Journal of Molecular Structure 1038 (2013) 242–249

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structural, Raman and dielectric behavior in $Bi_{1-x}Sr_xFeO_3$ multiferroic

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HIGHLIGHTS

- ▶ Multiferroic $Bi_{1-x}Sr_xFeO_3$ samples have been synthesized by citrate sol–gel method successfully.
- ▶ XRD confirms rhombohedral to pseudotetragonal transition on Sr doping.
- ▶ Raman spectra reveal blue shift of active phonon modes due to Sr doping.
- ▶ Sr^{2+} doping has a profound impact on the structural and dielectric properties.

ARTICLE INFO

Article history:
Received 15 November 2012
Received in revised form 24 January 2013
Accepted 26 January 2013
Available online 1 February 2013

Keywords:
Multiferroic
Sol–gel synthesis
X-ray diffraction
Raman scattering
Dielectric properties

ABSTRACT

The effect of Sr^{2+} doping on $Bi_{1-x}Sr_xFeO_3$ ($x = 0.0, 0.15, 0.175, 0.25$) multiferroic ceramics synthesized by citrate sol–gel method has been investigated by Rietveld analysis of X-ray powder diffraction data, Raman spectroscopy and dielectric measurement. X-ray diffraction along with the Rietveld-refinement showed a gradual change in crystal structure from rhombohedral ($R3c$) to pseudotetragonal ($P4/mmm$) with enhanced divalent Sr^{2+} ion concentration. All the 13 Raman modes predicted by group theory ($\Gamma_{R3c} = 4A_1 + 9E$) for $R3c$ structure of $Bi_{1-x}Sr_xFeO_3$ ($x = 0.0, 0.15, 0.175, 0.25$) were observed in the present study. The A_1-2 and E-4 modes are completely suppressed, while that of A_1-3, E-8 mode in $Bi_{1-x}Sr_xFeO_3$ ($x = 0.175, 0.25$) and E-2, E-5, and E-8 modes ($x = 0.25$) disappear completely as compared to parent BFO. The structural phase transition and weakening of long-range ferroelectric order with increasing doping concentration are thus further confirmed from Raman scattering spectra. The dielectric anomaly has been observed in dielectric constant and dielectric loss near 325 °C, 305 °C, 270 °C and 250 °C ($f = 10$ kHz) in $BiFeO_3$, $Bi_{0.85}Sr_{0.15}FeO_3$, $Bi_{0.825}Sr_{0.175}FeO_3$ and $Bi_{0.75}Sr_{0.25}FeO_3$, respectively.

1. Introduction

In recent years, multiferroic (MF) materials have attracted enormous attention that stems from two fold reasons: these materials exhibit two or more ferroic orders simultaneously in the same phase in a certain temperature range; and useful in a wide range of applications [1]. Among MF materials, $BiFeO_3$ (BFO) is one of the most promising due to coupling between ferroelectric and magnetic ordering at room temperature, leading to room temperature devices. $BiFeO_3$ has a rhombohedrally distorted perovskite structure (space group $R3c$) with chemical formula ABO_3 [2], high Curie temperature ($T_C \sim 1100$ K) and antiferromagnetic Neel temperature ($T_N = 643$ K) [3,4]. The ferroelectricity in BFO is attributed to the Bi^{3+} $6s^2$ lone pair electrons, where as magnetism is believed to originate from partially filled d orbital of Fe [5]. Also, BFO displays G-type canted antiferromagnetic with long-range cycloidal spatially modulated spiral spin structure [6].

Even though, magnetoelectric coupling could be observed at room temperature it is difficult to observe the ferroelectric loop of bulk BFO. The magnetic field sweeping and a large leakage current induced by defects, such as impurities, non-stoichiometry and oxygen vacancies make it difficult to achieve good ferroelectric properties. It is expected that doping in BFO as well synthesis by chemical route and thin films might get rid of the above problems. A suitable doping of rare earth (*RE*) ions (La, Pr, Nd, Gd, Ho etc.) at Bi-site [7–11] or substituting a part of Fe^{3+} ion by transition metal (*TM*) ions (Ti, Cr, Mn, etc.) [12–14] helps in minimizing the conductivity and hence the loss factor and also enhances the ferroelectric and ferro/antiferromagnetic ordering at room temperature.

Another possibility to improve the electric/magnetic properties of BFO could be the doping of divalent ions such as Ca^{2+}, Sr^{2+} or Ba^{2+} for Bi^{3+} [15–19]. The effect of Ba^{2+} doping in $BiFeO_3$ prepared by chemical synthesis route showed that magnetoelectric coupling increases with Ba^{2+} substitution with maximum coupling for 20% Ba doped $BiFeO_3$ [15]. A weak ferromagnetic ordering at room temperature for Ba and Ba–Ca co-doped $BiFeO_3$ was earlier observed [16]. Also, Ca and Sr doped $BiFeO_3$

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http://dx.doi.org/10.1016/j.molstruc.2013.01.065

reproduces antiferromagnetic behavior without enhancement of magnetization [17]. For $Bi_{0.75}Sr_{0.25}$ $FeO_{3-\delta}$ sample highest magnetic field induced polarization (P_r = 96 μC/cm) with lowest coercive field (H_c = 601 V/cm) at a field of 10 T has been reported [18]. Furthermore, the effect of Sr^{2+} doping on $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$ shows that both magnetic transition temperature (T_N) and ferroelectric transition temperature (T_C) decrease with Sr-doping [19].

We thus intend to investigate the effect of divalent Sr^{2+} ion doping on the crystal structure, Raman active phonon modes, and dielectric response (frequency as well as temperature dependent) of BFO multiferroics. In order to reduce the impurity formation ($Bi_2Fe_4O_9$, and $Bi_{25}FeO_{39}$), we have synthesized the series of $Bi_{1-x}Sr_xFeO_3$ (x = 0.0, 0.15, 0.175, 0.25) by citrate sol–gel method to have a systematic study of structure – property relationship. It is noticed that the divalent doping causes a change in the crystal structure at about Sr doping of x = 0.15. The weakening of long-range ferroelectric order with enhanced doping is further confirmed from Raman scattering spectra. In addition, a detailed dielectric study has also been discussed in the present work.

2. Experimental details

The polycrystalline samples of $Bi_{1-x}Sr_xFeO_3$ (x = 0.0, 0.15, 0.175, 0.25) were prepared by citrate sol–gel method. For citrate sol–gel method, equimolar amount of $Bi(NO_3)_2.6H_2O$, $Fe(NO_3)_2.9H_2O$ and $Sr(NO_3)$ were dissolved in deionized water and then calculated amount of citric acid were added (with molar amount of citric acid equal to total molar amount of nitrates in the solution). Then the homogenous solution was gently evaporated at 80 °C on hot plate to obtain gel. The dried powder was then calcined at 650 °C for 4 h to get the resultant substituted $BiFeO_3$ crystalline compounds. The obtained calcined powder was finally pressed into thin pallets of 10 mm diameter and 1–2 mm thickness and then sintered at high temperature 850 °C for 1.3 h in air.

The samples were further characterized by means of X-ray diffraction, Scanning electron microscopy, Raman spectroscopy and dielectric measurement. The X-ray diffraction were carried out with Cu $K\alpha_1$ (1.5406 Å) radiation using Bruker D8 Advance X-ray diffractometer over the angular range 20°–70° with a scanning rate of $2^\circ\ min^{-1}$ at room temperature working at 40 kV voltage and 40 mA current. The lattice parameters and other detailed structural information were obtained by the Rietveld refinement FullPROF program. The refined parameters included scale factor, background function (Chebyschev polynomial), profile parameters (pseudo-Voigt profile function), lattice parameters, atomic coordinates and isotropic temperature factors.

The Raman measurement were carried out using Labram HR800 micro-Raman spectrometer equipped with a 50x objective, an appropriate edge filter and a Peltier-cooled charge coupled device detector (1024 × 256 pixels of 26 μm). The spectra were excited with 488 nm radiations (2.53 eV) from an air-cooled Argon Laser. The laser power was always kept on 5 mW at the sample to avoid sample degradation, except in the laser power dependence experiments. After each spectrum had been recorded, a careful visual inspection was performed using white light illumination on the microscope stage in order to detect any change that could have been caused by the laser.

Microstructure and surface morphology of the samples have been examined by scanning electron microscopy at room temperature. The samples were thinned downed to 1.0 mm thick pellet, and high temperature silver paste was applied on their two major surfaces as electrodes for dielectric measurements. Dielectric measurements were were measured as a function of frequency (1 Hz – 1 MHz) between 300 K and 653 using 3532-50 LCR HiTester.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray powder diffraction patterns of the $Bi_{1-x}Sr_xFeO_3$ (x = 0.0, 0.15, 0.175, 0.25) samples (abbreviated as BFO, BSFO-15, BSFO-175 and BSFO-25 respectively) are shown in Fig. 1. From the X-ray diffraction (XRD) pattern, it is observed that pristine BFO sample crystallizes in distorted rhombohedral structure with $R3c$ space group where all the diffraction peaks matches well with the standard crystal data corresponding to the JCPDS file No. 86-1518, except a minor low-intensity impurity peak around 2θ = 28.42° associated with $Bi_2Fe_4O_9$. This observed impurity peak matches well with the JCPDS file No. 72-1832.

Furthermore, the diffraction peaks of Sr^{2+} doped BSFO-15, BSFO-175 and BSFO-25 samples revealed pseudotetragonal structure ($P4/mmm$ space group) are well matching with the earlier reported data [20]. It has been noticed that, all the peaks undergoes a shift in 2θ. The doubly splitted peaks as observed for pristine BFO at about 2θ (≈52° and 57°) becomes a single broadened peak for Sr doped BFO (please see inset of Fig. 1). This confirms a structural transformation and continual change of lattice constants from rhombohedral ($R3c$) to pseudotetragonal structure ($P4/mmm$). Furthermore, the intensity of impurity peak observed at 2θ = 28.42° was found to decrease continuously with Sr-doping leading to the fact that addition of Sr^{2+} at Bi-site is helpful in suppressing the secondary phase. Henceforth, the samples as prepared by sol–gel method have a single-phase rhombohedral (BFO) or pseudotetragonal (BSFO-15, BSFO-175 and BSFO-25) perovskite structure with all constituent components forming a solid solution rather than a mixture of Bi_2O_3, Fe_2O_3 or any other impurity phase except $Bi_2Fe_4O_9$ observed in pure BFO.

In order to further analyze the structural transformation measured XRD patterns of the samples were simulated based on Rietveld refinement using FullPROF program. The pseudo-Voigt profile functions convoluted with an axial divergence symmetry function were used to model the peak profile of pure BFO based on space group $R3c$ and Sr doped samples based on $P4/mmm$ space group. The lattice parameters and profile parameters were refined but atomic positions and anisotropic displacement parameters were kept fixed to the values given by earlier reported data [21,22]. As shown in Fig. 2, the stimulated XRD patterns coincide well with the measured XRD pattern with generally small R-values as mentioned in Table 1.

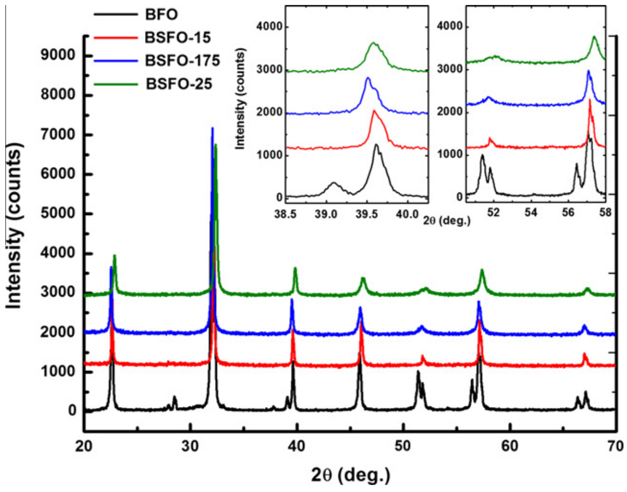

Fig. 1. X-ray powder diffraction pattern for $Bi_{1-x}Sr_xFeO_3$ (x = 0.0, 0.15, 0.175 and 0.25) samples.