Materials Chemistry and Physics 157 (2015) 116–123

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Ferroelectric and magnetic properties of the PMN-PT-nickel zinc ferrite multiferroic ceramic composite materials

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HIGHLIGHTS

- Multiferroic composites PMN-PT-ferrite have been obtained.
- Two compositions of PMN-PT were used to obtain composites.
- Ferroelectric–ferromagnetic properties at room temperature were achieved.
- The shape of the $M(T)$ curves is typical for this type composites.

ARTICLE INFO

Article history:
Received 4 January 2015
Received in revised form
17 February 2015
Accepted 12 March 2015
Available online 18 March 2015

Keywords:
Ceramics
Sintering
Microstructure
Dielectric properties
Magnetic properties

ABSTRACT

Multiferroic ceramic composites based on PMN-PT and Ni–Zn ferrite have been obtained and described in presented work. PMN-PT powders were synthesized by sol–gel method while nickel–zinc ferrite was obtained by classical ceramic method. Two compositions of PMN-PT were used i.e., $0.72PbMg_{1/3}Nb_{2/3}O_3$-$0.28PbTiO_3$ with rhombohedral symmetry and $0.63PbMg_{1/3}Nb_{2/3}O_3$-$0.37PbTiO_3$ with tetragonal one. In both cases the classical methods of calcination and final pressureless densification were used for obtaining of final ceramic composites. XRD, microstructure, EDS, dielectric, electrical and magnetic studies were performed for the obtained ceramic composite materials which confirmed ferroelectric and ferrimagnetic properties at room temperature.

1. Introduction

Solid solutions $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ (PMN-PT) with perovskite structure exhibit very good ferroelectric/relaxor and piezoelectric/electrostrictive properties which depend on the chemical composition (x) and technological methods [1]. A continuous transition from relaxor to normal ferroelectric properties takes place with increasing x. Morphotropic region is observed for $0.25 < x < 0.35$ [2]. With increasing x the maximum of the dielectric permittivity shifts from about $T_m = -3^oC$ for $x = 0$ to about $T_m = 227\ ^\circ C$ for $x = 0.5$ [3]. Morphotropic region of PMN-PT was investigated also in works [4,5]. The properties of solid solution PMN-PT make them useful for many applications for example for high frequency actuators and high power piezoelectric transducers etc. [6,7]. However, there are the problems during obtaining PMN-PT ceramics related with arising of unwanted pyrochlore phase [8,9]. It is the result of high volatility of PbO at high temperatures and the differential reactivity between MgO and Nb_2O_5. The pyrochlore phase degrades the electrophysical properties. Using the sol–gel method we can decrease the volume of pyrochlore phase.

Nickel–zinc ferrite with composition $Ni_{0.64}Zn_{0.36}Fe_2O_4$ has the spinel-type structure and belongs to soft ferrites with a high value of magnetic permeability and high resistance ρ ($10^5\ \Omega m$) [10]. Devices obtained from this material are used for example for signal processing, filters and broad-band transformers.

Mixing the upper described materials we have tried to obtain ceramic compositions which are multiferroic at room temperature

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http://dx.doi.org/10.1016/j.matchemphys.2015.03.025
0254-0584/

and can be characterized by a magnetic response to a variable electric field, or inversely, a polarization change in the external magnetic field. Similar effect was reached for example in [11–13]. In general obtained are also multiphase composites with additional, for example, polymer phase (called ceramic-polymer composites) [14]. In the case of the ferroelectromagnetic materials, a lot of other techniques of powder synthesizing such as molten salt synthesis, reaction sintering, columbite, sol–gel and co-precipitation methods are used, besides the classical method [15]. The ferroelectric and mechanical properties, altogether with the degree of ferroelectric and ferromagnetic subsystems' coupling in this type materials are mainly related to the properties of each components of the solid solution and their percentage [16–18]. Recently for example there were described ceramic composites based on best known piezoelectric PZT and zinc ferrite [14,19] and PMN-PT-ferrite composites [20,21]. Below described materials which have been obtained as a combination of ferroelectric/relaxor component i.e., $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ and ferrimagnetic component i.e., ($Ni_{0.64}Zn_{0.36}Fe_2O_4$) are an example of two component materials.

2. Experiment

PMN-PT solid solution was obtained by sol–gel technology described in [8]. PMN was obtained as a result of the reaction between $Mg(OC_2H_5)_2$ and $Nb(OC_2H_5)_5$ in alcohol. In a second step lead acetate (II) and ethylene glycol were added to the mixture according to the formula: $Pb(CH_3COO)_2 + 1/3\ Mg(Nb(OC_2H_5)6)_2 \rightarrow Pb(Mg_{1/3}Nb_{2/3})O_2(OC_2H_5)_2 + 2CH_3COOC_2H_5$. $PbTiO_3$ (PT) was obtained according to the formula: $Pb(CH_3COO)_2 + Ti(CH_3CH_2CH_2O)_4 \rightarrow PbTiO_2(CH_3CH_2CH_2O)_2 + 2CH_3COOC_3H_7$. Then the two liquid compositions PMN and PT were mixed together in ethylene glycol (with proper proportions for $x = 0.28$ and 0.37) to give the PMN-PT compound. Finally distilled water was added in order to begin hydrolysis of the obtained sol solution.

After passing the sol to gel, it was dried and then ground and sintered at $T = 550\ ^\circ C/4$ h in order to remove the organic parts. Dielectric and electromechanical properties of such obtained PMN-PT samples were described in [8,22]. Nickel–zinc ferrite $Ni_{0.64}Zn_{0.36}Fe_2O_4$ was obtained from the simple oxides Fe_2O_3, ZnO, NiO. The powders were mixed using Fritsch planetary ball mill for 15 h. The synthesis was conducted at conditions 1100 °C/4 h using calcination technique.

These two components were mixed in proportion 90% PMN-PT and 10% ferrite using Fritsch planetary ball mill for 15 h (wet in ethyl alcohol). After this the mixture was synthesized by calcination method with conditions: $T_{synth} = 950\ ^\circ C$, $t_{synth} = 8$ h. Final pressureless densification (sintering) of composite ceramic samples was conducted at $T_s = 1100\ ^\circ C$ by $t_s = 8$ h. Two compositions i.e., 0.73PMN-0.28PT-ferrite (abbreviated to PP28-F) and 0.63PMN-0.37PT-ferrite (abbreviated to PP37-F) were obtained. For electrical tests silver electrodes were applied on the both surfaces of the disk-shaped samples using paste burning method.

The X-ray tests at room temperature were performed using a Philips diffractometer (CuK_α radiation). Microstructure, EDS (Energy Dispersive Spectrometry) and EPMA (Electron Probe Microbeam Analysis) tests were carried out using a scanning microscope HITACHI S-4700. Magnetic properties were investigated using SQUID (MPMS XL-7 Quantum Design) magnetometer within the temperatures range from −271 °C to +27 °C and magnetic field up to 7 T. Dielectric and impedance measurements were performed using QuadTech 1920 LCR meter for a cycle of heating (at frequencies of the measurement field from 0.1 kHz to 1.0 MHz). Dielectric hysteresis loops P–E were investigated using Sawyer-Tower circuit and a Matsusada Inc. Heops-5B6 precision high voltage amplifier. Electromechanical measurements were carried out using an optical displacement meter (Philtec Inc., D63) and high voltage amplifier Heops. Data were stored on a computer disc using an A/D, D/A transducer card and LabView computer program.

3. Results and discussion

3.1. Crystal structure and microstructure

The density of 0.72PMN-0.28PT is 7.45 g/cm^3, while the density of 0.63PMN-0.37PT is equal to 7.21 g/cm^3. The densities of PP-F composite materials are similar (see Table 1).

Fig. 1 shows X-ray diffraction patterns of powder PMN-PT after synthesis, the ferrite powder and PP-F powders at room temperature. For rhombohedral 0.72PMN-0.28PT the (200) line should be a single maximum (R3*m* space group), while for tetragonal 0.63PMN-0.37PT the (200) line should consist of two components (P*m* and P4*mm* space groups). The X-ray analysis of obtained by us PMN-PT powders after synthesis exhibit rhombohedral symmetry for $x = 0.28$ and tetragonal one for $x = 0.37$. The XRD patterns of the synthesized powders of PMN-PT show lines belonging to perovskite phase with relatively small amount of pyrochlore phase. It is known that preparation of PMN using sol–gel method decreases the amount of unwanted pyrochlore phase [23]. Comparing the intensities of the reflections 29.08° (pyrochlore line 222) and of the reflections 31.2° (perovskite line 110) it has been stated than the amount of pyrochlore phase is higher for composite with $x = 0.37$.

X-ray diffraction pattern of ferrite powder $Ni_{0.64}Zn_{0.36}Fe_2O_4$ shows a single phase cubic spinel lines what stays in agreement with results of [24].

In case of the mixtures PP-F the X-ray the diffraction patterns we can see strong maxima originating from PMN-PT, as well as weak reflexes from the $Ni_{0.64}Zn_{0.36}Fe_2O_4$ ferrite. Since the synthesis of mixtures PP-F was performed by calcination method, the increase of the amount of the pyrochlore phase was observed and as a result for PP-F the amount of pyrochlore phase is higher than in PMN-PT without ferrite. In final compositions smaller amount of pyrochlore phase was observed for PP28-F (about 11%).

Energy-dispersive X-ray spectroscopy EDS (surface and local analyses) confirmed the assumed chemical composition of PP-F and the presence of maxima from elements originating in PMN-PT and elements originating in ferrite (Fig. 2). The obtained EDS examinations are comparable to the assumed proportions of the initial components, calculated by stoichiometry, while obtaining the PMN-PT-ferrite material. In Table 2 (for PP28-F) and in Table 3 (for PP37-F) are summarized assumed and measured individual components of the composite samples.

Fig. 3 presents microstructural SEM images of the ferrite ceramics (Fig. 3a), PMN-PT ceramic samples (Fig. 3b PP28 and Fig. 3c PP37), and fractured ceramic composite PP-F samples i.e., PP28-F

Table 1
Parameters of the PMN-PT ceramic samples and PP-F composite materials (dielectric properties for $f = 1$ kHz, d_{33} for $E = 0.5$ kV/mm and $f = 0.1$ Hz).

	PMN-PT28	PMN-PT37	PP28-F	PP37-F
ρ [g/cm^3]	7.45	7.21	7.46	7.47
T_m [°C]	132	187	123	182
ε_r	1860	1760	1860	1150
ε_m	6.290	6090	7.130	5840
tanδ at T_r	0.025	0.021	0.039	0.011
tanδ at T_m	0.024	0.032	0.095	0.063
P_S [μC/cm^2]	25.10	25.50	12.60	8.00
P_R [μC/cm^2]	21.00	22.16	8.42	4.51
E_C [kV/mm]	0.67	1.04	0.57	0.81
d_{33} [m/V] × 10^{-12}	400	457	368	20