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Raman vibrations and photovoltaic conversion in rare earth doped $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ (RE=Dy, Gd, Eu, Sm) ceramics

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Abstract

High-resolution Raman spectra, X-ray diffraction, oxygen vacancies, synchrotron X-ray absorption spectroscopy, magnetization, optical band gap, and photovoltaic (PV) conversion have been studied in BiFeO_3 (BFO) and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ (RE=Dy, Gd, Eu and Sm) multiferroic ceramics (7%Dy–BFO, 7%Gd–BFO, 7%Eu–BFO, and 7%Sm–BFO). 7%Dy–BFO exhibits a weak ferromagnetic behavior instead of the linear antiferromagnetic responses found in the other compounds. Optical transmissions reveal band gaps of 2.20–2.21 eV, which are slightly smaller than 2.24 eV in pure BFO. The current vs. voltage (I – V) characteristic curves of indium tin oxide (ITO)/ $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ ceramics/Au heterostructures suggest a p – n -junction-like behavior. The maximal PV power-conversion efficiencies under illumination of $\lambda=405$ nm in ITO/7%Dy–BFO/Au, ITO/7%Gd–BFO/Au, ITO/7%Eu–BFO/Au, and ITO/7%Sm–BFO/Au respectively reach 0.22%, 0.35%, 0.27%, and 0.24%, which are much larger than 0.017% in ITO/BFO/Au. The PV open-circuit voltage and short-circuit current can be reasonably described by a junction model as a function of illumination intensity.

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1. Introduction

Multiferroics, showing the coexistence of magnetic and ferroelectric features, have attracted much attention due to the potential applications of switchable devices employing electric polarization, magnetization, electronic conduction, and photoelectric effects [1–3]. Among the studied multiferroic materials, the perovskite bismuth ferrite BiFeO_3 (BFO) is the most widely investigated compound because of its antiferromagnetic (Néel temperature, $T_N \sim 630$ K) and ferroelectric ordering (Curie temperature, $T_C \sim 1100$ K) [1]. The magnetic moments of the Fe^{3+} ions in rhombohedral ($R3c$) BFO display

a G-type antiferromagnetic order such that each spin is surrounded by six anti-parallel neighbor spins [1,4]. The A-site Bi^{3+} has a stereochemically active $6s^2$ lone-pair, which results in hybridization of Bi $6p$ and O $2p$ states to cause an off-center displacement of Bi^{3+} toward O^{2-} to induce ferroelectric polarization [5].

Leakage currents and weak magnetic response are drawbacks for potentially useful applications of BFO [1]. To enhance the ferromagnetism with reduction of current leakage, many authors have studied the substitution of rare-earth elements for the Bi^{3+} ions in the A sites of the perovskite unit cell [6–18]. Enhanced ferromagnetic behavior has been observed in A-site doped $(\text{Bi}_{1-x}\text{RE}_x)\text{FeO}_3$ (RE=La, Nd, Er, Dy, Eu, and Sm) ceramics and thin films [6–18]. The weak ferromagnetism can be attributed to the canting of the antiferromagnetic spins by the

modification of the anti-parallel sublattice magnetization of Fe^{3+} due to the RE^{3+} substitution in the A sites of the perovskite unit cell.

Previous studies of doped BFO materials have focused on the structural and magnetic properties [7–25]. The $(\text{Bi}_{1-x}\text{La}_x)\text{FeO}_3$ ceramics have a rhombohedral $R3c$ symmetry for $x \leq 0.125$ [18]. The $(\text{Bi}_{1-x}\text{Nd}_x)\text{FeO}_3$ ceramics exhibit a rhombohedral symmetry for $x \leq 0.1$ and orthorhombic symmetry for $x = 0.15$ – 0.2 [19]. The $(\text{Bi}_{1-x}\text{Dy}_x)\text{FeO}_3$ ceramics for $x = 0.0$ – 0.1 and $(\text{Bi}_{0.85}\text{Dy}_{0.15})\text{FeO}_3$ nanowires exhibit ferromagnetic behavior with increasing Dy concentration and have an orthorhombic phase for $x = 0.15$ [12,13]. The $(\text{Bi}_{1-x}\text{Gd}_x)\text{FeO}_3$ nanoparticles exhibit a rhombohedral–orthorhombic structural transition at $x = 0.1$ [20]. An orthorhombic (or triclinic) phase begin to appear in $(\text{Bi}_{1-x}\text{Eu}_x)\text{FeO}_3$ ceramics for $x = 0.10$ [14–16]. Enhanced ferromagnetic responses were observed in higher concentrations of Eu doped BFO compounds due to structural distortions [14,15]. A structural transition from rhombohedral $R3c$ to orthorhombic $Pbnm$ was proposed for $(\text{Bi}_{1-x}\text{Eu}_x)\text{FeO}_3$ thin films with $x = 0.15$ [17]. The $(\text{Bi}_{1-x}\text{Sm}_x)\text{FeO}_3$ ceramics and thin films have shown enhanced magnetization as Sm concentration increases [21–25]. The $(\text{Bi}_{1-x}\text{Sm}_x)\text{FeO}_3$ ceramics show a magnetic structural transition from a spin cycloid to a G-type antiferromagnetic behavior at $x \sim 14$ mol% as Sm concentration increases [24,25]. The polycrystalline $(\text{Bi}_{0.85}\text{Sm}_{0.15})\text{FeO}_3$ exhibits an orthorhombic structure and weak ferromagnetic feature [25].

Direct optical band gaps of rhombohedral BFO thin films have been reported in the range of 2.55–2.75 eV [26–29]. The UV–visible transmissions of BFO nanoparticles [2] and single-crystalline BFO nanocubes (with average sizes of 50–200 nm) [30] respectively indicate band gaps of 2.18 and 2.1 eV. The optical band gaps (2.60–2.68 eV) of $(\text{Bi}_{1-x}\text{La}_x)\text{FeO}_3$ ($x = 0.0$ – 0.30) thin films decrease with increasing La concentration [9]. From first-principles density functional theory for BFO [31,32], oxygen vacancies (OVs) can shift the optical absorption to lower energy below the conduction band. An additional optical absorption peak appears at 2.2 eV in the OV rich condition [31].

BiFeO_3 thin films and crystals have shown photovoltaic (PV) responses and photoconductivity [33–39]. BFO is a p -type semiconducting material resulting from the loss of Bi^{3+} during the sintering process, which causes vacancies to act as p -type centers for accepting electrons [40]. First-principles calculations suggest that Bi vacancies (V_{Bi}) have lower formation energy than OVs under oxygen-rich conditions and V_{Bi} become the electron-acceptor defects [41]. The Fe–O bond length (~ 1.93 Å) in BFO is shorter than the Bi–O bond length (~ 2.31 Å), thus the formation of V_{Bi} is easier than formation of Fe vacancies [42]. The PV effects of (Ca, Sr, and Ba)-doped BFO ceramics with ITO and Au electrodes have shown strong dependences on ceramic thickness, light wavelength and intensity [43–46]. The PV open-circuit voltage and short-circuit current were described reasonably by a p - n -junction-like model, which is based on optically excited charges in the interface between ITO film and doped BFO ceramics [43,46].

This work is to explore structures, OVs, Raman vibrations, Fe valence, magnetization, optical band gaps, and PV effects in the A-site rare-earth doped $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ ($\text{RE} = \text{Dy, Gd, Eu, and Sm}$) ceramics. A p - n -junction-like model is used to describe the light-intensity-dependent PV open-circuit voltage and short-circuit current under illumination of $\lambda = 405$ nm.

2. Experimental procedure

BiFeO_3 (BFO), $(\text{Bi}_{0.93}\text{Dy}_{0.07})\text{FeO}_3$ (7%Dy–BFO), $(\text{Bi}_{0.93}\text{Gd}_{0.07})\text{FeO}_3$ (7%Gd–BFO), $(\text{Bi}_{0.93}\text{Eu}_{0.07})\text{FeO}_3$ (7%Eu–BFO), and $(\text{Bi}_{0.93}\text{Sm}_{0.07})\text{FeO}_3$ (7%Sm–BFO) ceramics were prepared by the solid state reaction method, in which Bi_2O_3 , RE_2O_3 ($\text{RE} = \text{Dy, Gd, Eu, and Sm}$), and Fe_2O_3 powders (purity $\geq 99.0\%$) were weighed in the ratios of 1.1:0:1.0 for BFO and 0.93:0.07:1.0 for $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$. 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 – 890°C (3 h) for $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ ceramics.

X-ray diffractions, oxygen vacancy concentrations, and grain morphologies of as-sintered ceramics were obtained using a Rigaku Multiplex Diffractometer with wavelengths $K\alpha_1$ (1.5406 Å) and $K\alpha_2$ (1.5444 Å) and a Hitachi S-3400N scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Micro-Raman spectra were measured using a Nanobase Model XperRam 200 Raman spectrometer equipped with a green laser of $\lambda = 532$ nm and a TE-cooled CCD detector. The Fe K -edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were recorded to determine oxidation states in the transmission mode at the 01C1 beam line at the National Synchrotron Radiation Research Center of Taiwan. The optical transmissions were measured using a Cary 5E UV–vis–NIR spectrometer. For photovoltaic effects (I – V characteristic curve, open-circuit voltage, short-circuit current, and power-conversion efficiency), ITO and Au films were deposited on ceramic surfaces by dc sputtering using the experimental configuration reported in our early study [47]. A diode laser of $\lambda = 405$ nm was used as the excitation source and the illuminated area (also area of ITO) is about 0.15 cm^2 . The sample thicknesses are 0.2 mm for BFO and 0.15 mm for $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$.

3. Results and discussion

X-ray diffraction (XRD) spectra of as-sintered samples are shown in Fig. 1(a), which show similar splittings in 2θ XRD peaks, suggesting a rhombohedral structure in BFO and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ compounds. As illustrated by the dashed line, XRD peaks of $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ compounds shift slightly to higher 2θ positions, due to the smaller radii (1.052–1.098 Å) of RE^{3+} ions compared with Bi^{3+} (1.17 Å) [48]. The stronger (100) and (200) peaks in $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ suggest a preferred (100) crystallographic orientation in the ceramic grains. Fig. 1(b) illustrates SEM grain morphologies and average oxygen atomic molar ratios

Fig. 1. (a) XRD spectra, (b) SEM EDS and (c) SEM grain morphologies of as-sintered ceramics at room temperature. “OA” is the average oxygen atomic ratio.

determined from different positions of each sample. The theoretical oxygen atomic ratio is 60% in the BiFeO_3 perovskite unit cell. $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ compounds exhibit

fewer OV than the pure BFO. OV concentrations in 7%Dy-BFO are slightly less than in 7%Gd-BFO, 7%Eu-BFO, and 7%Sm-BFO. Grain morphologies of as-sintered ceramics are

Fig. 2. Raman spectra of as-sintered BFO and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ (RE=Dy, Gd, Eu, and Sm) ceramics, and Fe_2O_3 , Bi_2O_3 , Dy_2O_3 , Gd_2O_3 , Eu_2O_3 , and Sm_2O_3 powders at room temperature.

shown in Fig. 1(c) and average grain sizes are respectively 2.1, 2.7, 2.6, 2.6, and 2.8 μm for BFO, 7%Dy-BFO, 7%Gd-BFO, 7%Eu-BFO, and 7%Sm-BFO.

Fig. 2(a) shows Raman vibration modes for BFO and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ (RE=Dy, Gd, Eu, and Sm) at room temperature. The Raman spectra of Fe_2O_3 , Bi_2O_3 , Dy_2O_3 , Gd_2O_3 , Eu_2O_3 , and Sm_2O_3 powders are given in Fig. 2(b) and suggest no residues in as-sintered ceramics. The Raman active modes of the $R3c$ rhombohedral BFO can be summarized as the irreducible representation, $\Gamma = 4A_1 + 9E$ [49–51]. BFO and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ exhibit similar Raman vibrations, confirming the same $R3c$ space group. The four dominant Raman vibrations are the $E(1)$ mode near 70 cm^{-1} , $E(\text{LO}2)$ mode near 130 cm^{-1} , $A_1(1)$ mode near 170 cm^{-1} , and $A_1(2)$ mode near 220 cm^{-1} [52]. The low-frequency Raman modes (below 170 cm^{-1}) and middle-frequency modes ($150\text{--}270\text{ cm}^{-1}$) are respectively associated with Bi and Fe atoms [52]. The higher Raman modes (above 260 cm^{-1}) mainly correlate to oxygen motions. The vibration mode near 220 cm^{-1} is the A_1 tilt mode of the FeO_6 octahedra. As illustrated by the dashed lines, the $E(\text{LO}2)$ and $A_1(2)$ modes shift significantly to higher

Fig. 3. Experimental Raman spectra and fitting modes in the region of $50\text{--}250\text{ cm}^{-1}$. The red line is the sum of fitting curves. The labeled numbers are frequencies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

frequencies upon substitution of lighter RE^{3+} (RE= Dy, Gd, Eu, and Sm) ions in the A-site Bi^{3+} positions. The shifts of the $A_1(2)$ modes imply that A-site RE^{3+} substitution affects the motions in the FeO_6 octahedra.

Fig. 3 shows fits of Raman modes in the region of $50\text{--}250\text{ cm}^{-1}$ by using the Lorentzian profile. $E(1)$, $E(2)$, $A_1(1)$, and $A_1(2)$ modes of $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ exhibit slightly broadened spectra compared with the pure BFO. These broadening phenomena likely result from lattice anharmonicity and disorder caused by randomness in the A-site substitution. As seen in Fig. 2(a), there is no frequency shift of the $E(1)$ mode, suggesting that the A-site RE^{3+} substitution does not affect the low-frequency vibration. Compared with the pure BFO, the relative intensities of the $A_1(1)$ mode in $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ were reduced, possibly due to the symmetry reduction of the FeO_6 oxygen octahedra by the A-site RE^{3+} substitution.

Fig. 4(a) displays the Fe K -edge XANES spectra of BFO, $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ (RE= Dy, Gd, Eu, and Sm) and the reference powders of FeO and Fe_2O_3 . The Fe K -edge XANES arises primarily from the $1s \rightarrow 4p$ transition [53]. There is no obvious Fe K -edge energy shift in BFO and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ compared with Fe_2O_3 . The absorption spectra confirm

Fig. 4. (a) Fe K -edge XANES spectra vs. photon energy and (b) Fourier transform amplitude of $k^2\chi(k)$ vs. interatomic distance without phase correction.

that the A-site substitution of $\text{Bi}^{3+} \rightarrow \text{RE}^{3+}$ does not change valence of Fe^{3+} ions in BFO and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$. As shown in Fig. 4(b), the Fourier transforms of the EXAFS $k^2\chi(k)$ spectra indicate that the A-site RE^{3+} doping does not obviously modify interatomic distances of Fe–O, Fe–Bi, and Fe–O–Fe bonds. These results suggest that the Fe–O–Fe bond angle (where the two Fe^{3+} are in the centers of neighboring FeO_6 octahedras) is not modified by the RE^{3+} substitution.

The hysteresis loops of magnetization vs. field at room temperature in Fig. 5 show linear antiferromagnetic responses in BFO and $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ ($\text{RE}=\text{Gd}, \text{Eu}$, and Sm). The magnetic susceptibilities are about 6.5×10^{-6} , 7.3×10^{-6} , 8.5×10^{-6} , and 1.3×10^{-5} emu/g Oe for BFO, 7%Sm-BFO, 7%Eu-BFO, and 7%Gd-BFO ceramics, respectively. 7%Dy-BFO exhibits a weak ferromagnetic loop as enlarged in the inset and the remanent magnetization is ~ 0.005 emu/g. First-principles density functional theory for BFO suggests that a weak magnetization may develop under oxygen-rich sintering condition [42]. The weak magnetization in 7%Dy-BFO may correlate to fewer OVAs as revealed in Fig. 1(b).

Fig. 6 shows optical transmission and $(ah\nu)^2$ vs. photon energy ($h\nu$). h and ν are Planck's constant and photon frequency, respectively. The optical absorption coefficient α is determined by

$$\alpha = -\ln(T)/d \quad (1)$$

Fig. 5. Magnetization hysteresis loops at room temperature. The inset is the hysteresis loop of 7% Dy-BFO.

Fig. 6. (a) Optical transmission and (b) $(ah\nu)^2$ vs. photon energy.

where T and d are the measured optical transmission and sample thickness, respectively. The optical band gap can be estimated using the Tauc relation [54],

$$(ah\nu)^2 = A(h\nu - E_g) \quad (2)$$

where E_g is the direct optical band gap between valence and conduction bands. E_g can be evaluated by extrapolating the

Fig. 7. (a) Open-circuit voltage (V_{oc}) and (b) short-circuit current density (J_{sc}) as light was switched on and off with increasing intensity. The labeled numbers are light intensities in mW/cm^2 .

straight line of the curves of $(\alpha h\nu)^2$ vs. $h\nu$ in Fig. 6(b). The E_g values of the $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ shift slightly toward lower photon energies in the range of 2.20–2.21 eV, which are smaller than $E_g \sim 2.24$ eV in pure BFO and the band gaps of 2.60–2.68 eV reported in $(\text{Bi}_{1-x}\text{La}_x)\text{FeO}_3$ ($x=0.0-0.30$) films [55]. The band gaps in BiFeO_3 nanoparticles show strong dependence on particle size and were correlated to microstrain and oxygen defects [56]. The slightly different band gaps (2.20–2.21 eV) in $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ may be associated with OV and grain sizes as shown in Fig. 1(b) and (c).

Fig. 7 shows photovoltaic (PV) open-circuit voltages (V_{oc}) and short-circuit current densities (J_{sc}) of ITO/BFO ceramic/Au and ITO/ $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ ceramic/Au structures as the laser ($\lambda=405$ nm) was switched on and off with increasing illumination intensity (I) by steps. The V_{oc} and J_{sc} are plotted in Fig. 8 as functions of illumination intensity. The V_{oc} exhibits a rapid increase as illumination intensity increases below $I \sim 50$ mW/cm^2 . At $I \sim 91$ mW/cm^2 , V_{oc} and J_{sc} are 0.7 V and 0.009 mA/cm^2 in ITO/BFO ceramic/Au, 0.74 V and 0.114 mA/cm^2 in ITO/7%Dy-BFO/Au, 0.75 V and 0.284 mA/cm^2 in ITO/7%Gd-BFO/Au, 0.68 V and 0.434 mA/cm^2 in ITO/7%Eu-BFO/Au, and 0.76 V and 0.362 mA/cm^2 in ITO/7%Sm-BFO/Au. These J_{sc} values are larger than $J_{sc} \sim 0.007$ mA/cm^2 reported in Au/BFO thin film/Au under illumination of $\lambda=532$ nm at $I \sim 20$ mW/cm^2 [3].

To describe V_{oc} and J_{sc} , we use a p - n -junction-like model between a n -type ITO film and a p -type ceramic [43]. The photodiode current i_d under a bias voltage V is expressed

Fig. 8. (a) V_{oc} and (b) J_{sc} as functions of illumination intensity. The solid lines are the theoretical fits with parameters given in (a).

as [57],

$$i_d = i_o \{ \exp[q(V - i_d R_s) / \xi k_B T] - 1 \} \quad (3)$$

where i_o , R_s and ξ are dark current, source resistance, and diode-quality factor, respectively. To estimate i_o , R_s and ξ , the characteristic curves of current vs. bias voltage were measured in the dark (without illumination) as shown in Fig. 9. By using Eq. (3) with $q = 1.6 \times 10^{-19}$ C and $T = 300$ K, we obtained $i_o = 5 \times 10^{-5}$ mA, $R_s = 6.2 \times 10^4 \Omega$ and $\xi = 13$ for BFO, $i_o = 5 \times 10^{-5}$ mA, $R_s = 1.7 \times 10^4 \Omega$ and $\xi = 6.5$ for 7%Dy-BFO, $i_o = 5 \times 10^{-5}$ mA, $R_s = 1.4 \times 10^4 \Omega$ and $\xi = 8$ for 7%Gd-BFO, $i_o = 5 \times 10^{-5}$ mA, $R_s = 1.9 \times 10^3 \Omega$ and $\xi = 6$ for 7%Eu-BFO, and $i_o = 5 \times 10^{-5}$ mA, $R_s = 2.6 \times 10^3 \Omega$ and $\xi = 8$ for 7%Sm-BFO. From Eq. (3), the illuminated i can be expressed as [43],

$$i = i_p - i_d = i_p - i_o \{ \exp\{[V - (i_d - i_p)R_s]q / \xi k_B T\} - 1 \} \quad (4)$$

where i_p , i_d , and V are the photovoltaic current, diode current, and measured voltage. As derived in Ref. [43], we use Eqs. (14) and (19) of Ref. [43] to fit short-circuit current (i_{sc}) and open-circuit voltage (V_{oc}) as a function of illumination intensity.

The solid lines in Fig. 8 are fits of V_{oc} and J_{sc} ($=i_{sc}/S$) with parameters given in Fig. 8(a). U_o is the voltage barrier across the depletion-region in the dark. The definition of B can be

Fig. 9. Characteristic curves of current vs. bias voltage without illumination. The solid lines are fits of Eq. (3) with parameters given in the Figure.

found in Eq. (6) of Ref. [43]. β is the optical attenuation length calculated directly from the optical transmission in Fig. 6(a). The measured attenuation lengths ($\beta = 1/\alpha$) at $\lambda = 405$ nm are respectively about 2.0, 1.0, 2.2, 1.4 and 1.3 μm for BFO, 7% Dy-BFO, 7%Gd-BFO, 7%Eu-BFO, and 7%Sm-BFO. The dielectric permittivities (ϵ_p) of BFO, 7%Dy-BFO, 7%Gd-BFO, 7%Eu-BFO, and 7%Sm-BFO ceramics are respectively about 100, 140, 160, 105, and 145 for measuring frequency $f = 1$ MHz at room temperature. The fits of V_{oc} agree reasonably well with experimental results. The fits of J_{sc} show discrepancy with the experimental curves in the low-illumination region likely due to current leakage. Note that this p - n -junction-like model only considers photo-excited electron-hole creation [43]. Other factors, such as OV, cation vacancies, domain structure, and grain boundaries may affect the electrical conductivity [58].

The dielectric permittivity and carrier density of n -type ITO thin films are respectively $\epsilon_n \sim 4$ near 3 eV [59] and $n_n \sim 10^{21} \text{ cm}^{-3}$ [60,61]. From Eq. (6) of Ref. [43], the carrier densities (n_p) of BFO, 7%Dy-BFO, 7%Gd-BFO, 7%Eu-BFO, and 7%Sm-BFO ceramics are respectively about 3×10^{20} , 1×10^{20} , 3×10^{18} , 2×10^{19} , and $3 \times 10^{19} \text{ cm}^{-3}$. The calculated depletion-region widths in the dark, $d_o \sim (U_0/B)^{1/2}$ [43], are respectively about 2, 5, 60, 20, and 15 nm for BFO, 7%Dy-BFO, 7%Gd-BFO, 7%Eu-BFO, and 7%Sm-BFO.

Fig. 10 shows curves of power-conversion efficiency (η) vs. load voltage (V) for several illumination intensities. The maximal PV power-conversion efficiencies (η_{max}) occur at the low-illumination intensities (~ 1 – 2 mW/cm^2) and are about 0.017%, 0.22%, 0.35%, 0.27%, and 0.24% for ITO/BFO/Au, ITO/7%Dy-BFO/Au, ITO/7%Gd-BFO/Au, ITO/7%Eu-BFO/Au, and ITO/7%Sm-BFO/Au, respectively. At $I = 125 \text{ mW/cm}^2$, the maximal power-conversion efficiencies for ITO/7%Dy-BFO/Au, ITO/7%Gd-BFO/Au, ITO/7%Eu-BFO/Au, and ITO/7%Sm-BFO/Au are respectively about 0.017%, 0.044%, 0.06%, and 0.05%. These PV power-conversion efficiencies are larger than $\eta_{max} \sim 0.007\%$ in ITO/(Bi_{0.90}Ca_{0.10})FeO_{2.95}

Fig. 10. Power-conversion efficiency vs. load voltage for various illumination intensities.

ceramic/Au (under $\lambda = 405$ nm) [43] and $\eta_{max} \sim 0.004\%$ in ITO/(Bi_{0.95}Sr_{0.05})FeO_{2.975} ceramic/Au (under $\lambda = 405$ nm) [46]. Compared with ITO/BFO/Au, ITO/(Bi_{0.93}RE_{0.07})FeO₃/Au structures exhibit stronger PV effects, which could be associated with microstructure. As shown in Fig. 1(a), (Bi_{0.93}RE_{0.07})FeO₃ compounds exhibit a relatively stronger (100) crystallographic orientation. Strong PV effects have also been observed in (100) oriented BFO films [62,63].

Fig. 11 shows external quantum efficiencies (EQE) calculated from the PV short-circuit current density as given in Fig. 8(b). The EQE is a measure of conversion efficiency from incident photons to conductive electrons, i.e.

$$\text{EQE} = (\text{electrons/s})/(\text{photons/s}) = hfJ_{sc}/q_e I \quad (5)$$

Fig. 11. External quantum efficiencies (EQE) vs. illumination intensity.

where I and q_e are light intensity and electron charge, respectively. The EQEs of $\text{ITO}/(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3/\text{Au}$ heterostructures reach maxima near $I=4 \text{ mW/cm}^2$ and then decrease rapidly with increasing illumination intensity. The maximal EQEs of $\text{ITO}/7\%\text{Dy-BFO}/\text{Au}$, $\text{ITO}/7\%\text{Gd-BFO}/\text{Au}$, $\text{ITO}/7\%\text{Eu-BFO}/\text{Au}$, and $\text{ITO}/7\%\text{Sm-BFO}/\text{Au}$ are about 3.6%, 4.5%, 5.0%, and 4.2%, respectively.

4. Conclusions

XRD and Raman spectra reveal that $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ ($\text{RE}=\text{Dy}, \text{Gd}, \text{Eu}$, and Sm) have a rhombohedral $R3c$ phase. Fe K -edge synchrotron absorption spectroscopy reveals that the valence of Fe^{3+} is not modified by the RE^{3+} ion ($\text{RE}=\text{Dy}, \text{Gd}, \text{Eu}$, and Sm) substitution in the A-site Bi^{3+} positions of the perovskite unit cell. 7%Dy-BFO shows a weak ferromagnetic response. The maximal PV power-conversion efficiencies under illumination of $\lambda=405 \text{ nm}$ are respectively about 0.017%, 0.22%, 0.35%, 0.27%, and 0.24% in $\text{ITO}/\text{BFO}/\text{Au}$, $\text{ITO}/7\%\text{Dy-BFO}/\text{Au}$, $\text{ITO}/7\%\text{Gd-BFO}/\text{Au}$, $\text{ITO}/7\%\text{Eu-BFO}/\text{Au}$, and $\text{ITO}/7\%\text{Sm-BFO}/\text{Au}$. The smaller band gaps (2.20–2.21 eV) in $(\text{Bi}_{0.93}\text{RE}_{0.07})\text{FeO}_3$ likely are associated with oxygen vacancies.

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