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Evidence of magnetoelectric coupling on calcium doped bismuth ferrite thin films grown by chemical solution deposition

L. V. Costa,[1] M. G. Ranieri,[1] M. Cilense,[2] E. Longo,[2] and A. Z. Simões[1,a)]
[1]*Department of Materials Science, São Paulo State University-Unesp—Engineering Faculty of Guaratinguetá, Dr. Ariberto Pereira da Cunha Avenue, 333, Pedregulho, 12516-410 Guaratinguetá-SP, Brazil*
[2]*Department of Physics-Chemistry, São Paulo State University-Unesp—Chemistry Institute Interdiciplinar Laboratory on Ceramics, Professor Francisco Degni Street, 14800-90 Araraquara-SP, Brazil*

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Magnetoelectric coupling was observed at room temperature in calcium modified bismuth ferrite $BiFeO_3$ (BFO) thin films deposited on $Pt/TiO_2/SiO_2/Si$ (100) substrates by the chemical solution deposition. Undoped and Ca-doped $BiFeO_3$ films were coherently grown at a temperature of 500 °C for 2 h. The highest doped BFO film has a tetragonal structure with *P4mm* space group, while BFO has a rhombohedral structure with space group *R*3*c*, which can be treated as a special triclinic structure. Room temperature magnetic coercive field indicates that the undoped film is magnetically soft with maximum magnetoelectric coefficient in the longitudinal direction was about 12 V/cm. Adding Ca^{2+} ions to BFO in high concentration decreases the remnant polarization and stabilizes the charged domain walls which interact with oxygen vacancies reducing coercive field. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4867123]

Among the single-phase multiferroic materials studied $BiFeO_3$ (BFO) with a rhombohedrally distorted perovskite structure with space group R3c, is the only one that exhibits both ferroelectricity and G-type antiferromagnetism at room temperature (with Curie temperature $Tc \sim 1103$ K and Néel temperature $T_N \sim 643$ K), which makes it most possible for applications at room temperature.[1] However, pure BFO has a serious high leakage current problem resulted from the charge defects such as oxygen vacancies and the cancellation of the ion magnetic moments due to its spatial periodic inhomogeneous spin structure,[2] which hindered its practical applications in multiferroic devices. To improve the properties of BFO, considerable efforts have been made, for instance, A-site substitution with La^{3+}, Nd^{3+}, Ce^{3+}, and Tb^{3+} (Refs. 3–6) and B-site substitution with Ni^{2+}, Cu^{2+}, Co^{2+}, Ti^{4+}, Zr^{4+},V^{5+} (Refs. 7 and 8), etc. Ramesh *et al.* studied the quasi-non-volatile and reversible modulation of electric conduction accompanied by the modulation of the ferroelectric state in Ca-doped $BiFeO_3$ films, using an electric field as the control parameter. The mechanism of this modulation in Ca-doped $BiFeO_3$ is based on electronic conduction as a consequence of the naturally produced oxygen vacancies that act as donor impurities to compensate calcium acceptors and maintain a highly stable Fe^{3+} valence state.[9] However, because the ferroelectricity of $BiFeO_3$ is primarily attributed to the Bi 6s lone-pair electrons, the ferroelectric properties and the T_c are expected to be less sensitive to strain.[10] However, few works related to this were reported. Therefore, in this paper, we prepared the A-site Ca doped BFO films with different compositions on $Pt/Ti/SiO_2/Si$ substrates by polymeric precursor method and investigated its influence on the structure and multiferroic properties.

a)Author to whom correspondence should be addressed. Electronic mail: alezipo@yahoo.com.

Calcium modified bismuth ferrite thin films were prepared by the polymeric precursor method, as described elsewhere.[11] The following compositions were prepared: BFO; BFOCa010; BFOCa020; and BFOCa030. The film thickness was reached by repeating 10 times the spin-coating and heating treatment cycles. The thickness of the annealed films was measured using scanning electron microscopy (SEM) (Topcom SM-300) at the transversal section. We have obtained films with thickness in the range of 340–360 nm. In this case, back scattering electrons were used. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 2000) and CuKα radiation. Top Au electrodes (0.5 mm diameter) were prepared for the electrical measurements by evaporation through a shadow mask at room temperature. The magnetoelectric coefficient measurements were attained in a dynamic lock-in technique. The dc magnetic bias field was produced by an electromagnet (Cenco Instruments J type). The time-varying dc field was achieved by a programmable dc power supply (Phillips PM2810 60 V/5 A/60 W). To measure the dc magnetic field, a Hall probe was employed. Additionally, an ac magnetic field up to 10 Oe with frequencies from 0.1 to 100 kHz was superimposed onto the dc field. The ac field was produced by a Helmholtz-type coil (180 turns with a diameter of 50 mm), driven by an ac current generated by a function generator (Philips PM5192). The amplitude of the ac field was calculated from the driving current measured by a multimeter (Keitley 196 System DMM). Samples were located in the magnetic field with surface perpendicular or parallel to the field direction, for longitudinal and transverse measurements, respectively.

Fig. 1 presents the XRD patterns of BFO and Ca doped BFO films deposited on platinum coated silicon substrates. The films were well crystallized at a processing temperature of 500 °C. The BFO and Ca doped BFO films self-organized

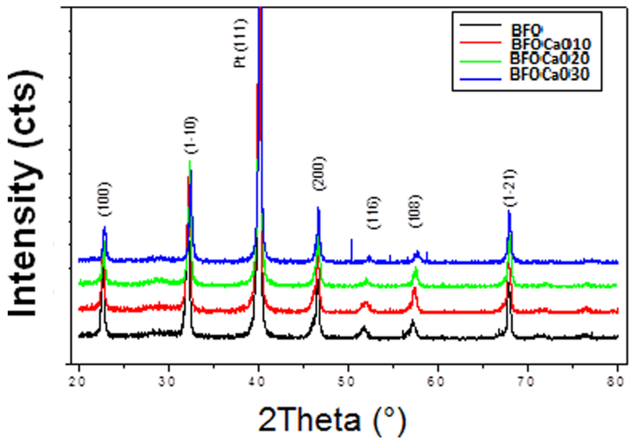

FIG. 1. X-ray diffraction of BFO, BFOCa010, BFOCa020, and BFOCa030 thin films deposited by the polymeric precursor method and annealed at 500 °C in static air for 2 h.

to produce (110)-preferred orientation with good crystallinity. With partial substitution of Ca ions for A-site bismuth ions, the (108) and (116) diffraction peaks of the film shifted toward a higher angle. No additional peak related to CaO could be assigned revealing partial substitution of calcium by bismuth in the crystal lattice and solid solution of Ca substitution in BFO. BFOCa030 film has a tetragonal structure with *P4mm* space group, while BFO has a rhombohedral structure with space group *R*3*c*, which can be treated as a special triclinic structure.[12]

The magnetoelectric coefficient versus dc bias magnetic field in the longitudinal and transversal directions reveals hysteretic behavior, as observed in the magnetic field cycles shown in Figures 2(a) and 2(b) for the BFOCa030. The maximum magnetoelectric coefficient of 12 V/cm Oe in the longitudinal direction is much larger than that previously reported for thin films as high as 3 V/cm Oe in the same direction at zero fields.[13] This is a consequence of the antiferromagnetic axis of BFOCa030 which rotates through the crystal with an incommensurate long-wavelength period of ~620 Å.[14] Early reports showed that the spiral spin structure leads to a cancellation of any macroscopic magnetization and would inhibit the observation of the linear magnetoelectric effect.[15] Significant magnetization (~0.5 μB/unitcell) and a strong magnetoelectric coupling have been observed in epitaxial thin films, suggesting that the spiral spin structure could be suppressed.[16] As can be seen in Fig. 2(c), the film is magnetically poled, initially there is an enhancement in saturation polarization, as expected. However, as the magnetic field increases, the polarization value drops, which can be attributed to disturbance created in grain alignment due the magnetic field.

The effect of divalent-ion-calcium doping on multiferroic $BiFeO_3$ films was investigated on Pt substrate using the soft chemical method through annealing at 500 °C for 2 h. Highest calcium concentration changes the local distortion and strain caused by the rhombohedral coexisting phase reflecting in physical properties of the system. Among these films studied, the BCFO30 showed strong magnetoelectric coupling in the longitudinal direction revealing hysteretic behavior. The A-site Ca doping with various contents has notable influences

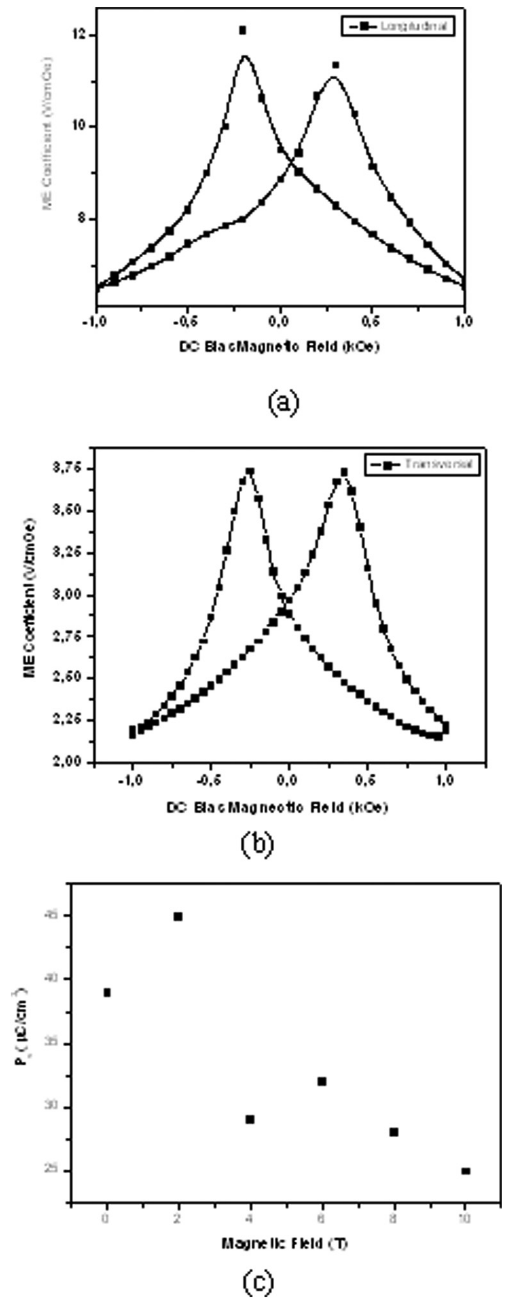

FIG. 2. The magnetoelectric coefficient dependence on dc bias magnetic field and the effect of magnetic poling on saturation polarization for BFOCa030 thin films deposited by the polymeric precursor method and annealed at 500 °C for 2 h at a 7 kHz ac magnetic field at room temperature. (a) Longitudinal, (b) transversal, and (c) magnetic field as a function of Ps.

on the electrical properties of the BFO films due the modification of the crystal structure and the reduction of charge defects. The results of these studies are very promising and suggest that BCFO30 thin films can be used as storage element in nonvolatile ferroelectric random access memories.

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