Enhanced photovoltaic effects in A-site samarium doped BiFeO 3 ceramics: The roles of domain structure and electronic state


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Enhanced photovoltaic effects in A-site samarium doped BiFeO$_3$ ceramics: The roles of domain structure and electronic state

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**Abstract**

This work reports enhanced photovoltaic (PV) responses of \((\text{Bi}_{1-x}\text{Sm}_x)\text{FeO}_3\) \((x = 0.0, 0.05, 0.10)\) ceramics (BFO100$_x$Sm) with ITO film under near-ultraviolet irradiation \((\lambda = 405\text{ nm})\). The ceramics were characterized by micro-Raman scattering, high-resolution transmission electron microscopy, and synchrotron X-ray absorption spectroscopy (XAS). A rhombohedral \(R\bar{3}c\) symmetry with tilted FeO$_6$ octahedra has been confirmed. The Fe K-edge absorption spectra reveal a slight shift toward higher energy as A-site Sm$^{3+}$ substitution increases. The oxygen K-edge XAS reveals an enhancement of hybridization between the O 2$p$ and unoccupied Fe 3$d$ states due to Sm doping. The optical band gaps are in the range of 2.15–2.24 eV. The maximal PV power-conversion and external quantum efficiencies respectively reach 0.37% and 4.1% in the ITO/BFO5Sm/Au heterostructure. The PV responses can be described quantitatively by a \(p-n\)-junction-like model. The domain structures and hybridization between the O 2$p$ and Fe 3$d$ states play important roles for the PV responses.

**1. Introduction**

Among perovskite multiferroic materials, the bismuth ferrite BiFeO$_3$ related systems are the most studied candidates because of their room-temperature antiferromagnetic behavior (Néel temperature, \(T_N\sim 630\text{ K}\)) and ferroelectric properties (Curie temperature, \(T_C \sim 1100\text{ K}\)) \([1]\). The ferroelectric polarization can be attributed to the hybridization of Bi 6$p$ and O 2$p$ states, which causes an off-center displacement of Bi$^{3+}$ toward O$^{2-}$ \([2]\). It was reported that the Curie temperature \(T_C\) in rare-earth-doped compositions of \((\text{Bi}_{1-x}\text{RE}_x)\text{FeO}_3\) \((\text{RE} = \text{La, Nd, Sm, Gd})\) decreases with decreasing average A-site ionic polarizability and tolerance factor \([3]\). Rhombohedral \(R\bar{3}c\) BiFeO$_3$ displays a G-type antiferromagnetic order, in which each spin in the Fe$^{3+}$ ions is surrounded by six anti-parallel neighbor spins \([1,4]\). However, leakage currents and weak magnetic behavior in BFO are drawbacks for applications \([1]\). To increase the ferroelectricity and ferromagnetism, many studies have focused on rare-earth substitution in the A-site Bi$^{3+}$ positions of the perovskite unit cell, resulting in improvements in the magnetic and ferroelectric properties \([5,6]\).

Early studies of rare-earth-doped BFO materials focused on structural and magnetic characterization \([3–16]\). The structures of \((\text{Bi}_{1-x}\text{RE}_x)\text{FeO}_3\) \((\text{RE} = \text{La, Nd, Sm, Gd})\) for \(x \leq 0.1\) correspond to the perovskite rhombohedral \(R\bar{3}c\) phase of BiFeO$_3$ \([3]\). The \((\text{Bi}_{1-x}\text{Sm}_x)\text{FeO}_3\) solid solutions show a ferroelectric rhombohedral phase for \(x = 0 – 12\%\), a coexistence of ferroelectric triclinic and orthorhombic phases for \(x = 12.5 – 20.0\%\), and a non-polar orthorhombic phase for \(x = 25\%\) at room temperature \([6]\). Ferroelectric polarization hysteresis loops appear in the range of \(0 \leq x \leq 17.5\%\) in \((\text{Bi}_{1-x}\text{Sm}_x)\text{FeO}_3\) ceramics \([6]\). Temperature-dependent dielectric permittivity results suggest that the magnetic Néel temperature \(T_N\) decreases with increasing Sm$^{3+}$ concentration for \(x = 1 – 8\%\) \([7]\). \((\text{Bi}_{1-x}\text{Sm}_x)\text{FeO}_3\) ceramics and thin films show enhanced magnetization with increasing Sm ratio \([12–16]\). \((\text{Bi}_{1-x}\text{Sm}_x)\text{FeO}_3\) ceramics show a magnetic structure transition from a spin cycloid to a G-type antiferromagnetic behavior at \(x \sim 14\%\) \([15,16]\).
Perovskite ferroelectric/piezoelectric oxides have been explored for photovoltaic (PV) applications for several decades because of easy electric-field-driven polarization [17–20], but a severe drawback for ferroelectric photovoltaic devices has been the low photovoltaic current under illumination. In recent photovoltaic studies [21–41], BFO thin films and crystals with various electrodes have shown properties with potential for PV applications. Pt/BFO/SRO and Pt/Sm:BFO/SRO thin films heterostructures showed significantly higher PV current densities in the low-resistance state under white-light illumination [30,31]. BFO has been considered a p-type semiconducting material resulting from the Bi\(^{3+}\) loss during the sintering process, which causes vacancies to act as p-type centers [42]. First-principles calculations suggested that Bi vacancies (V\(_{\text{Bi}}\)) have lower formation energy than oxygen vacancies under oxygen-rich condition and thus V\(_{\text{Bi}}\) become electron-acceptor defects [43].

The aim of this work is to investigate the electronic configurations and domain structures and their correlations in the PV responses of Sm\(^{3+}\) doped BFO polycrystalline ceramics with ITO and Au electrodes. Fe K-edge, Fe L\(_{2,3}\)-edge and oxygen K-edge synchrotron X-ray absorptions were measured to study electron structures and the hybridization of the O 2p and the unoccupied Fe 3d states. High-resolution TEM and diffraction were used to examine the nanoscale domain structures and symmetry. A theoretical p-n-junction-like model is used to quantitatively describe the PV open-circuit voltage and short-circuit current density as functions of illumination intensity.

2. Experimental procedure

BiFeO\(_3\) (BFO), (Bi\(_{0.95}\)Sm\(_{0.05}\))FeO\(_3\) (BFO5Sm), and (Bi\(_{0.90}\)Sm\(_{0.10}\))FeO\(_3\) (BFO10Sm) ceramics were prepared by the solid state reaction, in which Bi\(_2\)O\(_3\), Sm\(_2\)O\(_3\), and Fe\(_2\)O\(_3\) powders (purity ≥99.0 %) were weighed in the ratios of 1:1.0:1.0 for BFO, 0.95:0.05:1.0 for BFO5Sm, and 0.90:0.10:1.0 for BFO10Sm. The powders were mixed in an agate mortar with alcohol for more than 24 h and then were calcined at 800 °C for 3 h. The sintering temperatures were 830 °C (10 h) for BFO and 870 °C (3 h) for BFO5Sm and BFO10Sm ceramics. Grain morphologies, oxygen atomic ratios, and lattice structures were characterized using a Hitachi S-3400N scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and a Rigaku Multiplex Diffractometer. For SEM measurement, the samples were polished and thermally etched at 800 °C for 30 min. Standard deviations were calculated to estimate error ranges of oxygen atomic ratios. The average grain sizes were estimated by counting the number of grains intercepted by several straight lines sufficiently long to include most of grains on the SEM photomicrograph.

Micro-Raman spectra were measured using a Nanobase Model XperRam 200 Raman spectrometer equipped with a green laser of λ = 532 nm and a TE-cooled CCD detector. A high-resolution TEM (JEOL JEM-2100 LaB\(_6\)) was used to study domain structures and symmetries of the unit cells. To determine electronic states, the Fe K-edge synchrotron X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were obtained in transmission mode at the 01C1 beam line of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The soft X-ray absorption spectra (XAS) of the Fe L\(_{2,3}\)-edges and oxygen K-edge were studied in total electron yield via current mode at the 20A1 beam line of the NSRRC. For PV measurements (I–V characteristic curve, open-circuit voltage, short-circuit current, and power conversion efficiency), ITO (top electrode) and Au (bottom electrode) thin films were deposited on the ceramic surfaces by dc sputtering. A diode laser (λ = 405 nm) was used as the excitation source and the illuminated area (also ITO area) is ~0.15 cm\(^2\). The ceramic thicknesses are 0.2 mm for BFO and 0.15 mm for BFO5Sm and BFO10Sm.

Fig. 1. (a-c) SEM grain morphologies of thermally etched ceramics and (d) XRD spectra of as-sintered samples at room temperature. D and \(A_0\) are average grain size and average oxygen atomic ratio, respectively.
3. Results and discussion

Fig. 1(a–c) shows grain morphologies of thermally etched ceramics with average grain sizes (\(D\)) of 3.4, 1.8, and 1.3 \(\mu\)m for BFO, BFO5Sm, and BFO10Sm. As labeled in Fig. 1(a–c), the average oxygen atomic ratios (\(A_O\)) for BFO, BFO5Sm, and BFO10Sm are approximately 52.5 \(\pm\) 1.6%, 53.3 \(\pm\) 0.5%, and 55.6 \(\pm\) 0.6%, respectively. The average oxygen atomic ratios were determined from 15 to 18 spots in the region where ITO thin film was later deposited for the PV experiment. The average oxygen atomic ratio increases with increasing Sm concentration, suggesting that oxygen vacancies were reduced by the A-site Sm\(^{3+}\) substitution. This result is consistent with previous reports on rare-earth doped BiFeO\(_3\) materials [5]. XRD spectra of as-sintered samples are shown in Fig. 1(d), which show similar splittings in XRD peaks, suggesting a rhombohedral phase in all compounds. Compared with BFO, BFO5Sm and BFO10Sm exhibit stronger (1 0 0) and (2 0 0) peaks, suggesting a preferred (1 0 0) crystallographic orientation in the ceramic grains. As illustrated by the dashed line, XRD peaks of BFO5Sm and BFO10Sm shift toward higher 2\(\theta\), due to the smaller radius (1.098 Å) of the Sm\(^{3+}\) ion compared with 1.17 Å for the Bi\(^{3+}\) ion [44].

Fig. 2(a) shows Raman vibration modes in the range of 50–600 cm\(^{-1}\), including Fe\(_2\)O\(_3\), Bi\(_2\)O\(_3\), and Sm\(_2\)O\(_3\) powders. The Raman spectra suggest no second phase from incomplete reaction in the as-sintered Sm-doped compounds. The Raman active modes in the R\(^{3+}\) rhombohedral BFO can be represented by \(T = 4A_1 + 9E\) [45–47]. BFO, BFO5Sm, and BFO10Sm exhibit similar Raman vibrations, confirming the same R\(^{3+}\) space group. To identify the Sm\(^{3+}\) doping effects on atomic vibrations, the four dominant Raman modes, \(E(1), E(2), A_1(1),\) and \(A_2(2)\), were fitted by using a Lorentzian profile in the region of 50–250 cm\(^{-1}\) as shown in Fig. 2(b). The numbers labeled on peaks are Raman frequencies and full-width at half maximum (in parentheses). The low-frequency Raman modes (below 170 cm\(^{-1}\)) and mid-frequency modes (150–270 cm\(^{-1}\)) are respectively associated with Bi and Fe atoms [45]. 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. Major Raman modes, as illustrated by the dashed lines, shift significantly to higher frequencies with increasing Sm concentration, indicating that the A-site Bi\(^{3+}\) ions have been mostly substituted by lighter Sm\(^{3+}\) ions. The \(E(1), E(2), A_1(1),\) and \(A_2(2)\) modes of BFO5Sm and BFO10Sm exhibit broader spectra than BFO, possibly resulting from lattice anharmonicity and disorder caused by randomness of the A-site Sm\(^{3+}\) substitution.

Fig. 2 shows the high-resolution bright-field TEM images (top) and the selected-area diffraction patterns (SADPs). The inset in Fig. 2(a) shows the domain configuration of BFO measured from a two-beam condition via tilting technique. The arrows in the bright-field TEM images indicate various domain boundaries. BFO and BFO10Sm exhibit complex pinning domain structures at the boundary intersections, which can cause high strain and reduce electrical conductivity. BFO5Sm exhibits relatively homogeneous domain structures with linear domain walls. The domain morphology transforms from small nanodomains in (BFO) to large lamellar domains in the Sm-doped compounds, suggesting a transformation from the short-range-ordered to the long-range-ordered states. Enhanced electrical conductivity has been reported along uniform domain walls in (110)-oriented La\(^{3+}\) doped (10%) BFO thin films [48]. It was proposed that the enhanced conduction at the domain walls was driven by a local reduction in the electronic band gap [48]. Therefore, higher electrical conductivity can be expected in BFO5Sm because of uniform domain walls in the grain matrix. The SADPs were measured from representative grains along the [1 1 0] zone axis. The [1 1 0]-viewed SADPs reveal \(\frac{1}{2}(2\{111\})\) or \(\frac{1}{2}(000)\) superlattice diffraction spots without appearance of \(\frac{1}{2}(2\{000\})\) diffraction spots. Here, “o” and “e” represent odd and even Miller indices. This phenomenon can be attributed to the tilted FeO\(_6\) octahedra, indicating a predominantly rhombohedral R3\(^{\text{c}}\) symmetry [49,50]. The high-resolution TEM confirms the rhombohedral R\(^{3+}\) space group as suggested by the XRD (Fig. 1d) and Raman spectra (Fig. 2). The intensity of the \(\frac{1}{2}(2\{111\})\) superlattice diffraction is enhanced as Sm content increases, suggesting that the FeO\(_6\) octahedral tilting is enhanced by the Sm substitution.

Fig. 4 displays the Fe K-edge XANES spectra of BFO, BFO5Sm, BFO10Sm, and the reference powders FeO\(_2\) and Fe\(_2\)O\(_3\). The Fe K-edge absorption arises primarily from the 1\(s\) \(\rightarrow\) 4\(p\) electronic transition [51]. The Fe K-edge absorption is sensitive to the octahedral environment and local electrostatic interaction. As indicated by lines and labels in the inset, BFO shows a K-edge absorption peak at approximately 7133 eV, which is close to the K-edge energy of reference powder FeO\(_2\). This result suggests an Fe\(^{3+}\) oxidation state in BFO. The Fe K-edge absorption peaks in BFO5Sm and BFO10Sm appear respectively at approximately 7134 eV and 7136 eV, indicating that the oxidation state of Fe\(^{3+}\) does not transfer into Fe\(^{2+}\) as Sm concentration increases. It is also consistent with the EDS result (Fig. 1), in which BFO5Sm and BFO10Sm exhibit fewer oxygen vacancies. First-principles density functional theory suggests that the incorporation of oxygen vacancies can lead to the formation of the Fe\(^{2+}\) oxidation state [52]. As indicated by the arrow near
Fig. 3. Bright-field TEM images and selected-area diffraction patterns (SADPs).

Fig. 4. Fe K-edge and Sm L₂-edge absorption spectra vs. photon energy. The inset is an enlargement with energy labels for the absorption peaks.

7110 eV, weak pre-edge peaks appear at ~5 eV below the major absorptions and can be attributed to the dipole-forbidden 1s→3d transitions [51,53]. The 1s→3d pre-edge transition is associated with electric quadrupole and dipole states, and involves 4p mixing with the 3d orbital configuration around the Fe site [53]. Fig. 4 also shows the Sm L₂-edge absorption peaks near 7320 eV in BFO5Sm and BFO10Sm, due to the 2p→5d transition [54,55].

Fig. 5(a) shows the Fe L₂,3-edge XAS spectra, which correspond to the transition from the Fe 2p core level to the unoccupied Fe 3d states [56]. The spectra include the L₃ (2p₃/2) band at ~710 eV and the L₂ (2p₁/2) band at ~723 eV. The splittings of the L₂,3 absorptions are due to the t₂g and e₈ orbital configurations [57]. The absorption configurations and energy peaks of the Fe L₂,3 bands are similar to the L₂,3-edge band structures of α-Fe₂O₃ [58,59] and LaFeO₃ as found from first-principles calculations [57]. This result suggests that the dominant oxidation states of the Fe ion are Fe³⁺ in all three compounds and are consistent with the Fe K-edge spectra as revealed in Fig. 4. Fig. 5(b) shows the normalized O K-edge XAS due to the transition from the O 1s core level to O 2p states hybridized with the unoccupied Fe 3d orbital configurations [56,60,61]. The well-resolved profiles in BFO5Sm and BFO10Sm suggest crystalline structures as revealed in the (001) XRD peaks in Fig. 1(a) [62]. The A and B peaks can be identified as the t₂g and e₈ orbital bands separated by the ligand-field (LF) splitting [63,64]. The LF splitting is
associated with the local electrostatic interaction of oxygen with the Fe 3d orbitals [61]. The LF splitting between the $t_{2g}$ and $e_g$ bands are $\sim 1.3$ eV in BFO and $\sim 2$ eV in BF05Sm and BF010Sm. The intensity ratios between the $t_{2g}$ and $e_g$ bands are respectively about 1:8:1.7, 2:4:2.1, and 2:2:2.0 for BFO, BF05Sm, and BF010Sm.

In $\alpha$-Fe$_2$O$_3$, the LF splitting is about 1.3 eV and the intensity ratio of the $t_{2g}$ and $e_g$ bands is approximately 1:1 [60,61]. The intensities of the $t_{2g}$ and $e_g$ bands correlate to the number of Fe 3d holes modulated by the hybridization effects [61]. There are three $t_{2g}$ and two $e_g$ holes in Fe$^{3+}$ associated with the local electrostatic interaction of oxygen with the Fe 3d orbitals [61]. The LF splitting between the up-spin states is $\sim 1.3$ eV and the intensity ratio of $t_{2g}$ and $e_g$ hybridization is stronger than the $O \ 2p - e_g$ hybridization, thus a ratio of 1:1 could be experimentally observed [61]. However, as pointed out by Groot et al. [60], the splitting of the $d$ orbitals is complex and other mechanisms can affect the relative intensities of the $t_{2g}$ and $e_g$ bands, such as electronic exchange interactions and the non-stoichiometry effect. The intensities of the A and B peaks in Fig. 5(b) show strong dependence on the Sm concentration, although their absorption energies do not shift remarkably. This result suggests that the hybridization of the O 2p and Fe 3d states depends on the Sm atomic ratio. In BFO materials, the conduction band is mainly composed of the Fe 3d states hybridized with the O 2p state. Thus, the stronger hybridization of Fe 3d and O 2p in BF05Sm suggest an enhanced electrical conductivity. The energy positions and shapes of the O K-edge bands are very similar to the O K-edge structures of $\alpha$-Fe$_2$O$_3$ [61,63], confirming the Fe$^{3+}$ oxidation state in BFO, BF05Sm, and BF010Sm.

The broad C band in the region of 535–545 eV in Fig. 5(b) can be attributed to the mixture of Bi 6s, Sm 6s, Fe 4s/4p, and O 2p configurations [61,62]. BFO shows a broader C band than BF05Sm and BF010Sm, indicating a highly disordered configuration of electronic states. The broadness of the XAS lines has been considered as an intrinsic property of oxygen vacancies [65]. This result suggests that Sm doping can reduce oxygen vacancies. This phenomenon is consistent with the average oxygen atomic ratios obtained by SEM EDS as given in Fig. 1(c). As indicated by the arrow in Fig. 5(b), the pre-edge peaks occur at $\sim 2$ eV below the A peak and are correlated to the dipole transition from O 1s to O 2p up-spin states hybridized with the unoccupied Fe 3d up-spin states [62]. This implies that the Fe 3d$^3$ orbitals are in the high spin polarization with $\epsilon^2t^2_2$ electron configuration, as based on ligand-field theory [64].

Fig. 6 shows plots of optical transmission and $(\alpha h\nu)^2$ [2] vs. photon energy $(h\nu)$ measured by using a Cary 5E UV-Vis-NIR spectrometer. $h$ and $\nu$ are Planck’s constant and photon frequency. The optical absorption coefficient $\alpha$ was determined by $\alpha = -\ln(T)/d$, where $T$ and $d$ are the measured optical transmission and sample thickness. The optical band gap can be estimated using the Tauc relation [66], $(\alpha h\nu)^2 = A(h\nu - E_g)$, where $E_g$ is the optical band gap between valence and conduction bands, and $A$ is a material-dependent constant. $E_g$ can be evaluated by extrapolating the straight line portions of the curves of $(\alpha h\nu)^2$ vs. $h\nu$ as given in Fig. 6(b). BF05Sm and BF010Sm have smaller $E_g$ values of 2.18 eV and 2.15 eV than $E_g = 2.24$ eV in BFO. Rhombohedral BFO thin films have been reported with direct band gaps in the range of $\sim 2.55 - 2.75$ eV [67–70]. Band gaps of 2.18 and 2.1 eV were reported for BFO nanoparticles [71] and nanocubes (with sizes of 0.05–0.2 μm) [72]. Band gaps of BFO nanoparticles show strong dependence on particle size and were correlated to micro-strain and oxygen defects [73]. From first-principles density functional theory, the oxygen vacancies (OVs) in BFO can shift the optical absorption to lower energy below the conduction band [74,75]. The slightly different band gaps in BFO, BF05Sm, and BF010Sm may be correlated to OVs and grain sizes.

Fig. 7 shows PV open-circuit voltages $(V_{oc})$ and short-circuit current densities $(J_{sc})$ of ITO/(Bi$_{1-x}$Sm$_x$)FeO$_3$/Au heterostructures (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$^2$. [76]
as the laser (\( \lambda = 405 \text{ nm} \)) was switched on and off with increasing illumination intensity (\( I \)) by steps. The illumination-intensity dependent \( V_{oc} \) and \( J_{sc} \) are plotted in Fig. 8(a) and (b). The \( \text{ITO}/(\text{Bi}_{1-x}\text{Sm}_{x})\text{FeO}_{3}/\text{Au} \) heterostructures exhibit rapid increase in PV response below \( I \sim 50 \text{ mW/cm}^2 \). We apply a previously developed \( p-n \)-junction-like model to describe \( V_{oc} \) and \( J_{sc} \) as functions of illumination intensity [76]. The photodiode current \( i_d \) under a bias voltage \( V \) is expressed as [77].

\[
id = i_b \left\{ \exp \left[ \frac{q(V - i_d R_b)}{\varepsilon_0 \varepsilon_n kT} \right] - 1 \right\}.
\]

Here, \( i_b \), \( R_b \), and \( \varepsilon \) are dark current, source resistance, and diode-quality factor, respectively. To estimate \( i_d \), \( R_b \), and \( \varepsilon \), the characteristic curves were measured in the dark as shown in Fig. 9. By using Eq. (1) with \( q \sim 1.6 \times 10^{-19} \text{ C} \) and \( T = 300 \text{ K} \), we obtained \( i_b \), \( R_b \), and \( \varepsilon \) as given in Fig. 9. From Eq. (1), the illuminated \( i \) can be expressed as [76].

\[
i = i_p - i_d = i_p - i_b \exp[(V - (i_d - i_b) R_b) q / (\varepsilon_0 \varepsilon_n kT)] - 1.
\]

where \( i_p \), \( i_d \), and \( V \) are the photovoltaic current, diode current, and measured voltage. Through a considerable derivation [76], the PV open-circuit voltage \( V_{oc} \) and short-circuit current \( I_{sc} \) can be expressed as [76].

\[
V_{oc} = U_0 - B\beta^2 i_0 \left[ \exp(V_{oc} q / (\varepsilon_0 \varepsilon_n kT)) - 1 \right] 2 (qS\lambda I \text{hc})^2
\]

\[
i_{sc} = \frac{U_0}{R_s} - B\beta^2 \frac{i_{sc} + i_0 \exp[i_{sc} R_0 q / (\varepsilon_0 \varepsilon_n kT)] - 1}{R_s q (\varepsilon_0 \varepsilon_n kT)}
\]

\[
B = \frac{qI_{ph}}{2\varepsilon_0 \varepsilon_n}
\]

where \( S, h, c, \lambda \) are illumination area, light wavelength, Planck constant, light speed, and illumination intensity. \( U_0 \) is the voltage barrier across the depletion region in the dark. \( B \) is the optical attenuation length determined directly from the optical transmission in Fig. 6(a), i.e. \( \beta = -d / \ln(T) \). The measured \( B \) values at \( \lambda = 405 \text{ nm} \) are respectively about 2.0, 1.0, and 1.0 \( \mu \text{m} \) for \( \text{BFO}, \text{BFO}_{0.1}\text{Sm}_{0.9} \), and \( \text{BFO}_{0.1}\text{Sm}_{0.9} \). \( n_p \) and \( n_n \) are carrier densities of \( p \)-type \( (\text{Bi}_{1-x}\text{Sm}_{x})\text{FeO}_{3} \) and \( n \)-type ITO film, \( \varepsilon_p \) and \( \varepsilon_n \) are \( p \)-type and \( n \)-type dielectric permittivities. \( \varepsilon_p \) values of \( \text{BFO}, \text{BFO}_{0.1}\text{Sm}_{0.9} \), and \( \text{BFO}_{0.1}\text{Sm}_{0.9} \) ceramics are respectively about 100, 145, and 108 for measuring frequency \( f = 1 \text{ MHz} \) at room temperature. The reported carrier density [78] and dielectric permittivity [79] of \( n \)-type ITO thin films are \( n_n \sim 10^{21} \text{ cm}^{-3} \) and \( \varepsilon_n \sim 4 \) at photon energy of 3 eV. From Eq. (5), the calculated \( n_p \) values are about \( 3 \times 10^{20}, 3 \times 10^{19}, \) and \( 2 \times 10^{20} \text{ cm}^{-3} \) for \( \text{BFO}, \text{BFO}_{0.1}\text{Sm}_{0.9} \), and \( \text{BFO}_{0.1}\text{Sm}_{0.9} \) ceramics, respectively. The junction widths in the dark, \( d_j \sim (U_0/B)^{1/2} \) [76], are about 2, 17, and 3 nm for \( \text{BFO}, \text{BFO}_{0.1}\text{Sm}_{0.9} \), and \( \text{BFO}_{0.1}\text{Sm}_{0.9} \), respectively. The solid lines in Figs. 8(a) and (b) are fits of \( V_{oc} \) and \( J_{sc} \) by using Eqs. (3) and (4) with fitting parameters in Fig. 8(a). The theoretical fits of \( V_{oc} \) agree well quantitatively with experimental data. The fits of \( J_{sc} \) in Fig. 8(b) show discrepancies with the experimental points in the low-illumination region for \( \text{ITO}/\text{BFO}_{0.1}\text{Sm}_{0.9}/\text{Au} \), likely due to the leakage currents. Note that this \( p-n \)-junction-like model only considers the photo-excited electron-hole creation [76]. Other factors, such as oxygen and \( \text{Bi} \) vacancies, domain structure, electronic states, and charge recombination may influence the conductivity [73].

Fig. 8(c) shows external quantum efficiencies (EQE) calculated from the short-circuit current density \( J_{sc} \) in Fig. 8(b). The EQE is the conversion efficiency from incident photons to conduction electrons, i.e. \( \text{EQE} = \frac{h \nu J_{sc}}{qI_{ph}} \) [76], where \( I_{ph} \) and \( \nu \) are light intensity and electron charge. The maximal EQE of \( \text{ITO}/\text{BFO}_{0.1}\text{Sm}_{0.9}/\text{Au} \) reaches about 4%, which is significantly higher than the 0.00003% reported in the Pt/\( \text{ITO} \) crystal/\( \text{Pt} \) configuration under illumination of \( \lambda = 405 \text{ nm} \) [23], and is comparable to the 10% observed in ITO/BFO/SrRuO\(_3 \) at ultraviolet wavelength of \( \lambda = 325 \text{ nm} \) [41].

Fig. 10 gives curves of power-conversion efficiency (\( \eta \)) vs. load voltage \( (V) \) for several illumination intensities. The power-conversion efficiencies were calculated using \( P_{out} = P_{in} \eta \) and \( P_{out} \)
Fig. 8. (a) $V_{oc}$, (b) $J_{sc}$, and (c) external quantum efficiencies (EQE) as a function of illumination intensity. The solid lines in (a) and (b) are theoretical fits of Eq. (3) and (4) with parameters in (a). The dashed lines in (c) are guides for the eye.

Fig. 9. Characteristic curves of current vs. bias voltage without illumination. The solid lines are fits of Eq. (1) with parameters given in the Figure.

Fig. 10. Power-conversion efficiency ($\eta$) vs. load voltage for various illumination intensities.

are respectively the incident illumination power and electric power output measured from the curves of current vs. load voltage under illumination. The maximal PV power-conversion efficiencies ($\eta_{max}$) occur at low light intensities and reach respectively about 0.017%, 0.37%, and 0.13% for ITO/BFO/Au, ITO/BFO5Sm/Au, and ITO/BFO10Sm/Au. The microstructure, domain structures, polarization, and electronic states are believed to play important roles in the photovoltaic conductivity [80]. Compared with BFO as shown in Fig. 1(d), BFO5Sm and BFO10Sm ceramics exhibit a relatively stronger (1 0 0) orientation, which may enhance the photocurrent, similar to the effect of ordered polarization as reported in (1 0 0) oriented BFO films [81,82].

To compare the photovoltaic responses with previous reports, a brief summary of photovoltaic studies in some major perovskite ferroelectric and BFO-related materials is given in Table 1, including the results from this work. At low illumination intensity, the ITO/BFO5Sm/Au heterostructure has demonstrated comparable photovoltaic open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), power-conversion efficiency ($\eta_{max}$), and external quantum efficiency (EQE) with most other PV devices using perovskite ferroelectric and BiFeO$_3$ thin films and crystals as listed in Table 1.
4. Conclusions

Enhanced photovoltaic (PV) responses have been observed in ITO/[Bi1-xSmx]FeO3/Au heterostructures for x = 0.05 and 0.10 under near-ultraviolet irradiation of λ = 405 nm. The maximal PV power-conversion and external quantum efficiencies reach 0.37% and 4.1% in ITO/[Bi1-xSmx]FeO3/Au. The PV open-circuit voltage and short-circuit current density can be described quantitatively by a p-n-junction-like theoretical model as functions of illumination intensity. This work reveals that oxygen vacancies were reduced by A-site Sm3+ substitution. A slight shift toward higher energies was observed in the Fe K-edge absorption spectra due to the A-site Sm3+ substitution. Domain structures and hybridization between the O 2p and Fe 3d electronic configurations play important roles in the enhanced PV effects. The oxygen K-edge absorption indicates that the A-site Sm substitution enhances hybridization of the O 2p and unoccupied Fe 3d states. The optical band gaps of BFO, BFO5Sm, and BFO10Sm are respectively about 2.24, 2.18, and 2.15 eV.

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