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Effect of diamagnetic barium substitution on magnetic and photovoltaic properties in multiferroic BiFeO₃

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Spontaneous magnetization and photovoltaic (PV) effects have been measured in (Bi_{1-x}Ba_x)FeO_{3-δ} ceramics for $x = 0.05$, 0.10 , and 0.15 . The substitution of Ba²⁺ ion in the A site of the perovskite unit cell can effectively enhance the ferromagnetic magnetization. The heterostructure of indium tin oxide (ITO) film/(Bi_{1-x}Ba_x)FeO_{3-δ} ceramic/Au film exhibits significant PV effects under illumination of $\lambda = 405$ nm. The PV responses decrease with increasing Ba concentration. The maximum power-conversion efficiency in the ITO/(Bi_{0.95}Ba_{0.05})FeO_{2.95}/Au can reach 0.006%. A theoretical model based on optically excited current in the depletion region between ITO film and (Bi_{1-x}Ba_x)FeO_{3-δ} ceramics is used to describe the I-V characteristic, open-circuit voltage (V_{oc}), and short-circuit current density (J_{sc}) as a function of light intensity. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4862381>]

I. INTRODUCTION

Multiferroic BiFeO₃ (BFO) possesses a G-type antiferromagnetic order with a spatially modulated spin structure, which does not allow net magnetization.¹ The doped BFO ceramics and films of (Bi_{1-x}A_x)FeO_{3-δ} (A = La, Nd, Sm, Ca, Pb, Sr, and Ba) exhibited enhancement of ferromagnetic magnetization.^{2–8} Magnetizations of the doped specimens can be enhanced as the doping ion radius increases. Spontaneous magnetization of (Bi_{1-x}Ba_x)FeO_{3-δ} ceramics increases with Ba content.⁶ X-ray results of (Bi_{1-x}Ba_x)FeO_{3-δ} ($x = 0.15$ – 0.35) suggested a rhombohedral-tetragonal structural transition for $x = 0.35$.⁶ I-V curves of Bi_{1-x}Ba_xFeO_{3-δ} films ($x = 0$ – 0.2) exhibit a hysteresis associated with migration of oxygen vacancies.⁹

BFO films and crystals have been recently reported to have promising PV effects.^{10–13} The maximum power-conversion efficiencies in the Au/polycrystalline BFO/Pt films and indium tin oxide (ITO)/polycrystalline BFO/Pt films are 0.005% and 0.125%, respectively, at intensity (I) of 4.5 W/m².¹⁰ Physical mechanisms, such as asymmetric ferroelectric PV effect¹² and p-n junction model,¹³ have been used to explain the PV responses in BFO materials. BFO and ITO films have been reported to have p-type 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.^{14,15} PV results in the ITO/BFO ceramic/Au show dependences on BFO thickness, wavelength, and electric poling.^{16,17} The PV effect was attributed to photo-excited charge carriers in the interface between ITO film and BFO ceramic.¹⁶ Recent PV study of ITO/(Bi_{0.90}Ca_{0.10})FeO_{2.95} ceramic/Au exhibits a maximum power-conversion efficiency of 0.0072% under illumination of $\lambda = 405$ nm.¹⁸

II. EXPERIMENTAL PROCEDURE

(Bi_{0.95}Ba_{0.05})FeO_{2.975} (BFO5Ba), (Bi_{0.90}Ba_{0.10})FeO_{2.95} (BFO10Ba), and (Bi_{0.85}Ba_{0.15})FeO_{2.925} (BFO15Ba) ceramics were prepared by the solid state reaction method, in which Bi₂O₃, BaCO₃, 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 dried mixtures were calcined at 800 °C for 3 h. The sintering temperatures are in the range of 845–865 °C with dwell time of 3 h. For PV measurements, Au and ITO films were deposited on ceramics by dc sputtering. The thickness and illuminated area (also electrodes' area) of the samples are 0.2 mm and 0.15 cm². A diode laser of $\lambda = 405$ nm was used as the light source. The laser was incident perpendicular to the ITO surface.

III. RESULTS AND DISCUSSION

The magnetic hysteresis loops are given in Fig. 1 with spontaneous magnetizations of 0.02, 1.5, and 0.9 emu/g for BFO5Ba, BFO10Ba, and BFO15Ba, respectively. The ferromagnetic enhancement could be associated with distortion of the Fe-O-Fe bond angle due to Ba doping, which directly affects the Fe-O-Fe exchanging pathway. An enhancement of remanent magnetization was observed in BFO film due possibly to 180° exchange coupling of Fe⁴⁺.¹⁹

Figure 2 shows V_{oc} and J_{sc} as the laser was switched on and off with increasing intensity (I). $V_{oc}(I)$ and $J_{sc}(I)$ are plotted in Fig. 3. V_{oc} and J_{sc} at $I \sim 900$ W/m² are 0.58 V and 0.34 A/m² for BFO5Ba, 0.43 V and 0.14 A/m² for BFO10Ba, and 0.32 V and 0.008 A/m² for BFO15Ba. These values are comparable with $V_{oc} \sim 0.44$ V and $J_{sc} \sim 0.25$ A/m² at $I \sim 1 \times 10^3$ W/m² in graphene/BFO/Pt films,¹¹ and $V_{oc} \sim 0.62$ V and $J_{sc} \sim 0.04$ A/m² at $I \sim 910$ W/m² in ITO/BFO ceramic/Au.¹⁷

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FIG. 1. Magnetization loops at room temperature.

To understand V_{oc} and J_{sc} , a heterojunction between n-type ITO film and p-type BFO-Ba ceramic is considered. The diode current i_d under an applied voltage V can be expressed as¹⁸

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

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. bias 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 $i_o = 1 \times 10^{-17}$ A, $R_s = 3.6 \times 10^4 \Omega$, and $\xi = 1.4$ for BFO5Ba, $i_o = 1 \times 10^{-17}$ A, $R_s = 7.2 \times 10^4 \Omega$ and $\xi = 1.2$ for BFO10Ba, and $i_o = 1 \times 10^{-17}$ A, $R_s = 1 \times 10^6 \Omega$ and $\xi = 2.8$ for BFO15Ba. From Eq. (1), the measured current i can be expressed as a function of measured voltage under illumination by¹⁸

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

where i_p and i_d are the photo-induced and diode currents. The light intensity is assumed to decay only in the BFO-Ba side with a general form of $I(z) = I \exp(-z/\beta)$, where β is the

FIG. 2. (a) V_{oc} and (b) J_{sc} as light was switched on and off with increasing intensity labeled on the tops of illuminations. FIG. 3. Intensity-dependent (a) V_{oc} and (b) J_{sc} .

attenuation length. d_p is the depletion-region width in the BFO-Ba side. Then i_p is given by¹⁸

$$i_p = q d_p I S \lambda / h c \beta = i_d d_p / \beta, \quad (3)$$

where $i_l \equiv q S \lambda I / h c$. S is illuminated area. The charge densities in the ITO-side depletion region ($-d_n < x < 0$) and BFO-Ba depletion region ($0 < x < d_p$) are $\rho_n = q n_n$ and $\rho_p = q n_p$. Using Gauss's law, the potential step $-U$ across the depletion region can be expressed by¹⁸

$$-U = (-q/2\epsilon_0)(n_p d_p^2 / \epsilon_p + n_n d_n^2 / \epsilon_n), \quad (4)$$

where 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 depletion-region width d_n in the ITO is much less than d_p in the Ba-doped BFO, so d_p can be designated as d . Then Eq. (4) yields¹⁸

$$-U = -B d^2; \quad B = (q n_p / 2 \epsilon_0 \epsilon_p) (1 + n_p \epsilon_p / \epsilon_n n_n). \quad (5)$$

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

The dielectric permittivities (ϵ_p) of BFO5Ba, BFO10Ba, and BFO15Ba at room temperature are about 220, 240, and 170 for $f=1$ MHz, respectively. The ratio ϵ_p/ϵ_n is much smaller than n_p/n_p , so $n_p\epsilon_p/n_n\epsilon_n \ll 1$ in Eq. (5), which can be rewritten as $-U \cong -qd^2n_p/2\epsilon_o\epsilon_p$.

The voltage step across the depletion region is designated “ $-U_o$ ” without illumination. Illumination and applied voltage can change the depletion region width and change the $-U_o$ voltage step to $-U$. The measured voltage V across the diode then can be described by

$$V = U_o - U - (I_p - I_d)R_s, \quad (6)$$

where I_p-I_d is the measured current. For $V=0$ and no illumination, we designate the corresponding d as d_o . For the short-circuit (“sc”) case ($V=0$), Eq. (2) takes the form

$$i_{sc} = i_{psc} - i_o[\exp(i_{sc}R_sq/\xi kT) - 1], \quad (7)$$

where $i_{sc} = i_{psc} - i_d$. Eq. (6) becomes $V=0 = U_o - U_{sc} - i_{sc}R_s$, and we then use Eq. (5) to obtain

$$U_o - Bd_{sc}^2 - i_{sc}R_s = 0. \quad (8)$$

Based on Eqs. (3), (7), and (8), we obtain the relation¹⁸

$$i_{sc}R_s = U_o - B\{i_{sc} + i_o[\exp(i_{sc}R_sq/\xi kT) - 1]\}^2\beta^2/i_t^2. \quad (9)$$

Equation (9) can be used to fit the measured $J_{sc} = i_{sc}/S$ as a function of light intensity.

For the open-circuit (“oc”) case ($J=0$), Eqs. (2), (3), (5), and (6) take the respective forms

$$i_{oc} = 0 = i_{poc} - i_o[\exp(V_{oc}q/\xi kT) - 1], \quad (10)$$

$$i_{poc} = i_d d_{oc}/\beta; \quad U_{oc} = Bd_{oc}^2; \quad V_{oc} = U_o - U_{oc}. \quad (11)$$

Equations (10) and (11) give the relation¹⁸

$$V_{oc} = U_o - Bi_o^2[\exp(V_{oc}q/\xi kT) - 1]^2\beta^2/i_t^2. \quad (12)$$

Equation (12) can be used to fit the measured V_{oc} as a function of intensity.

The solid lines in Fig. 3 are fits of V_{oc} and J_{sc} by using Eqs. (12) and (9) with parameters in Fig. 3(a). The theoretical fits agree with experimental results well with reasonable parameters. From the fitting $B(\cong qn_p/2\epsilon_o\epsilon_p)$ values, the calculated carrier densities of BFO5Ba, BFO10Ba, and BFO15Ba are $n_p \sim 2.4 \times 10^{20} \text{ m}^{-3}$, $n_p \sim 2.7 \times 10^{21} \text{ m}^{-3}$, and $n_p \sim 9 \times 10^{26} \text{ m}^{-3}$, respectively. From Eq. (5), $d_o \sim (U_o/B)^{1/2}$, the depletion-region widths (d_o) for no illumination are about 9, 2.4, and 0.003 μm in BFO5Ba, BFO10Ba, and BFO15Ba, respectively. The calculated β values are 8.26, 5.2, and 0.18 mm for BFO5Ba, BFO10Ba, and BFO15Ba, respectively. These β values are based on absorption caused only by electron-hole creation, and are larger than actual values, because of other mechanisms, such as reflection by grain boundaries and charge recombination.

For measurements of power-conversion efficiency (η), an adjustable load resistance was used to obtain the relation between current and voltage of the load. Fig. 5 shows the curves of η versus voltage for several intensities. The maximum power-conversion efficiency (η_{max}) decreases with

FIG. 5. Curves of power-conversion efficiency versus voltage. The labeled numbers are intensities in W/m^2 .

increasing Ba content. As shown in Fig. 5(a), the η_{max} of BFO5Ba can reach 0.006%, which is larger than $\eta_{max} \sim 0.002\%$ in the ITO/BFO ceramic/Au structure¹⁷ and $\eta_{max} \sim 0.0025\%$ in the graphene/BFO/Pt.¹¹

IV. CONCLUSIONS

The Ba^{2+} substitution in BFO ceramic can effectively enhance ferromagnetic magnetization. The ITO/BFO5Ba ceramic/Au exhibits stronger PV effects than BFO10Ba and BFO15Ba under illumination of $\lambda = 405 \text{ nm}$. The model based on optically excited current can well describe the measured I-V characteristic curve (in the dark), V_{oc} , and J_{sc} as a function of light intensity. This model was used to estimate carrier density n_p , depletion width d_o , and attenuation length β .

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