses

On base of S2 sample the magnetic porous glasses (MPG) with average pore diameters ~65 nm have been prepared and have been filled by ferroelectrics KH_2PO_4 (KDP) from water solutions. Further, we have studied an effect of applied magnetic field on ferroelectric phase transitions T_C in nanocomposites KDP+MPG by dielectric spectroscopy. The results are shown in figure 6 where the dependency of shift (ΔT_C) of ferroelectric phase transition temperature T_C as a function of applied magnetic field B is presented. It is easy to see that the function $\Delta T_C(B)$ is linear in the diapason B = 1 – 10 T and corresponds to the dependency of magnetostriction coefficients for magnetic glasses obtained in [24].

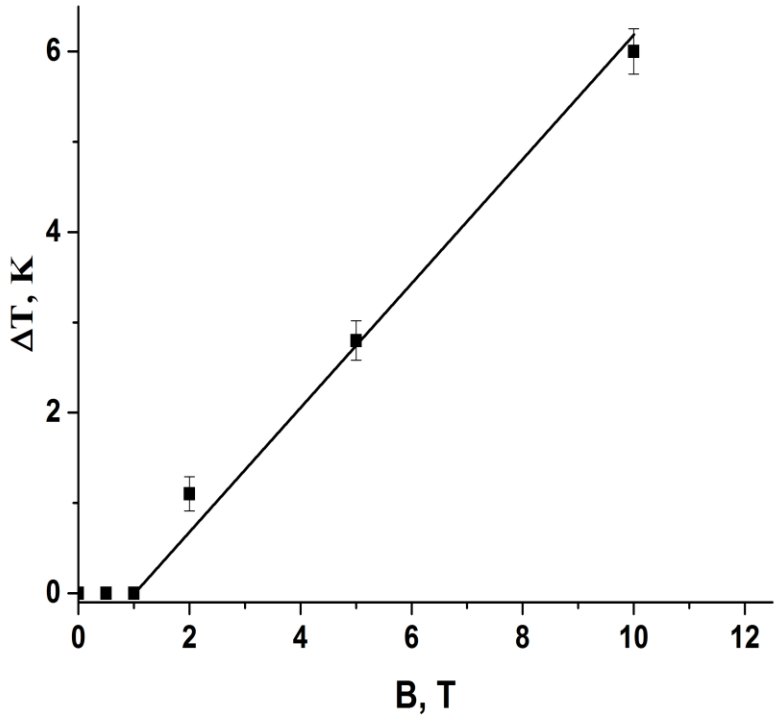

Figure 6 Dependency of ΔT_C vs applied magnetic field B

Further we have prepared NCM containing solid solution (1-x)KH_2PO_4 –(x)$(NH_4)H_2PO_4$ (KADP) (x=0-0.15) on base of our magnetic glasses with average pore diameter 50 (5) nm. KADP solid solutions were embedded into the pores from an aqueous solution with triple recrystallization. The average size of nanoparticles (~ 40 nm) has been estimated from broadening of elastic peaks. The phase diagram for the massive KH_2PO_4 (KDP) and $(NH_4)H_2PO_4$ (ADP) solid solutions are known [25,26] 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 [27] we have 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 obtained results for shifts of T_C on heating and on cooling and the differences $\Delta T=T_{C(heating)} - T_{C(cooling)}$ in NCM with KADP as the functions of ADP concentration and applied magnetic field are presented in table 1.

Table 1. Shifts of T_C in NCM containing KADP nanoparticles.

Samples and magnetic fields, T	$T_{C(cooling)}$, K	$T_{C(heating)}$, K	$\Delta T=T_{C(heating)} - T_{C(cooling)}$, K	T_C bulk, K
KDP B=0 T	120.4 ±0.1	126.2 ±0.1	5.8 ±0.2	~ 122
KDP B=10 T	126.7 ±0.1	130.9 ±0.1	4.2 ±0.2	
0.95KDP+0.05 ADP B=0 T	117.3 ±0.1	118.9 ±0.1	1.6 ±0.2	~ 104
0.95KDP+0.05 ADP B=10 T	117.4 ±0.1	120.4 ±0.1	3.0 ±0.2	
0.85KDP+0.15 ADP B=0 T	113.8 ±0.1	116.2 ±0.1	2.4 ±0.2	~ 73
0.85KDP+0.15 ADP B=10 T	114.0 ±0.1	117.5 ±0.1	3.5 ±0.2	

The observed shifts can be explained by the multidirectional influences of thermal compression (or expansion) plus positive magnetostriction of MAP glasses on cooling and heating depending on magnetic field and temperature variation of thermal expansion coefficients for KADP or KDP [28]. 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. It is worth noting that the effect of restricted geometry on T_C in NCM on base of magnetic glasses for the pure KDP is larger than in NCM with embedded KADP solid solutions. 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 [29] 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. For example in spherical inclusions of BaTiO3 in silica glasses the Curie temperature is shifted with respect to that of the bulk BaTiO3 by about +8.5 K. Also it was shown that the shift of T_C increases strongly with a growth of nanoparticle anisotropy.

3. Conclusion

It is shown that the magnetic alkali borosilicate glasses can be prepared by induction melting. The homogeneity of melt and obtained two-phase glasses is provided by a combination of convective and electromagnetic agitations. The studies of morphology and crystal structure confirm the presence of magnetic agglomerates consisting of magnetite nanoparticles in the matrix skeleton. The first measurements of dielectric response of nanocomposites KDP+MPG and DKDP+MPG in applied magnetic fields prove the possibility to govern by ferroelectric phase transition using magnetic field. It opens the way to the creation of multifunctional nanostructured materials on base of porous magnetic glasses.

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