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Structural, dielectric, thermal and electron magnetic resonance studies of magnetic porous glasses filled with ferroelectrics

A. Ciżman [a],*, W. Bednarski [b], T.V. Antropova [c], O. Pshenko [c], E. Rysiakiewicz-Pasek [a], S. Waplak [b], R. Poprawski [a]

[a] Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, Wrocław, Poland
[b] Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland
[c] Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Science, Nab.Makarova 2, Saint Petersburg, Russia

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ABSTRACT

Magnetic, dielectric and thermal properties of multiferroic nanoparticles were synthesized with a novel magnetic porous glass-based method. We report the properties of empty magnetic porous glasses and ones filled with $NaNO_2$ or KNO_3 ferroelectrics. It was shown that the ferroelectric nanocomposites obtained on the basis of porous glasses exhibit both ferroelectric and ferromagnetic properties. The dielectric permittivity and the ac conductivity were discussed as a function of frequency and temperature. For all obtained multiferroic nanocomposites the dielectric results show a ferroelectric-like behavior. The specific heat was measured using the DSC method and the anomaly of the ferroelectric phase transitions was indicated. We report on the magnetic properties of multiferroic nanocomposites investigated by EMR at two frequencies (X, S band). Both the temperature and the frequency dependencies of the narrow and broad resonance lines fulfilled a condition for the superparamagnetic behavior of porous glasses with ferroelectric particles inside. Finally, we were able to measure the ferroelectric polarization for magnetic porous glasses filled with $NaNO_2$ ferroelectrics. The particle-size dependent magnetic, dielectric and thermal properties of the obtained multiferroics nanocomposites were studied.

1. Introduction

Research on multiferroicity has increased in recent years. A great number of materials have shown a coupling between magnetism and ferroelectricity. One of the major problem of solid state physics is creating smart and novel multifunctional nanostructures with properties controlled by their size, morphology or the host matrix. The modern world of nanostructure materials have been pursued intensively in order to achieve high-quality structures with unique properties, based on porous glasses, ceramics or polymers which are able to solve real problems of modern engineering and science.

Over the last few years a significant increase in interest in nanoscale materials and their applications in novel electronic devices was observed. This is caused by unique properties of materials in nanoscale and their possible application in nanoscale devices. Multiferroics have achieved great attention due to a presence of magnetic and ferroelectric properties and their unusual magnetoelectric phenomena [1–5]. Multiferroics can be ferroelectric and ferromagnetic at the same time, moreover, the electric properties may affect the magnetic ones, and vice versa. $BiFeO_3$ is one of the best known multiferroic material which is the only material exhibiting good ferroelectromagnetism at room temperature [6]. Multiferroic materials are promising for a wide range of applications, such as different kinds of sensors, transducers, actuators or magnetoelectric memory cells. Now, all over the world materials scientists are looking for an answer if enhanced multiferroicity could exist on the nanoscale – a result that could have important technological implications. Small multiferroic elements have received a considerable attention because of their potential applications in nanotechnology such as memory elements in high density storage media or sensor elements. Nanoscale multiferroic elements based on magnetic porous matrices with different shapes and sizes can have totally different magnetic and electric properties than those of the bulk materials.

As can be seen, multiferroic nanocomposites seem to be a field full of challenging and interesting problems both for scientists and engineers. There are many methods to obtain multiferroic materials e.g. sol–gel, thin films, composites and porous glasses [7].

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* Corresponding author. Tel.: +48 713202955.
E-mail address: Agnieszka.Cizman@pwr.wroc.pl (A. Ciżman).

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Filling the magnetic porous matrix with ferroelectric materials is one of a method to obtain two interacting ferroelectric–ferromagnetic subsystems [7,8]. For industrial applications, stable remanent states, well-controlled switching behavior, and a little dependence on size variations are highly desirable. Understanding and controlling these properties of nanoscale multiferroic elements became a very important topic for current scientific research.

This paper is devoted to an investigation of the magnetic, dielectric and thermal properties of empty magnetic porous glasses and ones filled with $NaNO_2$ or KNO_3 ferroelectrics.

The bulk potassium nitrate (KNO_3) upon heating undergoes a phase transition from a phase II (orthorhombic crystal structure) to a phase I (rhombohedral crystal structure) at around 403 K [9–11]. When cooling, the phase I of KNO_3 does not directly revert back to the phase II, but it passes through a metastable phase III instead, which is ferroelectric in a temperature region of 397–383 K before it returns to the phase II.

Upon heating, the bulk sodium nitrite ($NaNO_2$) exhibits a first-order phase transition from a ferroelectric to a sinusoidal antiferroelectric phase at the Curie temperature $T_C = 436$ K, followed by a second-order phase transition to the paraelectric phase at the temperature $T_N = 438$ K [9,12–13].

2. Experimental details

2.1. Sample preparation

The magnetic porous glass was chosen as a hosting matrix for a formation of multiferroic nanocomposites. The starting two-phase alkali borosilicate glass modified by iron oxide–hematite (60% SiO_2, 15% B_2O_3, 5% Na_2O, 20% Fe_2O_3) was used to fabricate the magnetic porous matrices [8,14,15]. A thermal treatment of the initial glass at 823 K was applied to obtain the phase-separated glass. In order to remove the unstable sodium–boron phase the two-phase glass plates with dimensions of $10 \times 10 \times 0.5$ mm^3 were chemically etched in HCl solution. As a result we obtained microporous glass (MIP) which contains so-called secondary silica particles inside a porous space [16]. In order to remove the secondary silica from pores the MIP glasses were soaked in KOH solution. Thus macroporous glass (MAP) was obtained [17]. The chemical composition of the porous glasses are presented in Table 1.

It should be noted that in the Table 1 total maintenance of iron is given in recalculation on Fe_2O_3. Actually iron is located in glasses at different valency conditions namely Fe^{2+} and Fe^{3+}. This conclusion follows from the results of X-ray analysis according to which magnetite a chemical formula of which in an ionic kind it is possible to present as Fe^{3+} [Fe^{2+}, Fe^{3+}]O^4 is found out in glasses under study.

The absorption method (BET) was used to determine texture parameters of porous matrices. The porous glass exhibits a bimodal structure with average pore diameter of 5 nm and ~50 nm (labeled as Fe20MAP) and porosity of 60%, while for glass labeled as Fe20MIP the average pore diameter is 5 nm with porosity of ~15%. In order to determine the glass structure a powder X-ray diffraction (powder XRD) for Cu Kα emission wavelength of 1.54 Å and in an angular range from 5° to 100° at room temperature was used. A diffraction pattern obtained from the X-ray investigation for the glass Fe20-MIP and Fe20-MAP shows that both a position and an intensity of the diffraction peaks for porous magnetic glass (Fe20-MIP, Fe20-MAP) correspond to the crystal structures of magnetite [7,14]. The obtained size of magnetite nanoparticles is 168 ± 7 Å and 180 ± 5 Å for Fe20MIP and Fe20MAP, respectively.

Table 1
Chemical compositions of the magnetic porous glasses [7].

Glass component	Content, wt.%	
	Fe20-MIP	Fe20-MAP
Na_2O	0.5	1.0
B_2O_3	3.9	5.8
SiO_2	86.8	86.8
Fe_2O_3[a]	8.6	5.9
K_2O	0.2	0.5

[a] *Note:* The content of iron oxides is given in terms of Fe^{3+}.

Fig. 1 shows a structure of the Fe 20-MIP and Fe20-MAP which has been investigated by transmission electron microscopy (TEM) technique. The study of the glasses was realized with EM-125 electron microscope at an accelerating voltage of 75 kV with a resolution of 5 nm [14]. It is possible to see the agglomerates of nanoparticles of a ferriferous phase.

KNO_3-Fe20MIP and KNO_3-Fe20MAP samples were obtained by an immersion of empty magnetic porous glasses into melted potassium nitrate for several hours in order to enhance the filling factor of pores.

The immersion process of magnetic porous glasses into $NaNO_2$ liquid melt for 12 h was used to obtain the $NaNO_2$-Fe20MIP and $NaNO_2$-Fe20MAP multiferroic nanocomposites. All samples were polished to remove micro-crystallites from the sample surfaces.

2.2. Measurement techniques

The dielectric properties of magnetic porous glasses and multiferroic nanocomposites were determined using Novocontrol Alpha Impedance Analyzer at frequencies between 1 Hz and 10 MHz. The measurements were performed in the temperatures range of 120–480 K with the rate of 2 K/min. Ferroelectric hysteresis loops were measured with a homemade high-precision set-up based on Diamant–Drenck–Pepinsky (DDP) bridge. Electrical measurements were performed for porous samples coated with silver paint. Specific heat measurements were performed using a differential scanning calorimetry technique in the temperature range of 340–480 K with the heating rate of 2 K/min. During calorimetric measurements the samples were exposed to a dry N_2 atmosphere. Before each experiment the samples were dried at 390 K for 2 h in order to remove residual water from the pores. Electron magnetic resonance (EMR) studies were performed with a multi-frequency Bruker ElexSys E500 spectrometer. EMR investigation was carried out at X-band spectrometer (~9.5 GHz) with the aid of Oxford Instruments cryostat in the temperature range of 4–300 K and S-band (~3.5 GHz) was used at room temperature. EMR spectra were recorded as the first derivative of the microwave power (about 2 mW) absorption versus the external magnetic field in the range of 0.05–14 kG with the modulation amplitude of the magnetic field equal to 5G at the frequency of 100 kHz. An application of high magnetic field with the resolution of 8192 points per spectrum was necessary to obtain an accurate value of the spectral baseline and precise resonance fields. In EMR studies we used reduced samples with plate dimensions of about $4 \times 2 \times 0.5$ mm^3 and an external magnetic field was perpendicular to the plate, except measurements of the line anisotropy.

3. Results and discussion

3.1. Dielectric response in nanocomposites

The temperature dependence of the complex dielectric permittivity of empty Fe20MIP and Fe20MAP magnetic porous glasses is presented in Fig. 2. For both magnetic porous glasses: Fe20MIP and Fe20MAP the low ε' increases with the temperature. An enhanced dielectric permittivity ε' for Fe20MIP when compared