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Improvement in magnetoelectric and other physical properties of BSZT-NZF composites by microwave sintering

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ABSTRACT

A comparative study of conventional (CS) and microwave sintered (MS) magnetoelectric (ME) composites with compositional formula $0.90Ba_{0.9}Sr_{0.1}Zr_{0.04}Ti_{0.96}O_3$+$0.10Ni_{0.8}$ $Zn_{0.2}Fe_2O_4$ (BSZT-NZF) was done. The present report is on the achievement of comparable properties achieved by microwave sintering of the composites at an expense of less energy and time as compared to conventional sintering. The value of magnetoelectric coupling coefficient 'α' was found to be increased by 12.5% by microwave sintering. The value of α was 1.6 and 1.8 mV/cm-Oe for CS and MS composite sample respectively. The dielectric, ferroelectric and magnetic properties were found to be improved for MS composite sample.

1. Introduction

In recent, the magnetoelectric materials have been paid attention of the researchers because they exhibit both ferroelectric and ferromagnetic properties with magnetoelectric coupling. ME composites have strong magnetoelectric coupling while the single phase ME materials posses weak magnetoelectric coupling. Moreover the single phase ME materials also have temperature constraint [1–3]. Thus ME composites have potential applications in many multifunctional devices such as magnetic field sensors, multiple state memory element, transducers, actuators, sensors, non-volatile memory elements, oscillators and phase shifters etc. To improve the properties of such materials, lot of investigations have been done and it was found that not only the compositional modifications but also the processing techniques can affect the magnetoelectric coupling [4]. Now the challenge is to prepare such composites at low expense of money, energy and time. Some novel techniques like microwave processing, mechanochemical alloying, etc. are useful in saving time, energy and money. Microwave sintering technique is known for its fast firing as it heats the sample from inside uniformly. Due to which it takes the advantage over conventional sintering techniques in certain cases as it is materials dependent. A number of spinel ferrites and perovskite ferroelectrics such as $LiFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, $NiZnFe_2O_4$, $BaTiO_3$, $BaSrTiO_3$, $PbZrTiO_3$ etc. have been processed individually by microwave techniques [5–11]. For example, the DC resistivity of Li based ferrites was improved by using microwave sintering [5]. The use of microwave sintering is rarely used to prepare ME composites. In the present work is on the comparative study of structural, dielectric, ferroelectric, magnetoelectric properties of ME composites with compositional formula $0.90Ba_{0.9}Sr_{0.1}Zr_{0.04}Ti_{0.96}O_3 + 0.10Ni_{0.8}Zn_{0.2}Fe_2O_4$ prepared by conventional and microwave sintering.

2. Experimental

The individual phases ($Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $Ba_{0.9}Sr_{0.1}Zr_{0.04}Ti_{0.96}O_3$) were prepared by conventional solid state reaction route. AR grade (fine Sigma Aldrich with 99.9% purity) NiO, ZnO, Fe_2O_3 $BaCO_3$, $SrCO_3$, ZrO_2 and TiO_2 were used as raw materials. The mixing was carried out by ball-milling using zirconia balls and distilled water as milling media for both phases. The slurries of NZF and BSZT were dried and after that calcined in alumina crucibles at

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1000 °C and 1100 °C for 4 h respectively, and recalcined at 1000 °C and 1100 °C for 4 h respectively. The recalcined powder was then ball milled again and dried. The composites 0.90BSZT+0.10NZF were prepared by mixing the two phases by weight. A solution of 3% by weight of PVA was prepared in water and few drops of it were added as binder and the pellets having 2–3 mm thickness and 15 mm diameter were prepared using the uniaxial hydraulic press. The pellets were sintered in air as sintering atmosphere by conventional and microwave furnace at 1325 °C for 4 h and 20 min respectively. Temperature during microwave sintering was measured by IR- Sensor which was placed on the top of the furnace. The sensor was also connected to the PID controller for temperature reading and controlling. The structural characterizations of the samples were carried out by SEM and X-ray diffraction (XRD) using Cu-Kα radiation (λ = 1.541 Å). After sintering, the experimental density of the samples was determined using Archimedes' method. X-ray density of the samples was calculated using the lattice parameters. Phase identification of sintered pellets was done by using a D8Advance X-ray Diffractometer (XRD) (Bruker AXS) in a range of Bragg angles ($20° \leq 2\theta \leq 70°$) with step size of 0.02°. For measuring electrical properties, the sintered pellets were lapped and then electroded by using silver epoxy and heated at 400 °C for 30 min to ensure good ohmic contact. The dielectric properties were measured as a function of temperature using an Agilent 4284A LCR meter. P–E hysteresis loops were recorded by using an automated P–E loop tracer (manufactured by Marine India Pvt. Ltd) based on Sawyer-Tower circuit. For electric poling, samples were heated to 150 °C and a DC electric field (15 kV/cm) was applied for1h.Then the samples were cooled to room temperature in the presence of field. M–H loops were recorded using Lake Shore 735 VSM Controller, Model 662 interfaced with a computer. The magnetoelectric signal (voltage) was determined as a function of increasing DC magnetic field (0–1500 Oe) using7265 DSP lock-in amplifier in the presence of small AC magnetic field (H_{ac} = 10 Oe at 1 kHz). ME coefficient (α) was calculated from the magnetoelectric signal (δV) using the formula $\alpha = \delta V/tH_{ac}$, where δV is the magnetoelectric voltage generated after the application of magnetic field and 't' is the thickness of the sample and H_{ac} is the ac magnetic field.

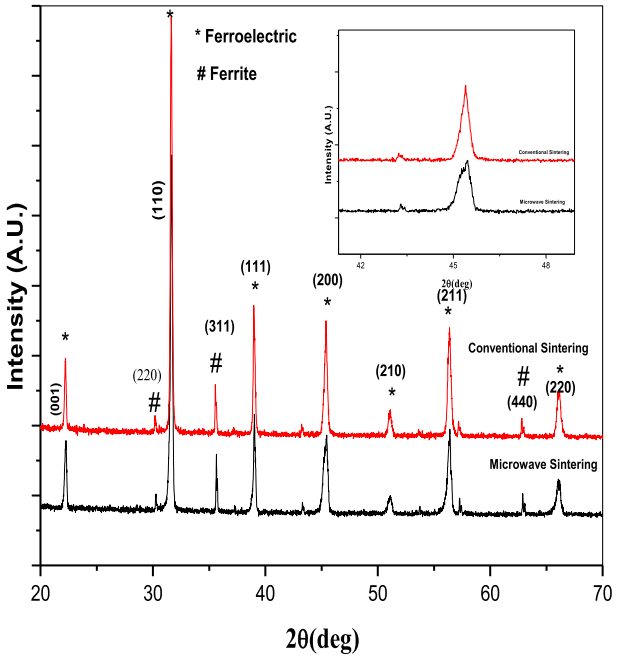

Fig. 1. XRD pattern for CS and MS composite samples.

3. Results and discussion

Fig. 1 shows the comparative XRD patterns for both CS and MS composite samples. These XRD patterns show well defined peaks with specific indices characteristics of cubic spinel structure of ferrite phase (NZF) and tetragonal perovskite structure of ferroelectric phase (BSZT). The calculated values of lattice parameters for both the samples are calculated by using Powder-X software with an error of 0.005. The values of lattice parameters are given in Table 1. The inset in Fig. 1 is showing the difference in XRD pattern of the two samples. From the calculated lattice parameters, the theoretical density '$d_{X\text{-}ray}$' was calculated and compared with experimental density 'd_{exp}'. It was found that higher relative density can be achieved with the help of microwave sintering technique. The values of $d_{X\text{-}ray}$, d_{exp} and relative density are given in Table 1. Fig. 2 shows the SEM micrographs for both CS and MS composite samples. From the figure it can be observed that samples prepared by microwave sintering technique are more homogeneous and dense as compared to the conventional sintered sample. Because after absorbing the microwave radiations, internal uniform heating takes place which results in homogeneous microstructure. While in conventional sintering the sample was heated by using heating elements. This causes the serious problem of non-uniform heating, thermal gradients, which in turn result in internal stresses in the specimen. It can also be observed that average grain size in MS samples is approximately same as CS sample. The calculated values of average grain size and experimental density of MS and CS samples are given in Table 1. From the table it can be observed that, a higher value of relative density is observed in case of MS sample as compared to CS sample. Hence, the composite samples with better densification and similar grain size can be prepared in short interval of time by microwave sintering.

The variation of dielectric constant and tangent loss 'tanδ' as function of temperature (at 10 kHz) for both samples is shown in Fig. 3. MS sample was found to have high dielectric constant and low dielectric loss as compared to CS sample. Both the samples exhibited similar temperature dependence of dielectric constant. Dielectric constant increases with increase in temperature and shows a peak at a particular temperature called Curie temperature (T_c), which is a characteristic of ferroelectric behavior. The values of room temperature dielectric constant (ε_{RT}), tangent loss ($\tan\delta_{RT}$), dielectric constant at T_c (ε_{max}) and tangent loss at T_c for CS and MS samples at 10 kHz are given in Table 1. From the table it is observed that, MS sample was found to have higher dielectric constant as compared to the CS composite sample. Whereas, tangent loss is lower in MS sample as compared to CS sample, which may be attributed to the low porosity and dense microstructure in the case of MS composite sample.

Table 1
Structural, dielectric parameters and magnetoelectric coefficient 'α' for CS and MS samples.

Parameters	CS sample	MS sample
Lattice constant 'a' (Ferroelectric phase) Å	3.9901	3.9812
Lattice constant 'c' (Ferroelectric phase) Å	4.0142	4.0012
Lattice constant 'a' (Ferrite phase) Å	8.3381	8.3405
Experimental density (gm/cm^3)	6.29	6.55
X-ray density (gm/cm^3)	6.94	6.99
Relative density (%)	90.6	93.7
Grain size (μm)	1.50	1.46
ε_{RT}	2440	2950
$\tan\delta_{RT}$	0.02	0.013
ε_{RT} at T_c	3530	4070
$\tan\delta_{RT}$ at T_c	0.007	0.006
α (mV/cm-Oe)	1.6	1.8