Journal of Magnetism and Magnetic Materials 324 (2012) 3052–3057

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Magnetic, magnetoelectric and dielectric behavior of $CoFe_2O_4$–$Pb(Fe_{1/2}Nb_{1/2})O_3$ particulate and layered composites

J. Kulawik, D. Szwagierczak, P. Guzdek *

Institute of Electron Technology, Kraków Division, Zabłocie 39, 30-701 Kraków, Poland

ARTICLE INFO

Article history:
Received 12 October 2011
Received in revised form
26 April 2012
Available online 11 May 2012

Keywords:
Bulk composite
Layered composite
Relaxor-ferrite
Magnetic properties
Magnetoelectric effect

ABSTRACT

Magnetic, magnetoelectric and dielectric properties of multiferroic $CoFe_2O_4$–$Pb(Fe_{1/2}Nb_{1/2})O_3$ composites prepared as bulk ceramics were compared with those of tape cast and cofired laminates consisting of alternate ferrite and relaxor layers. X-ray diffraction analysis and Scanning Electron Microscope observations of ceramic samples revealed two-phase composition and fine grained microstructure with uniformly distributed ferrite and relaxor phases. High and broad maxima of dielectric permittivity attributed to dielectric relaxation were found for ceramic samples measured in a temperature range from −55 to 500 °C at frequencies 10 Hz–2 MHz. Magnetic hysteresis, zero-field cooled (ZFC) and field cooled (FC) curves, and dependencies of magnetization on temperature for both magnetoelectric composites were measured with a vibrating sample magnetometer in an applied magnetic field up to 80 kOe at 4–400 K. The hysteresis loops obtained for composites are typical of a mixture of the hard magnetic material with a significant amount of the paramagnet. The bifurcation of ZFC–FC magnetizations observed for both composites implies spin-glass behavior. Magnetoelectric properties at room temperature were investigated as a function of *dc* magnetic field (0.3–7.2 kOe) and frequency (10 Hz–10 kHz) of *ac* magnetic field. Both types of composites exhibit a distinct magnetoelectric effect. Maximum values of magnetoelectric coefficient attained for the layered composites exceed 200 mV/(cm Oe) and are almost three times higher than those for particulate composites.

1. Introduction

Multiferroics are materials which exhibit two or more ferroic properties (ferroelectricity, ferromagnetism and ferroelesticity). If a material is simultaneously ferromagnetic and ferroelectric, magnetoelectric effect can be observed. In such materials applied magnetic field causes a dielectric polarization or external electric field results in an induced magnetization.

Multiferroic properties are shown by some single-phase materials. The best known is $BiFeO_3$. Iron-based relaxors – lead iron niobate, tantalate and tungstate – being also single phase multiferroics, have been scarcely investigated [1–8]. Single phase multiferroics are rare and typically show weak magnetoelectric effect. The majority of these materials have also low Néel or Curie temperature far below room temperature.

However, a strong magnetoelectric effect can be attained as the "product property" in composites. In the 1970s, the first multiferroic composite based on piezoelectric $BaTiO_3$ and ferrimagnetic $CoFe_2O_4$ has been reported. Since then, many multiferroic composites have been fabricated as bulk ceramics, bilayers, multilayers, thin films, nanostructures [9–24].

Due to a possibility to switch ferromagnetic properties by an external electric field and ferroelectric properties by a magnetic field, multiferroic materials are very attractive for numerous applications including magnetic field sensors, memory devices, transducers, filters, waveguides, switches, phase invertors.

$CoFe_2O_4$ (CFO) ferrite is a well-known hard magnetic material with Curie temperature of about 800 K, high coercivity, moderate saturation magnetization and good chemical stability [25–28]. Due to its large magnetostriction it is a good candidate component of composites with high magnetoelectric effect.

$Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) is a ferroelectric relaxor which has a high dielectric constant, undergoes a diffuse phase transition at about 385 K, is relatively easy to prepare as a single phase and can be sintered at low temperatures (<1050 °C). PFN exhibits two antiferromagnetic transitions with Néel temperatures in the range 140–155 K and 9–19 K [1,2].

This paper is devoted to composite multiferroics being a combination of cobalt ferrite and PFN relaxor. Two different procedures were used to prepare the investigated composites-one was sintering of bulk ceramic samples, and the second was tape casting, lamination and co-sintering of alternate ferrite and

* Corresponding author. Tel.: +48 663047567; fax: +48 012 6563626.
E-mail address: pguzdek@ite.waw.pl (P. Guzdek).

0304-8853/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2012.04.056

relaxor layers. The properties of the developed materials were characterized by X-ray diffraction analysis, scanning electron microscopy, dielectric, magnetic and magnetoelectric coefficient measurements.

2. Experimental

Synthesis of PFN was carried out by a two step "wolframite" method. The wolframite $FeNbO_4$ was prepared by ball-milling Fe_2O_3 and Nb_2O_5 in stoichiometric proportions in isopropyl alcohol for 8 h and subsequent calcination at 1000 °C for 4 h. The reaction product was then mixed by ball milling with PbO, dried, pelletized and calcined at 800 °C for 4 h in a covered crucible. The addition of 1 mol% MnO_2 was introduced to the batch in order to improve resistivity. Synthesis of $CoFe_2O_4$ ferrite was performed by a conventional solid state reaction at 1050 °C for 10 h. The syntheses products were ball-milled for 8 h. CFO–PFN composites were prepared by two methods. Bulk ceramic samples were fabricated by sintering at 950 °C for 2 h the mixture of ferrite and relaxor, previously ball-milled, granulated and pressed into pellets. The layered composites were prepared by tape casting, lamination and co-sintering of alternately stacked ferrite and relaxor layers.

Slurries for tape casting are composed of the relaxor or the ferrite powder, polyvinyl butyral as a binder, fish oil as a dispersant, polyethylene glycol and dibutyl phthalate as plasticizers, toluene and isopropyl alcohol as solvents. Tape casting was performed using a table top tape caster (R.Mistler, TTC-1200). The tapes were dried at 50 °C and cut by a laser (Oxford Laser, E-355-3-G-OA) into rectangular sheets. Six layers of the ferrite and five layers of the relaxor were stacked alternately and pressed isostatically (Pacific Trinetics Corporation, IL-4008PC) under a pressure of 35 MPa for 10 min at 70 °C. Then burnout of organic components was carried out in the temperature range 100–500 °C, followed by sintering at 950 °C for 2 h.

Phase compositions of the synthesized CFO and PFN powders and CFO–PFN ceramics were examined by a Philips X'Pert diffractometer. Microstructures of bulk ceramic and multilayer samples were investigated using a FEI and a Jeol scanning electron microscopes.

Dielectric properties of composites were investigated using a LCR QuadTech meter in a temperature range from −55 to 350 °C and in a frequency range 10 Hz–2 MHz.

Magnetic properties of the samples were studied using a vibrating sample magnetometer (PPMS Ever Cool, 9 T, Quantum Design) in the temperature range 4–400 K. Hysteresis loops were determined at a magnetic field changing in a range from −80 to 80 kOe. Magnetization versus temperature measurements were carried out as a function of magnetic field (1–85 kOe). Zero-field cooled and field cooled magnetization curves in the presence of a magnetic field of 100 Oe were determined in the temperature range 4–400 K. In the case of multilayer composites the direction of the applied magnetic field was parallel to the layers.

The magnetoelectric effect was evaluated at room temperature by a dynamic lock-in method (AGH University of Science and Technology), which has been described previously in the literature [12]. The samples were placed in *dc* magnetic field created by an electromagnet and *ac* sinusoidal magnetic field produced by Helmholtz coils. The applied *dc* field was perpendicular or parallel to the sample surface. The induced voltage between sample surfaces was measured with a lock-in amplifier (Stanford Research System, model SR 830) with an input resistance of 100 MΩ and a capacitance of 25 pF. The lock-in amplifier was used in differential mode. To measure the *dc* and *ac* magnetic field, a Hall probe SM 102 was applied. ME coefficients were determined for various magnitudes of the *dc* static magnetic field (0.3–7.2 kOe) and different frequencies of the *ac* modulation field (10 Hz–10 kHz).

3. Results and discussion

X-ray diffraction analysis has shown the presence of ferrite and relaxor phases in the sintered particulate composites. Additional phases were not found which implies the lack of chemical interaction between the composite components. SEM images revealed dense and fine-grained microstructure and uniform distribution of the ferrite and relaxor phases in the samples.

Relaxor and ferrite tapes are characterized by a good smoothness, flexibility and strength. Thicknesses of the dried tapes are 100–150 μm. Fig. 1 illustrates a cross-section of the sintered CFO–PFN layered composite. No delaminations, cracks or the formation of interlayer is observed at the relaxor-ferrite interfaces after cofiring process. Both layers are well sintered and fine-grained with grain sizes of 0.5–2 μm for the relaxor and below 0.5 μm for the ferrite phase.

As can be seen from Fig. 2, the bulk composite exhibits broad and high maxima of dielectric permittivity, at the level of 10^3–10^4 in the frequency range 10 Hz–1 MHz, decreasing and shifting to higher temperatures with increasing frequency. The positions of these maxima do not correspond to the peaks related to diffuse phase transition of the pure PFN relaxor phase (563 K and 385 K at 1 kHz for the composite and the relaxor, respectively). Thus, the observed broad maxima are suggested to be attributed to dielectric relaxation in both the ferrite and relaxor components of the bulk composite. In multilayer composites, alternate ferrite and relaxor layers form capacitors connected in series. Thus, the dielectric permittivity of the layered composite is much lower

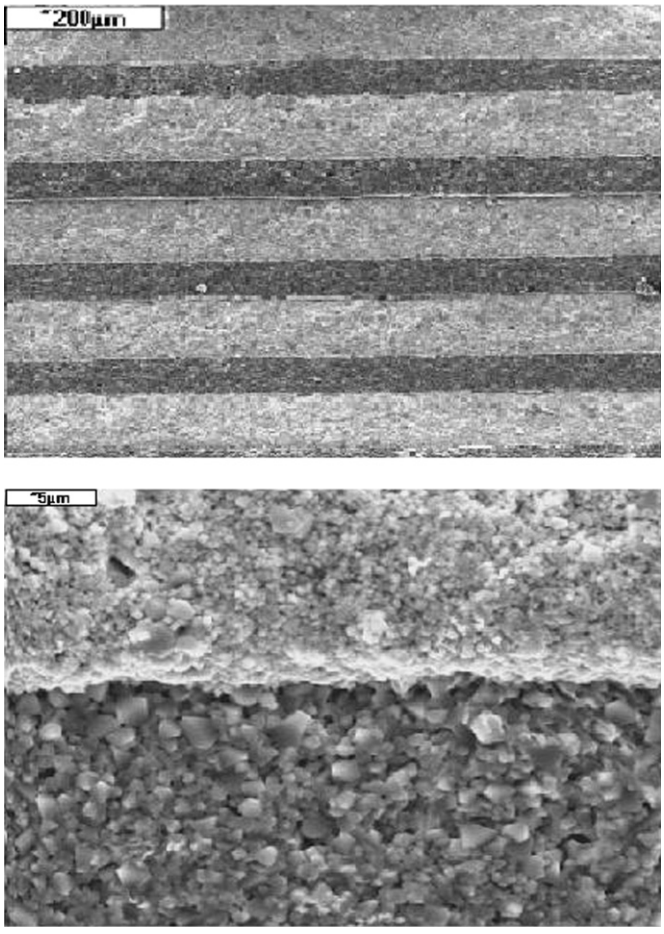

Fig. 1. SEM micrograph of a fractured cross-section of layered $CoFe_2O_4$–PFN composite consisting of ferrite (dark) and relaxor (light) layers.