Journal of Magnetism and Magnetic Materials 385 (2015) 418–427

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Synthesis and characterization of $La_{0.75}Ca_{0.15}Sr_{0.05}Ba_{0.05}MnO_3$–$Ni_{0.9}Zn_{0.1}Fe_2O_4$ multiferroic composites

Md. D. Rahaman [a,*], S.H. Setu [a], S.K. Saha [b], A.K.M. Akther Hossain [b]

[a] Deparment of Physics, University of Dhaka, Dhaka 1000, Bangladesh
[b] Department of Physics, Bangladesh University of Engineering and Technology (BUET), Ramna, 1000 Dhaka, Bangladesh

ARTICLE INFO

Article history:
Received 21 December 2014
Received in revised form
1 March 2015
Accepted 6 March 2015
Available online 11 March 2015

Keywords:
Manganite–ferrite composites
Sintering
X-ray diffraction
Dielectric response
Magnetic property
Magnetoelectric voltage coefficient

ABSTRACT

In the present work, we report on structural, dielectric, impedance spectroscopic studies and magnetoelectric properties of $(1-x)$ $La_{0.75}Ca_{0.15}Sr_{0.05}Ba_{0.05}MnO_3$ (LCSBMO)+(x) $Ni_{0.9}Zn_{0.1}Fe_2O_4$ (NZFO) ($x=0.0$, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) composites. The composites were prepared by the solid state reaction route. The coexistence of a cubic spinel NZFO phase and a tetragonal LCSBMO phase in the composites is confirmed by the X-ray diffraction measurement. Scanning electron microscopy images reveal that NZFO particles were distributed non-uniformly with some porosity in the LCSBMO matrix. Frequency dependent dielectric constant shows usual dielectric dispersion behavior, which may be attributed to the Maxwell–Wagner type interfacial polarization. At higher frequencies ($\geq 10^5$ Hz), due to electronic and ionic polarizations only, the dielectric constant is independent of frequency. Complex impedance shows semicircular arc due to the domination of grain boundary resistance and electric modulus confirms the presence of hopping conduction. The AC conductivity (σ_{AC}) obeys the power law and the linearity of $\log \omega^2$ versus $\log \sigma_{AC}$ plots indicates that the conduction mechanism is due to small polaron hopping. Low frequency dispersion in permeability is due to domain wall motion and the frequency stability of permeability indicates that the arrangement of the magnetic moment in the polarization process can keep up with the external field. The maximum magnetoelectric voltage coefficient of ~40 mV Oe^{-1} cm^{-1} for $x=0.8$.

1. Introduction

Magnetoelectric (ME) effect which occurs due to interaction between electric and magnetic dipole in ferroelectric–ferromagnetic multiferroic materials [1] has brought about much interest, not only for technological applications in possible miniaturization and integration for electronic devices such as waveguides, switches, transducers, modulators, magnetic storage systems, read heads for hard disks, sensing devices, electrically controlled microwave phase shifters or ferromagnetic resonance devices, magnetically controlled electro-optic or piezoelectric devices, broadband magnetic field sensors, and magnetoelectric memory cells due to their capability of monitoring magnetization/electric polarization as a function of external electric/magnetic field, but also from the view point of fundamental scientific understanding [2–7]. With the development of science and technology, rapid development of miniaturized digital circuits, and excellent high-frequency characteristics of the microwave devices, single-phase multiferroic materials like Cr_2O_3, $BiFeO_3$, $Pb(Fe_{0.5}Nb_{0.5})O_3$, etc. [3,8,9] cannot satisfy the requirement of much technological applications because they normally have a feeble ME effect at room temperature as well as a Neel temperature far below room temperature [10]. Then there have been resurgence among the researchers for the dual phase composite materials based on the concept of "product property" [11] to mitigate the requirements of miniaturization and excellent high frequency performance of the electronic devices. Although reported values for the dual phase composites are 10–100 times higher than the ME coefficient for single phase multiferroics [12] but their practical applications are still at infancy.

In the recent years, large numbers of manganite–ferrite (hard and soft) composites have been produced and investigated such as $La_{0.67}Sr_{0.33}MnO_3/(Zn_{0.6}Fe_{0.4})[Ni_{0.4-x}Cu_xFe_{1.6}]O_4$ [13], $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3/CoFe_2O_4$ [14], LCMO/$NiFe_2O_4$ [15–17], $La_{2/3}(Ca_{0.6}Ba_{0.4})_{1/3}MnO_3/NiFe_2O_4$ [18], $La_{0.7}Sr_{0.3}MnO_3/NiFe_2O_4$ [19], $La_{0.7}Sr_{0.3}MnO_3/CuFe_2O_4$ [20, 21], $La_{0.7}Sr_{0.3}MnO_3/ZnFe_2O_4$ [22], $La_{0.67}Ca_{0.33}MnO_3/CuFe_2O_4$ [23], $La_{0.7}Sr_{0.3}MnO_3/CoFe_2O_4$ [24, 25], $La_{0.67}Ca_{0.33}MnO_3/Fe_3O_4$ [26, 27], $Cu_{0.7}Cd_{0.3}Fe_2O_4/La_{0.67}Sr_{0.33}Mn_{0.98}Co_{0.02}O_3$ [28], $L_{0.67}Sr_{0.33}MnO_3/BaFe_{11.3}(ZnSn)_{0.7}O_{19}$ [29], $La_{2/3}Sr_{1/3}MnO_3/BaFe_{12}O_{19}$ [30], $La_{0.7}Sr_{0.3}MnO_3/SrFe_{12}O_{19}$ [31], and $SrFe_{12}O_{19}/La_{1-x}Ca_x$

---

[*] Corresponding author. Fax: +880 28613642.
E-mail address: dalilurrahaman1976@gmail.com (Md.D. Rahaman).

http://dx.doi.org/10.1016/j.jmmm.2015.03.024
0304-8853/

MnO_3 [32] with a view to enhance the magnetoresistance because the introduction of high resistivity second phase in the manganites has the barrier effect to the tunneling process and also causes the magnetic disorder near the grain boundary.

However, to our knowledge, no reports are available in the literature on magnetoelectric (ME) properties of $(1-x)$ [$La_{0.75}Ca_{0.15}Sr_{0.05}Ba_{0.05}MnO_3$] (LCSBMO)+$(x)$ [$Ni_{0.9}Zn_{0.1}Fe_2O_4$] (NZFO) composites. As a magnetostrictive phase, we have selected NZFO due to its mixed spinel (AB_2O_4) structure. NZFO is a combination of $NiFe_2O_4$ (NFO) which has inverse spinel structure while $ZnFe_2O_4$ (ZFO) has normal spinel structure. The incorporation of Zn^{2+} into the NFO spinel cell pushes the inverse structure to acquire mixed spinel [33,34]. The NZFO ferrite is highly magnetostrictive and resistive, since a Jahn–Teller ion such as Zn^{2+} has a high coupling coefficient [35]. From an application point of view, NZFO is one of the most versatile, reasonable material for general use in both high- and low-frequency devices because of their high electric resistivity (exceeds 10^7 Ω m), high value of magnetic permeability, low dielectric loss, good chemical stability, low coercivities, high mechanical hardness, low porosity, reasonable cost and high Curie temperature, which further depends on the compositions and heat treatment of the samples [36–43].

On the other hand, $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) is known for its simple perovskite crystal structure and dopant-controlled Curie temperature accompanied by a metal-to-insulator transition (MIT) above room temperature [44]. The doping at A site (the divalent alkali-earth metal ions) of these manganites can both lead to the appearance of Mn^{4+} ions which produces Mn^{3+}–O–Mn^{4+} double-exchange function [45] and change the average radius of A-site ions to adjust the bond length and bond angle of ABO_3 oxygen octahedrons and to influence double-exchange function [46,47]. We have selected $La_{0.75}Ca_{0.15}Sr_{0.05}Ba_{0.05}MnO_3$ (LCSBMO) as the matrix which is a mixture of $La_{0.7}Ca_{0.3}MnO_3$, LSMO, and $La_{0.7}Ba_{0.3}MnO_3$, respectively because light doping of Sr^{2+} and Ba^{2+} for Ca^{2+} ions caused a shift of paramagnetic (PM) to ferromagnetic (FM) transition temperature (T_c) to a higher value close to room temperature as well as improves the electrical and magetotransport properties [48–50]. On the other hand, the simultaneous of Sr–Ba results in a Mn^{3+}/Mn^{4+} mixed valence state creating mobile charge carriers and canting of Mn spins [51].

In the present study, we have studied the structural, morphological, electrical, magnetic, and magnetoelectric properties of $(1-x)$ LCSBMO+(x) NZFO composites.

2. Experimental details

2.1. Materials and method

The $(1-x)$ $La_{0.75}Ca_{0.15}Sr_{0.05}Ba_{0.05}MnO_3+(x)$ $Ni_{0.9}Zn_{0.1}Fe_2O_4$ (x=0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) composites were prepared using the following steps. First, a pure polycrystalline $La_{0.75}Ca_{0.15}Sr_{0.05}Ba_{0.05}MnO_3$ (LCSBMO) and $Ni_{0.9}Zn_{0.1}Fe_2O_4$ (NZFO) were prepared using the conventional solid state reaction method. For the preparation of LCSBMO powders, high purity ($>99\%$) powders of La_2O_3, $CaCO_3$, $SrCO_3$, $BaCO_3$, Mn_2O_3 were mixed in stiochiometric proportions and ground for 4 h in order to achieve homogeneity in the mixed powder. Then the mixed powders were calcined in air at 900 °C for 6 h with a heating rate of 10 °C/min and cooling rate of 5 °C/min in a furnace to establish the course of nucleation for the grain growth and to felicitate the decomposition of the substituent oxides/carbonates. The calcined powders were again ground to make fine powders. A similar procedure has been followed to prepare NZFO ferrite powder using NiO, ZnO, and Fe_2O_3 (with a purity higher than 99%) as starting materials. For preparing the composites, we have mixed LCSBMO and NZFO powders together according to the stoichiometric ratios and ground for 2 h to allow good mechanical mixing with small amount of diluted polyvinyl alcohol (PVA) as binder. The mixed powder was palletized into small disks (1.3 cm diameter and ~0.2 cm thickness) and toroids (outer diameter 1.3 cm, inner diameter 0.7 cm and thickness ~0.2 cm) using a steel die and a hydraulic press with a uniaxial pressure of 5000 psi and sintered 1200 °C for 5 h in a closed alumina crucible in atmospheric air followed and cooled at room temperature by adjusting the cooling rate to yield the final product. The heating rate and cooling rate was set at 10 °C/min and 5 °C/min, which is an essential and important process to achieve the required oxygen content in the material. Composites were sintered with different temperatures since the sintering process is key issue to develop the most appropriate structure for the application, complete the inter-diffusion of the component metal ions into the desired crystal lattice and to establish the appropriate valencies for the multi-valent ions by proper oxygen control [52,53].

2.2. Characterizations

The phase formation of all the composites were characterized by a Philips PanAnalytic Xpert Pro X-ray diffractometer with a Cu anode (Cu-Kα radiation source with λ=1.541 Å) with the step size 0.02 operating at 40 kV and 30 mA at room temperature and 1 °C/min scanning speed, by collecting the data in a 2θ range of 10–70°. The lattice parameters were calculated from XRD data. The microstructure of the composites was analyzed using a scanning electron microscope (SEM) (JEOL JSM-6460, Japan). For electrical measurement samples were painted conducting silver paste on either side to ensure good electrical contacts. The toroids were wrapped with 4-turns copper wire to measure magnetic permeability. The frequency dependence of dielectric constant and magnetic permeability were measured using a Wayne Kerr Impedance Analyzer (B 6500 series) in the frequency region 100 Hz to 120 MHz [54]. The complex electric modulus ($M^*(\omega) = 1/\varepsilon^* = 1/\varepsilon' - j\varepsilon''$) has been determined using real and imaginary components of the dielectric permittivity. The ME effect was obtained by applying an AC magnetic field superimposed on a DC magnetic field on the sample, and then measuring the output signal with applied DC magnetic field. An electromagnet was used to provide a dc magnetic field of up to 0.86 T. A signal generator was used to drive the Helmholtz coil to generate an ac magnetic field of 0.0008 T. The output voltage generated from the composite was measured by a Keithley electrometer (Model 2000) as a function of dc magnetic field. ME voltage coefficient, α_{ME}, was calculated using relation, $\alpha_{ME} = V/H_{AC} \times d$, where V is the ME voltage across the sample surface and H_{AC} is the amplitude of the sinusoidal magnetic field and d is the thickness of the sample [54].

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1(a) and (b) shows the XRD of $La_{0.75}Ca_{0.15}Sr_{0.05}Ba_{0.05}MnO_3$ (LCSBMO) manganite and $Ni_{0.9}Zn_{0.1}Fe_2O_4$ (NZFO) ferrite sintered at 1200 °C. From Fig. 1(a), it is observed that the diffraction pattern for LCSBMO shows all the allowed reflection lines corresponding to single-phase tetragonal structure. The lattice parameters for LCSBMO are $a=b=3.8625$ Å and $c=12.4822$ Å. On the other hand, from Fig. 1(b), it is observed that the XRD diffraction pattern for NZFO shows all the allowed reflection lines corresponding to single-phase cubic spinel structure. The lattice constant of NZFO was determined by the method described elsewhere [54,55]. The calculated lattice constant (a_0) was found to be 8.394 Å for NZFO