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Determination of A.C. Conductivity of Nano-Composite Perovskite BaTi_{1-x}Fe_xO₃ Prepared by the Solid State Technique

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Abstract : Barium Titanate BaTiO₃ is known for both its electric and magnetic properties. The synthesis and characterization of iron doped barium titanate; BaTi_{1-x}Fe_xO₃ (x = 0.5) was investigated with a view to understand its structural, magnetic and electrical properties. A finest possible sample of Iron doped micro particles of BaTiO₃ (BTO) with possible tetragonal structure via a solid-state route was prepared. Prepared samples of BaTi_{1-x}Fe_xO₃ (x = 0.5) was (BTFO)were structural characterized by X-ray diffraction (XRD) then XRD data fitted by Rietveld refinement. The dielectric constant measurements of the samples were carried out at 10MHz. Vibrating Sample Magnetometer (VSM)measurements revealed the magnetic nature of Iron doped BaTiO₃. Magnetic Moment verses Temperature plot took at 1Teslaand Magnetic Moment verses Magnetic field plot took at low temperature (10K). Ferroelectric hysteresis loop traced at the electric field in-between -15 to +15 (KV/cm). Details of the preparation technique, experimental results, data analysis, and the interpretation will be presented.

Key words: Particle size, XRD, FE-SEM, BDS, Post annealing atmosphere, Perovskite.

1. Introduction

Barium Titanate (BaTiO₃) is one of the most extensively investigated and widely used perovskite oxides as a material for thermistors¹, multilayer ceramic capacitors (MLCCs)², electro-optic devices³, and dynamic random access memories⁴, because of its high dielectric constant^{5,6} and ferroelectric property⁷. In view of the current trend of miniaturization in the fabrication of electronic devices with improved properties and high reliability, nanoscale BaTiO₃ materials are desirable. For MLCCs, in particular, improved performance can be obtained by decreasing the thickness of the ceramic layer with a decrease of the particle size⁸.

Furthermore, ceramics produced from agglomerate-free nanosized powders with a narrow sized istribution have shown unique consolidation and compaction properties⁹. Another important reason for synthesizing nanosizedBaTiO₃ is as an attempt to understand the finite size effect on the ferroelectricity in nanoscale materials, which is much debated in the literature.^{10,11,12}In this case, the highly dispersed nanocrystals have the benefit of precise investigation into the dependence of ferroelectricity on the particle size for an individual nanoparticle¹³.

The traditional solid-state reaction¹⁴ and wet-chemical processing, including sol–gel processing¹⁵, oxalate route¹⁶, and homogeneousprecipitation¹⁷, have been used to produce BaTiO₃materials. To form a pure crystalline phase, however, a calcinations step above 700^oC was necessary in all these methods, which led to coarse and chemically bonded aggregates. Although the synthesis of BaTiO₃ by an alkoxide–hydroxide sol–precipitation process did not require further calcination at an elevated temperature, it also produced agglomerated and irregular-shaped powders with a broad size distribution ^{18,19}. The hydrothermalmethod has been used to prepare highly dispersed BaTiO₃ powders, whereas it was found to be inadequate to further downsize the particle size to become smaller than several tens of nanometer^{20,21,22}.

Crystalline BaTiO₃ particles with diameters smaller than 10 nm have been synthesized by the decomposition of bimetallic alkoxide precursors in organic solvents²³ and the "benzyl alcohol route."^{24,25} Nevertheless, the nonaqueous reaction approaches have shown advantages in the subtle control of the crystallization and particle growth^{24,25}.

2. Experimental Method

The sample was prepared with the solid state reaction method using stoichiometric amounts of BaCO₃, TiO₂, andFe₂O₃²⁶.The X-ray diffraction (XRD) experiments were carried out on Philips X'Pert PRO powder diffractometer (Cu K α = 1.5406 Ű) 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 Full Prof 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 hours. Next post-annealing at 1200 °C for 6 hours was carried out. BaTiO₃ is known to have a perovskite structure where 3dtransition metals can be easily doped and substitute for titanium, due to their strong resemblance to the titaniumion in size and valence. Consequently, the content of Ti and Fe in Ba(Ti_{0.5}Fe_{0.5})O₃ can be controlled by stoichiometric proportions of BaCO₃, TiO₂ and Fe₂O₃ in 1:0.5:0.5 molarratio. The similar method has been adopted in Ref.^{27,28} to prepare other composition Ba(Ti_{1-x}Fe_x)O₃.

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 (BaTiO₃)is in good agreement with reported values $a=b=3.99370 \text{ A}^0$ and $C=4.02045\text{A}^0(\alpha = \beta = \gamma = 90^{\circ})^{29}$. 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. 1



Fig. 2

Dielectric measurement was performed using broad band dielectric spectrometer (Novocontrol Tech., Germany) at ac signal 1 V @ frequency 1 Hz to 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–BaTiO₃ 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–BaTiO₃ reflections. Besides, it is also noticed that the full-width at half-maximum (FWHM) increases after annealing in vacuum.



Fig.3 Log–log scale plot of the real, imaginary and resultant ac conductivity with frequency variation at different measurement temperatures for BTFO samples.

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. Figure 1 shows the XRD patterns of the Fe-doped BaTiO₃ ceramics at doping levels of x = 0.5 as expected, the BaTiO₃ ceramics without Fe doping showed only tetragonal structure. At doping level of 0.5%, only tetragonal structure was observed, without detectable presence of any other phases. The presence of hexagonal phases was clearly observed, and the XRD diffraction peaks for the hexagonal phases became more significant with the increase of doping level (Fig.1). This have a better view on the evolution behaviors of the tetragonal and hexagonal phases in the Fe-doped BaTiO₃ ceramics. Fig. 1 shows the XRD profile fit for selected samples. The refined cell parameters. XRD pattern of the BTFO samples (Fig. 1) is drastically different from the XRD pattern of the BaTiO₃ (BTO) sample Fig. 1. The BTO sample was obtained by heating the pellet form of BaTiO₃powder at 1273 K for 6 h. High purity (99.9%) BaTiO₃powder was procured from Sigma–Aldrich Chemicals. XRD pattern of the BTO sample matched to tetragonal structure with space group P4mm. The lattice parameters (a = 3.9963 A°, c = 4.0229 A°, V = 64.25 A $^{\circ}$) of BTO sample were in good agreement to reported value^{25,27}. On the other hand, patterns of BTMO samples are best fitted into 12R type hexagonal structure with space group R3m^{28,31}. This means the structure of Fe doped BTO samples are stabilized into lower symmetric BaFeO₃ type structure. Cell volume has also increased the BTFO samples.



Fig. 4 and 4(a) The FE-SEM picture of the BTFO-1000 sample indicated a nearly uniform distribution of spherical shaped particles over the surface. Viewing the agglomeration effect among particles, no attempt was made to estimate the particle size from FE-SEM pictures.





Fig.6 shows the field dependence of magnetization at 300 K for different sample. The magnetic parameters H_c (coercivity), MR(remanent magnetization) and H_{irr} (irreversible field) are indicated for BTFO-1000⁰C

Magnetization versus field (M–H) for the samples was measured at magnetic field, as illustrated in Fig 6. 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. Fig. 2(a-b) shows typical surface morphology (FE-SEM) of BTFO and BTO samples. The image of BTFO sample (Fig. 2a) shows more of diffused particles takingnearly spherical shaped with average size 60–80 nm. Theparticles of the heat-treated BTFO sample (Fig. 8)shaped into rectangular rod/thick plate with length 2–5 mm,width 800 nm to 1.2 mm and thickness 500–800 nm. Fig 8(a)In EDX analysis, several points on the100 mm _100 mm surface area of the sample were examined using electron probe size 1 to 2 μ m. The micro point analysis of EDX spectrum revealed the presence of Ba, Ti, Fe, C, O as the main constituents of the material . The EDX spectrum in lines can mode over a length 40 mm The plate shape of the particles, also reported by Wu et al.³², are moreclear in BTO sample (Fig. 2(b) with length 2–4.5 mm, width 1–1.5 mm and thickness 700–800 nm. The chemical routed BTMO-CP-B sample on the other hand, showed bimodal distribution with the diameter of 700–800 nm and 200–400 nm for large and small of particles, respectively.

Conclusion:

The structural, surface morphological, ferroelectric, and magnetic properties of $BaTi_{0.5}Fe_{0.5}O_3$ (where, x =0.5) ceramics are investigated as functions of different concentration of Fe. Phase transformation from tetragonal to hexagonal of BTFO ceramics are strongly influence. The hexagonal phase of BTFO, which is generally a high temperature phase, is stabilized at room temperature by co-substituting of Fe. At x=0.5, the bulk sample showed both ferroelectric and ferromagnetic signature. High permittivity barium titanate dioxide (BTO) is often used for dielectrics in commercial multilayer ceramic capacitors, actuators applications, and microelectromechanical system (MEMS) applications are durable stable, high insulating characteristic against voltage. BTO system is especially known for its promising for environmental friendly applications. Different solid solutions in the system have been synthesized via solid state reaction route. The BaTi_{0.5}Fe_{0.5}O₃ ceramic was prepared by the solid state reaction method, and co-precipitation method. XRD patterns showed that this material crystallizes in a perovskite-type single phase tetragonal structure with space group R3m. FE-SEM image shows well crystallite structure in the order of micro meter grain size to nano meter scale for solid state reaction method and mechanical alloyed. In particularly, the spherical shape particle image is observed. The chemical composition of the samples was identified by EDX. The frequency and temperature dependence of dielectric study have been performed for Fe doped BaTiO₃ samples. The present research demonstrates that crystalline with a tetragonal structure can be fabricated at low and high temperature. These materials should serve as an ideal candidate for fundamental studies of ferroelectricity and ferromagnetic.

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