

Effect of Barium Substitution on Ferroelectric and Magnetic Properties of Bismuth Ferrite

Rajasree Das and Kalyan Mandal

S. N. Bose National Centre for Basic Sciences, Kolkata 700 098, India

We successfully synthesized $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x = 0.0, 0.20, 0.25$) replacing Bi by Ba using a chemical synthesis route. The phase and crystal structure of the samples were studied by X-ray diffraction (XRD). Peaks in the XRD shifted toward lower θ value with the increase in Ba concentration due to the increase in the unit cell size. Detail thermal behavior was performed by differential scanning calorimetry and differential thermal analysis (DTA) to investigate the change in magnetic and ferroelectric transition temperature, respectively, due to Ba substitution. Magnetic, dielectric, and magnetoelectric properties of the samples were also studied in detail. Antiferromagnetic bismuth ferrite was converted to ferromagnetic materials at room temperature on incorporating Ba in the crystal structure. Polarization versus electric field (P - E loop) and dielectric constant were also found to change significantly in the presence of a magnetic field in the aforementioned samples. Appreciable magnetodielectric effect $[\epsilon_r(H) - \epsilon_r(0)]/\epsilon_r(0)$ also indicated effective magnetoelectric coupling within the materials.

Index Terms—Fatigue resistance, ferroelectric transition, magnetoelectric coupling, multiferroics.

I. INTRODUCTION

BISMUTH ferrite (BFO) is one of the most interesting members [1] of multiferroic family, which shows large magnetoelectric coupling in single phase at room temperature (RT). It has been studied by many groups worldwide due to its importance in fundamental research, as well as in commercial applications.

BFO has a rhombohedrally distorted perovskite structure that belongs to the $R3c$ space group [2]. Compared to other multiferroics, BFO exhibits a higher ferroelectric Curie temperature ($T_C \sim 830^\circ\text{C}$) and a high G -type antiferromagnetic (AFM) ordering ($T_N \sim 370^\circ\text{C}$) temperature [3]. At RT, pure bismuth ferrite shows an AFM nature because of its complicated cycloidal spin structure with a wavelength λ of about 62 nm along the $[110]_h$ axis at RT. Though BFO is considered as a promising candidate for magnetic storage or in the applications of spintronics devices [4], leakage current due to oxygen vacancies or impurities is the major problem in BFO. It has been observed that doping [5]–[7] with ions at A-sites and B-sites reduce the leakage current in BFO and enhance the multiferroic properties.

Though Ba-doped BFO shows promising results, few reports are available on this composition [8]–[10]. In this study, Ba-doped BFO are prepared using a chemical route different from the paper of Wang *et al.* [10]. The temperature dependence of magnetic and dielectric behaviour, fatigue resistance, and magnetoelectric properties are investigated in details, which show some interesting results.

II. EXPERIMENTAL DETAILS

$\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ceramics ($x = 0.0, 0.2$, and 0.25) are prepared by chemical synthesis route in ambient atmosphere.

Starting chemicals, such as $\text{Ba}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, and $\text{Fe}(\text{NO}_3)_3$, are weighed according to the stoichiometric compositions, all supplied by Sigma-Aldrich, St. Louis, MO, with a purity of 99.9%. Solutions of these chemicals are mixed and dried up at 80°C . Homogeneous powders are calcined in two steps: 1) at 500°C for 4 hr and 2) at appropriate temperatures between 865°C and 885°C for 2 hr to get single-phase ceramics. For the measurement of electrical properties, pellets with diameter of 5 mm and thickness of 1 mm are prepared and sintered at 850°C . Both sides of the pellet are pasted with silver paste to connect electric wires for the measurements of dielectric and magnetoelectric properties.

Phase and structure of the samples are determined by X-ray diffraction (XRD) using CuK_α radiation (PANalytical). The magnetic properties of BFO are measured using a vibrating sample magnetometer (VSM; Lake Shore Cryotronics, Westerville, OH) up to a maximum field of 16 kOe at RT. Impedance analyzer (Agilent 4294 A) is used to measure the change in dielectric constant of the samples within the frequency range 40 Hz to 1 MHz. Ferroelectric hysteresis loops are studied by a polarization versus electric field (P - E) loop tracer (Marine India).

III. RESULTS AND DISCUSSIONS

A. Structural Analysis

Fig. 1 shows the XRD pattern of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x = 0.0, 0.20, 0.25$). Except the first one, all other samples show single-phase perovskite structure, which implies that the doping does not lower the stabilization of BiFeO_3 . BiFeO_3 shows additional low intensity peaks of Bi_2O_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ at $2\theta \approx 27.6^\circ, 33.2^\circ$, and 30.52° . As Bi is more volatile than Fe, iron-rich phases, such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, are usually formed while preparing BFO. But those impurities disappear in Ba-doped BFO as $\text{Ba}(\text{NO}_3)_2$ in the solid solution could accelerate the formation of BiFeO_3 perovskite structure. Peak positions shift toward left with the increase of doping concentration, indicating increment in the lattice parameter. Thus, Ba substitution leads to an increase in the unit cell volume since the ionic radius of Ba^{+2} (2.173 Å) is larger than that of Bi^{+3} (1.55 Å). Separation

