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Microwave-Hydrothermal synthesis of $BaTiO_3 + NiCuZnFe_2O_4$ nanocomposites

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ABSTRACT

The nano-sized $BaTiO_3$ and NiCuZn ferrite powders were synthesized using Microwave-Hydrothermal (M-H) system at 160 °C/45 min. The ferroelectric and ferrite phases were confirmed by the XRD and surface morphologies were studied by SEM and TEM. The size of the powders that were synthesized using M-H system was found to be 40–60 nm. The $xBaTiO_3 + (1-x)NiCuZnFe_2O_4$ nano-composites were prepared at different weight percentages. The room temperature hysteresis loops were taken on the present composite samples in the field of 5 kOe. The value of coercivity and saturation magnetization was found to be increasing with the decrease of $BaTiO_3$ content in the composites. The frequency variation dielectric constant (ε), dissipation factor (D), initial permeability (μ_i) and quality factor (Q) were studied at room temperature in the frequency range of 1 kHz–1 MHz region. From these studies it was observed that the present composites were useful for the fabrication of Multilayer Chip Inductors (MLCI).

1. Introduction

Materials, which have coupled magnetic, electric and structural order parameters that result in simultaneous ferromagnetism, ferroelectricity and ferroelasticity, have recently attracted a great deal of attention [1–7] not only from the view point of the materials science but also because of their potential practical applications in spintronics, information storage, sensors and design of new type electronic devices. These types of materials are known as multiferroics. Very few single phase materials exhibit the coexistence of strong ferromagnetism and ferroelectricity. These materials have been synthesized in the laboratory and explained why there are few magnetic ferroelectrics from theoretical and experimental point of view [8]. More efforts have been focused on composite of two different materials individually possessing ferromagnetic or ferroelectric properties. Therefore, the construction of composite materials exhibiting coexistence of ferromagnetic and ferroelectric properties should be significant.

From the survey of literature, it is found that $BaTiO_3 + NiCuZn$ ferrite composites were prepared using sol–gel, auto combustion [9], solid state reaction [10] and oxalate precipitation [11] methods. However, detailed investigation of dielectric properties were not undertaken in any of these studies. Hence, for the first time nanocomposites of $xBaTiO_3 + (1-x)Ni_{0.53}Cu_{0.12}Zn_{0.35}Fe_{1.88}O_4$ (where $x = 0$, 30, 50, 70 and 100 wt%) were prepared using the nanopowders of $BaTiO_3$ and NiCuZn ferrite which were synthesized using the Microwave-Hydrothermal (M-H) method [12–14]. The electrical, dielectric and magnetic properties were measured on the sintered nano-composite samples and the obtained results are presented in this paper.

2. Experimental

In the present investigation, $Ni_{0.53}Cu_{0.12}Zn_{0.35}Fe_{1.88}O_4$ was prepared using pure nickel nitrate [$Ni(NO_3)_2{\cdot}6H_2O$], copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$], zinc nitrate [$Zn(NO_3)_2{\cdot}6H_2O$] and ferric nitrate [$Fe(NO_3)_2{\cdot}9H_2O$]. These reagents were dissolved in 50 ml of de-ionized water. An aqueous NaOH solution was added to the mixture until the desired pH (pH > 10) value was obtained.

$BaTiO_3$ powders were synthesized using barium chloride ($BaCl_2{\cdot}2H_2O$) and titanium chloride ($TiCl_4$) solutions. Sodium hydroxide (NaOH) was used as alkaline neutralizer. NaOH (0.1 M) was dissolved in a 10 ml of boiled double-distilled water to which a 0.002 mol of $BaCl_2$ and an equivalent amount of 2 M of $TiCl_4$ were added. The pH of the resultant mixture was found to be ≥13. Controlling of pH is the key factor to synthesize the nano-powder.

$Ni_{0.53}Cu_{0.12}Zn_{0.35}Fe_{1.88}O_4$ and $BaTiO_3$ precipitation was then separately transferred into double-walled digestion vessels that have an inner liner and cover made up of Teflon PFA and an outer high strength layer made up of ultem polyetherimide and then treated using M-H method at 160 °C/45 min. The M-H treatment was performed using a microwave accelerated reaction system (MARS-5, CEM Corp., Mathews, NC). This system uses 2.45 GHz microwave frequency and can be operated at 0–100% full power (1200 ± 50 W). The reaction vessel was connected to an optical probe to monitor and control the temperature during synthesis. The product was separated by centrifugation and then washed repeatedly with de-ionized water, followed by drying in an Oven overnight at 100 °C. The phase identification

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of powders was performed using X-ray diffraction (XRD) with Cu Kα radiation. Particle size and morphology of the powders were determined using a Transmission Electron Microscopy (TEM) (Model JEM-2010, JEOL, Tokyo, Japan).

The synthesized nano-powders of NiCuZn ferrite and $BaTiO_3$ were mixed at different weight percent and named as $BaTiO_3$ (sample 1), 30 wt% of NiCuZn ferrite + 70 wt% of $BaTiO_3$ (sample 2), 50 wt% of NiCuZn ferrite + 50 wt% of $BaTiO_3$ (sample 3), 70 wt% of NiCuZn ferrite + 30 wt% of $BaTiO_3$ (sample 4) and NiCuZn ferrite (sample 5).

The powders were uniaxially pressed into toroidal samples and pellets. After binder was burnt out at 300 °C, the specimens were sintered at 910 °C/30 min using microwave sintering method [15]. The sintered samples were characterized using XRD and Scanning Electron Microscopy (SEM). The bulk density of the present samples was measured using the Archimedes's method. The properties such as dielectric constant (ε) and dissipation factor (D); initial permeability (μ_i) and quality factor (Q) were measured over a wide frequency range (100 Hz–1 MHz) using LCR meter (Kokuyo Electric Co., Japan model no. KC-605). The magnetic properties such as saturation magnetization (M_s) and coercive field of the samples were measured with the hysteresis loop tracer at room temperature in the pulsed field of 5 kOe.

3. Results and discussion

Figs. 1 and 2 give the XRD patterns of the as-synthesized powders of NiCuZn ferrite and $BaTiO_3$, respectively. It can be seen from the figures that the powders possess pure spinel structure and tetragonal perovskite structure, respectively. No other phases

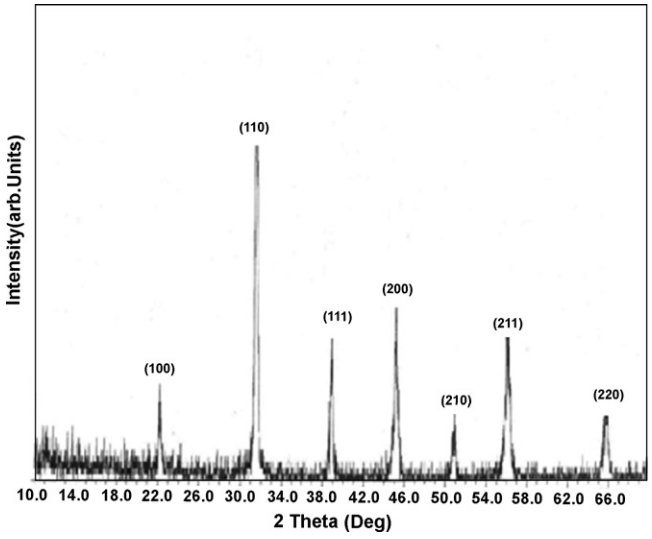

Fig. 1. XRD pattern of $BaTiO_3$ powder.

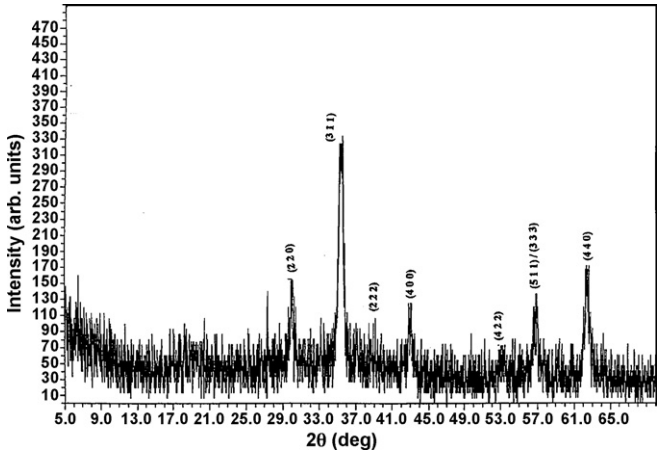

Fig. 2. XRD pattern of NiCuZn ferrite powder.

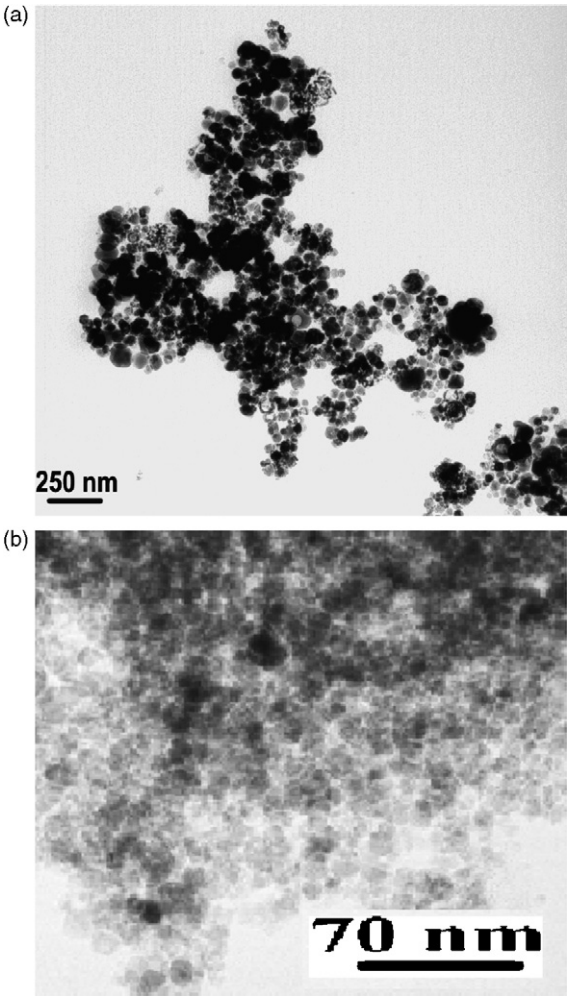

Fig. 3. TEM picture of (a) $BaTiO_3$ powder and (b) NiCuZn ferrite.

were detected in the XRD patterns. The particle size (D_m) of the as-synthesized powders has been estimated with the help of XRD patterns using Scherrer's equation: $D_m = K\lambda/\beta \cos\theta$, where K is a constant, β is the full width half maxima, λ is the wavelength of X-rays used and θ is the diffraction angle. The particle size calculated from the above formula for the NiCuZn ferrite and $BaTiO_3$ powder is ~30 and ~50 nm, respectively.

Fig. 3a gives the TEM picture of the as-synthesized NiCuZn ferrite powder and Fig. 3b gives the TEM picture of the as-synthesized $BaTiO_3$ powder. From the TEM pictures the particle size was calculated and was found to be ~20 and ~40 nm for NiCuZn ferrite and $BaTiO_3$ powder, respectively.

To use the present composite materials for the fabrication of Multilayer Chip Inductors (MLCI) and LC filters, the samples have to be sintered well below the melting point (970 °C) of electrode material (silver) to stop the silver diffusion. Therefore, in the present investigation the composites were sintered at 910 °C/30 min using microwave sintering method [15].

Fig. 4 shows the XRD pattern of the sintered composite samples. It can be observed that NiCuZn ferrite phase and a $BaTiO_3$ phase coexist in the composite. The peaks in the XRD pattern were identified and it was found that no intermediate phase or interfacial phase was observed. This indicates that complete solid solution has been occurred between the $BaTiO_3$ and NiCuZn ferrite. Table 1 shows the bulk density, porosity, particle size and lattice constant of the present sintered composites. The average