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Review

Lanthanum doped $BiFeO_3$ powders: Syntheses and characterization

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ABSTRACT

A soft chemistry route was employed to fabricate single-phase lanthanum modified $BiFeO_3$ (BFO) powders. Effects of lanthanum concentration on the phase formation, grain size and morphologies of BFO powders were systematically investigated. X-ray diffraction results indicated that perovskite phase have been synthesized at the temperature of 850 °C/2 h while infrared data indicates no traces of carbonate. Raman analysis reveals that lanthanum atom substitutes bismuth into the BFO site. A homogeneous size distribution of BFO powders was evidenced by scanning electron microscopy.

Contents

1. Introduction

Perovskite and related compounds are widely investigated because of their multiferroic, photocatalytic, and magnetic properties which are useful for applications in thin-film capacitor, nonvolatile memory, nonlinear optics, and photoelectrochemical cell [1–4]. Most perovskite phases are prepared by solid-state reactions between the corresponding oxides at temperature above 1000 °C. Recently, solution based methods have been widely developed for various perovskite nanomaterials synthesis [5]. Bismuth ferrite, one of the very few multiferroics with a simultaneous coexistence of ferroelectric and antiferromagnetic order parameters in perovskite structure, has attracted much attention for many decades since 1960. $BiFeO_3$ (BFO) has a ferroelectric Curie temperature T_c of 850 °C and an antiferromagnetic Neel temperature of 370 °C [6,7]. However, potential applications of BFO in the memory devices, sensors, satellite communications, optical filters and smart devices were greatly limited due to its low insulation resistance caused by the reduction of Fe^{3+} species to Fe^{2+} and oxygen vacancies for charge compensation [8,9]. Although great achievements have been made for BFO thin films prepared by the pulsed-laser deposition (PLD) method [10,11], it was hard to avoid generating impurity phases by the conventional solid-state reaction in bulk materials. BFO perovskites could only stabilize within a narrow ranged temperature. Up to date, the synthesis of single-phase BFO ceramics is still a challenging issue. In the solid-state route, nitric acid leaching was required to eliminate the impurity phases, such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$, after calcination of mixed bismuth and iron oxides [12], which resulted in coarser powders and the poor reproducibility. Most recently, Wang et al. [8] and Pradhan et al. [13] prepared pure BFO phase ceramics by a rapid liquid-phase sintering technique. The crystallization temperature of BFO in these methods was required above the ferroelectric Curie temperature T_c, which implied that the volatilization

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of bismuth was hard to avoid. Moreover, Ghosh et al. [14] made pure phase bismuth ferrite nanopowders by the tartaric acid based sol–gel method coupled with the additional calcination process. Accordingly, it is interesting to synthesize and investigate single-phase BFO-based solid solution with no other ferroelectric end member. Up to now, two main methods are reported to prepare single-phase BFO ceramics; one involves rapid liquid-phase sintering and the other leaching of the impurity phase with dilute nitric acid. These methods lead to ceramics with high leakage current, which is the main obstacle for its practical applications. So, an alternative method for preparing high quality BFO ceramics is desired. Few works have been done to prepare BFO powders by using the soft chemistry method. The advantage of soft chemical routes was that microcrystallines could be synthesized at a much lower temperature, and also energy saving and cost effective. Previous work demonstrated that lanthanum substitution reduces the strain behavior of BFO films. From leakage current density values we noted that La^{+3} substitution for Bi^{+3} is an effective way to reduce bismuth vacancies that are accompanied by oxygen vacancies decreasing the film conductivity [15]. Cheng et al. [16] have obtained $Bi_{1-x}La_xFeO_3$ ceramics with $x = 0$, 0.1, 0.2, and 0.3 by solid-state reaction, starting from metal oxides. Below 10% La doping, Bi_{1-x} La_xFeO_3 maintains the rhombohedral structure of $BiFeO_3$. However, for $Bi_{0.8}La_{0.2}FeO_3$ and Bi 0.7 $La_{0.3}FeO_3$, the structures change to the orthorhombic and tetragonal, respectively. The authors have observed that La doping significantly reduces electric leakage, enhances the ferromagnetic moment due to the broken cycloid spin structure caused by the changes in the crystalline structure. In other work, [17] Augustin et al. have obtained single-phase perovskite structure of La^{3+} substituted nanocrystalline strontium ferrite prepared by citrate combustion method using metal nitrate salts as cation precursors and citric acid as a fuel. A phase transition from cubic to orthorhombic has been observed with increasing La^{3+} substitution. In view of the fact that recently, more and more efforts have been undertaken to develop nontoxic lead-free piezoelectric materials, we report in this work the syntheses and characterization of La-doped bismuth ferrite powders prepared from chemical method. The main advance of this paper is to report the efficiency of chemical solution to obtain single-phase lanthanum modified bismuth ferrite powders. Comments were addressed to changes on crystal structure and morphology of the grains.

2. Experimental procedure

The procedure of $Bi_{1-x}La_xFeO_3$ (BFO) synthesis, based on the polymeric precursor method, also called Pechini method [18], starts from the fact that certain α-hydroxycarboxylic organic acids can form polybasic, acid chelates with a wide range of cations. After addition of a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, with homogeneous cation distribution. Iron (III) nitrate nonahydrate, 99.5% purity (Merck) and bismuth nitrate, 99.5% purity (Aldrich) were used as raw materials. The bismuth and iron precursor solutions were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of Fe and Bi solutions were mixed and homogenized by stirring at 90 °C. $Bi_{1-x}La_xFeO_3$ powders with $x = 0$, 0.08, 0.15 and 0.30 were prepared from the metal citrate complex polyesterified with ethylene glycol. The molar ratio of metal/citric acid/ethylene glycol was 1/4/16. In this work, an excess of 5 wt% Bi was added to the solution aiming at compensating some unavoidable bismuth oxide loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Most of the organic matter is subsequently eliminated at temperatures as low as 300 °C, forming a dark residue containing reactive oxides with well-controlled stoichiometry. The formed porous product was crushed and heated in an alumina crucible at 850 °C for 2 h to eliminate residues of organic material. The resulting powder was milled in attritor with zirconia balls in an acetone medium for 40 min using a procedure according to the literature [19].

Phase analysis was monitored using an X-ray diffractometer (XRD, Model D500, Siemens). Infrared spectroscopy (Model 400-IR/FT, IMPACT) was used to indicate the presence of carbonates in bismuth ferrite powders. The FT-Raman analyses were done in a FRS/100/S Bruker spectrometer, using a Nd:YAG laser. XANES spectra were collected at the Bi and Fe K-edges being measured with a Si (2 2 0) monochromator in the D04B-XAFS1 beam line at the Brazilian Synchrotron Light Laboratory (LNLS). Data were collected at room temperature using energy steps of 2 eV and an integration time of 3 s. A scanning electron microscopy (SEM, Model SM-300, Topcon) was used to study their particle size and powder morphology.

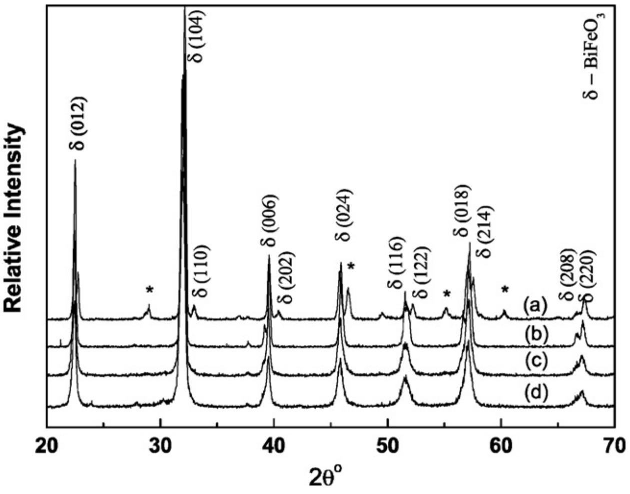

Fig. 1. X-ray data for $Bi_{1-x}La_xFeO_3$ powders calcinated at 850 °C for 2 h as a function of lanthanum content: (a) $x = 0$; (b) $x = 0.08$; (c) $x = 0.15$ and (d) $x = 0.30$.

3. Results and discussion

Crystallinity of lanthanum modified BFO powders calcinated at 850 °C for 2 h was studied by XRD analyses (Fig. 1). Upon La substitution at the Bi site, powders free of secondary phases were noted indicating the formation of solid solution. Also, as the lanthanum content increases, fewer peaks are observed in the pattern. This behavior can be ascribed to change of crystal structure as already discussed in Ref. [20]. XRD data reveal that $BiFeO_3$ was obtained by the soft chemistry method with rhombohedral distorted perovskite structure. The La-modified $BiFeO_3$ powders were also fitted. One feature that should be noted is that with increasing La composition, the intensity of some diffraction peaks, becomes weak and tends to disappear, whereas some others tend to appear near $x = 0.30$. The XRD pattern is becoming close to those of orthorhombic structure. This result obviously indicates a structural phase transition near $x = 0.30$, which is consistent with other reports [21,22] but different from those on epitaxial films [23]. This is reasonable since in the thin-film form, not only La substitution but also the in-plane stress has effects on structure [24,25]. The presence of $Bi_{24}Fe_2O_{29}$ as minor phases (marked with *) is presented in the BFO compound as a low-level impurity phase.

Infrared spectra of powders were recorded (Fig. 2). Typical band characteristics of oxygen–metal bonds were observed in the 450–640 cm^{-1} region. Independently of lanthanum content the samples are free of carbonates. This result is satisfactory from a technological point of view since many properties are dependent on the purity of the raw powders, especially carbonate traces. That can results in porous ceramics due to CO_2 elimination. The O–H bond stretching near 3400 cm^{-1} could be attributed to adsorbed water due to the contact of the sample with the environment.

Raman spectra are illustrated in Fig. 3. The presence of Raman-active modes can be used to evaluate the structural order degree at short-range. The modes located at 212, 316, 377, 445, 537 and 635 cm^{-1} are caused by internal vibration of FeO_6 octahedra, whereas below 200 cm^{-1} must be addressed to different sites occupied by bismuth within the perovskite units. The bands located at 97, 120 and 145 cm^{-1} are related to Bi atoms of perovskite layer and corresponds to a rigid layer. The Raman spectrum of the BLFO sam-

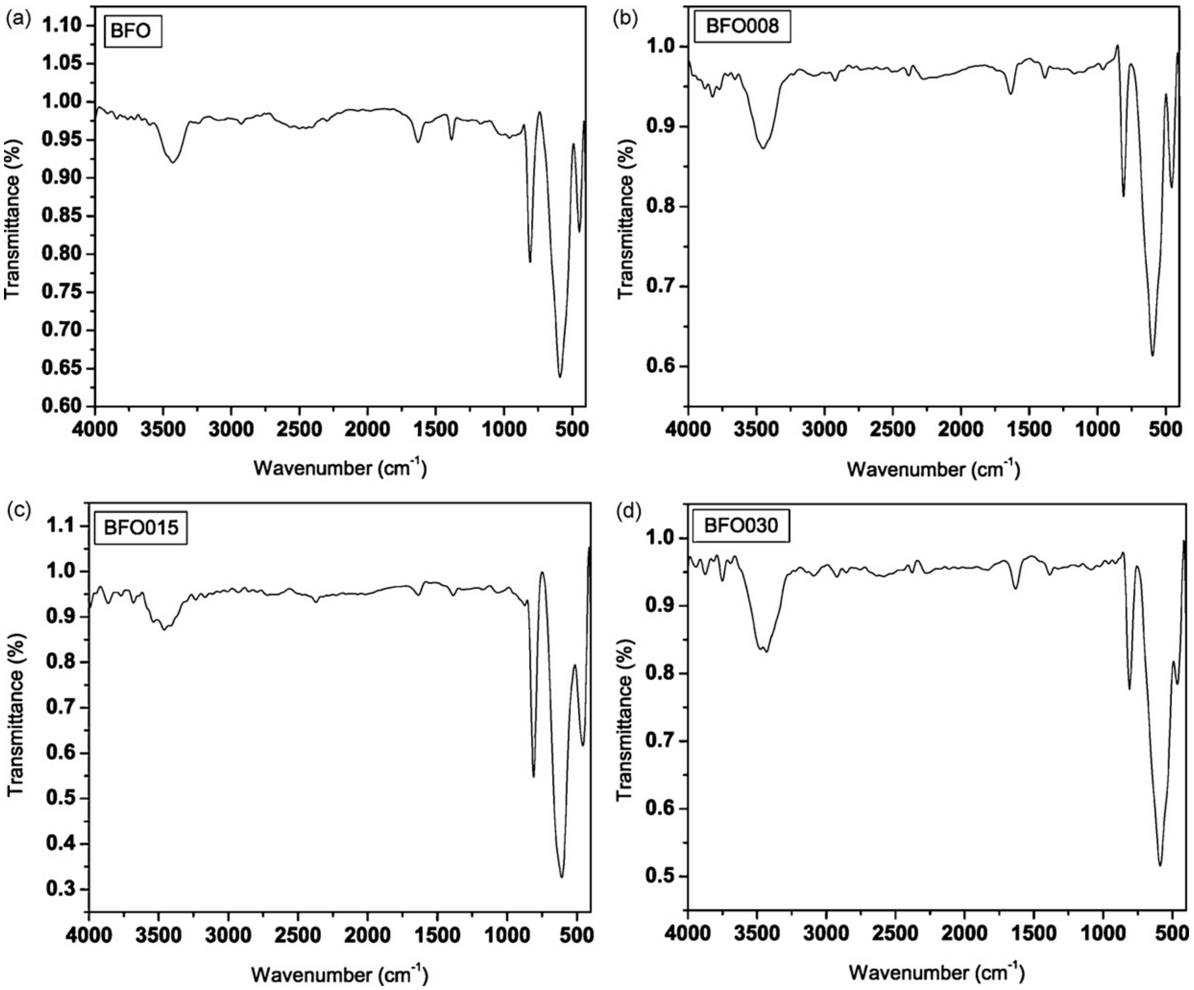

Fig. 2. Infrared data for $Bi_{1-x}La_xFeO_3$ powders calcinated at 850 °C for 2 h as a function of lanthanum content: (a) $x = 0$; (b) $x = 0.08$; (c) $x = 0.15$ and (d) $x = 0.30$.

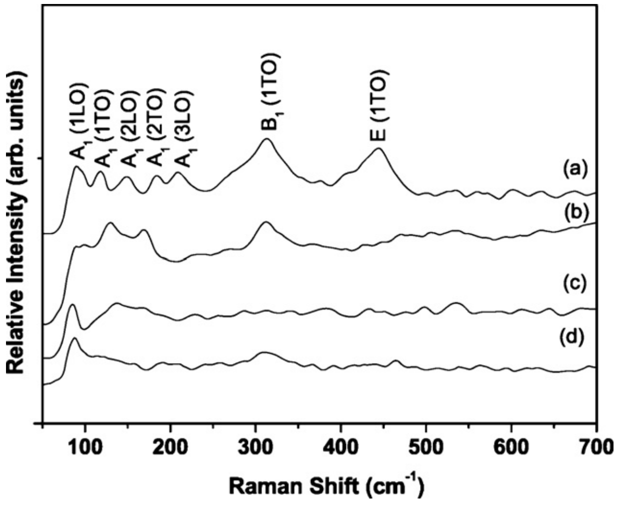

Fig. 3. Raman spectra for $Bi_{1-x}La_xFeO_3$ powders calcinated at 850 °C for 2 h as a function of lanthanum content: (a) $x = 0$; (b) $x = 0.08$; (c) $x = 0.15$ and (d) $x = 0.30$.

ples (Fig. 3(b and c)) showed the same BFO bands, but its intensity showed a decrease accompanied by a slight shift to a higher range of energy frequencies. These bands are located at 118 and 147 cm^{-1} for the BFO and 127 and 168 cm^{-1} for the BLFO. These displacements indicate that the lanthanum atom substitutes bismuth into the BFO site. Small changes observed in all spectra can be associated with the preparation method, average crystal size and structural order degree. In this way, it was noted that changes which occur above 200 cm^{-1} in the BLFO powders are caused by structural distortion and reduction of vibrations in the FeO_6 octahedra caused by substitution with lanthanum.

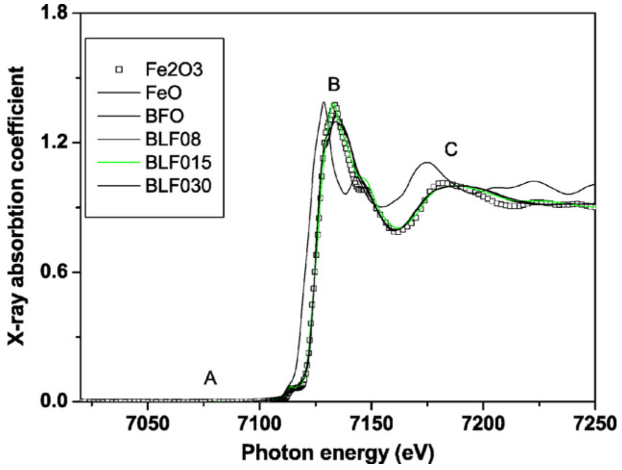

Fig. 4. XANES spectra for bismuth ferrite powders calcinated at 850 °C for 2 h as a function of lanthanum content.

Fig. 4 shows the Fe K-edge XANES spectra of the lanthanum modified BFO powders. For the purpose of comparison, the XANES

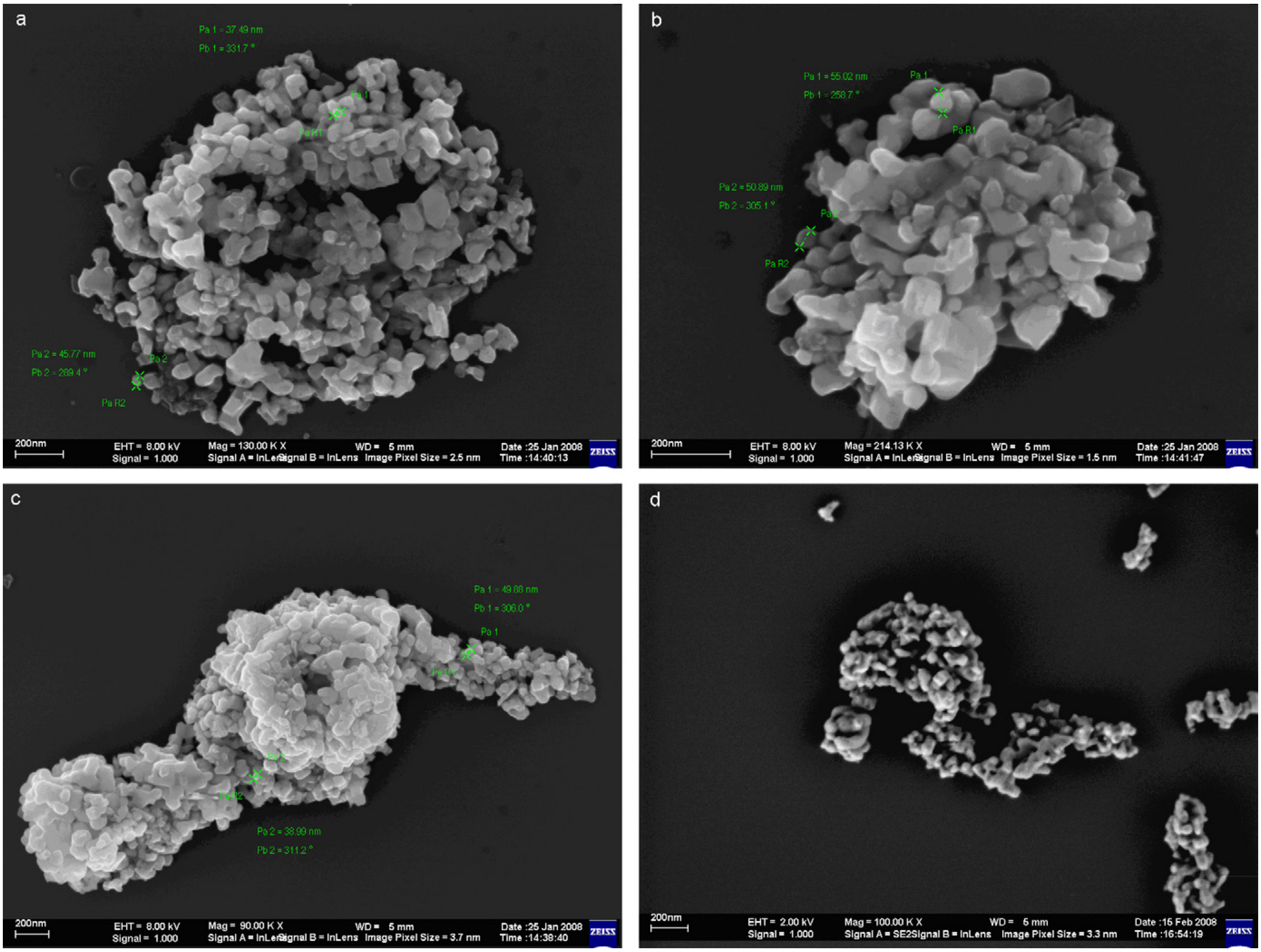

Fig. 5. SEM micrographs for $Bi_{1-x}La_xFeO_3$ powders calcinated at 850 °C for 2 h as a function of lanthanum content: (a) $x = 0$; (b) $x = 0.08$; (c) $x = 0.15$ and (d) $x = 0.30$.

spectrum of BFO, FeO and Fe_2O_3 powders are also shown. The iron atoms present a 3+ valence state in the BFO system once its curve is quite similar to Fe_2O_3 phase. Peak *A* corresponds to the 1*s*-3*d* electric dipole–forbidden transition, whereas Peak *C* signifies the dipole–allowed transition (empty orbital 4*p*). Peak *B* known as a shoulder peak is caused by the shakedown process in which 2*p* electron in the oxygen 2*p* band partially transfers to the Fe3*d* orbital, so called ligand-to-metal charge transfer process. In this way, we observe changes in the symmetry of BFO and BFO08 compositions when compared to the BLF015 and BLF030 samples. That indicates that iron atoms have different symmetries. In this direction, a structural change is occurring from BFO to BLF030 composition.

The effect caused by lanthanum addition on the morphology and shape of the grains was evaluated by SEM analysis (Fig. 5). A large number of elongated and circular agglomerates which is typical of chemical methods were evident for all compositions. As it can be seen, addition of lanthanum caused a structural distortion leading to grains in a plate-like morphology. No precipitates were evident in the grain boundary indicating the formation of a continuous solid solution. On the other hand, BFO system consists of a mixture of rod-like and plate-like grains. The rod-like grains might be originated from an anisotropic behavior of bismuth ferrite. That indicates change in the kinetics of the grain growth. By roughly estimation and using the Scherrer formula, it was found that the individual particle size was approximately 30 nm.

4. Conclusions

In summary, we have developed and optimized a simple way to prepare single-phase bismuth ferrite samples. The powders prepared under the optimized conditions show lanthanum composition dependent structure and microstructure properties. A structure phase transition from rhombohedral to orthorhombic is observed near $x = 0.30$. XANES spectra evidenced iron atoms in a 3+ valence state while SEM analysis reveal structural distortion leading to a different grain shape after lanthanum addition. Finally, we fabricated single-phase lanthanum modified bismuth ferrite powders from the soft chemistry route.

Acknowledgments

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