Magnetic properties of PMN-PT/LSMO multiferroic composite ceramics

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Dielectric and magnetic properties of multiferroic composite materials based on solid solutions of lead magnesium niobate-lead titanate ($(0.87Pb(Mg_{1/3}Nb_{2/3})O_3-0.13PbTiO_3$) and lanthanum strontium manganite ($La_{0.76}Sr_{0.24}MnO_3$ were studied. Materials sintered at temperature below 1000°C demonstrated coexistence of ferroelectric and ferromagnetic ordering. It was shown, that external DC magnetic field impacts on electric field dependence of materials dielectric constant.

Keywords: ferroelectric ceramics, multiferroics, multiferroic composites, magnetic properties.

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1. Introduction

Multiferroics, as materials that combine several types of microscopic ordering, such as ferromagnetic and ferroelectric, represent a promising class of functional materials for electronics and sensors [1]. Unfortunately, the currently known single-phase (natural) multiferroics do not have the characteristics that make it possible to develop competitive devices based on them [2]. In the most studied single-phase multiferroics, such as bismuth ferrite and compounds based on it, the temperatures of phase transitions of electric- and magnetic-ordered states are quite far from each other, which leads to a weakly expressed interaction of the electric and magnetic subsystems, i.e. to weak coupling coefficients [3]. In addition, in many natural multiferroics, nature of the magnetoelectric coupling leads to weakly expressed magnetoelectric and magnetodielectric effects [4]. In this regard, it seems promising to develop artificial multiferroic media based on alternating layers or mixture of magnetic and ferroelectric particles, i.e., multiferroics based on bulk or layered composites [5].

In this paper, a new multiferroic composite was studied. Perovskite-like lanthanum-strontium manganite (LSMO, $La_{1-x}Sr_xMnO_3$), known for its high magnetic susceptibility, magnetization and magnetocaloric effect, is used as a magnetic material [6]. Previously, attempts were made to realize multiferroic 0−3- and 2−2-composites based on LSMO as a magnetic component and solid solutions of barium-strontium titanate, barium zirconate and barium-calcium titanate as ferroelectric component [7–12]. The small values of magnetoelectric coupling obtained in these papers do not yet allow the use of these materials for the development of new electronic components. Higher magnetoelectric coupling values were obtained in composites based on LSMO and lead-containing ferroelectrics such as lead zirconate titanate and lead magnoniobate. But only layered 2−2-composites based on laminated and thin-film heterostructures were stuided for now [13–16]. In this work, we will consider a bulk 0−3-composite with a ferroelectric component represented by the well-known perovskite lead magnoniobate-lead titanate (PMN-PT, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$), which exhibits high values of polarization, dielectric constant, electrocaloric effect and piezoelectric coefficients [17]. The choice of such materials for creating composite was based on their manufacturability and the ability to easily vary the Curie temperatures over a wide temperature range by changing the mole fractions of the solid solution components. The average synthesis temperature of ceramics based on PMN-PT is about 1200°C, which is by 200°C lower than the synthesis temperature of ceramics based on LSMO. Due to this, when annealing PMN-PT/LSMO composite mixture at temperatures below 1200°C it is more likely to obtain a composite of type 0−3 (magnetic particles in a ferroelectric matrix), rather than a single-phase four-component solid solution $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3-LaMnO_3-SrMnO_3$.

The ceramic samples under study were prepared by conventional high temperature sintering route. For the manufacture of $0.87Pb(Mg_{1/3}Nb_{2/3})O_3-0.13PbTiO_3$(0.87PMN−0.13PT) magnesium niobate $MgNb_2O_6$ was first produced. Chemically pure powders of magnesium oxide MgO and niobium (V) oxide Nb_2O_5 were weighed in stoichiometric proportions, mixed, ground and annealed in air at 1100°C for 2 h. Grinding and mixing here and subsequently were carried out in a planetary ball mill „PULVERISETTE 7 premium line" Fritsch for 20 min in isopropyl alcohol with grinding bodies made of zirconium dioxide with a diameter of 3 mm at speed of 800 rpm. After this, chemically pure powders of lead oxide (II) PbO, $MgNb_2O_6$

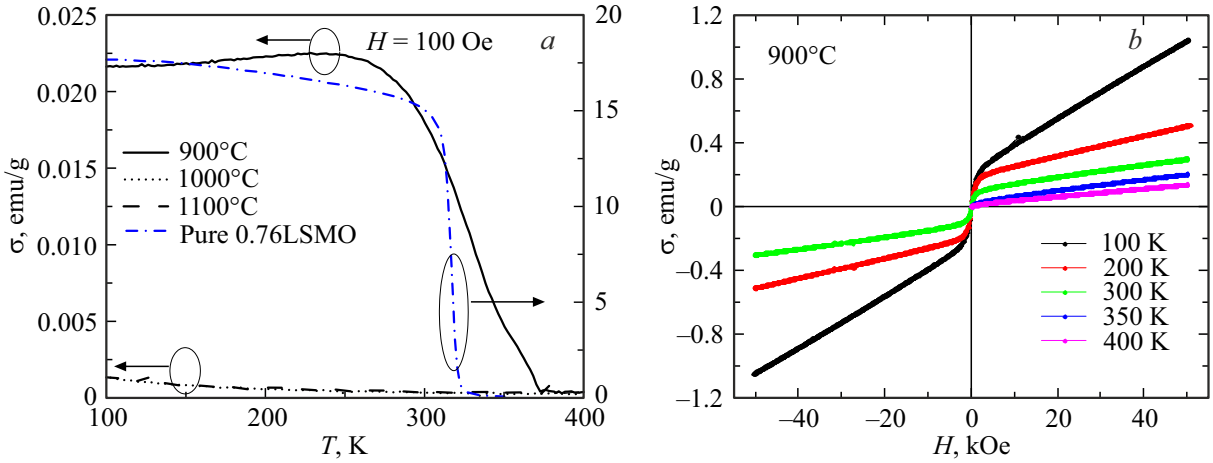

Figure 1. *a* — temperature dependences of the specific magnetization of samples manufactured at different temperatures, measured in magnetic field $H = 100$ Oe; *b* — field dependences of specific magnetization for composite manufactured at a temperature of 900°C, measured at different temperatures.

and titanium oxide (IV) TiO_2 were also weighed in stoichiometric proportions, mixed, grinded and annealed in an air atmosphere at 1200°C for 1 h in a closed crucible. To compensate the lead loss during annealing, the lead oxide was taken in an excess of 2 mol.%.

To produce $La_{0.76}Sr_{0.24}MnO_3$ (0.76LSMO), chemically pure lanthanum carbonate hexahydrate $La_2(CO_3)_3 \cdot 6H_2O$, strontium carbonate $SrCO_3$ and manganese (IV) oxide MnO_2 were taken in the required stoichiometric proportions. Then the mixture was ground and annealed in air at 1400°C for 2 h.

To create composites, the prepared powders were taken in molar ratio of 90% (0.87PMN–0.13PT)/10% (0.76LSMO) and 80% (0.87PMN–0.13PT)/20% (0.76LSMO). The resulting mixture was grinded in the ball mill in isopropyl alcohol, then the resulting suspension was dried at a temperature 180°C for 5 h. The average particle size after grinding was approximately 1 μm. The resulting dry powder was pressed in a cylindrical mold with a force of 5 tons. A four percent aqueous solution of methylcellulose was used as a binder. The resulting samples were disk-shaped with diameter of 12 mm and thickness of 2 mm. The resulting samples were annealed in air at temperatures of 900, 1000 and 1100°C. Then the samples were thinned on both sides to a thickness of 0.5 mm, polished, the electrodes were made with silver-palladium paste. The disk plane-parallel capacitors obtained in this way were used to study the electrical characteristics. Also, to compare the dielectric and magnetic properties 0.87PMN–0.13PT and 0.76LSMO (pure) samples were prepared, synthesized at temperatures of 1230 and 1400°C, respectively.

To study the electrical conductivity of the obtained samples, B2987A Keysight electrometer was used. Composites based on 90% (0.87PMN–0.13PT)/10% (0.76LSMO) showed the resistivity of 0.125 MΩ · m, and composites 80% (0.87PMN–0.13PT)/20% (0.76LSMO) — only 10 kΩ · m. Due to high conductivity further composites based on 80% (0.87PMN–0.13PT)/20% (0.76LSMO) were excluded from the study. Measurements of dielectric constant and loss tangent, as well as capacitance-voltage curves were carried out using Agilent E4980A precision RLC meter and F32-ME Julabo liquid thermostatic bath. Temperature dependences of dielectric constant were measured at frequencies of 100 kHz and 1 MHz, field dependences — at 1 kHz and 1 MHz.

The magnetic characteristics of the resulting composites were studied in the Department of Solid State Magnetism of the Federal State Autonomous Educational Institution of Higher Education „El'tsin UrFU". The field and temperature dependences of specific magnetization were measured using MPMS-XL7 EC magnetic measuring unit (Quantum Design, USA) with a primary transducer based on a superconducting quantum interference sensor (SQUID magnetometer). The magnetic field is created by a superconducting solenoid with a wound wire made of Nb_3Sn. The measurements were carried out in the temperature range 100–400 K in magnetic fields with strength below 50 kOe. Figure 1, *a* shows the temperature dependence of the specific magnetization of ceramic samples manufactured at different temperatures. The sample manufactured at temperature of 900°C has two magnetic phases with Curie points 330 and 370 K. Samples prepared at temperatures of 1000 and 1100°C are paramagnetic at temperatures above 100 K. Figure 1, *b* shows the field dependences of the specific magnetization of sample manufactured at temperature of 900°C.

No magnetic hysteresis was detected in the curves $\sigma(H)$ for samples manufactured at temperatures of 900, 1000 and 1100°C. On this basis, we can conclude that these samples are soft magnetic materials with low coercive force values, $H_C \cdot H_C$ strongly depends on the grain size of the magnetic phase, so we can conclude that the studied compounds are microcrystalline. Above 20 kOe, a linear increase in the specific magnetization is observed for these samples, which is apparently due to the presence of a paramagnetic matrix.

Figure 2 shows the temperature dependences of the dielectric constant and loss tangent of samples manufactured at different temperatures. The increase of dielectric constant with increase rising of sintering temperature is associated with an increase in the samples density during the formation of a monophase solid solution. There is a noticeable drop in the absolute value of the dielectric constant of the composites, and the shift in the Curie temperature to lower temperatures compared to pure 0.87PMN–0.13PT. The dielectric constant for the initial ceramics 0.87PMN–0.13PT, which we synthesized earlier at a temperature of 1230°C, was 22000 at frequency of 100 kHz. The Curie temperature for them was 60°C.

The capacitance-voltage characteristics of the composites were studied in the magnetic field of magnitude $H_{\max} = 5$ kOe and in its absence ($H = 0$), the field was directed perpendicular to the electrodes. Figure 3, *a* shows normalized effect of the magnetic field on the value of the dielectric constant at different DC electric fields for composite sample manufactured at temperature of 900°C. At frequency of 1 kHz, the overall tunability of the sample, defined as $\varepsilon(0)/\varepsilon(E_{\max}) - 1$, at maximum electric field

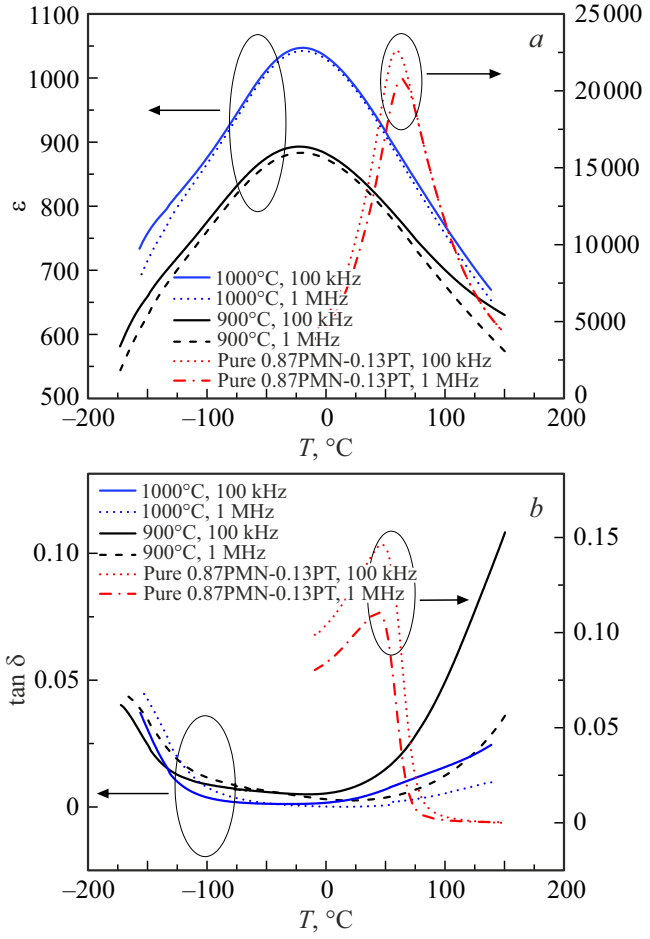

Figure 2. Temperature dependences of dielectric constant (*a*) and dielectric loss tangent (*b*) of samples manufactured at different temperatures.

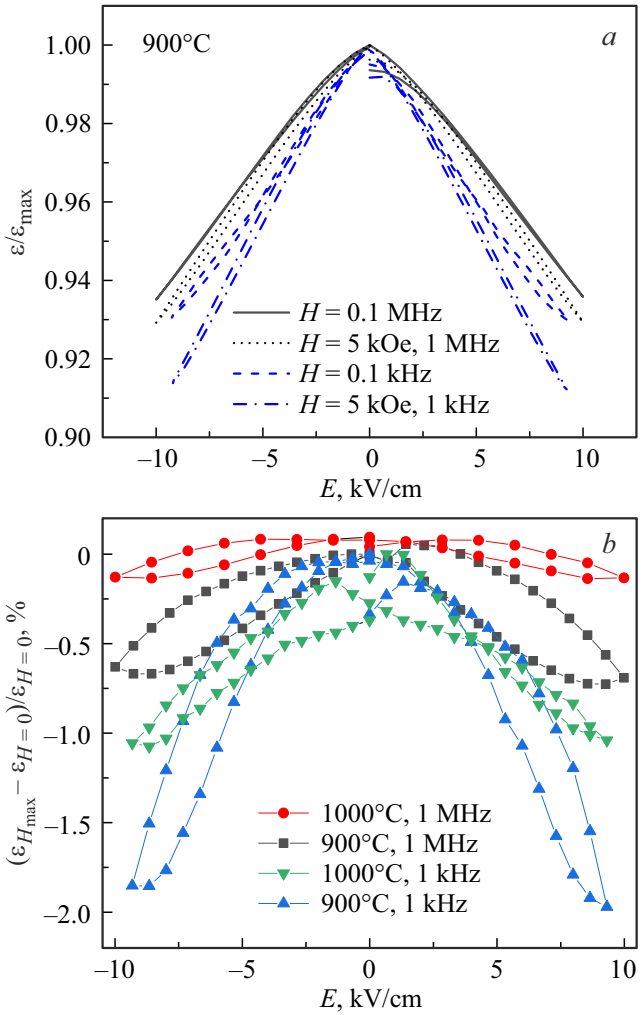

Figure 3. *a* — dielectric permittivity vs. strength of the external electric field for composite manufactured at a temperature 900°C, when magnetic field is applied and removed; *b* — normalized difference in dielectric permittivity values in the presence and absence of magnetic field for samples manufactured at different temperatures.

of 10 kV/cm reaches 7.5%, the application of the magnetic field of 5 kOe increases the tunability to 9.8% (Figure 3, *b*).

Finally, we can conclude that multiferroic composites based on PMN-PT and LSMO prepared by solid-phase high-temperature synthesis showed the presence of a small magnetoelectric coupling. In particular, it was found that for the studied compositions in the considered ranges of electric and magnetic fields (below 10 kV/cm and below 5 kOe, respectively), the increase in the DC magnetic field leads to increase in electric tunability of composite capacitive structures. Further studies must be carried out with aim to increase the magnetodielectric effect in such composites. For example, further studies of the influence of particle size in the initial charge before mixing the composite and a more detailed study of temperatures and synthesis times seems resonable. It is also necessary to study the effect of various

additives, such as magnesium titanate, in order to reduce the composite conductivity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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