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Dielectric properties of two-phase and porous ferriferous glasses

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In the present contribution we have studied the dielectric properties of two-phase sodium borosilicate glasses doped by iron oxide and of porous media based on them. The temperature dependences of dielectric permittivity and conductivity for all samples have been obtained, and the impedance spectroscopy analysis for porous magnetic glasses has been done. The obtained data allow us to estimate the values of activation energies for porous samples.

Keywords: dielectric spectrometry, sodium borosilicate glass with magnetic atoms.

1. Introduction

It is well known that the materials embedded into different natural or artificial dielectric porous media change their physical properties due to the size effect and restricted geometry. For example, a giant growth of dielectric permittivity [1, 2] at low frequencies, substantial increment of conductivity in a paraelectric phase [3] and change of a phase transition type [4, 5] were defined for $NaNO_2$ embedded into 7 nm porous glass. For active porous media one can expect an additional influence of a matrix on the macroscopic physical properties of embedded material.

The global aim of our study is a production of novel multifunctional nanocomposite material with two spatially separated but interacted subsystems: magnetic and ferroelectric. There is one important point: the interface between both subsystems must be very large to support an observable interaction. One of the ways to produce these systems is the embedding of a ferroelectric into a magnetic porous matrix. As a magnetic matrix it is possible to use the so-called magnetic porous glass. For example, it can be prepared by chemical etching of two-phase sodium borosilicate glass doped by hematite (α-Fe_2O_3). In present paper we have studied dielectric properties of the initial two-phase magnetic glasses (nonporous) doped by various concentrations of hematite and of porous magnetic glasses, based on them. The dielectric measurements are very important part of characterization, because for the aim mentioned above we need a matrix, which demonstrates not only magnetic properties, but also a large value of dielectric permittivity ε. It is known that the majority of materials with high ε demonstrates a high piezoelectric response and one can expect an appearance of strong interaction between magnetic and ferroelectric subsystems due to elastic strains and a large interface between them.

2. Samples and experimental methods

We have studied dielectric properties of three types of two-phase ferriferous glasses Fe25 (50% SiO_2–20% B_2O_3–5% Na_2O–25% Fe_2O_3), Fe20 (60% SiO_2–15% B_2O_3––5% Na_2O–20% Fe_2O_3) and Fe15 (60% SiO_2–20% B_2O_3–5% Na_2O–15% Fe_2O_3) [6], basic two-phase alkali borosilicate glasses (7% Na_2O, 23% B_2O_3, 70% SiO_2 – SBS) and properties of two types of porous magnetic glasses: microporous glass (Fe20MIP) with an open-ended network of pores with the average diameter of 6 (±2) nm and porosity 15%, obtained after one-stage chemical etching of two-phase magnetic glass containing 20% of hematite, and macroporous open-ended glass (Fe20MAP) with the average pore size of 23 (±2) nm and porosity 60%, produced by two-stage etching of the same initial two-phase glass [6, 7]. The chemical compositions of porous glasses were 0.3–1.0% Na_2O, 3–7% B_2O_3, 70–90% SiO_2 and 3–15% iron oxide, depending on the composition of initial two-phase ferriferous glasses. The heat treatment of all glasses (including SBS) was performed at 550 °C and as a result the dendrite interconnected net of channels enriched by borosilicate phase was formed. All samples were rectangular plates 10×10 mm with a thickness of 2 mm for two-phase glasses and 0.45 mm for porous samples.

For study of dielectric response we have used a dielectric spectrometer Novocontrol BDS 80, which operates in the temperature range from –160 °C to 400 °C and in the frequency range 3 mHz to 20 MHz. The measurements were performed in dry nitrogen atmosphere at the frequency range from 0.1 Hz to 10 MHz and in the temperature diapason 300–550 K. Before measurements all samples were annealed at 380 K for a removal of possible remnant water.

3. Results and discussions

3.1. Two-phase magnetic glasses

Initially we have measured a dielectric response of two-phase glasses doped by different hematite admixtures and we have compared the obtained results with

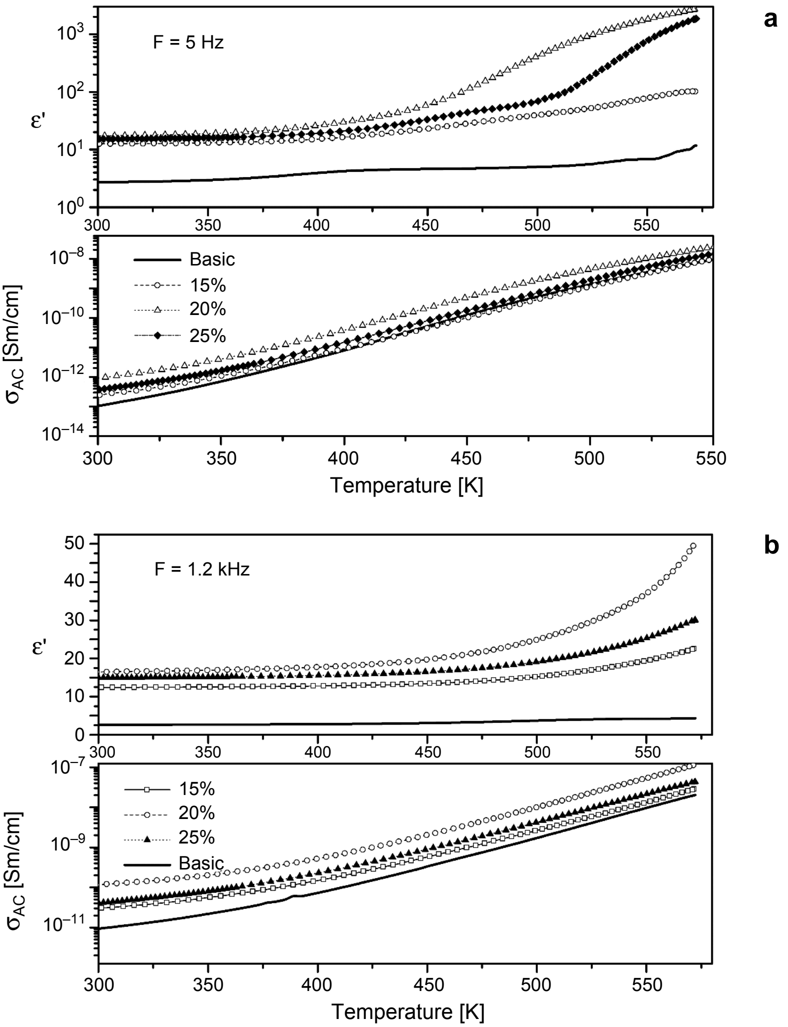

Fig. 1. Temperature dependences of dielectric permittivity ε' (top) and AC conductivity σ_{AC} (bottom) for the initial two-phase magnetic glasses with different concentrations of iron oxide and for the basic nonporous glasses (without iron oxide) – solid lines at 5 Hz (**a**) and 1.2 kHz (**b**).

a dielectric response for basic SBS glass – glass without hematite. In Figures 1**a** and 1**b**, the dielectric permittivity ε' and AC conductivity ($\sigma_{AC} = \sigma' = \omega\varepsilon_0\varepsilon''$) corresponding to different types of glasses are presented at the measuring frequency 5 Hz and 1.2 kHz. For all magnetic two-phase glasses, the value of dielectric permittivity is larger than for basic glass (~10 times at RT). For Fe15 glasses ε' increases monotonically, but for Fe20 and Fe25 glasses we have observed a growth of ε' above ~400–450 K at low frequencies, depending on iron oxides concentration. For example, at high temperature ε' for Fe20 becomes ~100 times larger than at RT. The increase in frequency leads to the shift (Fig. 1**b**) of the anomaly to higher temperatures. Thus an introduction of hematite increases dielectric permittivity. This result conforms to the studies of dielectric properties and to AC conductivity carried out for $40SiO_2–30Na_2O–1Al_2O_3–(29 - x)B_2O_3 \cdot xFe_2O_3$ (mol%) and $0.0 \le x \le 29.0$ [8], $20Li_2O–31B_2O_3–34SiO_2–(15 - x)NiO \cdot xFe_2O_3$ ($x = 2.5, 5, 7.5, 10$ and 12.5 mol%) [9] and $(0.7 - x)SiO_2–0.3Na_2O–xFe_2O_3$ ($0.0 \le x \le 0.20$ mol%) [10] glasses at increasing iron oxide concentration. The principal difference in the $\varepsilon'(T)$ dependences is an observation of unexpected growth for Fe20 and Fe25 above 400–450 K as it is mentioned above. Our ACM (atomic force microscopy) measurements [11] have shown that iron oxide forms large agglomerates with characteristic sizes 940 (±40) nm for Fe25, 340 (±20) nm for Fe20 and Fe15. The analysis of X-rays diffraction data [11] has shown that in Fe15 glasses a coexistence of β-Fe_2O_3 (~90 wt%) with diffraction size $d = 198$ (±32) Å and ~10 wt% of magnetite (Fe_3O_4) with $d =$ $= 455$ (±46) Å is observed. Agglomerates in Fe20 glasses consist of magnetite nanoparticles with $d = 151$ (±7) Å only while in Fe25 glasses we have a small (~3%) admixture of β-Fe_2O_3 phase to the dominant Fe_3O_4 phase. Here it is necessary to note that the transformation of initial α-Fe_2O_3 oxide into β-Fe_2O_3 and Fe_3O_4 at preparation of sodium borosilicate ferriferous glasses was observed for the first time: earlier the transformation of hematite into magnetite only at preparation of similar ferriferous glasses was reported in the paper [8] for concentration of α-Fe_2O_3 above 20 mol% in the initial mixture. The AFM and X-rays data permit us to suppose that the difference of internal organization ("friable" agglomerates in Fe25 and more compact in Fe15 and Fe20 glasses) and composition of iron oxides nanoparticles could be responsible for anomalies in observed $\varepsilon'(T)$ and $\sigma_{AC}(T)$. Usually, the conductivity in conventional alkali borosilicate glasses is ionic and has a thermoactivation nature [12–15], but it is shown [9, 10] that the introduction of iron oxides leads to an increase in both σ_{AC} and σ_{DC} due to the deposit of electron conductivity. Unfortunately, the correlations between the self-organization and the internal structure of iron oxides agglomerates and relaxation processes in these ferriferous glasses are insufficiently known. To determine the parameters of relaxation processes and contributions of various types of conductivity, we are going to perform the additional measurements in future.

3.2. Porous magnetic glasses

In the next step, Fe20 glass was chosen as a base for porous glasses because of the largest value of dielectric permittivity and the presence of monophase Fe_3O_4 admixture with ferrimagnetic properties [11]. X-ray diffraction has shown that after one- and two-stage etching, the average diffraction size of magnetite particles does not change and corresponds to those observed in two-phase Fe20 glasses. The chemical analysis has shown that the total amount of iron oxide decreases 3–5 times after one and two-stage etching for Fe20MIP and Fe20MAP glasses accordingly. In Figure 2, the temperature dependence of ε' and σ_{AC} for porous magnetic glasses with different pore diameters, for initial two-phase Fe20 glass and for basic two-phase SBS glass are presented. One can see that after chemical etching, the value of dielectric permittivity and conductivity decreases, but for Fe20MIP glass, the value of ε' does not differ

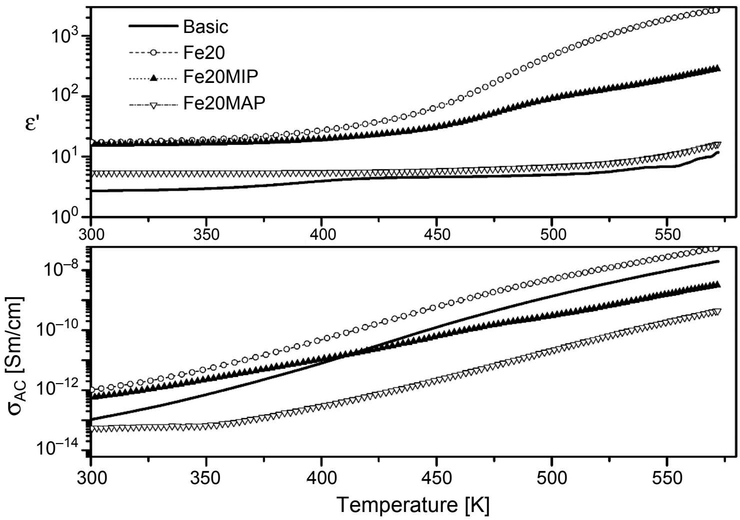

Fig. 2. Temperature dependences of dielectric permittivity ε' and conductivity σ_{AC} for microporous (Fe20MIP), macroporous (Fe20MAP) magnetic glasses, for two-phase Fe20 glass and basic (nonporous) alkali borosilicate glass at 5 Hz.

essentially from ε' observed for initial magnetic glass Fe20 at temperature below 350 K, and above the temperature Fe20MIP glass demonstrates a more smooth rise of dielectric permittivity than Fe20. At the same time, for all types of Fe20 glasses, ε' remains higher than for basic SBS glasses. In the case of Fe20MAP the dielectric permittivity and conductivity strongly reduce, relatively to the initial two-phase Fe20 and the Fe20MIP glass. It could be connected with a fact that the channels in Fe20MAP are practically empty because this glass loses the large part of iron oxide and sodium borate phases after two-stage etching. So it is possible to conclude that the reduction of iron oxide concentration and sodium borate fraction leads to a decrease in dielectric permittivity and σ_{AC}, but these ferriferous glasses keep the common for conventional sodium borosilicate porous glasses peculiarities above 400–450 K, associated with high-temperature relaxation process due to trapping of free charge carriers on internal “matrix–pore” interface [16, 17].

3.3. DC-conductivity

We have analyzed the temperature dependence of DC-conductivity for basic two-phase, two-phase Fe20, Fe20MIP and Fe20MAP glasses. For this aim the hodographs (Nyquist diagrams $Z''(\omega)$ vs. $Z'(\omega)$) of impedance at each temperature were plotted. Experimental curves at high frequencies have been well approximated by semicircles. The intersections of these semicircles with $Z'(\omega)$-axis give the estimated values of DC-conductivity (σ_{DC}). The products $\sigma_{DC}T$ for all types of glasses in Arrhenius coordinates are presented in Fig. 3. The upper series of symbols for every type of ferriferous glasses corresponds to heating, the lower – to cooling. For the basic SBS

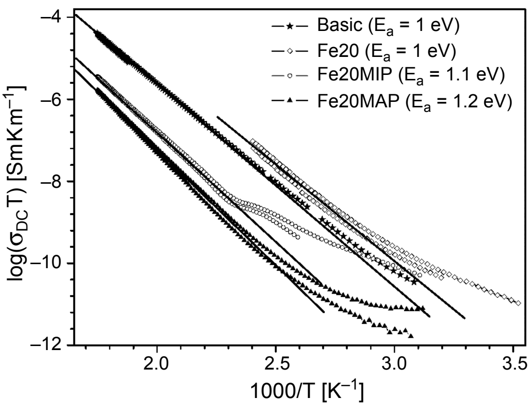

Fig. 3. Temperature dependences of $(\sigma_{DC}T) = f(1/T)$ in Arrhenius coordinates on heating (upper set of symbols) and on cooling (lower set of symbols) for the basic SBS, Fe20, Fe20MIP and Fe20MAP glasses and their approximations by Arrhenius law – solid lines.

glass, the results obtained at heating and at cooling coincide. The high-temperature parts of these dependences are well fitted by Arrhenius law: $\sigma_{DC}T = \sigma_0 \exp(-E_a/kT)$ (σ_0 is a constant and E_a – activation energy) and demonstrate the thermal activation behavior. The solid lines in Fig. 3 correspond to these approximations. For Fe20MIP this approach is suitable for the temperature interval above 435 K only. At low temperature σ_{DC} differs essentially from Arrhenius law and the origin of this phenomenon will be discussed further.

The values of activation energy have been determined from a slope of the approximation line and are equal to 1.2±0.1 eV for Fe20MAP, 1.1±0.1 eV for Fe20MIP and 1.0±0.1 eV for basic two-phase and two-phase Fe20 glasses. It is known that the properties of the SiO_2–Na_2O–B_2O_3 ternary system in different composition ranges can be described in the framework of the simple model including two concentration parameters: $K = [SiO_2]/[B_2O_3]$ and $R = [Na_2O]/[B_2O_3]$, where the concentrations are indicated in molar percents. In particular, in the papers [13, 18] it has been shown that the activation energy of ionic conductivity depends on the ratio $[Na_2O]/[B_2O_3]$ only and the increases at decreasing R achieve 0.91 (±0.02) eV for $R = 0.43$ and 0.93 (±0.02) eV for $R = 0.35$. In our glasses $R = 0.304$ for basic SBS glass and 0.33 for two-phase Fe20 glass and the obtained E_a are in a good agreement with the results in papers [13, 18]. For Fe20MIP and Fe20MAP glasses, the ratio R is essentially smaller: R ~ 0.1–0.2, and in principle, the obtained values of E_a for Fe20MIP and Fe20MAP glasses correspond to the expected ones for ionic current in these ferriferous porous glasses. Comparing σ_{DC} for the basic SBS and Fe20 glasses with practically equal R-parameters (Fig. 3), one can see that the presence of iron oxides in Fe20 glass leads to a considerable growth of DC conductivity integrally but does not change the activation energy. Indeed it is known [19] that the electronic conductivity of bulk magnetite increases at the growth of temperature ~3 times in temperature interval 240–500 K, *i.e.*, this increase can give a small input in the slope of $\sigma_{DC}T$ dependence since ionic conductivity increases more than 100 times as early as in temperature interval 300–400 K. To compare the results for Fe20MIP and Fe20MAP glasses in Fig. 3, it is easy to see that elimination of secondary silica and iron oxide from channels at the production of MAP glasses from MIP ones leads to decreasing of DC conductivity and to disappearance of anomaly in a vicinity of 400 K observed for Fe20MIP. Thus it is possible to conclude that the channels content of Fe20MIP glasses plays a principal role in DC conductivity at low temperatures. At present the available information is insufficient for decoding of a mechanism (or mechanisms) of DC conductivity at low temperatures (below 400 K) in MIP glass due to very complicated chemical composition of material in the channels containing the mixture of Na_2O, B_2O_3 and iron oxides components. It requires additional measurements.

4. Conclusions

The dielectric measurements of initial two-phase glasses doped by different amounts of hematite (α-Fe_2O_3) have shown an increase in dielectric permittivity and conductivity in relation to the basic SBS glass. Fe20 glass demonstrates the largest value of dielectric permittivity and conductivity and this type of magnetic glasses has been chosen as a base for porous magnetic matrices. The values of ε' and σ_{AC} for magnetic glasses decrease after chemical etching, but dielectric permittivity of Fe20MIP and Fe20MAP glasses remains higher than for the basic SBS glass. The σ_{AC} conductivity of Fe20MIP glasses in the temperature range 300–400 K stays higher than for SBS glass. Temperature dependences of DC-conductivity of two-phase sodium borosilicate (basic) glass, two-phase ferriferous Fe20 glass and porous Fe20MIP and Fe20MAP glasses were obtained from the hodographs of impedance. These dependences demonstrate thermal activation behavior. The estimated values of activation energies are equal to 1.2±0.1 eV for Fe20MAP, 1.1±0.1 eV for Fe20MIP magnetic glasses and 1.0±0.1 eV for basic two-phase and two-phase Fe20 glasses. It is shown that the principal role in DC conductivity for Fe20MIP glass at temperature below 400 K plays the secondary silica and iron oxide in channels.

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References

[1] Pan'kova S.V., Poborchii V.V., Solov'ev V.G., *The giant dielectric constant of opal containing sodium nitrate nanoparticles*, Journal of Physics: Condensed Matter **8**(12), 1996, pp. L203–L206.

[2] Colla E.V., Fokin A.V., Kumzerov Yu.A., *Ferroelectrics properties of nanosize KDP particles*, Solid State Communications **103**(2), 1997, pp. 127–130.

[3] Kinka M., Banys J., Naberezhnov A., *Dielectric properties of sodium nitrite confined in porous glass*, Ferroelectrics **348**(1), 2007, pp. 67–74.

[4] KUTNJAK Z., VODOPIVEC B., BLINC R., FOKIN A.V., KUMZEROV YU.A., VAKHRUSHEV S.B., *Calorimetric and dielectric studies of ferroelectric sodium nitrite confined in a nanoscale porous glass matrix*, Journal of Chemical Physics **123**(8), 2005, article 084708.

[5] NABEREZHNOV A., FOKIN A., KUMZEROV YU., SOTNIKOV A., VAKHRUSHEV S., DORNER B., *Structure and properties of confined sodium nitrite*, The European Physical Journal E **12**(Supplement 1), 2003, pp. 21–24.

[6] STOLYAR S.V., ANFIMOVA I.N., ANTROPOVA T.V., DROZDOVA I.A., *The new two-phase ferriferous alkali borosilicate glasses for creation of the nanoporous materials with magnetic properties*, Nanosystems, Nanomaterials, Nanotechnologies **9**(2), 2011, pp. 433–440, (in Russian).

[7] VASILEVSKAYA T.N., ANTROPOVA T.V., *Small-angle X-ray scattering study of the structure of glassy nanoporous matrices*, Physics of the Solid State **51**(12), 2009, pp. 2537–2545.

[8] DANTAS N.O., AYTA W.E.F., SILVA A.C.A., CANO N.F., SILVA S.W., MORAIS P.C., *Effect of Fe_2O_3 concentration on the structure of the SiO_2–Na_2O–Al_2O_3–B_2O_3 glass system*, Spectrochimica Acta Part A **81**(1), 2011, pp. 140–143.

[9] EL-DESOKY M.M., SALEM S.M., KASHIF I., *Magnetic and electrical properties of lithium borosilicate glasses containing nickel and iron oxides*, Journal of Materials Science: Materials in Electronics **10**(4), 1999, pp. 279–283.

[10] SALMAN F.E., MEKKI A., *Dielectric study and ac conductivity of iron sodium silicate glasses*, Journal of Non-Crystalline Solids **357**(14), 2011, pp. 2658–2662.

[11] PORECHNAYA N., PLYASTCOV S., KOROLEVA E., GOLOSOVSKY I., KIBALIN YU., *Structure and properties of two-phases magnetic glasses and porous matrices based on these glasses*, Proceedings of V International Conference "Actual Problems of Solid State Physics", Minsk, October 18–21, 2011, Vol. 3, pp. 203–205, (in Russian).

[12] CATCHINGS R.M., *Thermally stimulated conductivity studies of trapping centers in alkali-borosilicate glasses*, Journal of Applied Physics **50**(4), 1979, pp. 2813–2816.

[13] GRANDJEAN A., MALKI M., SIMONNET C., *Effect of composition on ionic transport in SiO_2–B_2O_3––Na_2O glasses*, Journal of Non-Crystalline Solids **352**(26–27), 2006, pp. 2731–2736.

[14] AKIRA DOI, *Thermally stimulated currents in lithium-sodium disilicate glasses*, Journal of Materials Science **17**(7), 1982, pp. 2087–2094.

[15] MAIA L.F., RODRIGUES A.C.M., *Electrical conductivity and relaxation frequency of lithium borosilicate glasses*, Solid State Ionics **168**(1–2), 2004, pp. 87–92.

[16] GUTINA A., ANTROPOVA T., RYSIAKIEWICZ-PASEK E., VIRNIK K., FELDMAN YU., *Dielectric relaxation in porous glasses*, Microporous and Mesoporous Materials **58**(3), 2003, pp. 237–254.

[17] GUTINA A., RYSIAKIEWICZ-PASEK E., FELDMAN YU., *Nonexponential dynamics in porous glasses*, Glass Physics and Chemistry **27**(4), 2001, pp. 394–399.

[18] GRANDJEAN A., MALKI M., MONTOUILLOUT V., DEBRUYCKER F., MASSIOT D., *Electrical conductivity and 11B NMR studies of sodium borosilicate glasses*, Journal of Non-Crystalline Solids **354**(15–16), 2008, pp. 1664–1670.

[19] Belov K.P., *Electronic processes in magnetite (or "Enigmas of magnetite")*, Physics-Uspekhi (Advances in Physical Sciences) **36**(5), 1993, pp. 380–391.

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