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Raman Vibrations, Domain Structures, and Photovoltaic Effects in A-Site La-Modified BiFeO$_3$ Multiferroic Ceramics

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Micro-Raman spectroscopy, X-ray diffraction, high-resolution transmission electron microscopy (TEM), oxygen vacancies, synchrotron X-ray absorption spectroscopy, magnetizations, optical band gaps, and photovoltaic (PV) effects have been studied in (Bi$_{1-x}$La$_x$)$_3$Fe$_2$O$_7$ (BFO100:xL) ceramics for $x = 0.0$, 0.05, 0.10, and 0.15. XRD, Raman spectra, and TEM confirm a rhombohedral $R3c$ symmetry with the tilted FeO$_6$ oxygen octahedra in all compounds. The low-frequency Raman vibrations become broader and shift toward higher frequencies as La$^{3+}$ increases. Fe K-edge synchrotron X-ray absorptions reveal that Fe$^{3+}$ valence and Fe–O–Fe bond angle are not modified by the La$^{3+}$ substitution. All compounds exhibit a linear antiferromagnetic feature. Optical transmission reveals band gaps in the range of 2.22–2.24 eV. The heterostructures of indium tin oxide (ITO) film/(Bi$_{1-x}$La$_x$)$_3$Fe$_2$O$_7$ ceramics/Au film show a $p$-$n$ junction-like $I$-$V$ characteristic behavior. The maximal PV power conversion efficiency can reach 0.19% in ITO/BFO15L/Au under illumination of $\lambda = 405$ nm. A junction-like theoretical model can reasonably describe open-circuit voltage and short-circuit current as a function of illumination intensity.

I. Introduction

Bismuth ferrite BiFeO$_3$ (BFO) materials have been widely studied because of their room-temperature antiferromagnetic ($T_N$=630 K) and ferroelectric ordering ($T_C$ ~1100 K). BFO has a rhombohedral perovskite $R3c$ structure, in which the cations (Bi$^{3+}$ and Fe$^{3+}$) displace along the [111]$_c$ direction with FeO$_6$ octahedra rotated antiphase around the rhombohedral axis. A-site Bi$^{3+}$ has a stereochemically active $6s^2$ lone pair, which causes a hybridization of Bi 6$p$ and O 2$p$ states, and causes an off-centering displacement of Bi$^{3+}$ toward O$^{2-}$ to induce ferroelectricity. The magnetic moment of Fe$^{3+}$ ions of BFO are in a G-type AFM ordering such that each spin is surrounded by six antiparallel neighbor spins. The dynamics of domain walls in polycrystalline BFO plays an important bridging role between local conductivity and macroscopic electromechanical properties. Electric leakage, low remanent polarization, and weak magnetoelectric coupling have limited BFO for applications. To reduce the current leakage and suppression of the magnetic spin cycloid, many studies have focused on the substitution of rare-earth elements onto the A-site Bi$^{3+}$ ions of the perovskite cell. La doping in BFO ceramics can improve magnetic response, and reduce the leakage current and dielectric loss. Rhombohedral $R3c$ symmetry of (Bi$_{1-x}$La$_x$)$_3$Fe$_2$O$_7$ has been reported in different La concentration ranges, for example, $x \leq 0.125, 0.15 \leq x \leq 0.20, 0.25 \leq x \leq 0.30$. From synchrotron XRD and high-resolution TEM, an incommensurately modulated phase has been observed for $0.19 \leq x \leq 0.30$. An orthorhombic $Pnma$ symmetry was proposed for $x \geq 0.50$. First-principles calculations using density functional theory (DFT) in (Bi$_{1-x}$La$_x$)$_3$Fe$_2$O$_7$ show that the most stable phases are rhombohedral $R3c$ for $x = 0.1$ and orthorhombic $Pnma$ for $x = 0.2$ and 0.3. According to the Kohn–Sham energy, the phase boundary between $R3c$ and $Pnma$ symmetries was predicted near $x = 0.30$. Two degenerate orthorhombic $Pnma$ and $Pnma_2$ structures are theoretically stable in the region of $0.3 \leq x \leq 0.65$. Weak ferromagnetic magnetization has been observed in A-site rare-earth-doped (Bi$_{1-x}$A)$_3$Fe$_2$O$_7$ (A = La, Nd, Sm, Er) ceramics. Unsatuated ferroelectric hysteresis loops have been observed in (Bi$_{1-x}$La$_x$)$_3$Fe$_2$O$_7$ ceramics. The magnitudes of remanent magnetization ($M_r$) and coercive field ($H_c$) increase with La content, perhaps due to the suppression of the cycloidal spin structure and increased magnetoelectric coupling. The weak ferromagnetism in (Bi$_{1-x}$La$_x$)$_3$Fe$_2$O$_7$ ceramics can be attributed to the canting of the antiferromagnetic spins by the modification of the antiparallel sublattice magnetization of Fe$^{3+}$. Recent work of Nd-substituted BFO ceramics has suggested that homogeneity of sample can be improved by using multiple heating cycles. BiFeO$_3$ has been considered a $p$-type semiconducting material resulting from the loss of Bi$^{3+}$ cations during the high-temperature synthesis process, which causes vacancies to act as $p$-type centers for accepting electrons. First-principles calculations suggested that Bi vacancies ($V_{Bi}$) have lower formation energy than oxygen vacancies under oxygen-rich condition and $V_{Bi}$ become the electron-acceptor defects. In BFO, the Fe–O bond length (~1.93 Å) is shorter than the Bi–O bond length (~2.31 Å), thus the formation of Bi vacancies is easier than formation of Fe vacancies. $p$-type BFO and $n$-type ITO films have been reported,respectively, with carrier densities of $n_p$~10$^{20}$ cm$^{-3}$ and $n_p$~10$^{20}$ cm$^{-3}$. BFO films and crystals have shown interesting photovoltaic
PV responses and photoconductivity. PV properties of the alkaline-earth (Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\))-doped BFO ceramics with ITO (top) and Au (bottom) electrodes have shown dependences on thickness, light wavelength, and intensity. The PV open-circuit voltage and short-circuit current have been described by a theoretical model, which is based on the photo-excited carriers in the interface.

The Raman spectra of BFO ceramics reveal two anomalies in the vicinities of the Neel temperature (\(T_N\approx 645\) K) and of 140–200 K, the temperature range of a spin-reorientation transition. Direct optical band gaps of 2.55–2.75 eV have been reported for rhombohedral BFO films. Based on optical transmission and the Tauc equation, optical band gaps of (Bi\(_{1-x}\)La\(_x\))FeO\(_3\) (\(x = 0.0–0.30\)) films are in the range of 2.60–2.68 eV and decrease with increasing La concentration.

Previous studies of A-site-doped BFO materials have focused on structure, and on photo-induced electric and optical properties. However, the correlations among optical responses, domain structure, oxygen vacancies, vibration modes, electronic valence, magnetic response, and A-site substitution cation still lack exploration. This work is mainly to study the effects of La\(^{3+}\) doping on structural symmetry, domain structure, oxygen vacancies, Fe valence, Fe–O–Fe interatomic distance, magnetization, optical band gap, and PV effects of (Bi\(_{1-x}\)La\(_x\))FeO\(_3\) (\(x = 0.0–0.15\)) prepared under the same synthesizing conditions.

II. Experimental Procedure

BiFeO\(_3\) (BFO), (Bi\(_{0.95}\)La\(_{0.05}\))FeO\(_3\) (BFO5L), (Bi\(_{0.90}\)La\(_{0.10}\))FeO\(_3\) (BFO10L), and (Bi\(_{0.85}\)La\(_{0.15}\))FeO\(_3\) (BFO15L) ceramics

![Fig. 1. (a) SEM grain morphologies, (b) XRD spectra, and (c) Raman spectra of as-sintered ceramics. "G" and "O" represent average grain sizes and oxygen atomic ratios determined by SEM EDS.](image-url)
were prepared by the solid-state reaction, in which Bi$_2$O$_3$, La$_2$O$_3$, and Fe$_2$O$_3$ powders (purity $\geq$99.0%) were weighed, respectively, in the respective ratios of 1.1:0:1.0, 0.95:0.05:1.0, 0.90:0.10:1.0, and 0.85:0.15:1.0. The powders were mixed in an agate mortar with alcohol as a medium for more than 24 h. The dried mixtures were calcined at 800°C (3 h) for all compounds, and then sintered at 830°C (10 h) for BFO and 870°C (3 h) for BFO5L, BFO10L, and BFO15L.

X-ray diffraction, grain morphologies, and oxygen vacancies of the as-sintered ceramics were, respectively, measured using a Rigaku Corporation (Tokyo, Japan) Multiplex Diffractometer and a Hitachi Corporation (Tokyo, Japan) S-3400N scanning electron microscope (SEM/EDS). A high-resolution TEM (JEM-2100 LaB$_6$, JEOL Ltd., Tokyo, Japan) was used to study the symmetry groups and domain structures. Micro-Raman spectra were measured using a Raman instrument (XperRam 200; Nanobase Inc., Seoul, Korea) equipped with a green laser of $\lambda = 532$ nm. To determine the oxidation states, the synchrotron X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of Fe K-edge were recorded in transmission mode at the 01C1 beam line of the National Synchrotron Radiation Research Center in Taiwan. The soft X-ray absorption spectra (XAS) of the Fe L$_3$-edge were studied in total electron yield via sample current mode at the 6.3.1.1 beam line of the Advanced Light Source Berkeley National Laboratory. The soft X-ray absorption spectra (XAS) of the Fe L$_3$-edge were studied in total electron yield via sample current mode at the 6.3.1.1 beam line of the Advanced Light Source Berkeley National Laboratory. For PV effects, ITO and Au films were deposited on ceramic surfaces by dc sputtering. The sample thickness and illuminated area (also area of ITO) are 0.2 mm and $\sim$0.15 cm$^2$. A diode laser of $\lambda = 405$ nm was used for illumination. The optical transmission of ITO film is $\sim$80% at $\lambda = 405$ nm. The optical transmission spectra were measured using a Cary 5E UV-Vis-NIR spectrometer (Agilent Technologies, Santa Clara, CA).

III. Results and Discussion

Grain morphologies of the as-sintered ceramics are shown in Fig. 1(a) and the average grain sizes (as represented by “$G$”) are, respectively, 2.1, 4.5, 4.1, and 2.0 $\mu$m for BFO, BFO5L, BFO10L, and BFO15L. Figure 1(a) also gives average oxygen molar ratios measured from five different positions of each sample as indicated by “O”. The theoreti-
The relative intensity of the $E(2)$ mode grows as La concentration increases and the suppression of the $A_1(1)$ mode is possibly due to the change in symmetry of the FeO$_6$ octahedra. The $E(4)$ and $E(8)$ modes near 280 and 480 cm$^{-1}$ associate with atomic vibrations between A (or B)-site atoms and oxygen.\textsuperscript{50} The prominent $E(8)$ mode in BFO10L is possibly due to the enhancement of the La–O vibration.

The high-resolution TEM images and the selected area diffraction patterns (SADPs) were obtained for BFO, BFO5L, BFO10L, and BFO15L as shown in Fig. 3. The SADPs were measured from representative grains along the [110] zone axis. The [110]-viewed SADPs reveal 1/2(111) superlattice diffractions attributed to the tilted FeO$_6$ oxygen octahedra, indicating a rhombohedral $R3c$ symmetry in (Bi$_{1-x}$La$_x$)FeO$_3$ ($x = 0.0–0.15$).\textsuperscript{51,52} The TEM result confirms the rhombohedral phase as suggested in the XRD spectra [Fig. 1(b)]. Figure 3(c) reveals split diffraction spots (twinning) in BFO10L, suggesting the existence of twin planes corresponding to invariant plane shear as a variant boundary in martensite, which has been observed in ferroelectric materials and non-ferroic alloys.\textsuperscript{53,54}

Figure 4 shows the high-resolution TEM domain structures in micrometer and nanometer scales. Compared with BFO10L, BFO5L and BFO15L show more homogeneous domain structures with domain wall widths of about 2–3 nm. Lamellar domains, such as 71° and 109° domains in rhombohedral structure, are often observed in crystal and ceramic grains, and serve to minimize the microstructural free energy.\textsuperscript{54} The inset in Fig. 4(a) is a dark-field image viewed in a two-beam condition near the [110]-zone axis and imaged by a distortion vector $g_0 = [111]$, which shows complicated domains. As indicated by the dashed circle in Fig 4(c), BFO10L exhibits complex pinning domain structures at the boundary intersections, which can cause high strain and decrease charge conductivity. Enhanced electric conductivity has been reported along uniform domain walls in the (110)-oriented La$^{3+}$-doped BFO films.\textsuperscript{55}

Figure 5(a) displays the Fe K-edge XANES spectra of (Bi$_{1-x}$La$_x$)FeO$_3$, and the referenced powders of FeO and Fe$_3$O$_4$. These absorption spectra reveal that the valence of Fe...
shown in Fig. 5(b), indicate that the A-site La$^{3+}$ doping does not cause valence change in Fe$^{3+}$ as revealed in the Fe K-edge absorption. The Fourier transforms of the EXAFS $k^2 \chi(k)$ spectra as shown in Fig. 5(c) indicate that the Fe-O bond angle is not modified by the La$^{3+}$ substitution. Figure 5(c) shows the peak area normalized Fe L$_3$-edge XAS spectra and a shoulder feature develops at 706.4 eV with La doping. By comparing the evolution of the shoulder for Fe$_2$O$_3$ and a shoulder feature develops at 706.4 eV with La doping. By comparing the evolution of the shoulder for Fe$_2$O$_3$ and Fe$_3$O$_4$, pure BFO and La$^{3+}$-doped BFO fit within the trend. The Fe energy is referenced to the Fe metal peak as determined by the XANES and XPS.$^{26}$ The result is consistent with the Fe$^{3+}$ valence as revealed in the Fe K-edge absorption.

The magnetization versus field plots at room temperature in Fig. 6 show no hysteresis loops. Instead, all compounds exhibited a similar linear antiferromagnetic behavior. The magnetization versus field plots in Fig. 6 show no hysteresis loops. Instead, all compounds exhibited a similar linear antiferromagnetic behavior. The first-principles DFT,$^{57,58}$ the presence of oxygen vacancies can shift the optical absorption edge to lower energy below the conduction band. An additional optical absorption peak appears at 2.2 eV for larger concentration of oxygen vacancies.$^{57}$ The band gap in BFO can be engineered from 2.09 to 2.32 eV by controlling particle sizes.$^{59}$ The decrease in band gap with decreasing particle size was attributed to the appearance of defect-induced levels between the conduction and valence bands, oxygen defects, and Coulombic interactions.$^{59}$

where $T$ and $d$ are the measured optical transmission and sample thickness, respectively. The optical band gap can be estimated using the Tauc relation as follows,$^{45}$

$$\alpha = -\frac{\ln(T)}{d}$$

(1)

$$\alpha h v^2 = A(h v - E_g)$$

(2)

where $E_g$ is the direct band gap between valence and conduction bands. $E_g$ can be evaluated by extrapolating the straight lines of the curves of $(\alpha h v)^2$ vs $h v$ as shown in Fig. 7(b). The (Bi$_{1-x}$La$_x$)FeO$_3$ ($x = 0.0-0.15$) ceramics show slightly different optical absorption edges ($E_g$) in the range of 2.22-2.24 eV, which are smaller than band gaps of 2.60-2.68 eV for (Bi$_{1-x}$La$_x$)FeO$_3$ films ($x = 0.0-0.30$). From first-principles DFT,$^{57,58}$ the presence of oxygen vacancies can shift the optical absorption edge to lower energy below the conduction band. An additional optical absorption peak appears at 2.2 eV for larger concentration of oxygen vacancies.$^{57}$

The band gap in BFO can be engineered from 2.09 to 2.32 eV by controlling particle sizes.$^{59}$ The decrease in band gap with decreasing particle size was attributed to the appearance of defect-induced levels between the conduction and valence bands, oxygen defects, and Coulombic interactions.$^{59}$ Thus, the variation in band gaps (2.22-2.24 eV) in (Bi$_{1-x}$La$_x$)FeO$_3$ is associated with oxygen vacancies and grain sizes.

Figure 8 shows open-circuit voltages ($V_{oc}$) and short-circuit current densities ($J_{sc}$) of ITO/(Bi$_{1-x}$La$_x$)FeO$_3$ ceramic/Au heterostructures as the laser was switched on and off with increasing intensity ($I$). The illuminated $V_{oc}$ and $J_{sc}$ are plotted in Fig. 9 as a function of illumination intensity. The ITO/(Bi$_{1-x}$La$_x$)FeO$_3$ ceramics/Au exhibit larger $V_{oc}$ and $J_{sc}$ than values obtained in the ITO/BFO ceramic/Au. For instance, at $I \sim 910 \text{ W/m}^2$, $V_{oc}$ and $J_{sc}$ are 0.7 V and 0.09 A/m$^2$ in ITO/BFO ceramic/Au, 0.82 V and 2.07 A/m$^2$ in ITO/BFO5L/Au, 0.83 V and 0.58 A/m$^2$ in ITO/BFO10L/Au, and 0.78 V and 0.95 A/m$^2$ in ITO/BFO15L/Au. These PV values are larger than $V_{oc} \sim 0.44$ V and $J_{sc} \sim 0.25$ A/m$^2$ reported in graphene/polycrystalline BFO/Pt films under standard white light (AM 1.5) of 1000 W/m$^2$. $^{36}$

To understand the PV responses, a junction between $n$-type ITO film and $p$-type La$^{3+}$-doped BFO ceramic has been proposed to describe $V_{oc}$ and $J_{sc}$ as a function of illumination intensity. $^{38}$ We use Shockley’s sign convention, the diode current $i_d$ under a bias voltage $V$ is expressed as,$^{38}$
\[ i_d = i_o \left[ \frac{q(V - i_d R_s)}{\xi k T} - 1 \right] \]

(3)

where \( R_s \) and \( \xi \) are source resistance and diode quality factor. To estimate \( i_o \), \( R_s \), and \( \xi \), the characteristic curves of current versus bias voltage were measured in the dark as shown in Fig. 10. By using Eq. (3) with \( q = 1.6 \times 10^{-19} \) C, \( k_B = 1.38 \times 10^{-23} \) J/K, and \( T = 300 \) K, we obtained \( i_o = 5 \times 10^{-8} \) A, \( R_s = 6.2 \times 10^4 \) \( \Omega \), and \( \xi = 13 \) for BFO, \( i_o = 6.3 \times 10^4 \) \( \Omega \), and \( \xi = 13 \) for BFO5L, \( i_o = 5 \times 10^{-8} \) A, \( R_s = 3.5 \times 10^3 \) \( \Omega \), and \( \xi = 13 \) for BFO10L, and \( i_o = 1.26 \times 10^4 \) \( \Omega \), and \( \xi = 13 \) for BFO15L. The quality factor \( \xi \) depends on grain size.

The measured voltage \( V \) can be expressed as a function of measured voltage under illumination by,

\[ i = i_p - i_d = i_p - i_o \left[ \exp\left(\frac{V - (i_d - i_p)R_s}{\xi k T}\right) - 1 \right] \]

(4)

where \( i_p \) and \( i_d \) are photovoltaic and diode currents. Through considerable derivations, short-circuit current \( (i_{sc}) \) and open-circuit voltage \( (V_{oc}) \) can be expressed as

\[ i_{sc} = \frac{U_o}{R_s} - B \frac{\xi}{\lambda} \frac{i_o}{R_s} \left[ \exp\left(\frac{i_{sc}R_s}{\xi k T}\right) - 1 \right] \]

(5)

\[ V_{oc} = U_o - B \frac{\xi}{\lambda} \frac{i_o}{R_s} \left[ \exp\left(\frac{V_{oc}q}{\xi k T}\right) - 1 \right] \]

(6)

\[ i_l = q \lambda I / h c; B = (q n_p / 2 e n_p e_p) \left( 1 + n_p e_p / e_n n_o \right) \]

(7)

where \( S, \lambda, \) and \( c \) are illumination area, wavelength, and light speed. \( U_o \) is the voltage step across the depletion region at dark and \( \beta \) is the attenuation length. From Fig. 7, the measured attenuation lengths \( (\beta = 1/\lambda) \) at \( \lambda = 405 \) nm are, respectively, about 2.0, 2.2, 2.1, and 2.0 \( \mu m \) for BFO.
BFO, BFO10L, and BFO15L. $n_p$ and $n_n$ are carrier densities of p-type La-doped BFO ceramics and n-type ITO film. $\varepsilon_p$ and $\varepsilon_n$ are, respectively, dielectric permittivities of p-type-doped BFO ceramics and n-type ITO film. The $\varepsilon_p$ values of BFO, BFO5L, BFO10L, and BFO15L ceramics are, respectively, about 100, 200, 160, and 155 for frequency $f= 1$ MHz at room temperature. The solid lines in Fig. 9 are theoretical fits of $V_{oc}$ and $J_{sc}$ ($J_{sc}/S$) by using Eqs. (5) and (6) with fitting parameters given in Fig. 9(a). The fits of $V_{oc}$ agree reasonably well with experimental results. The fits of $J_{sc}$ show slight discrepancy with the experimental values in the low illumination region possibly due to current leakage.

The estimated carrier densities ($n_p \sim 2\varepsilon_0\varepsilon_p / q$) of BFO, BFO5L, BFO10L, and BFO15L ceramics are, respectively, $5.1 \times 10^{25}$, $0.6 \times 10^{25}$, $2.7 \times 10^{25}$, and $1.7 \times 10^{25}$ m$^{-3}$. The unilluminated depletion region widths [$d_0 \sim (U_0 / B)^{1/2}$]$^{38}$ of BFO, BFO5L, BFO10L, and BFO15L are, respectively, about 1.6, 14.5, 3.5, and 5.2 nm, which are smaller than the depletion layer (few hundred nanometers) between ITO and BFO films.$^{32}$ Note that this junction-like model only considers the photo-excited electron-hole creation. Other factors, such as current leakage, oxygen vacancies, internal reflection, domain structure, and charge recombination can also influence PV conductivity.$^{62}$

Figure 11 shows curves of power conversion efficiency ($\eta$) versus load voltage ($V$) for several intensities. The maximal PV power conversion efficiencies $\eta_{\text{max}}$ of ITO/BFO/Au, ITO/BFO5L/Au, ITO/BFO10L/Au, and ITO/BFO15L/Au at $I=2$ W/m$^2$ can, respectively, reach 0.014%, 0.17%, 0.031%, and 0.19%, which are larger than $\eta_{\text{max}} \sim 0.0025\%$ in graphene/polycrystalline BFO/Pt films (under white light of $I \sim 10^3$ W/m$^2$)$^{36}$, $\eta_{\text{max}} \sim 0.005\%$ in Au/polycrystalline BFO/Pt,$^{35}$ and $\eta_{\text{max}} \sim 0.007\%$ in ITO/(Bi$_{0.90}$Ca$_{0.10}$)FeO$_2$/Au (under illumination of $\lambda = 405$ nm).$^{38}$

**IV. Summary**

High-resolution TEM, XRD, and micro-Raman spectra reveal a rhombohedral $R3c$ symmetry in (Bi$_{1-x}$La$_x$)FeO$_3$ ($x = 0.0–0.15$). The low-frequency Raman modes become broader and shift toward higher frequency as La$^{3+}$ increases. The Fe K-edge synchrotron absorption confirms that Fe$^{3+}$ valence and Fe–O–Fe bond angle are not modified by the La$^{3+}$ substitution. The maximal power conversion efficiency of ITO/BFO15L/Au can reach 0.19%. The homogeneous domain structure plays an important role in the enhanced PV responses of BFO5L and BFO15L. A $p$–$n$ junction-like model based on optically excited charges in the depletion region between ITO and (Bi$_{1-x}$La$_x$)FeO$_3$ can reasonably describe $V_{oc}$ and $J_{sc}$ as a function of illumination intensity. The smaller band gaps ($2.22–2.24$ eV) in (Bi$_{1-x}$La$_x$)FeO$_3$ ($x = 0.0–0.15$) ceramics can be correlated with oxygen vacancies and grain sizes.

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**References**
