Journal of Magnetism and Magnetic Materials 341 (2013) 112–117

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Preparation and characterization of $BaTiO_3$+$MgCuZnFe_2O_4$ nanocomposites

M. Kanakadurga, P. Raju, S.R. Murthy [*]

Department of Physics, Osmania University, Hyderabad 500007, India

ARTICLE INFO

Article history:
Received 25 September 2012
Received in revised form
6 April 2013
Available online 17 April 2013

Keywords:
Composites
Ferrite
Ferroelectrics
Mechanical milling
Magnetic properties
Magnetoelectric coefficient

ABSTRACT

MgCuZn ferrite and $BaTiO_3$ powders with the crystallite sizes 88 nm and 82 nm were prepared using a high energy mechanical milling and sintering method. The prepared powders were characterized using X-ray diffractometer (XRD), Fourier transform infrared spectrometer and scanning electron microscope (SEM). The nanopowders were mixed to obtain the composites with composition $x$$BaTiO_3$+(1−$x$) $Mg_{0.48}Cu_{0.12}Zn_{0.4}Fe_2O_4$ (where x=0–1) using a mechanical milling. The presence of ferroelectric ($BaTiO_3$) phase and ferrimagnetic (MgCuZn ferrite) phase has been confirmed using XRD and SEM. Ferroelectric hysteresis loops and magnetic hysteresis loops have been recorded at room temperature. In polarization–electric-field curves (P–E), the remanent polarization and coercive fields display little asymmetry. When the amount of ferrite phase is increased, the ferroelectric coercive field also increases. The saturation magnetization decreases with an increase of phase fraction of $BaTiO_3$, because the interaction between magnetic grains is weakened by the existence of nonmagnetic (ferroelectric) phase that is distributed in the magnetic phase. The electrical properties were measured on the composites at 1 MHz. The static magnetoelectric (ME) voltage coefficient $(dE/dH)_H$ was measured by change in ME output voltage with respect to dc bias magnetic field at a constant applied magnetic field.

1. Introduction

Ferroelectric–ferromagnetic composite materials have attracted wide attention from many researchers because of their interesting electromagnetic properties and magnetoelectric effects [1–3]. Ferrite–ferroelectric composite materials can provide both inductance and capacitance. Hence, these materials can be used to design and produce the passive electromagnetic frequency interference (EMI) filters, integrating inductive and capacitive elements in one package [4,5]. These components have intensive industrial applications for suppressing electromagnetic frequency interference in electronic circuitry. The filters performance can be optimized by adjusting the inductive and capacitive properties of ferrite–ferroelectric composite materials through compositional variation [6]. Compositional variation means, customizing filters properties. The important factor, in the preparation of capacitive–inductive composites for multilayer chip inductors and EMI filters, is the selection of proper composition of ferrite and ferroelectric materials [7]. It is also important that the chemical reactions between two constituent materials should not take place during the preparation of a composite material [8,9]. This will help to stop the degradation of dielectric and magnetic properties of the composite. High energy mechanical milling, a physical method, is chosen for preparing the materials constituting the composite, since other methods such as chemical methods involve chemical manipulations and rections during the preparation of the constituents of the composite, which may influence the degradation of magnetic and electrical properties [10,11]. Moreover, for physical methods, the raw materials used for the preparation of the constituents, are more economical when compared with those of other chemical methods.

With the rapid development of mobile communication and information technology, passive electronic components, such as surface mount devices (SMD), with small size, high efficiency and low cost, are required [12]. Chip inductors, one of the passive SMD, are important components for the electronic products such as notebook computers, hard disk drive, video cameras, mobile phones, etc., which require small dimensions, light weight and better functions [12–15]. As a result of fast development of wireless communication industry, mobile handsets continue to shrink in size and simultaneously offer increasingly complex functions. This raises the requirements both for miniaturization and performance on all components used. In particular, multilayer chip inductor (MLCI) needs to be made even smaller in size while providing high performance for high frequency circuit applications. The traditional wire wound inductors, with no magnetic shielding, can be miniaturized to a certain limit [9]. This leads to the development of new materials for MLCI.

From the earlier work done on ferrites, NiCuZn ferrites and MgCuZn ferrites were found to be suitable materials for the use in

[*] Corresponding author.
E-mail address: ramanasarabu@gmail.com (S.R. Murthy).

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.04.037

MLCI applications due to better electromagnetic properties [16–19]. However, MgCuZn ferrite was found to be a better material than NiCuZn ferrite for MLCI, owing to its high resistivity, Curie temperature and low cost. Moreover, the magnetostriction constant for MgCuZn ferrite is lower than that of NiCuZn ferrites and hence, the ferrite possesses better magnetic properties [20–22]. As a result, further miniaturization of multilayer chip inductors can be achieved with MgCuZn ferrites [19]. Multiferroic composite materials that display a coexistence of ferroelectric and ferromagnetic responses attracted the current interest because of their potential for several novel device applications such as high frequency MLCI applications, EMI filters and sensors etc [7]. In a multiferroic composite, electromagnetic coupling is facilitated by elastic interaction between ferroelectric and ferrimagnetic components via piezoelectric effect and magnetostriction [7]. In the current work, the constituent materials selected were: BaTiO3, a ferroelectric material with large piezoelectricity and $Mg_{0.48}Cu_{0.12}Zn_{0.4}Fe_2O_4$, (MCZ ferrite) a ferrimagnetic material with low magnetostriction, so that composites of $BaTiO_3$–$Mg_{0.48}Cu_{0.12}Zn_{0.4}Fe_2O_4$ combine the ferroelectricity and ferrimagnetism. When both ferrimagnetic phase and a ferroelectric phase coexist in a single material, novel properties such as magneto-electric, magneto-optic and other coupling mechanisms are expected due to interaction between the magnetization and electric polarization [4,5]. The possibility of these interesting coupling effects motivates us to study ferrite–ferroelectric composites. In the present investigation, the composites were prepared using a high energy mechanical milling method. To our knowledge, there are no reports on the preparation of MgCuZn ferrite and $BaTiO_3$ nanocomposites using the high energy mechanical milling method and their electrical and magnetic studies. The prepared samples were characterized using XRD, FTIR and SEM. Ferroelectric hysteresis loops and magnetic hysteresis loops have been recorded at room temperature and the obtained results are presented in this paper.

2. Experimental method

For the preparation of $Mg_{0.48}Cu_{0.12}Zn_{0.4}Fe_2O_4$ (MCZ), a mixture of Fe_2O_3 (99.8% purity), CuO (99.7%), MgO (99.0%) and ZnO (99.9%), all from Aldrich, were used as received without further purification. The required amounts were weighed and mixed accordingly in a vial to achieve the stoichiometry. Mechanical milling was carried out for 20 h in the hardened WC vial together with 10 12 mm WC balls, using a Retsch Co. high energy planetary ball mill. Ball to powder mass charge ratio of 14:1 was chosen. The speed of the mill was set at 400 rpm with interval at 40 min. The powders were analyzed by Fourier Transform Infrared spectrometer [(FTIR, Brucker tensor 27] at intervals of 5 h grinding time to confirm the ferrite phase formation. Finally, the powder grounded for 20 h, has been examined from the X-ray diffraction (XRD) spectrum using X-Pert PAN Analytical diffractometer.

Pure barium oxide (BaO) and titanium dioxide (TiO_2) powders were taken in stoichiometric ratio and mixed in the mechanical mill for the preparation of $BaTiO_3$ (BT). The total grinding time used was 16 h. At the end of 5 h, 10 h and 16 h grinding time, the powders were analyzed using XRD and FTIR. In this case also, ball to powder mass charge ratio of 14:1 with mill speed of 400 rpm were used.

The prepared powders of MCZ and BT were mixed at different mol%, to obtain composites, $x BaTiO_3+(1-x)Mg_{0.48}Cu_{0.12}Zn_{0.4}Fe_2O_4$ {where $x=$[0 (MCZ), 0.2 (MCZBT1), 0.4 (MCZBT2), 0.5 (MCZBT3), 0.6 (MCZBT4), 0.8 (MCZBT5), 1.0 (BT)]}. The mixed powders were milled in a Retsch Co. high energy planetary ball mill for 10 h, 15 h, 20 h and 40 h under air atmosphere with the same milling conditions mentioned above. The powders were milled for 40 h to reach a steady state where the particles have become homogenized in size and shape. The milling parameters (speed, milling time and purity of chemicals) have been controlled carefully to reduce the defects and then to obtain nanocomposites with desired morphology. The 40 h milled powders were uniaxially pressed into toroids and pellets and then sintered at 850 °C/2 h in air atmosphere.

X-ray diffractometer (XRD) with CuK_α radiation was used to identify the structure of the composites. The bulk density of the sintered composites was measured using the Archimedes principle. Magnetic measurements were carried out using vibrating sample magnetometer (VSM; Lakeshore, Model 7404). Ferroelectric hysteresis loops were recorded under an alternative electric field using a ferroelectric test system. The microstructure of sintered composite materials was studied using scanning electron microscope (SEM; Model JEOL, Tokyo, Japan). For electrical measurements, the disk samples were coated with silver paste on both sides. The dielectric constant (ε), dissipation factor (D), initial Permeability (μ_i) and quality factor (Q) of the sintered composite specimens were measured using LCR meter (Kokuyo Electric Co., Japan model no. KC-605) at 1 MHz. The composites are poled electrically and magnetically before measuring the magnetoelectric coefficient (ME effect). The electric poling was carried out in a 1.5 kV/cm dc field, during constant cooling of samples from 140 °C to room temperature. Magnetic poling was done at a constant dc magnetic field (5 kOe) for 20 min by mounting the sample centrally in between the pole pieces of a dc electromagnet using a sample holder. The stray charges developed during poling were removed by grounding the plates of the sample holder. The ME signals were measured by means of electric potential that is developed across the sample, as a function of applied increasing dc magnetic field. The output ME voltage generated in the sample was measured using Keighley's electrometer (Model 614). The static ME voltage coefficient $(dE/dH)_H$ is measured by change in ME output voltage with respect to dc bias magnetic field at a constant applied magnetic field.

3. Results and discussion

The formation of spinel structure in the ferrite sample, can be confirmed using FTIR spectral analysis [23]. Fig. 1 shows the FTIR spectra of MgCuZn ferrite powder at different grinding times (10 h, 15 h and 20 h). For 10 h and 15 h milled sample, the spinel cubic structure bands are not formed, suggesting that it is a intermediary phase consisting of Mg, Cu, Zn, and Fe, which nucleates at interfaces and grows by interdiffusion under interfacial metastable equilibrium. For 20 h milled powders, the formation of cubic spinel structure is confirmed. The vibrational frequencies of IR bands of MCZ ferrite are observed in the range $\nu_1=582\ cm^{-1}$ and $\nu_2=443\ cm^{-1}$, which are attributed to tetrahedral and octahedral sites of the spinel structure [23,24], are in well agreement with the reported values [25]. The figure also reveals the confirmation of metal–oxide bonding of MgCuZn ferrite [26,27], in which the absorption bands vary with the milling time of the samples. A change in the intensity of absorption bands as seen from the FTIR spectra is attributed to the difference in the ferrite phase formation during milling. The additional bands observed in the figure are due to partial phase formation. It is observed from the figure that there exist prominent bands near 3400 cm^{-1} and 1450 cm^{-1}, suggesting the presence of considerable amounts of water (H_2O) and OH^{-1} in the sample [28] which are attributed to the stretching modes of H–O–H bending vibrations of free or absorbed water [29,30].