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Calcium-doping effects on photovoltaic response and structure in multiferroic BiFeO₃ ceramics

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Photovoltaic (PV) effects, power-conversion efficiencies, and structures have been systematically measured in (Bi_{1-x}Ca_x)FeO_{3-δ} ceramics for $x = 0.05$, 0.10 , and 0.15 . The heterostructures of indium tin oxide (ITO) film/(Bi_{1-x}Ca_x)FeO_{3-δ} ceramics/Au film exhibit significant PV effects under illumination of $\lambda = 405$ nm. The maximum power-conversion efficiency in the ITO/(Bi_{0.90}Ca_{0.10})FeO_{2.95} (BFO10C)/Au can reach 0.0072%, which is larger than 0.0025% observed in the graphene/polycrystalline BFO/Pt films [Zang *et al.*, Appl. Phys. Lett. **99**, 132904 (2011)]. A theoretical model based on optically excited current in the depletion region between ITO film and Ca-doped BFO ceramics is used to describe the I-V characteristic, open-circuit voltage, and short-circuit current density as a function of illumination intensity. This work suggests that the Ca-substitution can reduce the rhombohedral distortion and stabilize the single-phase structure. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4823856>]

I. INTRODUCTION

Photovoltaic (PV) effects in ferroelectric perovskite oxides, such as LiNbO₃,¹ BaTiO₃,² Pb(Zr,Ti)O₃ (PZT),^{3,4} and La-doped PZT⁵⁻⁹ have been reported for dependences on light wavelength, thickness, and ion substitution. However, most of these materials have not been considered for PV applications due to small power-conversion efficiencies. The maximal power-conversion efficiencies are about 0.005% under sunlight and 0.28% under narrow-band ultraviolet in the La-doped PZT films.⁹ Recent studies have shown promising PV and photostrictive properties in BFO films and crystals.¹⁰⁻²² The maximal power-conversion efficiencies in the Au/polycrystalline BFO/Pt films and indium tin oxide (ITO)/polycrystalline BFO/Pt films capacitors are about 0.005% and 0.125%, respectively, at intensity (I) of 4.5 W/m².¹⁴ The maximal power-conversion efficiency in the graphene/polycrystalline BFO/Pt films is about 0.0025% at $I \sim 10^3$ W/m².¹⁵ A high external quantum efficiency of 10% under illumination of $\lambda = 340$ nm was reported in the epitaxial ITO/BFO/SrRuO₃ films.²²

Several PV mechanisms have been proposed for BFO, including asymmetric ferroelectric PV effect,^{4,16} domain-wall model,¹⁷ and p-n junction model.²² BFO and ITO films have exhibited p- and n-type semiconductivities with carrier densities of $n_p \sim 10^{23}$ m⁻³ and $n_n \sim 10^{26}$ – 10^{27} m⁻³, respectively.²²⁻²⁴ The recent PV results observed in the ITO/BFO ceramic/Au heterostructure show dependences on BFO thickness, light wavelength, and electric poling.^{25,26} The PV responses can be attributed to photo-excited charge

carriers in the interface between BFO ceramic and ITO film.²⁵

Recent structural results of (Bi_{1-x}Ca_x)FeO_{3-δ} suggested ferroelectric rhombohedral (or monoclinic) phase and paraelectric tetragonal (or pseudo-tetragonal or orthorhombic) phase, respectively, for $0 \leq x \leq 0.1$ and $0.18 \leq x \leq 0.5$, with a two-phase coexistence for the intermediate compositions.²⁷⁻³² The electric properties of (Bi_{1-x}Ca_x)FeO_{3-δ} ceramics are sensitive to the oxygen pressure during synthesizing process and the conductivity can change from p-type semiconduction to an ion conduction.³¹ A p-n junction could be formed in Ca-doped BiFeO₃ thin films (with coplanar platinum electrodes) by oxygen vacancy movement under an electric-field application.³²

II. EXPERIMENTAL PROCEDURE

The (Bi_{0.95}Ca_{0.05})FeO_{2.975} (BFO5C), (Bi_{0.90}Ca_{0.10})FeO_{2.95} (BFO10C), and (Bi_{0.85}Ca_{0.15})FeO_{2.925} (BFO15C) ceramics were prepared by the solid state reaction method, in which Bi₂O₃, CaO, and Fe₂O₃ powders (purity $\geq 99.0\%$) were weighed in 0.95:0.1:1.0, 0.90:0.20:1.0, and 0.85:0.3:1.0 ratios, respectively. The powders were mixed in an agate mortar with alcohol as a medium for more than 24 h. The chemical reactions are $0.95\text{Bi}_2\text{O}_3 + 0.1\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow 2(\text{Bi}_{0.95}\text{Ca}_{0.05})\text{FeO}_{2.975}$, $0.90\text{Bi}_2\text{O}_3 + 0.2\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow 2(\text{Bi}_{0.90}\text{Ca}_{0.10})\text{FeO}_{2.95}$, and $0.85\text{Bi}_2\text{O}_3 + 0.3\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow 2(\text{Bi}_{0.85}\text{Ca}_{0.15})\text{FeO}_{2.925}$, respectively. The dried mixtures were calcined at 800 °C for 3 h for all compositions. The sintering temperatures are in the range of 845–925 °C with dwelling time of 3 h.

A Rigaku Multiplex Diffractometer with radiations of K α_1 (1.5444 Å) and K α_2 (1.5406 Å) was used for structure analysis. For PV measurements, Au and ITO films (~ 100 nm) electrodes were deposited on ceramics by dc sputtering deposition.

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The thickness and illuminated area (also electrodes' area) of samples are 0.2 mm and $\sim 0.15 \text{ cm}^2$.

III. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) spectra are shown in Fig. 1 with grain morphologies in the insets. BFO5C shows a rhombohedral structure at room temperature, the same as the pure BFO ceramic.²⁷ As Ca content increases, the XRD reflections of BFO10C and BFO15C become narrower and shift slightly to higher 2θ positions, mainly due to the smaller ionic radius of the Ca^{2+} ion (0.99 Å) compared with the Bi^{3+} ion (1.03 Å) in the A site of the perovskite unit cell. BFO15C shows no splitting in all XRD peaks, revealing a single-phase pseudocubic structure. This result suggests that Ca doping in BFO can reduce rhombohedral distortion and volume of unit cell. Based on the (110) reflections, the calculated lattice parameters of the pseudocubic structure for BFO10C and BFO15C are, respectively, $a \sim 3.951 \text{ Å}$ and $a \sim 3.910 \text{ Å}$, which are close to the pseudocubic lattice parameters predicted in Ref. 33. In addition, BFO10C and BFO15C show no second phase, suggesting that the Ca-substitution in the A site of the perovskite unit cell can stabilize the single-phase structure.

For PV measurements, a diode laser of $\lambda = 405 \text{ nm}$ was used as the illumination source. The laser beam was incident perpendicular to the sample surface with ITO film. Figure 2 shows open-circuit voltage (V_{oc}) and short-circuit current

density (J_{sc}) as the laser was switched on and off with increasing intensity (I). V_{oc} and J_{sc} are plotted in Fig. 3 as a function of illumination intensity. BFO10C exhibits stronger PV responses than BFO5C and BFO15C, especially for J_{sc} . Both V_{oc} and J_{sc} exhibit strong dependences on illumination intensity for $I < 1000 \text{ W/m}^2$. V_{oc} and J_{sc} at $I \sim 900 \text{ W/m}^2$ are about 0.45 V and 0.053 A/m^2 for BFO5C, 0.47 V and 0.46 A/m^2 for BFO10C, and 0.45 V and 0.32 A/m^2 for BFO15C. These PV responses are comparable with $V_{oc} \sim 0.44 \text{ V}$ and $J_{sc} \sim 0.25 \text{ A/m}^2$ at $I \sim 1 \times 10^3 \text{ W/m}^2$ observed in the heterostructure of graphene/polycrystalline BFO/Pt films.¹⁵ The poled lead lanthanum zirconated titanate (PLZT) (3/52/48) piezoelectric ceramic has $J_{sc} \sim 2 \times 10^{-4} \text{ A/m}^2$ at $I \sim 2 \times 10^3 \text{ W/m}^2$ under illumination of $\lambda = 366 \text{ nm}$.⁵

To understand the illuminated V_{oc} and J_{sc} , we consider a heterojunction diode consisting of an n-type ITO layer and a p-type Ca-doped BFO ceramic. The analysis is similar to that presented by Fahrenbruch and Bube³⁴ in their Fig. 6.9 and Eq. (6.13) with two exceptions. The first exception is that they discuss the photo-induced current i_p in terms of an intensity spectrum over wavelength, whereas we derive an expression for i_p based on monochromatic light. The second exception is that they use the sign convention that applies to ordinary diodes, that a large positive V gives a large positive i , and a large negative V gives a small negative i of magnitude i_o . We use Shockley's sign convention,³⁵ which for a photodiode the sign of the output current i is positive.

The expression of diode current under an applied voltage V can be expressed as

FIG. 1. XRD spectra at room temperature. Insets are grain morphologies observed by SEM.

FIG. 2. (a) Open-circuit voltage V_{oc} and (b) short-circuit current density J_{sc} as light was switched on and off with increasing incident intensity labeled on the tops of illuminations.

FIG. 3. Intensity-dependent (a) V_{oc} and (b) J_{sc} . The solid lines are the theoretical fits with parameters given in Figure.

$$i_d = i_o \{ \exp[q(V - i_d R_s) / \xi k T] - 1 \}, \quad (1)$$

where R_s and ξ are the source resistance and diode-quality factor. To find i_o and R_s , the characteristic curves of current vs. voltage were measured in the dark as shown in Fig. 4. By using Eq. (1) with $q = 1.6 \times 10^{-19}$ C, $k = 1.38 \times 10^{-23}$ J/K, and $T = 300$ K, we obtained $i_o = 1 \times 10^{-15}$ A, $R_s = 75\,000 \, \Omega$, and $\xi = 1.6$ for BFO5C, $i_o = 1 \times 10^{-15}$ A, $R_s = 13\,000 \, \Omega$, and $\xi = 1.4$ for BFO10C, and $i_o = 1 \times 10^{-15}$ A, $R_s = 28\,000 \, \Omega$, and $\xi = 1.6$ for BFO15C. ξ usually vary from 1 to 3 for

FIG. 4. Characteristic curves of current versus applied dc voltage in the dark.

homojunction and heterojunction diodes.³⁴ Sen and Tyagi predicted that ξ should depend on grain size.³⁶

For brevity, below, we introduce a “thermal voltage constant” V_T , which has dimensions voltage and is proportional to T , given by $V_T \equiv \xi k T / q$. Based on Eq. (1), the measured current i can be expressed as a function of measured voltage under illumination by

$$i = i_p - i_o \{ \exp\{[V - (i_d - i_p)R_s] / V_T\} - 1 \}, \quad (2)$$

where i_p and i_d is the photo-induced and diode currents. We now consider the photo-induced current i_p in Eq. (2). Because the energy gap in the ITO exceeds the photon energy, the light intensity is assumed to decay only in the BFO-Ca side with a general form of $I(z) = I \exp(-z/\beta)$, where β is the attenuation length for which $\beta \gg d_p$. d_p is the depletion-region width in the Ca-doped BFO side. The absorbed intensity I_a in the depletion region can be estimated by $I_a = I d / \beta$. The creation rate of electron-hole pairs is estimated to be the absorbed intensity divided by the photon energy, $I_a / (hc/\lambda)$. Then, i_p is given by the following equation, in which for brevity we introduce the “illumination current constant” $i_l \equiv q S \lambda I / hc$, which has dimension of current:

$$i_p = q d_p I S \lambda / hc \beta = i_l d_p / \beta, \quad (3)$$

where S is the illuminated area. The depletion width d_p is related to the potential step $-U$ across the entire depletion region of the diode, and $-U$ is found by the following standard derivation. In the ITO-side depletion region ($-d_n < x < 0$), the net charge density $\rho_n = q n_n$ comes from the ionized donors that have donated electrons to the conduction band. Similarly, in the Ca-doped BFO depletion region ($0 < x < d_p$), $\rho_p = q n_p$ comes from the acceptors that have accepted electrons from the valence band. Using Gauss’s Law in the region $-d_n < x < 0$, the position-dependent E field is

$$E(x) = \int_{-d_n}^x (\rho_n / \epsilon_o \epsilon_n) dx' = (\rho_n / \epsilon_o \epsilon_n)(x + d_n). \quad (4)$$

Then, the total contribution from the n-type ITO and p-type Ca-doped BFO sides to $-U$ is

$$\begin{aligned} -U &= - \int_{-d_n}^0 E(x) dx - \int_0^{d_p} E(x) dx \\ &= (-q/2\epsilon_o)(n_p d_p^2 / \epsilon_p + n_n d_n^2 / \epsilon_n), \end{aligned} \quad (5)$$

where ϵ_o is the vacuum permittivity and ϵ_p and ϵ_n are the dielectric permittivities. The requirement that there is no net charge in the depletion region gives $d_n = (n_p / n_n) d_p$. The carrier densities of p-type BFO film and n-type ITO film are $n_p \sim 10^{23} m^{-3}$ and $n_n \sim 10^{26} - 10^{27} m^{-3}$, respectively.²²⁻²⁴ Thus, the depletion-region width d_n in the ITO is much less than d_p in the Ca-doped BFO side, so d_p can be designated as simply d . Then, Eq. (5) yields

$$\begin{aligned} -U &= -(q d^2 n_p / 2 \epsilon_o \epsilon_p)(1 + n_p \epsilon_p / \epsilon_n n_n) = -B d^2, \\ B &= (q n_p / 2 \epsilon_o \epsilon_p)(1 + n_p \epsilon_p / \epsilon_n n_n). \end{aligned} \quad (6)$$

The room-temperature dielectric permittivities (ϵ_p) of BFO5C, BFO10C, and BFO15C ceramics are, respectively, about 120, 90, and 170 for measuring frequency $f = 1$ MHz. The ratio ϵ_p/ϵ_n is much smaller than n_n/n_p , so $n_p\epsilon_p/n_n\epsilon_n \ll 1$ in Eq. (6), and using the above numerical values it can be rewritten approximately as

$$-U = -Bd^2 \cong -qd^2 n_p / 2\epsilon_o \epsilon_p. \quad (7)$$

The voltage step across the depletion region (p side minus n side) is designated “ $-U_o$ ” without illumination. We assume unilluminated ohmic contacts to the ITO and Ca-doped BFO, which together will provide an emf $+U_o$, which can be assumed to change little when current flows due to illumination of the ITO–Ca-doped BFO junction. Illumination and/or externally applied voltage can change the depletion region width and correspondingly change the $-U_o$ voltage step to $-U$. The measured voltage V across the diode then can be described by

$$V = U_o - U - (I_p - I_d)R_s, \quad (8)$$

where $I_p - I_d$ is the measured current. For $V = 0$ and no illumination, we designate the corresponding d value as d_o . The parameters U_o and β should be independent of I and V . To find them, we use Eqs. (3), (7), and (8)

$$\beta = q\lambda SI[(U_o - i_{sc}R_s)/B]^{1/2}/hci_{psc}, \quad (9)$$

$$U_o = (V_{oc}i_{psc}^2 - i_{sc}R_s i_{poc}^2)/(i_{psc}^2 - i_{poc}^2). \quad (10)$$

We now consider the short and open circuits with corresponding subscripts “ sc ” and “ oc ,” respectively. For the short-circuit $V = 0$ case, Eq. (2) takes the form

$$i_{sc} = i_{psc} - i_o[\exp(i_{sc}R_s/V_T) - 1], \quad (11)$$

where $i_{sc} = i_{psc} - i_d$. The only unknown in Eq. (11) is i_{psc} , and in Eq. (3) for i_{psc} the unknowns are d_{sc} and β , so for known light intensity I and measured i_{sc} we can solve Eq. (3) to estimate the ratio d_{sc}/β , which is given by

$$d_{sc}/\beta = i_{psc}/i_l = \{i_{sc} + i_o[\exp(qi_{sc}R_s/\xi kT) - 1]\}/i_l. \quad (12)$$

For the short-circuit case, Eq. (8) becomes $V = 0 = U_o - U_{sc} - i_{sc}R_s$, and we then use Eq. (7) to obtain

$$U_o - Bd_{sc}^2 - i_{sc}R_s = 0. \quad (13)$$

By squaring Eq. (12) and substituting into Eq. (13), we obtain one of the two desired relations between U_o and β :

$$i_{sc}R_s = U_o - B\{i_{sc} + i_o[\exp(i_{sc}R_s/V_T) - 1]\}^2\beta^2/i_l^2. \quad (14)$$

Eq. (14) can be used to fit the measured $i_{sc} = J_{sc}S$ as a function of illumination intensity I .

For the open-circuit case ($J = 0$), Eqs. (2), (3), (7), and (8) take the respective forms

$$i_{oc} = 0 = i_{poc} - i_o[\exp(V_{oc}/V_T) - 1], \quad (15)$$

$$i_{poc} = i_l d_{oc}/\beta, \quad (16)$$

$$U_{oc} = Bd_{oc}^2, \quad (17)$$

$$V_{oc} = U_o - U_{oc}. \quad (18)$$

Combining Eqs. (15)–(18) gives us the other relation between U_o and β

$$V_{oc} = U_o - Bi_o^2[\exp(V_{oc}/V_T) - 1]^2\beta^2/i_l^2. \quad (19)$$

By solving Eqs. (14) and (19) simultaneously, we can find U_o and β . The expression for β^2 is

$$\beta^2 = (V_{oc} - i_{sc}R_s)i_l^2/B\{[i_{sc} + i_o[\exp(i_{sc}R_s/V_T) - 1]]^2 - i_o^2[\exp(V_{oc}/V_T) - 1]^2\}. \quad (20)$$

Using this β^2 expression, U_o can be found from either Eq. (14) or (19). U_o and β can be estimated using the measured i_{sc} and V_{oc} for one I , then Eqs. (14) and (19) can be used to fit the measured J_{sc} and V_{oc} respectively as a function of intensity.

The solid lines in Fig. 3 are fits of V_{oc} and J_{sc} by using Eqs. (14) and (19), respectively, with parameters given in Fig. 3(a). The theoretical fits agree with experimental results well with physically reasonable parameters. In particular, the i_o value may appear small, but it does allow for a reverse current contribution, which significantly reduces the short-circuit current density, and minimizing such reduction is a well-known design consideration for p-n junction PV devices.

From the fitting $B(\cong qn_p/2\epsilon_o\epsilon_p)$ values listed in Fig. 3(a), the calculated carrier densities of BFO5C, BFO10C, and BFO15C are, respectively, $n_p \sim 1.1 \times 10^{21} \text{ m}^{-3}$, $n_p \sim 1.0 \times 10^{19} \text{ m}^{-3}$, and $n_p \sim 1.9 \times 10^{20} \text{ m}^{-3}$, which are smaller than $n_p \sim 10^{23} \text{ m}^{-3}$ in BFO film.²² From Eq. (7), $d_o \sim (U_o/B)^{1/2}$, the depletion-region widths for no

FIG. 5. Illuminated curves of (a) current density (J) versus voltage and (b) power-conversion efficiency (η) versus voltage for BFO5C ceramic.

FIG. 6. Illuminated curves of (a) current density (J) versus voltage and (b) power-conversion efficiency (η) versus voltage for BFO10C ceramic.

illumination are $d_o \sim 2.6 \mu\text{m}$, $d_o \sim 23 \mu\text{m}$, and $d_o \sim 7.3 \mu\text{m}$ for BFO5C, BFO10C, and BFO15C, respectively. The depletion layer between ITO and BFO films was estimated to be few hundred nanometers.²² The theoretical attenuation lengths (β) are about 15.2, 15.9, and 6.4 nm for BFO5C, BFO10C, and BFO15C, respectively. These β values are calculated for absorption caused only by electron-hole creation

FIG. 7. Illuminated curves of (a) current density (J) versus voltage and (b) power-conversion efficiency (η) versus voltage for BFO15C ceramic.

and are much larger than actual values, because of other absorption and dissipation mechanisms, such as internal reflection by grain boundaries and charge recombination.

For measurement of power-conversion efficiency (η), an adjustable load resistance (R_L) was used to obtain the relation between current and voltage of the load. The curves of illuminated total current density (J) and power-conversion efficiency (η) versus total voltage (V) for several intensities are given in Figs. 5–7, respectively. The maximum power-conversion efficiency shifts to higher voltages as illumination intensity increases. BFO10C exhibits stronger power-conversion efficiencies than BFO5Ca and BFO15C. As shown in Fig. 6(b) for BFO10C, the η - V curve at $I \sim 451 \text{ W/m}^2$ shows a maximum power conversion of $\eta_{\text{max}} \sim 0.0075\%$, which is larger than $\eta_{\text{max}} \sim 0.002\%$ in the ITO/BFO ceramic/Au structure²⁶ and $\eta_{\text{max}} \sim 0.0025\%$ in the graphene/polycrystalline BFO/ Pt structure.¹⁵

IV. CONCLUSIONS

Strong intensity-dependent photovoltaic effects are observed in the heterostructures of ITO film/($\text{Bi}_{1-x}\text{Ca}_x$) $\text{FeO}_{3-\delta}$ ceramics/Au film under illumination of $\lambda = 405 \text{ nm}$. The BFO10C exhibits stronger maximum power-conversion efficiency (η_{max}) than BFO5C and BFO15C. The maximum power-conversion efficiency (η_{max}) in the ITO/BFO10C ceramic/Au can reach 0.0072%. The theoretical model can well describe the experimental results of I-V characteristic (at dark), illuminated open-circuit voltage V_{oc} , and short-circuit current density J_{sc} as a function of illumination intensity. This model was used to estimate physical parameters of charge carrier density (n_p), optical attenuation length (β), and depletion-region width (d_o). The heterovalent substitution from Bi^{3+} to Ca^{2+} could cause the occurrences of oxygen vacancies and an iron change of $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+}$. The PV responses in the ITO/($\text{Bi}_{1-x}\text{Ca}_x$) $\text{FeO}_{3-\delta}$ ceramics/Au mainly depend on physical parameters and microstructure in the depletion region, such as carrier density and depletion width. In addition, oxygen vacancy, grain size, and the distribution of Fe^{3+} and Fe^{4+} ions in ceramics also affect the transport of charge carriers. This work suggests that the Ca-substitution in ($\text{Bi}_{1-x}\text{Ca}_x$) $\text{FeO}_{3-\delta}$ ceramics can reduce the rhombohedral distortion toward a pseudocubic cell.

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