Enhanced photovoltaic effects in A-site samarium doped BiFeO₃ ceramics: The roles of domain structure and electronic state

Authors: C.- S. Tu, C.- S. Chen, P.- Y. Chen, H.- H. Wei, V. Hugo Schmidt, C.- Y. Lin, J. Anthoniappen, and J.- M. Lee

NOTICE: this is the author's version of a work that was accepted for publication in Journal of the European Ceramic Society. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in [Journal of the European Ceramic Society](#), VOL# 36, ISSUE# 5, (2015), DOI: [10.1016/j.jeurceramsoc.2015.12.019](#).

C.- S. Tu, C.- S. Chen, P.- Y. Chen, H.- H. Wei, V. Hugo Schmidt, C.- Y. Lin, J. Anthoniappen, and J.- M. Lee, "Enhanced photovoltaic effects in A-site samarium doped BiFeO₃ ceramics: The roles of domain structure and electronic state," Journal of the European Ceramic Society 36, 1149-1157 (2015). doi: 10.1016/j.jeurceramsoc.2015.12.019.

Enhanced photovoltaic effects in A-site samarium doped BiFeO₃ ceramics: The roles of domain structure and electronic state

Chi-Shun Tu^{a,*}, Cheng-Sao Chen^b, Pin-Yi Chen^c, Hsiu-Hsuan Wei^a, V.H. Schmidt^d, Chun-Yen Lin^a, J. Anthoniappen^e, Jenn-Min Lee^f

^a Department of Physics, Fu Jen Catholic University, New Taipei City 24205, Taiwan

^b Department of Mechanical Engineering, Hwa Hsia University of Technology, New Taipei City 23567, Taiwan

^c Department of Mechanical Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan

^d Department of Physics, Montana State University, Bozeman, MT 59717, USA

^e Department of Physics, University of San Carlos, Cebu 6000, Philippines

^f National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

ABSTRACT

This work reports enhanced photovoltaic (PV) responses of (Bi_{1-x}Sm_x)FeO₃ ($x=0.0, 0.05, 0.10$) ceramics (BFO100xSm) with ITO film under near-ultraviolet irradiation ($\lambda=405$ nm). The ceramics were characterized by micro-Raman scattering, high-resolution transmission electron microscopy, and synchrotron X-ray absorption spectroscopy (XAS). A rhombohedral R3c symmetry with tilted FeO₆ octahedra has been confirmed. The Fe *K*-edge absorption spectra reveal a slight shift toward higher energy as A-site Sm³⁺ 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 BiFeO₃ related systems are the most studied candidates because of their room-temperature antiferromagnetic behavior (Néel temperature, $T_N \sim 630$ K) and ferroelectric properties (Curie temperature, $T_C \sim 1100$ 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 Bi³⁺ toward O²⁻ [2]. It was reported that the Curie temperature T_C in rare-earth-doped compositions of (Bi_{1-x}RE_x)FeO₃ (RE = La, Nd, Sm, Gd) decreases with decreasing average A-site ionic polarizability and tolerance factor [3]. Rhombohedral R3c BiFeO₃ displays a G-type antiferromagnetic order, in which each spin in the Fe³⁺ 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 Bi³⁺ 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 (Bi_{1-x}RE_x)FeO₃ (RE = La, Nd, Sm, Gd) for $x \leq 0.1$ correspond to the perovskite rhombohedral R3c phase of BiFeO₃ [3]. The (Bi_{1-x}Sm_x)FeO₃ 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 (Bi_{1-x}Sm_x)FeO₃ ceramics [6]. Temperature-dependent dielectric permittivity results suggest that the magnetic Néel temperature (T_N) decreases with increasing Sm³⁺ concentration for $x=1-8\%$ [7]. (Bi_{1-x}Sm_x)FeO₃ ceramics and thin films show enhanced magnetization with increasing Sm ratio [12–16]. (Bi_{1-x}Sm_x)FeO₃ ceramics show a magnetic structure transition from a spin cycloid to a G-type antiferromagnetic behavior at $x \sim 14\%$ [15,16].

Fig. 1. (a-c) SEM grain morphologies of thermally etched ceramics and (d) XRD spectra of as-sintered samples at room temperature. $\bar{D}$ and $\bar{A}_O$ are average grain size and average oxygen atomic ratio, respectively.

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_{Bi}) have lower formation energy than oxygen vacancies under oxygen-rich condition and thus V_{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 2*p* and the unoccupied Fe 3*d* 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), $(\text{Bi}_{0.95}\text{Sm}_{0.05})\text{FeO}_3$ (BFO5Sm), and $(\text{Bi}_{0.90}\text{Sm}_{0.10})\text{FeO}_3$ (BFO10Sm) ceramics were prepared by the solid state reaction, in which Bi_2O_3 , Sm_2O_3 , and Fe_2O_3 powders (purity $\geq 99.0\%$) 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 $\lambda = 532$ nm and a TE-cooled CCD detector. A high-resolution TEM (JEOL JEM-2100 LaB₆) 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 ($\lambda = 405$ nm) was used as the excitation source and the illuminated area (also ITO area) is ~ 0.15 cm² [2]. The ceramic thicknesses are 0.2 mm for BFO and 0.15 mm for BFO5Sm and BFO10Sm.

3. Results and discussion

Fig. 1(a–c) shows grain morphologies of thermally etched ceramics with average grain sizes ($\bar{D}$) of 3.4, 1.8, and 1.3 μm for BFO, BFO5Sm, and BFO10Sm. As labeled in Fig. 1(a–c), the average oxygen atomic ratios ($\bar{A}_O$) 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 (100) and (200) peaks, suggesting a preferred (100) crystallographic orientation in the ceramic grains. As illustrated by the dashed line, XRD peaks of BFO5Sm and BFO10Sm shift toward higher 2θ , 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_2O_3 , Bi_2O_3 , and Sm_2O_3 powders. The Raman

Fig. 2. (a) Raman spectra in the region of 50–600 cm^{-1} and (b) fitting modes in the region of 50–250 cm^{-1} . The labeled numbers are frequencies and full-width at half maxima (in parentheses). The red line is the sum of the fitting curves.

spectra suggest no second phase from incomplete reaction in the as-sintered Sm-doped compounds. The Raman active modes in the $R3c$ rhombohedral BFO can be represented by $\Gamma = 4A_1 + 9E$ [45–47]. BFO, BFO5Sm, and BFO10Sm exhibit similar Raman vibrations, confirming the same $R3c$ 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 $A_1(2)$, 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 $A_1(2)$ 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. 3 shows the high-resolution bright-field TEM images (top) and the selected-area diffraction patterns (SADPs). The inset in Fig. 3(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 $[1\bar{1}0]$ zone axis. The $[1\bar{1}0]$ -viewed SADPs reveal $1/2(111)$ (or $1/2(000)$) superlattice diffraction spots without appearance of $1/2(00e)$ 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 $R3c$ symmetry [49,50]. The high-resolution TEM confirms the rhombohedral $R3c$ space group as suggested by the XRD (Fig. 1d) and Raman spectra (Fig. 2). The intensity of the $1/2(111)$ 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 and Fe_2O_3 . The Fe K-edge absorption arises primarily from the $1s \rightarrow 4p$ 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 Fe_2O_3 . 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 L_2 -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 $1s \rightarrow 3d$ transitions [51,53]. The $1s \rightarrow 3d$ 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 L_2 -edge absorption peaks near 7320 eV in BFO5Sm and BFO10Sm, due to the $2p \rightarrow 5d$ transition [54,55].

Fig. 5(a) shows the Fe $L_{2,3}$ -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 L_3 ($2p_{3/2}$) band at ~ 710 eV and the L_2 ($2p_{1/2}$) band at ~ 723 eV. The splittings of the $L_{2,3}$ absorptions are due to the t_{2g} and e_g orbital configurations [57]. The absorption configurations and energy peaks of the Fe $L_{2,3}$ bands are similar to the $L_{2,3}$ -edge band structures of α -Fe $_2$ O $_3$ [58,59] and LaFeO $_3$ as found from first-principles calculations [57]. This result suggests that the dominant oxidation states of the Fe ion are Fe $^{3+}$ in all three compounds and are consistent with the Fe K-edge spectra as

Fig. 5. (a) Fe $L_{2,3}$ -edges and (b) O K-edge absorption spectra vs. photon energy.

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 t_{2g} and e_g 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 splittings between the t_{2g} and e_g bands are ~ 1.3 eV in BFO and ~ 2 eV in BFO5Sm and BFO10Sm. 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, BFO5Sm, and BFO10Sm.

In α -Fe₂O₃, 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 iron and thus an intensity ratio of 3:2 is expected without the hybridization effect in α -Fe₂O₃ [61]. As the e_g orbitals shift toward the oxygen ligands, the O 2p- e_g hybridization is stronger than the O 2p- t_{2g} 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 state hybridized with the O 2p state. Thus, the stronger hybridization of Fe 3d and O 2p in BFO5Sm 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 α -Fe₂O₃ [61,63], confirming the Fe³⁺ oxidation state in BFO, BFO5Sm, and BFO10Sm.

The broad C band in the region of 535–545 eV in Fig. 5(b) can be attributed to the mixture of Bi 6p, Sm 6s, Fe 4s/4p, and O 2p configurations [61,62]. BFO shows a broader C band than BFO5Sm and BFO10Sm, 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 ~ 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 orbitals are in the high spin polarization with $e_g^2 t_{2g}^3$ electron configuration, as based on ligand-field theory [64].

Fig. 6 shows plots of optical transmission and $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) measured by using a Cary 5E UV-Vis-NIR spectrometer. h and ν are Planck's constant and photon frequency. The optical absorption coefficient α 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). BFO5Sm and BFO10Sm have smaller E_g values of 2.18 eV and 2.15 eV than $E_g \sim 2.24$ eV in BFO. Rhombohedral BFO thin films have been reported with direct band gaps in the range of ~ 2.55 – 2.75 eV [67–70]. Band gaps of 2.18 and 2.1 eV were reported respectively 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, BFO5Sm, and BFO10Sm 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)FeO₃/Au heterostructures

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

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 .

Table 1

Comparison of PV studies in perovskite ferroelectric and BiFeO₃ materials. PZT = Pb(Zr,Ti)O₃; PLZT = (Pb,La)(Zr,Ti)O₃; BSFCO = (Bi_{0.9}Sm_{0.1})(Fe_{0.95}Co_{0.05})O₃; LSCO = (La_{0.67}Sr_{0.33})CoO₃; LSMO = (La,Sr)MnO₃; STO = SrTiO₃; SRO = SrRuO₃; AZO = Al₂O₃-ZnO. ITO is indium tin oxide. FTO is a commercial glass substrate.

Photovoltaic heterostructures	V _{oc} (V)	J _{sc} (mA/cm ²)	Light wavelength λ (nm)	Light intensity (mW/cm ²)	Efficiency (%)
Pt/PZT(52/48)/Ni [17]	0.8	6 × 10 ⁻⁵	300–390	1.0	
Pt/PZT(20/80)/Pt [18]		8 × 10 ⁻³	350–450	10	
ITO/poly-PZT(53/47)/ITO [19]	0.25	5 × 10 ⁻⁶	632	0.45	0.22
Nb:STO/PLZT(3/52/48)/LSMO [20]	0.7	0.0008		0.06	0.28
ITO/PZT/Cu ₂ O/Pt [83]	0.4	4.5	Sunlight	100	0.57
ITO/BFO/SRO [21]	0.3	4 × 10 ⁻⁴	435	0.75	
Pt/BFO/Pt [22]	20	0.05	375	100	
Pt/BFO crystal/Pt [23]	13	0.001	405		3 × 10 ⁻⁵ (EQE)
ZnO:Al/BFO/LSCO [24,25]	0.22	0.004	White light	1	
Pt/BFO/SRO [26]	0.08	0.063	White light	100	
Pt/BSFCO/Pt [27]	0.9	5 × 10 ⁻⁵	White light	100	
Pt/0.9BFO-0.1YCrO ₃ /Pt [28]	0.51	0.00148	Sunlight	100	
Pt/BFO/STO [29]	3.9	2.6 × 10 ⁻⁴	White light	100	
Nb:STO/BFO/Au [32]	0.04	6	White light	285	0.03
Ag/Pt-BFO NTs/Ag [33]	0.2		Sunlight	10	0.5
AZO/poly-BFO/FTO [34]	0.63	0.13	Sunlight	100	0.0208 7 (EQE) at λ = 340 nm
Fe/BFO/LSMO/STO [35]	0.21	6 × 10 ⁻⁴	White light	20	
Au/BFO/Au [36]		0.0075	532	<20	
Graphene/poly-BFO/Pt [37]	0.44	0.025	Sunlight	100	
ITO/poly-BFO/Pt [38]	0.1	0.0025		0.45	0.125
Pt/BFO/Pt [40]	16	0.12	White light	285	
ITO/BFO/SRO [41]	0.8–	1.5	Sunlight	285	10 (EQE) at λ = 325 nm
ITO/BFO ceramic/Au (this work)	0.58	0.005	405	10	0.005 0.16 (EQE)
TO/BFO5Sm ceramic/Au (this work)	0.7	0.094	405	10	0.25 3.0 (EQE)

as the laser (λ = 405 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 ITO/(Bi_{1-x}Sm_x)FeO₃/Au heterostructures exhibit rapid increase in PV response below *I* ~ 50 mW/cm². 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].

$$i_d = i_0 \left\{ \exp \left[\frac{q(V - i_d R_s)}{\xi k_B T} \right] - 1 \right\}. \quad (1)$$

Here, *i*₀, *R*_s, and ξ are dark current, source resistance, and diode-quality factor, respectively. To estimate *i*₀, *R*_s, and ξ , the characteristic curves were measured in the dark as shown in Fig. 9. By using Eq. (1) with *q* = 1.6 × 10⁻¹⁹ C and *T* = 300 K, we obtained *i*₀, *R*_s, and ξ as given in Fig. 9. From Eq. (1), the illuminated *i* can be expressed as [76].

$$i = i_p - i_d = i_p - i_0 \left(\exp \left[\frac{q(V - (i_d - i_p) R_s)}{\xi k_B T} \right] - 1 \right). \quad (2)$$

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].

$$V_{oc} = U_0 - B \beta^2 i_0^2 \frac{[\exp(V_{oc} q / \xi k_B T) - 1]^2}{(q S \lambda I / h c)^2} \quad (3)$$

$$i_{sc} = \frac{U_0}{R_s} - B \beta^2 \frac{i_{sc} + i_0 [\exp(i_{sc} R_s q / \xi k_B T) - 1]^2}{R_s (q S \lambda I / h c)^2} \quad (4)$$

$$B = \frac{q n_p}{2 \varepsilon_0 \varepsilon_p} \left(1 + \frac{n_p \varepsilon_p}{\varepsilon_n n_n} \right) \quad (5)$$

where *S*, λ , *h*, *c*, and *I* 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. β is the optical attenuation length determined directly from the optical transmission in Fig. 6(a), i.e. $\beta = -d / \ln(T)$. The measured β values at λ = 405 nm are respectively about 2.0, 1.0 and 1.0 μm for BFO, BFO5Sm, and BFO10Sm. *n*_p and *n*_n are carrier densities of *p*-type (Bi_{1-x}Sm_x)FeO₃ ceramics and *n*-type ITO film. ε_p and ε_n are *p*-type and *n*-type dielectric permittivities. ε_p values of BFO, BFO5Sm, and BFO10Sm ceramics are respectively about 100, 145, and 108 for measuring frequency *f* = 1 MHz at room temperature. The reported carrier density [78] and dielectric permittivity [79] of *n*-type ITO thin films are *n*_n ~ 10²¹ cm⁻³ and ε_n ~ 4 at photon energy of 3 eV. From Eq. (5), the calculated *n*_p values are about 3 × 10²⁰, 3 × 10¹⁹, and 2 × 10²⁰ cm⁻³ for BFO, BFO5Sm, and BFO10Sm ceramics, respectively. The junction widths in the dark, *d*₀ ~ (*U*₀/*B*)^{1/2} [76], are about 2, 17, and 3 nm for BFO, BFO5Sm, and BFO10Sm, respectively.

The solid lines in Figs. 8(a) and (b) are fits of *V*_{oc} and *J*_{sc} (= *i*_{sc}/*S*) 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 ITO/BFO5Sm/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 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. $EQE = h f J_{sc} / q_e I$ [76], where *I* and *q_e* are light intensity and electron charge. The maximal EQE of ITO/BFO5Sm/Au reaches about 4%, which is significantly higher than the 0.00003% reported in the Pt/BFO crystal/Pt configuration under illumination of λ = 405 nm [23], and is comparable to the 10% observed in ITO/BFO/SrRuO₃ at ultraviolet wavelength of λ = 325 nm [41].

Fig. 10 gives curves of power-conversion efficiency (η) vs. load voltage (*V*) for several illumination intensities. The power-conversion efficiencies were calculated using *P*_{out}/*P*_{in}, *P*_{in} 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 (η) 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 (η_{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 (100) orientation, which may enhance the photocurrent, similar to the effect of ordered polarization as reported in (100) 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 (P_{out}/P_{in}), and external quantum efficiency (EQE) with most other PV devices using perovskite ferroelectric and BiFeO₃ thin films and crystals as listed in Table 1.

4. Conclusions

Enhanced photovoltaic (PV) responses have been observed in ITO/(Bi_{1-x}Sm_x)FeO₃/Au heterostructures for $x = 0.05$ and 0.10 under near-ultraviolet irradiation of $\lambda = 405$ nm. The maximal PV power-conversion and external quantum efficiencies reach 0.37% and 4.1% in ITO/BFO5Sm/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.

Acknowledgement

This work is supported by the Ministry of Science and Technology of Taiwan under Project Nos. MOST 104-2221-E-030-014, 104-2221-E-146-001, and 102-2221-E-131-006.

References

- [1] G. Catalan, J.F. Scott, Physics and applications of bismuth ferrite, *Adv. Mater.* 21 (2009) 2463–2485.
- [2] P. Ravindran, R. Vidya, A. Kjekshus, H. Fjellvåg, O. Eriksson, Theoretical investigation of magnetoelectric behavior in BiFeO₃, *Phys. Rev. B* 74 (2006) 224412 (18pp).
- [3] S. Karimi, I.M. Reaney, Y. Han, J. Pokorny, I. Sterianou, Crystal chemistry and domain structure of rare-earth doped BiFeO₃ ceramics, *J. Mater. Sci.* 44 (2009) 5102–5112.
- [4] I. Sosnowska, T. Peterlin-Neumaier, E. Steichele, Spiral magnetic ordering in bismuth ferrite, *J. Phys. C* 15 (1982) 4835–4846.
- [5] D.C. Arnold, Composition-driven structural phase transitions in rare-earth doped BiFeO₃ ceramics: a review, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* 62 (2015) 62–82.
- [6] X. Chen, Y. Wang, Y. Yang, G. Yuan, J. Yin, Z. Liu, Structure, ferroelectricity and piezoelectricity evolutions of Bi_{1-x}Sm_xFeO₃ at various temperatures, *Solid State Commun.* 152 (2012) 497–500.
- [7] Y.B. Yao, W.C. Liu, C.L. Mak, Pyroelectric properties and electrical conductivity in samarium doped BiFeO₃ ceramics, *J. Alloys Compd.* 527 (2012) 157–162.
- [8] S.-T. Zhang, Y. Zhang, M.-H. Lu, C.-L. Du, Y.-F. Chen, Z.-G. Liu, Y.-Y. Zhu, N.-B. Ming, X.Q. Pan, Substitution-induced phase transition and enhanced multiferroic properties of Bi_{1-x}La_xFeO₃ ceramics, *Appl. Phys. Lett.* 88 (2006) 162901 (3pp).
- [9] Q.H. Jiang, C.W. Nan, Synthesis and properties of multiferroic La-modified BiFeO₃ ceramics, *J. Am. Ceram. Soc.* 89 (2006) 2123–2127.
- [10] Y.H. Lin, Q. Jiang, Y. Wang, C.W. Nan, L. Chen, J. Yu, Enhancement of ferromagnetic properties in BiFeO₃ polycrystalline ceramic by La doping, *Appl. Phys. Lett.* 90 (2007) 172507 (3pp).
- [11] G.L. Yuan, S.W. Or, J.M. Liu, Z.G. Liu, Structural transformation and ferroelectromagnetic behavior in single-phase Bi_{1-x}Nd_xFeO₃ multiferroic ceramics, *Appl. Phys. Lett.* 89 (2006) 052905 (3pp).
- [12] G.L. Yuan, S.W. Or, Multiferroicity in polarized single-phase Bi_{0.875}Sm_{0.125}FeO₃ ceramics, *J. Appl. Phys.* 100 (2006) 024109 (5pp).
- [13] D. Maurya, H. Thota, A. Garg, B. Pandey, P. Chand, H.C. Verma, Magnetic studies of multiferroic Bi_{1-x}Sm_xFeO₃ ceramics synthesized by mechanical activation assisted processes, *J. Phys.: Condens. Matter* 21 (2009) 026007 (6pp).
- [14] X. Xu, T. Guoqiang, R. Huijun, X. Ao, Structural, electric and multiferroic properties of Sm-doped BiFeO₃ thin films prepared by the sol–gel process, *Ceram. Int.* 39 (2013) 6223–6228.
- [15] S. Maruyama, V. Anbusathaiah, A. Fennell, M. Enderle, I. Takeuchi, W.D. Ratcliff, Change in the magnetic structure of (Bi,Sm)FeO₃ thin films at the morphotropic phase boundary probed by neutron diffraction, *Appl. Mater.* 2 (2014) 116106 (7pp).
- [16] V.A. Khomchenko, J.A. Paixão, B.F.O. Costa, D.V. Karpinsky, A.L. Kholkin, I.O. Troyanchuk, V.V. Shvartsman, P. Borisov, W. Kleemann, Structural, ferroelectric and magnetic properties of Bi_{0.85}Sm_{0.15}FeO₃ perovskite, *Cryst. Res. Technol.* 46 (2011) 238–242.
- [17] V. Yarmarkin, B. Goltzman, M. Kazanian, V. Lemanov, Barrier photovoltaic effects in PZT ferroelectric thin films, *Phys. Solid State* 42 (2000) 522–527.
- [18] F. Zheng, J. Xu, L. Fang, M. Shen, X. Wu, Separation of the Schottky barrier and polarization effects on the photocurrent of Pt sandwiched Pb(Zr_{0.20}Ti_{0.80})O₃ films, *Appl. Phys. Lett.* 93 (2008) 172101 (3pp).
- [19] B. Chen, Z. Zuo, Y. Liu, Q.-F. Zhan, Y. Xie, H. Yang, G. Dai, Z. Li, G. Xu, R.-W. Li, Tunable photovoltaic effects in transparent Pb(Zr_{0.53}Ti_{0.47})O₃ capacitors, *Appl. Phys. Lett.* 100 (2012) 173903 (4pp).
- [20] M. Qin, K. Yao, Y.C. Liang, High efficient photovoltaics in nanoscaled ferroelectric thin films, *Appl. Phys. Lett.* 93 (2008) 122904 (3pp).
- [21] W. Ji, K. Yao, Y.C. Liang, Bulk photovoltaic effect at visible wavelength in epitaxial ferroelectric BiFeO₃ thin films, *Adv. Mater.* 22 (2010) 1763–1766.
- [22] J. Seidel, D. Fu, S.-Y. Yang, E. Alarcón-Lladó, J. Wu, R. Ramesh, J.W. Ager III, Efficient photovoltaic current generation at ferroelectric domain walls, *Phys. Rev. Lett.* 107 (2011) 126805 (4pp).
- [23] M. Alexe, D. Hesse, Tip-enhanced photovoltaic effects in bismuth ferrite, *Nat. Commun.* 2 (2011) 256 (5pp).
- [24] R.K. Katiyar, A. Kumar, G. Morell, J.F. Scott, R.S. Katiyar, Photovoltaic effect in a wide-area semiconductor-ferroelectric device, *Appl. Phys. Lett.* 99 (2011) 092906 (3pp).
- [25] R.K. Katiyar, A. Kumar, G. Morell, J.F. Scott, R.S. Katiyar, Erratum: photovoltaic effect in a wide-area semiconductor-ferroelectric device, *Appl. Phys. Lett.* 99 (2011) 092906, *Appl. Phys. Lett.* 2011;99:159902 (1pp).
- [26] R.K. Katiyar, P. Misra, S. Sahoo, G. Morell, R.S. Katiyar, Enhanced photoresponse in BiFeO₃/SrRuO₃ heterostructure, *J. Alloys Compd.* 609 (2014) 168–172.
- [27] V.S. Puli, D.K. Pradhan, R.K. Katiyar, I. Coondoo, N. Panwar, P. Misra, D.B. Chrisey, J.F. Scott, R.S. Katiyar, Photovoltaic effect in transition metal modified polycrystalline BiFeO₃ thin films, *J. Phys. D: Appl. Phys.* 47 (2014) 075502 (6pp).
- [28] Y. Sharma, P. Misra, R.K. Katiyar, R.S. Katiyar, Photovoltaic effect and enhanced magnetization in 0.9(BiFeO₃)-0.1(YCrO₃) composite thin film fabricated using sequential pulsed laser deposition, *J. Phys. D: Appl. Phys.* 47 (2014) 425303 (6pp).
- [29] R.K. Katiyar, P. Misra, G. Morell, R.S. Katiyar, Effect of poling on photovoltaic properties in highly oriented BiFeO₃ thin films, *Integr. Ferroelectr.* 157 (2014) 168–173.
- [30] R.K. Katiyar, P. Misra, G.L. Sharma, G. Morell, J.F. Scott, R.S. Katiyar, Unipolar resistive switching and associated photoresponse in Sm doped BiFeO₃ thin film grown by RF sputtering, *Mater. Res. Soc. Symp. Proc.* 157 (2013) 7, <http://dx.doi.org/10.1557/opl.2013.072>.
- [31] R.K. Katiyar, Y. Sharma, D.G.B. Diestra, P. Misra, S. Kooriyattil, S.P. Pavunny, G. Morell, B.R. Weiner, J.F. Scott, R.S. Katiyar, Unipolar resistive switching in planar Pt/BiFeO₃/Pt structure, *AIP Adv.* 5 (2015) 037109 (6pp).
- [32] T.L. Qu, Y.G. Zhao, D. Xie, J.P. Shi, Q.P. Chen, T.L. Ren, Resistance switching and white-light photovoltaic effects in BiFeO₃/Nb-SrTiO₃ heterojunctions, *Appl. Phys. Lett.* 98 (2011) 173507 (3pp).
- [33] G.G. Khan, R. Das, N. Mukherjee, K. Mandal, Effect of metal doping on highly efficient photovoltaics and switchable photovoltage in bismuth ferrite nanotubes, *Phys. Status Solidi RRL* 6 (2012) 312–314.
- [34] W. Dong, Y. Guo, B. Guo, H. Liu, H. Li, H. Liu, Photovoltaic properties of BiFeO₃ thin film capacitors by using Al-doped zinc oxide as top electrode, *Mater. Lett.* 91 (2012) 359–361.
- [35] R. Guo, L. You, Y. Zhou, Z.S. Lim, X. Zou, L. Chen, R. Ramesh, J. Wang, Non-volatile memory based on the ferroelectric photovoltaic effect, *Nat. Commun.* 4 (2013) 1990 (5pp).
- [36] T. Choi, S. Lee, Y.J. Choi, V. Kiryukhin, S.W. Cheong, Switchable ferroelectric diode and photovoltaic effect in BiFeO₃, *Science* 324 (2009) 63–66.
- [37] Y. Zang, D. Xie, X. Wu, Y. Chen, Y. Lin, M. Li, H. Tian, X. Li, Z. Li, H. Zhu, H.T. Ren, D. Plant, Enhanced photovoltaic properties in graphene/polycrystalline BiFeO₃/Pt heterojunction structure, *Appl. Phys. Lett.* 99 (2011) 132904 (3pp).
- [38] B. Chen, M. Li, Y. Liu, Z. Zuo, F. Zhuge, Q.F. Zhan, R.W. Li, Effect of top electrodes on photovoltaic properties of polycrystalline BiFeO₃ based thin film capacitors, *Nanotechnology* 22 (2011) 195201 (5pp).
- [39] W. Ji, K. Yao, Y.C. Liang, Evidence of bulk photovoltaic effect and large tensor coefficient in ferroelectric BiFeO₃ thin films, *Phys. Rev. B* 84 (2011) 094115 (5pp).
- [40] S.Y. Yang, J. Seidel, S.J. Byrnes, P. Shafer, C.H. Yang, M.D. Rossell, P. Yu, Y.H. Chu, J.F. Scott, J.W. Ager III, L.W. Martin, R. Ramesh, Above-bandgap voltages from ferroelectric photovoltaic devices, *Nat. Nanotechnol.* 5 (2010) 143–147.
- [41] S.Y. Yang, L.W. Martin, S.J. Byrnes, T.E. Conry, S.R. Basu, D. Paron, L. Reichertz, J. Ihlefeld, C. Adamo, A. Melville, Y.H. Chu, C.H. Yang, J.L. Musfeldt, D.G. Schlom, J.W. Ager III, R. Ramesh, Photovoltaic effects in BiFeO₃, *Appl. Phys. Lett.* 95 (2009) 062909 (3pp).
- [42] M. Khodabakhsh, C. Sen, H. Kassaf, M.A. Gulun, I.B. Misirliglu, Strong smearing and disappearance of phase transitions into polar phases due to inhomogeneous lattice strains induced by A-site doping in Bi_(1-x)A_(x)FeO₃ (A: La, Sm, Gd), *J. Alloys Compd.* 604 (2014) 117–129.
- [43] Q. Xu, M. Sobhan, Q. Yang, F. Anariba, K.P. Ong, P. Wu, The role of Bi vacancies in the electrical conduction of BiFeO₃: a first-principles approach, *Dalton, Transactions* 43 (2014) 10787–10793.
- [44] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Cryst. A* 32 (1976) 751–767.
- [45] P. Hermet, M. Gofinet, J. Kreisel, Ph. Gosez, Raman and infrared spectra of multiferroic bismuth ferrite from first principles, *Phys. Rev. B* 75 (2007) 220102(R) (4pp).

- [46] J. Hlinka, J. Pokorny, S. Karimi, I.M. Reaney, Angular dispersion of oblique phonon modes in BiFeO₃ from micro-Raman scattering, *Phys. Rev. B* 83 (2011) 020101(R) (4pp).
- [47] J. Bielecki, P. Svedlindh, D.T. Tibebe, S. Cai, S.-G. Eriksson, L. Börjesson, C.S. Knee, Structural and magnetic properties of isovalently substituted multiferroic BiFeO₃: insights from Raman spectroscopy, *Phys. Rev. B* 86 (2012) 184422 (16pp).
- [48] J. Seidel, P. Maksymovych, Y. Batra, A. Katan, S.Y. Tang, Q. He, A.P. Baddorf, S.V. Kalinin, C.H. Yang, J.C. Yang, Y.H. Chu, E.K.H. Salje, H. Wormeester, M. Salmeron, R. Ramesh, Domain wall conductivity in La-doped BiFeO₃, *Phys. Rev. Lett.* 105 (2010) 197603 (3pp).
- [49] D.I. Woodward, I.M. Reaney, Electron diffraction of tilted perovskites, *Acta Crystallogr. B* 61 (2005) 387–399.
- [50] C.W. Tai, S.H. Choy, H.L.W. Chan, Ferroelectric domain morphology evolution and octahedral tilting in lead-free (Bi_{1/2}Na_{1/2})TiO₃–(Bi_{1/2}K_{1/2})TiO₃–(Bi_{1/2}Li_{1/2})TiO₃–BaTiO₃ ceramics at different temperatures, *J. Am. Ceram. Soc.* 91 (2008) 3335–3341.
- [51] L.A. Grunes, Study of the K edges of 3d transition metals in pure and oxide form by X-ray-absorption spectroscopy, *Phys. Rev. B* 27 (1983) 2111–2131.
- [52] C. Ederer, N.A. Spaldin, Influence of strain and oxygen vacancies on the magnetoelectric properties of multiferroic bismuth ferrite, *Phys. Rev. B* 71 (2005) 224103 (9pp).
- [53] T.E. Westre, P. Kennepohl, J.G. DeWitt, B. Hedman, K.O. Hodgson, E.I. Solomon, A multiplet analysis of Fe K-Edge 1s → 3d pre-edge features of iron complexes, *J. Am. Chem. Soc.* 119 (1997) 6297–6314.
- [54] E. Beaurepaire, J.P. Kappler, X-ray-absorption near-edge structure study in mixed-valent samarium systems, *Phys. Rev. B* 41 (1990) 6768–6776.
- [55] J. Chaboy, A. Marcelli, T.A. Tyson, Influence of double-electron transitions on the EXAFS L edges of rare-earth systems, *Phys. Rev. B* 49 (1994) 11652–11661.
- [56] T. Higuchi, W. Sakamoto, N. Itoh, T. Shimura, T. Hattori, T. Yogo, Valence state of Mn-doped BiFeO₃–BaTiO₃ ceramics probed by soft X-ray absorption spectroscopy, *Appl. Phys. Express* 1 (2008) 011502 (3pp).
- [57] H. Ikeno, I. Tanaka, T. Miyamae, T. Mishima, H. Adachi, K. Ogasawara, First principles calculation of Fe L_{2,3}-edge X-ray absorption near edge structures of iron oxides, *Mater. Trans.* 45 (2004) 1414–1418.
- [58] P.S. Miedema, F.M.F. Groot, The iron L edges: Fe 2p X-ray absorption and electron energy loss spectroscopy, *J. Electr. Spectrosc. Relat. Phenom.* 187 (2013) 32–48.
- [59] J.P. Crocombette, M. Pollak, F. Joliet, N. Thomat, M. Gautier-Soyer, X-ray-absorption spectroscopy at the Fe L_{2,3} threshold in iron oxides, *Phys. Rev. B* 52 (1995) 3143–3150.
- [60] F.M.F. de Groot, M. Gnom, J.C. Fuggle, Oxygen 1s x-ray-absorption edges of transition-metal oxides, *Phys. Rev. B* 40 (1989) 5715–5723.
- [61] Z.Y. Wu, S. Gota, F. Jollet, M. Pollak, M. Gautier-Soyer, C.R. Natoli, Characterization of iron oxides by x-ray absorption at the oxygen K edge using a full multiple-scattering approach, *Phys. Rev. B* 55 (1997) 2570–2577.
- [62] D.H. Douma, R. Ciprian, A. Lamperti, P. Lupo, E. Cianci, D. Sangalli, F. Casoli, L. Nasi, F. Albertini, P. Torelli, A. Debernardi, Experimental versus ab initio x-ray absorption of iron-doped zirconia: trends in O K-edge spectra as a function of iron doping, *Phys. Rev. B* 90 (2014) 205201 (7pp).
- [63] Y. Ma, P.D. Johnson, N. Wassdahl, J. Guo, P. Skytt, J. Nordgren, S.D. Kevan, J.-E. Rubensson, T. Boske, W. Eberhardt, Electronic structures of α-Fe₂O₃ and Fe₃O₄ from O K-edge absorption and emission spectroscopy, *Phys. Rev. B* 48 (1993) 2109–2111.
- [64] C.J. Ballhausen, Introduction to Ligand-Field Theory, McGraw-Hill, New York, 1962.
- [65] D.-Y. Cho, J.-M. Lee, S.-J. Oh, H. Jang, J.-Y. Kim, J.-H. Park, A. Tanaka, Influence of oxygen vacancies on the electronic structure of HfO₂ films, *Phys. Rev. B* 76 (2007) 165411 (5pp).
- [66] Y. Xu, M. Shen, Structure and optical properties of nanocrystalline BiFeO₃ films prepared by chemical solution deposition, *Mater. Lett.* 62 (2008) 3600–3602.
- [67] S.R. Basu, L.W. Martin, Y.H. Chu, M. Gajek, R. Ramesh, R.C. Rai, X. Xu, J.L. Musfeldt, Photoconductivity in BiFeO₃ thin films, *Appl. Phys. Lett.* 92 (2008) 091905 (3pp).
- [68] X.S. Xu, T.V. Brinzari, S. Lee, Y.H. Chu, L.W. Martin, A. Kumar, S. McGill, R.C. Rai, R. Ramesh, V. Gopalan, S.W. Cheong, J.L. Musfeldt, Optical properties and magnetochromism in multiferroic BiFeO₃, *Phys. Rev. B* 79 (2009) 134425 (4pp).
- [69] A. Anshul, A. Kumar, B.K. Gupta, R.K. Kotnala, J.F. Scott, R.S. Katiyar, Photoluminescence and time-resolved spectroscopy in multiferroic BiFeO₃: effects of electric fields and sample aging, *Appl. Phys. Lett.* 102 (2013) 222901 (5pp).
- [70] X. Chen, H. Zhang, T. Wang, F. Wang, W. Shi, Optical and photoluminescence properties of BiFeO₃ thin films grown on ITO-coated glass substrates by chemical solution deposition, *Phys. Status Solidi A* 209 (2012) 1456–1460.
- [71] F. Gao, X. Chen, K. Yin, S. Dong, Z. Ren, F. Yuan, T. Yu, Z. Zou, J.M. Liu, Visible-light photocatalytic properties of weak magnetic BiFeO₃ nanoparticles, *Adv. Mater.* 19 (2007) 2889–2892.
- [72] U.A. Joshi, J.S. Jang, P.H. Borse, J.S. Lee, Microwave synthesis of single-crystalline perovskite BiFeO₃ nanocubes for photoelectrode and photocatalytic applications, *Appl. Phys. Lett.* 92 (2008) 242106 (3pp).
- [73] P.S.V. Mocherla, C. Karthik, R. Ubig, M.S. Ramachandra, C. Sudakar, Tunable bandgap in BiFeO₃ nanoparticles: the role of microstrain and oxygen defects, *Appl. Phys. Lett.* 103 (2013) 022910 (5pp).
- [74] S. Ju, T.Y. Cai, First-principles studies of the effect of oxygen vacancies on the electronic structure and linear optical response of multiferroic BiFeO₃, *Appl. Phys. Lett.* 95 (2009) 231906 (3pp).
- [75] S.J. Clark, J. Robertson, Energy levels of oxygen vacancies in BiFeO₃ by screened exchange, *Appl. Phys. Lett.* 94 (2009) 022902 (3pp).
- [76] C.S. Tu, C.M. Hung, Z.R. Xu, V.H. Schmidt, Y. Ting, R.R. Chien, Y.-T. Peng, J. Anthoninappen, Calcium-doping effects on photovoltaic response and structure in multiferroic BiFeO₃ ceramics, *J. Appl. Phys.* 114 (2013) 124105 (6pp).
- [77] W. Shockley, H.J. Queisser, Detailed balance limit of efficiency of p-n junction solar cells, *J. Appl. Phys.* 32 (1961) 510–519.
- [78] H. Kim, C.M. Gilmore, A. Piqué, J.S. Horwitz, H. Mattoussi, H. Murata, Z.H. Kafafi, D.B. Crissey, Electrical, optical, and structural properties of indium-tin-oxide thin films for organic light-emitting devices, *J. Appl. Phys.* 86 (1999) 6451–6461.
- [79] G. Giusti, J. Bowen, Q. Ramasse, G. Rey, E. Blackburn, L. Tian, I.P. Jones, J.S. Abell, Dielectric properties of pulsed-laser deposited indium tin oxide thin films, *Thin Solid Films* 524 (2012) 249–256.
- [80] N.A. Spaldin, S.-W. Cheong, R. Ramesh, Multiferroics: past, present, and future, *Physics Today* 63 (2010) 38–43.
- [81] R. Nechache, C. Harnagea, S. Licocchia, E. Traversa, A. Ruediger, A. Pignolet, F. Rosei, Photovoltaic properties of Bi₂FeCrO₆ epitaxial thin films, *Appl. Phys. Lett.* 98 (2011) 202902 (3pp).
- [82] A. Bhatnagar, A.R. Chaudhuri, Y.H. Kim, D. Hesse, M. Alexe, Role of domain walls in the abnormal photovoltaic effect in BiFeO₃, *Nat. Commun.* 4 (2013) 2835 (8pp).
- [83] D. Cao, C. Wang, F. Zheng, W. Dong, L. Fang, M. Shen, High-efficiency ferroelectric-film solar cells with an n-type Cu₂O cathode buffer layer, *Nano Lett.* 12 (2012) 2803–2809.