



Dielectric relaxations in pure, La-doped, and (La, Co)-codoped BiFeO₃: Post-sintering annealing studies

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ABSTRACT

Pure, La-doped, and (La,Co)-codoped BiFeO₃ ceramic samples were prepared by solid-state reaction. By means of dielectric permittivity, electric modulus spectroscopy, and impedance analysis, the dielectric properties of the samples were systematically investigated in the temperature range of 140–330 K and frequency range of 20–10⁷ Hz. Three, two, and one dielectric relaxations were found in pure, La-doped, and (La,Co)-codoped samples, respectively, in the investigated temperature window. Post-sintering annealing studies reveal that both *p*- and *n*-types carriers coexist in the samples with the *p*-type carriers (holes) being the major carriers acting as relaxing species. The dielectric properties are determined by the competition between the *n*-type carriers (electrons) and the holes. La-doping and (La,Co) dual doping enhance the role played by the holes. Impedance analysis shows that the low-temperature (high-frequency) relaxation is a polaronic relaxation resulting from the hopping motion of holes inside grains. The middle-temperature (frequency) and high-temperature (low-frequency) relaxations are Maxwell-Wagner relaxations caused by the hopping motion of holes blocked by grain boundaries and sample-electrode contacts, respectively. These results underscore the role of sample preparing conditions in the dielectric properties of BiFeO₃ and suggest that optimizing the preparing procedures would be a promising strategy to achieve superior properties of BiFeO₃.

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1. Introduction

Materials exhibiting two or all three coupled ferroic orders of ferro/antiferromagnetics, ferroelectrics, and ferroelastics are termed as multiferroics [1,2]. Multiferroic behavior endows materials with the “product” properties, leading to various types of new physical phenomena in the materials and offering the potential for multifunctional devices which are unachievable by conventional ferroic materials [3,4]. The great potential for practical applications as well as the rich physics, have led to a tremendous flurry of research interest in multiferroic materials in recent years. Unfortunately, because the ferroelectric ordering (which requires the cations to have an empty *d* orbital) is incompatible with the ferromagnetic ordering (non-empty *d* orbital is needed), there are enumerable multiferroic materials exist in nature [5]. Additionally, the observed multiferroic behavior of most multiferroics frequently

occurs in a low temperature range of $T < 50$ K [6], which strongly limits the applications of these materials. BiFeO₃ is so far the only known room-temperature multiferroic material. It, therefore, goes to the fore front of research in the multiferroic realm.

A formidable problem limiting the practical application of BiFeO₃, is the relatively high leakage current. Although, many strategies, including for example doping [7], sample processing [8–11], film strain [12–15], etc. have been adopted to solve the problem, it is still difficult to achieve better ferroelectric and magnetic properties simultaneously in single-phase BiFeO₃. A prerequisite for solving the problem is to completely understand the mechanism of the leakage current. Physically, the current can be contributed by weakly localized electrons/holes and/or ions. The hopping motions of these carriers not only yield conduction but also create polarization [16]. Therefore, dielectric spectroscopy can provide useful insight into the microscopic features of the conducting/relaxing species.

So far, the dielectric measurements were performed extensively on BiFeO₃ thin films [12,17–19] and ceramics [20–33]. The results

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are considerable discrepancies, providing strong motivation for further studies. Two main features of the dielectric properties of BiFeO₃ can be extracted: (1) only one relaxation with an activation energy of ~1.0 eV was found in thin film system [12,17,19], and (2) up to four relaxations were reported in ceramic samples. For clarity, these relaxations are termed as L1-L4 in the order of ascending temperature. Details of them are summarized in Table 1. Different mechanisms were proposed for L2-L4. For example, charge carriers hopping between Fe²⁺ and Fe³⁺ ions [26,27], reorientations of Fe²⁺ - Fe³⁺ dipoles [33], the migration of singly charged oxygen vacancies [28], etc. were argued to be putative mechanism for L2; Maxwell-Wagner relaxation due to grain boundaries [26] and migrations of oxygen vacancies [27] were proposed as possible mechanism for L3; defect ordering [26], short-range motion of doubly charged oxygen vacancies [12], and interfacial polarization [33] were considered to be the mechanism for L4.

It is noteworthy that, although the reported mechanisms for these relaxations are inconsistent, there is a consensus that these relaxations are strongly related to oxygen vacancies. It is well-known that oxygen vacancies and their migration play a crucial role in determining the (di)electric, magnetic, and optical properties of BiFeO₃ [34–36]. Therefore, detailed investigations of the influence of oxygen vacancy on the dielectric behavior can not only deepen the understanding of the mechanism of the leakage current, but also be helpful for optimizing the preparation conditions for future potential applications. In the present work, the dielectric properties of the nominally pure, La-, and (La, Co)-doped BiFeO₃ samples after different annealing treatments were studied.

2. Experimental details

The ceramics of BiFeO₃ (BFO), Bi_{0.9}La_{0.1}FeO₃ (BLFO), and Bi_{0.9}La_{0.1}Fe_{0.97}Co_{0.03}O₃ (BLFCO) were prepared by the modified solid-state reaction method with high purity (99.99%) starting powders of Bi₂O₃, Fe₂O₃, La₂O₃, and Co₃O₄. These materials were carefully weighed and stoichiometrically mixed in an agate mortar for 5 h and then calcined at 800 °C for 6 h followed by furnace cooling. The resultant powders were re-ground 1 h and pressed into pellets with the size of 12 mm diameter and about 1 mm thickness under a uni-axial pressure of 20 Mpa. Finally, the pellets were sintered at 850 °C for 40 min and quenched to room temperature in air resulting in less Bi deficiency. Annealing treatments were performed in flowing (200 ml/min) O₂ and N₂ (both with purity >99.999%) at different temperatures for 2 h.

Phase purity of the sintered pellets was characterized by X-ray diffraction (XRD) performed on a MXP18AHF diffractometer (MARK, Japan) with Cu K α radiation. The morphology and microstructure of the sample were examined using a field emission scanning electrical microscope (SEM, Model S-4800, Hitachi Co., Tokyo, Japan). Dielectric properties in both temperature and frequency domains were measured using a Wayne Kerr 6500B precise impedance analyzer (Wayne Kerr Electronic Instrument Co., Shenzhen, China) with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system (Partulab Co., Wuhan, China). The temperature domain dielectric properties were

measured at fixed frequencies by varying temperature with a heating rate of 2 K/min. The frequency domain dielectric properties were measured at fixed temperatures by scanning frequency from 10² to 10⁶ Hz. The amplitude of ac measuring signal was 100 mV. Electrodes were made by printing silver paste on both sides of the disk-type samples.

3. Results and discussion

3.1. Structure, morphology, and general dielectric properties characterization

Fig. 1 shows the XRD patterns of BFO, BLFO, and BLFCO. The patterns for the three samples are identified to be a rhombohedral structure with R3c space group. All the main peaks can be indexed based on JCPDS Card No. 74-2493. Very minor second phase possibly referring to Bi₂Fe₄O₉ or Bi₂₅FeO₃₉ indicated by an asterisk was observed in BLFCO. SEM images of surface morphology, shown in the insets of Fig. 1, reveal that the grain size is non-uniform. The grains with an average size around 110, 140, and 160 μ m for BFO, BLFO, and BLFCO, respectively, are densely packed together with some small pores.

Fig. 2 summarizes the temperature (*T*) dependent dielectric properties of the three samples under the selected frequencies of 10², 10³, 10⁴, 10⁵, 5 \times 10⁵, and 10⁶ Hz. It is clearly seen that the samples of BLFO and BLFCO show colossal dielectric constant (CDC, with dielectric constant ϵ' > 10³) behavior characterized by a steplike increase in ϵ' and accompanied by a thermally activated relaxation in loss tangent ($\tan \delta$). The CDC behavior of BLFO is contributed by two relaxation processes, whereas in BLFCO, the behavior is contributed by one relaxation process. Although the CDC behavior is not found in BFO, the sample shows at least two relaxation processes. In order to describe the relaxations clearly, we discuss them in each sample in the following parts.

3.2. Dielectric properties of BFO

In order to get deep insight into the physical nature of the relaxations in BFO, we performed detailed dielectric measurements on BFO in the frequency domain. Fig. 3(a) displays the spectroscopic plots of $\tan \delta$ recorded at a series of temperatures. With increasing temperature, up to three relaxations can be seen. To clearly see

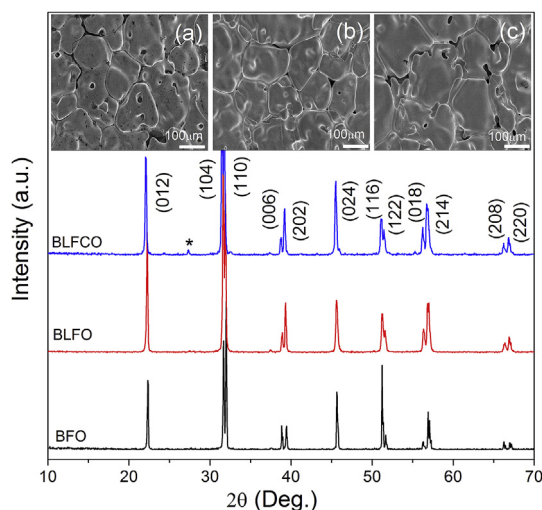


Fig. 1. XRD patterns for the pure, La-doped, and (La, Co) codoped samples. Insets are the SEM images for the pure (a), La-doped (b), and (La, Co) codoped (c) samples.

Table 1
Relaxations reported in BiFeO₃ ceramics.

Relaxation	Appearing temperature	Activation energy	Typical reference(s)
L1	Around 25 K	~30 meV	[20]
L2	100–250 K	0.25–0.45 eV	[24,26]
L3	Around RT	0.5–0.6 eV	[24,26]
L4	Above RT	~1.0 eV	[24,26]

RT is short for room temperature.

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