

Magnetoelectric coupling in multiferroic Ba(Fe_{0.01}Ti_{0.99})O₃ nanowires

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ABSTRACT

In the present work, structural, microstructural and magnetoelectric (ME) coupling of multiferroic Ba(Fe_{0.01}Ti_{0.99})O₃ (BFT1) nanowires have been studied. BFT1 nanowires were prepared by a hydrothermal method with reaction temperature 180 °C for 48 hours. The X-ray diffraction shows that BFT1 is polycrystalline with cubic phase. The calculated value of distortion ratio (c/a) is ~ 1. No impurity or extra phase is observed. The micrographs by transmission electron microscopy reveal nanowires like structure of BFT1 with diameter lie in the range of ~ 40 - 50 nm and length greater than 1.5 μm. The ME coefficient measurement shows that the ME coupling under the effect of both ac and dc bias. It shows strong dependence on ac and dc bias applied field. The value of linear coefficient (α) called ME coefficient is calculated as ~ 16 mV/Oecm at a fixed frequency of 850 Hz. This ME coefficient α corresponds to induction of polarization by a magnetic field or of magnetization by an electric field. The observed optimum dc bias field at which the maximum magneto-electric coupling occurs is ~ 750 Oe. The magnetization hysteresis shows strong ferromagnetism. Copyright © 2012 VBRI Press.

Keywords: Multiferroic; nanowires; magnetoelectric (ME) coupling; ferromagnetism.



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Introduction

Over the past decade in scientific community, one-dimensional multiferroic nanostructures, like nanorods, nanowires, nanotubes, etc. have received considerable attention. They are promising candidates for realizing nanoscale electronic, optical, and mechanical devices because they retain wire-like connectivity despite their nanoscale radial dimension [1]. The synthesis of multiferroic nanostructures with controllable size and shape is essential for fundamental studies. Among various multiferroic materials, transition metal doped BaTiO₃ is the best material, possessing a perovskite structure with Curie temperature of 132 °C [2-4]. The synthesis of transition metal doped BaTiO₃ nanostructures are of great importance

and has attracted much attention due to its novel shape and size dependent properties. For instance, the ferroelectric Curie temperature of the zero dimensional BaTiO₃ nanoparticles decreases progressively with particles size [5-6]. On the other hand one dimensional BaTiO₃ nanowires still retain their ferroelectric properties, and non-volatile polarization domains with dimensions can be induced in the nanowires. This further open ups the possibility of fabricating BaTiO₃ nanowire-based nonvolatile memory devices and for many more applications [7, 8]. The polarization within individual ferroelectric domains of the nanowire generally orient along the wire axis.

By definition, a single phase multiferroic is a material that simultaneously possesses two or more ferroic order parameters- ferromagnetism and ferroelectricity [9]. The important property that makes this material attractive is the magnetoelectric (ME) effect, i.e. the induction of magnetization by an electric field or polarization by a magnetic field [10]. The preparation of such materials provide opportunities for potential applications in spintronics, magneto-electric sensors in optoelectronics and microwave electronics, multi-state memory devices with dual magnetic and electric controls, magnetic recording read heads and also to encode the information in electric polarization and magnetization to obtain four logic states [11,12]. The ME effect can be either intrinsic in single phase materials or extrinsic, in composite materials. The M-E behavior in multiferroics is found to be strongly dependent on the material properties such as dielectric constants, piezoelectric constants, and spatial architecture of the material characterized by the volume fractions of the phases, the shape and orientation of particles of these phases, their connectivity and mutual positions [12]. In compounds with no time-reversal and no space inversion symmetries, an intrinsic magneto-electric coupling occurs. In such materials, an applied electric field, E , displacing the magnetic ions, eventually changes the exchange interaction between them and hence the magnetic properties of the compound [13].

According to Landau theory [14,15], the ME effect is described in the Gibbs-Free energy (F) of the system in the terms of an applied magnetic field H and an applied electric field E .

$$-F(E, H) = \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j + \frac{1}{2} \mu_0 \mu_{ij} H_i H_j + \alpha_{ij} E_i H_j + \frac{\beta_{ijk}}{2} E_i H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_j E_k + \dots$$

where the first term on the right hand side explains the contribution resulting from the electrical response to an electric field, where ϵ_0 is the permittivity of free space, and the relative permittivity $\epsilon_{ij}(T)$ is a second-rank tensor which is independent of E_i in non-ferroic materials. The second term is the magnetic equivalent of the first term, where $\mu_{ij}(T)$ is the relative permeability and μ_0 is the permeability of free space. The third term describes linear magnetoelectric coupling via $\alpha_{ij}(T)$; the third-rank tensors $\beta_{ijk}(T)$ and $\gamma_{ijk}(T)$ represent higher-order (quadratic) magnetoelectric coefficients. The magnetoelectric effects can then easily be established in the form $P_i(H_j)$ or $M_i(E_j)$. The former is obtained by differentiating F with respect to

E_i , and then setting $E_i = 0$. A complementary operation involving H_i establishes the latter. One obtains:

$$P_i = \alpha_{ij} H_j + \frac{\beta_{ijk}}{2} H_j H_k + \dots$$

$$\mu_0 M_i = \alpha_{ji} E_j + \frac{\gamma_{ijk}}{2} E_j E_k + \dots$$

The linear ME coupling coefficient (α) can be introduced either electrically ($\alpha_E = dM/dH$) or magnetically ($\alpha_H = dP/dH = \epsilon_0 \epsilon_r dE/dH$). Landau and Lifshitz were the first to observe the ME effect in 1957 and later it was confirmed in an antiferromagnetic single crystal Cr₂O₃. Subsequently, observations of ME effect in many other multiferroic crystals have been reported. However, ME effect in these materials is usually small and for the materials to be technologically viable, large ME coupling must be demonstrated. So, much attention is given in developing multiferroics possessing higher ME coupling coefficients. For potential application of such materials, theoretical studies on the ME coupling are very important. Various researchers have worked on different aspects of ME effect in nanomaterials. Liu *et al.* [16] studied the static ME coupling using Landau's theory with the consideration of residual strains. Nan *et al.* [17] used green's function method combined with perturbation theory to study the composite of BaTiO₃ and CoFe₂O₄. Duan *et al.* [18] reported that the atomic displacement at Fe/BaTiO₃ (001) interface caused by ferroelectric switching change the overlap between atomic orbital at the interface that affects the magnetization at the interface. Despite all these, we need to focus on the size, shape and surface effects on the stability of ME coupling for nanoscale materials.

In order to realize the potential application of 1-D BaTiO₃ nanostructures, it is necessary to develop synthetic methods to fabricate these nanostructures. Several methods such as sol-gel, templating methods, hydrothermal method, etc. are reported for the fabrication of BaTiO₃. Among them, hydrothermal method has been referred as a versatile, low cost and environmentally friendly method for preparation of BaTiO₃ nanostructures. Here in, we report the hydrothermal fabrication of Ba(Fe_{0.01}Ti_{0.99})O₃ (BFT1) nanowires and present their structural, microstructural, ferromagnetic and magneto-electric coupling effect.

Experimental

BFT1 nanowires were fabricated via hydrothermal process, and the typical synthesized process is described as the following. The chemicals used for the preparation of BFT1 precursor were barium acetate (Loba Chemie, 98% purity), tetra-n-butyl orthotitanate (Merck, 98%), ferric chloride (Merck, 96%), ethanol (Merck, 99.9%) and NaOH (Nice, 98%). Initially 0.01M of high purity tetra-n-butyl-orthotitanate was dissolved in ethanol to form a uniform solution by stirring and also 0.01M of barium acetate was dissolved in de-ionized water uniformly. Subsequently, the previous solution was slowly introduced into the later solution along with 1% doping of ferric chloride. The pH value of the mixed solution was adjusted to 13.0 by adding NaOH. The mixture was then transferred to an auto clave (filled up to about 80% capacity) where it was immediately

sealed and placed in the furnace. The hydrothermal reaction for BFT1 was carried out at 180 °C for 48 hours. After cooling down at room temperature, BFT1 solution was filtered and washed with distilled water and ethanol for several times to remove the absorbed impurities, and finally dried at 80 °C in an oven for 8 hours. The crystal structure was investigated by X-ray diffraction (XRD) using X'Pert PRO PAN alytical system. Microstructure was determined by transmission electron microscopy (TEM) using TECNAI G²T30, U-TWIN. Magnetization measurements were performed using vibrating sample magnetometer (VSM-735). The Magneto electric (ME) effect of was performed by using Dynamic Magnetolectric coupling measurement Setup.

Results and discussion

The purity and crystallinity of the synthesized sample was examined by the powder XRD technique. The XRD pattern of BFT1 prepared at 180 °C /48h is shown in **Fig. 1**, exhibiting that the product is made up of good crystallization. It is found that the present multiferroic system is polycrystalline in nature with *Pm3m* space group in a cubic phase. The value of distortion ratio (*c/a*) is ~ 1. The diffraction pattern in the $2\theta = 40^\circ\text{--}50^\circ$ region is usually characteristic of the presence of either cubic or tetragonal BaTiO₃ structure. In this case, no splitting of cubic (200) into tetragonal (200) and (002) reflections at about 45° can be observed. The XRD pattern for BFT1 shows cubic symmetry with lattice constants $a = 4.0336\text{\AA}$. The broad XRD lines indicate the products are resulting of nanosize.

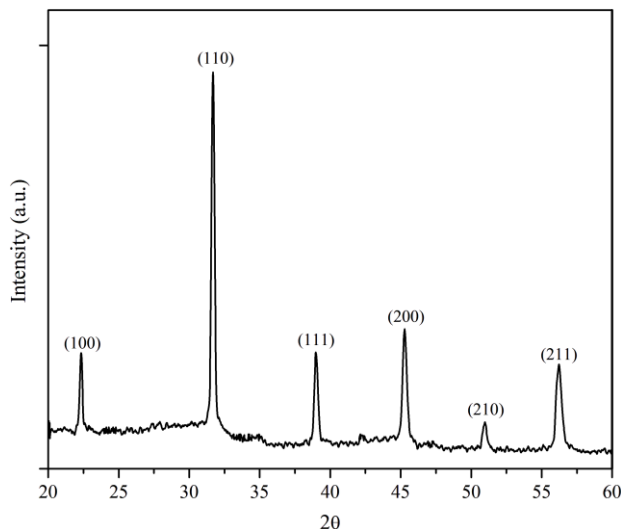


Fig. 1. XRD pattern of BFT1 nanowires.

Fig. 2 reveals the morphology and structure of BFT1. It shows that BFT1 consists of wires of diameter of the range 40-50 nm and length greater than 1 μm. For BFT1 the nucleation and growth process takes place by Ostwald ripening process. Along with Ostwald ripening, it can be expected that particle growth occurs by a coalescence mechanism, i.e., oriented attachment [19].

In this process Fe³⁺ ions replace the Ti⁴⁺ ions and due to their difference in ionic radii, larger crystals with their greater volume to surface area ratio, are more energetically favored than smaller crystals and represent a lower energy

state. For materials with an anisometric crystal lattice, 1D growth is more easily obtained due to the energy difference between different crystals faces which have different atomic density and atoms on different facets have a different number of unsatisfied bonds or broken bonds. Hence, leads to different growth mechanisms and varied growth rates.

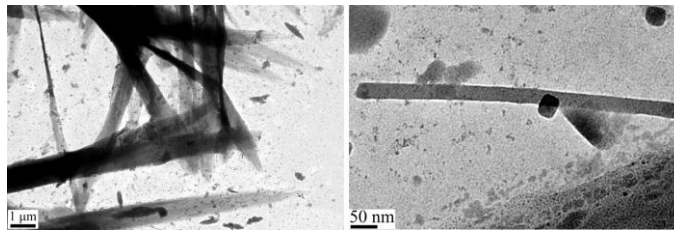


Fig. 2. TEM images of BFT1 nanowires.

The main hypothesis about the role of oriented attachment in hydrothermal conditions is that under dispersed conditions, the anisotropic particles are formed by successive collisions without grain rotation and can lead to various particle shapes. Whereas under agglomerated conditions, alignment by grain rotation can occur if the particles are in contact. However, since the crystallographic alignment can be satisfied at any point of the particle's surface, the final particle can result from several attachment events along the same surface, giving an uncontrollable shape. This alternative can be effective under both agglomerated and dispersed conditions: in agglomerates, the presence of an adhered compound may lead to oriented agglomerates and, under dispersed conditions; the steric hindrance may lead to effective collisions in only one crystallographic direction. This leads to the formation of BFT1 nanowires.

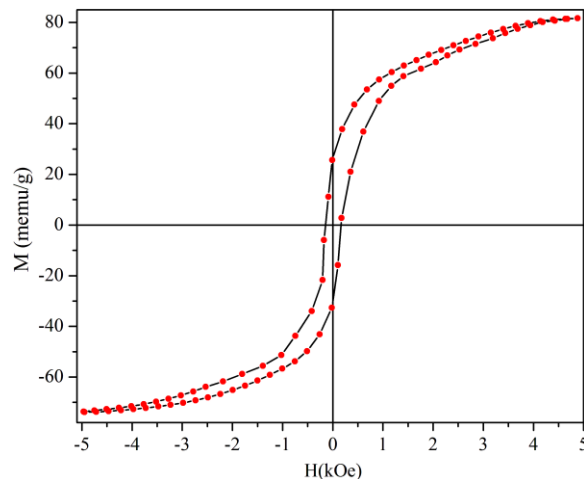


Fig. 3. Magnetization hysteresis (*M-H*) loop of BFT1 nanowires.

Fig. 3 shows ferromagnetism in BFT1 with a typical hysteresis loop with saturation magnetization, $M_s \sim 82.23$ memu/g, remnant magnetization, $M_r \sim 31.91$ memu/g and coercive field, $H_c \sim 122.68$ Oe at room temperature. The Fe³⁺ ions substituting for Ti⁴⁺ introduce oxygen vacancies into BaTiO₃. An electron trapped in the oxygen vacancy constitutes an F-center, where electron occupies an orbital which overlaps the *d*-shell of both iron neighbors and these oxygen vacancies may act as a kind of medium through

which super-exchange interactions between neighboring Fe^{3+} ions occur. This exchange interaction leads to ferromagnetic coupling.

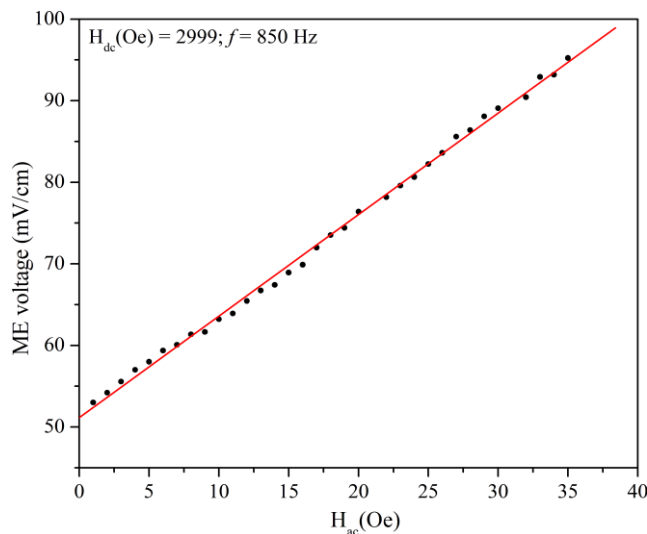


Fig. 4. ME Voltage as a function of the amplitude of the ac field.

We measured the magnetically induced ME effect, which involves the determination of the voltage on BFT1 electrodes under applied magnetic fields. Fig. 4 shows the linear ME effect in BFT1. The experiment involves the measurement of the induced voltage as a function of variable amplitude of the applied ac field at a fixed frequency of 850 Hz, which was produced by couple of Helmholtz coils. According to the theory induced voltage should have a linear relationship with amplitude of the ac applied field:

$$\alpha = \frac{1}{t_c} (\partial V / \partial H_{ac})$$

where V is the induced voltage, H_{ac} is the amplitude of the applied ac magnetic field, α is the ME coupling coefficient which corresponds to induction of polarization by a magnetic field or of magnetization by an electric field and t_c is the thickness of the BFT1 [20]. That confirms the theoretical linear relation. The calculated value of α is ~ 16 mV/Oe cm.

Fig. 5 shows the induced voltage versus dc bias field measured at fixed frequency of 850 Hz of the applied ac magnetic field. The shape of the curve shows the nonlinear behavior and the height of the peak is related to the strength of the ME coupling. The graph also indicates the optimum dc bias field at which the maximum magneto-electric coupling occurs which is the critical parameter for the operation of multiferroic sensors and devices to maximize the energy conversion between the fields. The observed optimum dc bias field is \sim around 750 Oe.

Conclusion

We have synthesized BFT1 nanowires through hydrothermal method with reaction temperature 180°C , kept for 48 hours. XRD pattern revealed the cubic structure for BFT1. TEM reveals that the average width of BFT1

nanowires is $\sim 40\text{-}50$ nm and length about greater than 1.5 μm . The $M\text{-}H$ hysteresis at room temperature for BFT1 shows ferromagnetism with $M_s \sim 82.23$ memu/g, $M_r \sim 31.91$ memu/g and $H_c \sim 122.68$ Oe. For BFT1 the magnetoelectric coupling was observed and the calculated value of linear ME coefficient $\alpha \sim 16$ mV/Oe cm. The observed optimum dc bias field at which the maximum magneto-electric coupling occurs is \sim around 750 Oe.

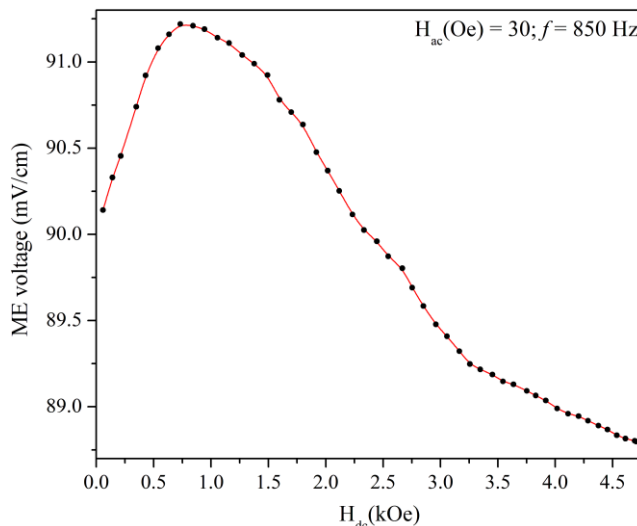


Fig. 5. ME Voltage as a function of the dc applied magnetic field under constant applied ac magnetic field.

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