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Dielectric and magnetic studies of $BaTi_{0.5}Fe_{0.5}O_3$ ceramic materials, synthesized by solid state sintering

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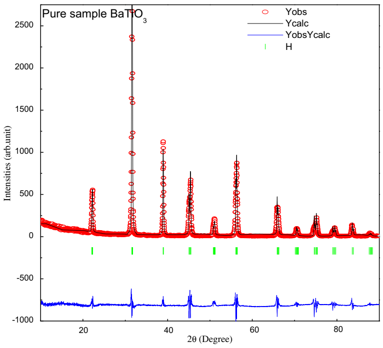
HIGHLIGHTS

- Powdered crystal XRD was studied by pure sample $BaTiO_3$ and Fe doped using solid state techniques.
- Powder XRD diffraction and BDS analysis were reported.
- Crystalline properties were studied by VSM.
- Conductivity, impedance dielectric loss studied.

GRAPHICAL ABSTRACT

XRD patterns of $BaTiO_3$ of pure sample by using of Full-prof suite software.



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ABSTRACT

A comparative study of the surface morphology, dielectric and magnetic properties of the $BaTi_{0.5}Fe_{0.5}O_3$ (BTFO) ceramics materials. This has been carried out by synthesizing the samples in different routes. BTFO samples have shown single phased 12R type hexagonal structure with $\overline{R3m}$, P4mm space group. Interfacial effects on the dielectric properties of the samples have been understood by Cole–Cole plots in complex impedance and modulus formalism. It has been identified that huge dielectric constant (10^3–10^6) at lower frequencies is largely contributed by the heterogeneous electronic microstructure at the interfaces of grains. Modulus formalism has identified the effects of both grain and grain boundary microstructure on the dielectric properties, particularly in chemical routed samples. The order of grain boundary resistivity suggests the semiconductor/insulator class of the material. The grain boundary resistivity of the mechanical alloyed samples is remarkably lower than the solid state and chemical routed samples. Few samples have of the samples have exhibited signature of ferromagnetism at the room temperature.

Introduction

In recent year the magnetoelectric multiferroics, in which the ferromagnetism and ferroelectricity coexist, is emerging more and more attractive because of the potential applications in multiple state memory elements, magnetic valve, filtering device, etc. [1,2]. The magnetic control of ferroelectricity or the electric control of ferromagnetism (magnetoelectric coupling) could open new the way to device concepts and the doping of ferroelectric materials with magnetic ions. This has been is actively studied as a route to obtain such coupling. Fe doped $BaTiO_3$ single crystals display

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ferromagnetic behaviour but the ferroelectricity is suppressed for doping concentrations above 0.5% [3]. As an alternative attempt to search for room temperature magnetoelectrics, the substitution of B-site d^0 cations in ferroelectric perovskite oxides by magnetic d_n cations was revitalized recently. Take $Ba(Ti_{1-x}Fe_x)O_{3-\delta}$ as an example, coexistence of room temperature ferroelectricity and ferromagnetism is revealed in a tetragonal polymorph [4–6]. Room temperature ferromagnetism was also realized in the transition-metal doped hexagonal polymorph [7–10]. The introduce a ferromagnetic property into a ferroelectric material originally without ferromagnetism by itself, one of the common approaches is to dope magnetic impurities into the ferroelectric host material [4]. The other approach is to combine a ferroelectric material and a ferromagnetic material together into a composite material, which subsequently shows multiferroic properties. Tetragonal $BaTiO_3$, a well-known ferroelectric material with a perovskite structure [11–15]. It is well-known that tetragonal $BaTiO_3$ ceramics possesses good ferroelectricity, and this suggests that the Fe-doped $BaTiO_3$ ceramics has been expected multiferroic properties if the Fe dopants can introduce ferromagnetism into the ferroelectric ceramic. Ferromagnetism has been observed in hexagonal Fe-doped $BaTiO_3$ ceramics at low doping levels [16].

Materials and method

The sample was prepared with the solid state reaction method using stoichiometric amounts of $BaCO_3$, TiO_2, and Fe_2O_3 [17]. The X-ray diffraction (XRD) experiments were carried out on Philips X'Pert PRO powder diffractometer (Cu $K\alpha = 1.5406$ Å) with a scan step of 0.050, Vibrating sample magnetometer is measured during ferromagnetic properties (VSM, Lakeshores Model 7404). The data refinement was performed with Rietveld method on FullProf software package. Thoroughly grinding and pellet pressing (12 mm in diameter) were performed prior to each step of sintering. Most samples were sintered at the preliminary sintering 1000 °C for 6 h. Next post-annealing at 1200 °C for 6 h was carried out. $BaTiO_3$ is known to have a perovskite structure where 3*d* transition metals can be easily doped and substitute for titanium, due to their strong resemblance to the titanium ion in size and valence. Consequently, the content of Ti and Fe in $Ba(Ti_{0.5}Fe_{0.5})O_3$ can be controlled by stoichiometric proportions of $BaCO_3$, TiO_2 and Fe_2O_3 in 1:0.5:0.5 M ratio. The similar method has been adopted in Ref. [18,19] to prepare other composition $Ba(Ti_{1-x}Fe_x)O_3$.

Results and discussion

Fig. 1 shows XRD profiles of pure samples. The profiles were fitted using FULL-PROF-Suite program. XRD pattern of the samples matched into tetragonal structure with space group P4mm. There was no trace of significant impurity phase in the samples. Lattice parameters of pure sample ($BaTiO_3$) is in good agreement with reported values $a = b = 3.99370$ Å and $c = 4.02045$ Å ($\alpha = \beta = \gamma = 90°$) [20]. Fig. 2 shows XRD profiles of bulk samples. The profiles were fitted using FULL-PROF-Suite program. XRD pattern of the samples matched into hexagonal structure with space group R3m. There was no trace of significant impurity phase in the samples. Fig. 2(a) and (b) lattice parameters of pure sample are in good agreement with reported values $a = b = 5.698508$ Å, $c = 27.981369$ Å (CPT-1150) and $a = b = 5.689721$ Å, $c = 27.913567$ (CPT-1150 °C) [21–23].

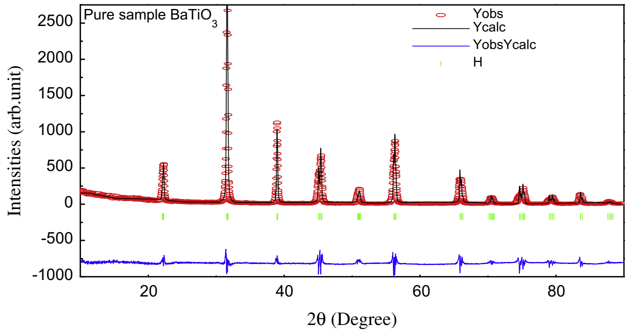

Fig. 1. XRD patterns of $BaTiO_3$ of pure sample by using of full-prof suite software.

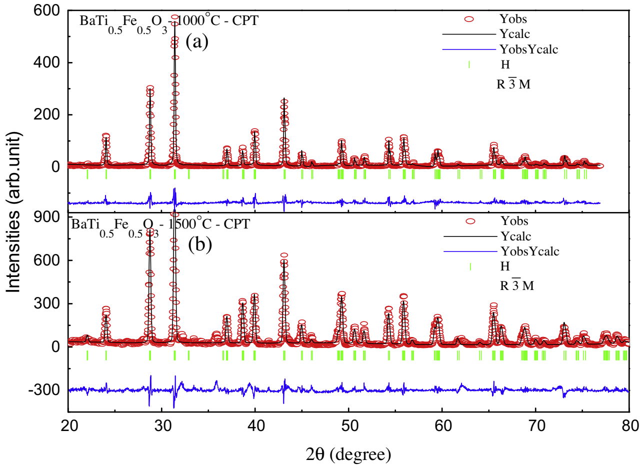

Fig. 2. (a) and (b) Corresponding to Rietveld refinement spectra of $BaTi_{0.5}$ $Fe_{0.5}O_3$ – 1000 °C and 1500 °C – CPT.

Dielectric measurement was performed using broad band dielectric spectrometer (Novocontrol Tech., Germany) at ac signal 1 V @ frequency 1 Hz–10 MHz and temperature range 298–473 K. The pellets with diameter of 12 mm were used for dielectric measurements. The pellet-shaped samples were sandwiched between two gold-coated plates and the plates were connected to the BDS with shielded cables. Fig. 1 shows the XRD patterns of the as-prepared and annealed $Ba(Ti_{0.5}Fe_{0.5})O_3$ ceramics. The standard XRD pattern of 6H–$BaTiO_3$ is also exhibited at the bottom of the figure for comparison. The XRD data indicate no structural difference between the two samples. All ceramics have a hexagonal perovskite structure, with the appearance of only 6H–$BaTiO_3$ reflections. Besides, it is also noticed that the full-width at half-maximum (FWHM) increases after annealing in vacuum. Magnetization versus field (M–H) for the samples was measured at magnetic field, as illustrated in Fig. 8. These M–H loops apparently show hysteresis, suggesting that all ceramics are ferromagnetic at room temperature. Moreover, it is noticed that the magnetization reach saturation even at the maximum magnetic field. It is implied that the M–H curves for the samples consist of two components: a magnetic hysteresis loop.

Ac conductivity

Fig. 3 shows the frequency (*f*) dependence of the real part (σ') of ac conductivity at selected temperatures in the range 298–473 K for the sample. BTFO samples showed nearly a frequency independent conductivity at lower frequencies. The highly insulating nature (low conductivity 10^{-11}–10^{-8} S/cm) and constant conductivity over a wide range of lower frequencies of the samples are useful for designing good quality resistors.

Impedance study

We have analyzed the real (Z') and imaginary (Z'') parts of the complex impedance of different samples using the Cole–Cole plot.