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Dielectric and Magnetic properties of $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ ceramics

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Abstract

The polycrystalline samples of $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ ($x = 0, 0.1, 0.2, 0.25, 0.3, 0.4$ and $x = 1$) were prepared by the conventional solid state reaction method. The effect of substitution in $BiFeO_3$ by $Ba_{0.8}Sr_{0.2}TiO_3$ on the structural, dielectric and magnetic properties was investigated. X-ray diffraction study showed that these compounds crystallized at room temperature in the rhombohedral distorted perovskite structure for $x \leq 0.3$ and in cubic one for $x = 0.4$. As $Ba_{0.8}Sr_{0.2}TiO_3$ content increases, the dielectric permittivity increases. This work suggests also that the $Ba_{0.8}Sr_{0.2}TiO_3$ substitution can enhance the magnetic response at room temperature. A remanent magnetization M_r and a coercive magnetic field H_C of about 0.971 emu/g and 2.616 kOe, respectively were obtained in specimen with composition $x = 0.1$ at room temperature.

Keywords: C. Dielectric properties; C. Magnetic properties; D. Perovskite; Ceramics

1. Introduction

Multiferroic materials exhibit ferroelectric and magnetic properties simultaneously within a single phase. These materials are considered to offer potential in novel devices such as multi-state memory devices, transducers and sensors [1,2]. In the conventional mechanism of ferroelectricity in perovskite, an off-centring of B-site cations, requires the B site to have an empty *d* orbital, which is incompatible with magnetic ordering from partially filled *d* shells [3]. Thus, there are very few single phase multiferroic materials in nature. Bismuth ferrite $BiFeO_3$ is one of multiferroic materials [4]. $BiFeO_3$ is ferroelectric below $T_C \approx 830$ °C and G-type antiferromagnetic below $T_N \approx 370$ °C, with cycloidal spin magnetic arrangement [5]. $BiFeO_3$ crystallizes in a rhombohedral structure at room temperature with $R3c$ space group [6]. The preparation of $BiFeO_3$ in the bulk form without traces of impurities has been a difficult task. Sosnowska et al. [5] observed an impurity peak of $Bi_2Fe_4O_9$ and Tabares-Munoz et al. [7] that of $Bi_{46}Fe_2O_{72}$. Therefore, $BiFeO_3$–ABO_3 solid–solution systems such as $PbTiO_3$ [8], $BaTiO_3$ [9–11] and $NaNbO_3$ [12] and $SrTiO_3$ [13], have attracted great attention as a means to increase structural stability. Furthermore, $BiFeO_3$ ceramic is characterized by high leakage, small permittivity, high dielectric losses and multiple thermally activated relaxations in kHz range [14,15].

$Ba_{0.8}Sr_{0.2}TiO_3$ is a prototype ferroelectric material with several excellent ferroelectric properties ($T_C = 75$ °C, and $\varepsilon_r \sim 11{,}500$) [16] better than $BaTiO_3$ (T_C: 120 °C, and $\varepsilon_r \sim 9000$) [17], the structure of $Ba_{0.8}Sr_{0.2}TiO_3$ has tetragonal phase at room temperature [16], and is expected that both ferroelectricity and ferromagnetism still coexist in the compound formed when mixed with $BiFeO_3$.

The aim of the present work is to study the structural, dielectric and magnetic properties of the $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ ceramics with $x = 0.1, 0.2, 0.3, 0.4$ and 1.

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2. Experimental

The $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ ($x = 0$, 0.1, 0.2, 0.25, 0.3, 0.4 and $x = 1$) ceramics were prepared using solid state reaction method. For compositions in the range $0 \leq x \leq 0.4$ compositions, high purity Bi_2O_3, Fe_2O_3, TiO_2, $BaCO_3$ and $SrCO_3$ powders were carefully weighed in stoichiometric proportions and thoroughly mixed in agate mortar for 2 h. Bismuth oxide was taken in 5% mole excess to compensate bismuth loss during sintering process. In order to obtain single phase samples, the powders were then pressed into discs and calcined rapidly at 600 °C for 1 h and later at 800 °C for 2 h with intermediate grindings. After calcination, samples were grounded for 2 h and pressed into pellets, then heated at 830 °C for 1 h in air with a high heating rate. For the composition $x = 1$, the appropriate mixture of powder was calcined at 1100 °C for 12 h. After being carefully milled, the powder was then pressed into pellets, and finally sintered at 1320 °C for 3 h.

The crystal structures of the sintered samples were examined by an X-ray diffraction (XRD, XPERT-PRO) with Cu Kα radiation ($\lambda = 1.5406$ Å), 0.02° scan step and 1 s/step counting time. The microstructure of the samples was examined by a scanning electron microscopy (Zeiss Ultra plus 40, Germany). The dielectric measurements were studied using LCR meter HP 4284A. The temperature and frequency ranges were between 30 and 600 °C and 100–1000 kHz, respectively. The magnetization hysteresis (M–H) loop was performed using vibrating sample magnetometer (NanoMOKE2 of Germany) superconducting quantum interference device (SQUID) at room temperature.

3. Results and discussion

3.1. Phase purity and microstructures

The X-ray diffraction (XRD) patterns were analyzed to confirm the phase purity, the symmetry and to calculate the lattice parameters for all compositions of the solid solution $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$. A profile matching of the XRD spectra was made using the "Fullproof" software [18].

The analysis of the XRD patterns reveals that all the samples exhibit single phase characteristics with no trace of other impurity phases (e.g., $Bi_2Fe_4O_9$, $Bi_{46}Fe_2O_{72}$, etc.). The rhombohedral distorted perovskite structure of $BiFeO_3$ with $R3c$ space group is conserved as $xBa_{0.8}Sr_{0.2}TiO_3$ content increases up to $x = 0.3$ and at $x = 0.4$, it transforms into cubic structure ($Pm3m$). Fig. 1a and b shows the X-ray diffraction patterns of $(BiFeO_3)_{0.8}$–$(Ba_{0.8}Sr_{0.2}TiO_3)_{0.2}$ and $(BiFeO_3)_{0.6}$–$(Ba_{0.8}Sr_{0.2}TiO_3)_{0.4}$ ceramics respectively as examples. A similar phase transition from rhombohedral to cubic was observed at $x = 0.3$ for $(1-x)BiFeO_3$–$xBaTiO_3$ [9,10]. The structure and lattice parameters of different compositions in the system $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ are listed in Table 1. The lattice constant is not increasing monotonically with increase in x, but shows fluctuation. The ionic radii of Ba^{2+} ($r(Ba^{2+}) = 1.36$ Å) and Sr^{2+} ($r(Sr^{2+}) = 1.18$ Å) are larger then that of Bi^{3+} ($r(Bi^{3+}) = 1.03$ Å), while the radius of Ti^{4+} ($r(Ti^{4+}) = 0.605$ Å) is smaller than that of Fe^{3+} ($r(Fe^{3+}) = 0.645$ Å) [19]. So substitution of Ba and Sr in A site will result in an increase in crystal lattice constant while it is the reverse for the Ti substitution on site B. So, incorporation of $Ba_{0.8}Sr_{0.2}TiO_3$ is responsible for the fluctuation of the lattice constant.

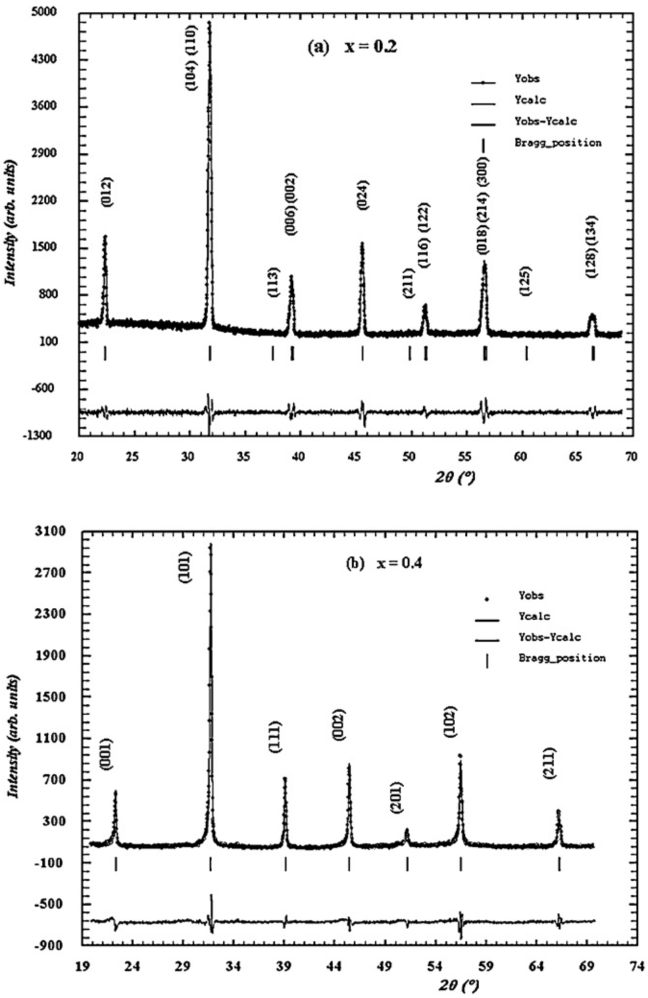

Fig. 1. XRD patterns for a rhombohedral and cubic ceramics samples of $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ with (a) $x = 0.2$ and (b) $x = 0.4$.

The SEM micrographs of $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ samples with different compositions are shown in Fig. 2. Fig. 2a shows the surface of the specimen with composition $x = 0.1$. The microstructure was heterogeneous with bimodal grain size distribution, consisting of large grains of ~8 μm and small grains of 3–4 μm. We can notice also that the substitution of $BiFeO_3$ by $Ba_{0.8}Sr_{0.2}TiO_3$ reduces the grain size and hence increases the volume fraction of grain boundaries and the

Table 1
Structure and lattice parameters of different compositions in the system $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$.

Composition $(1-x)BiFeO_3$–x $Ba_{0.8}Sr_{0.2}TiO_3$	Structure	Lattice parameters	
		a (Å)	α (°)
$x = 0.1$	Rhombohedral	5.638(2)	59.382(6)
$x = 0.2$	Rhombohedral	5.620(6)	60.157(1)
$x = 0.3$	Rhombohedral	5.619(7)	60.159(4)
$x = 0.4$	Cubic	3.987(9)	–