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Tailoring microstructure and photovoltaic effect in multiferroic Nd-substituted BiFeO₃ ceramics by processing atmosphere modification

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A B S T R A C T

This study highlights significant effects of processing atmosphere ratio (O₂/N₂) on microstructure, impurity phases, atomic hybridization, band gap, and photovoltaic properties in (Bi_{0.93}Nd_{0.07})FeO₃ (BFO7Nd) ceramics. A Rietveld-refinement analysis indicates increased oxygen and bismuth vacancies in the specimens processed in the O₂-rich atmosphere (hereafter called O₂-rich-atmosphere specimens). In the matrix containing mainly Fe³⁺ ions, Fe⁴⁺ cations were identified with O₂ concentration decreasing in the atmosphere by Fe K/L-edges synchrotron X-ray absorption. Oxygen K-edge absorption reveals reduced hybridizations of the O 2p-Fe 3d and the O 2p-Bi 6sp orbitals in the O₂-rich-atmosphere specimens. Photovoltaic effects in the ITO/BFO7Nd/Au heterostructures under near-ultraviolet irradiation ($\lambda = 405$ nm) exhibit strong dependences on O₂/N₂ ratio. A *p-n*-junction model was used to describe open-circuit voltage and short-circuit current density as functions of irradiation intensity. The calculated carrier densities (in BFO7Nd ceramics) and *p-n*-junction widths (in the dark) are $\sim 10^{23} \text{ m}^{-3}$ and a few hundred nanometers, respectively.

1. Introduction

Bismuth ferrite BiFeO₃ (BFO) is the only known multiferroic material possessing ferroelectric (FE) and magnetic responses simultaneously above room temperature. BFO materials have shown potential applications in multistate memories [1,2], gas sensors [3], and photovoltaic (PV) sensors [4]. Substantial PV effects under near-ultraviolet irradiation have been reported in the heterostructure consisting of a *p*-type A-site rare-earth (RE) substituted BiFeO₃ ceramic layer and an *n*-type indium tin oxide (ITO) thin film [4,5]. The irradiation intensity-dependent PV open-circuit voltage and short-circuit current can be described quantitatively by a *p-n*-junction-like model based on photo-excited electron-hole generation [4,5]. The experimental direct band gaps of BFO and (Bi_{1-x}Sm_x)FeO₃ polycrystalline ceramics occur in the range of ~ 2.15 - 2.24 eV [5]. The first-principles calculated band gap of pure BFO ceramic is ~ 2.25 eV [4]. It was proposed that the domain structure and orbital hybridization between the O 2p and the Fe 3d orbitals play key roles in the PV effects [5].

BFO has a typical linear antiferromagnetic (AFM) character below the Néel temperature ($T_N \sim 630$ K) and a FE rhombohedral *R3c* space group with a rotation of FeO₆ octahedra below the Curie temperature

($T_C \sim 1100$ K) [2,6]. Electronic structure calculations in perovskite oxides indicated that atomic hybridization between the B-site metal 3d and the O 2p orbitals is responsible for the FE properties [7]. Enhancements of FE polarization, magnetization, and electromechanical properties have been extensively explored in A-site rare-earth (RE) substituted BFO [8–12]. Oxygen K-edge synchrotron X-ray absorption in (Bi_{1-x}RE_x)FeO₃ (*RE* = Nd, Gd, La) ceramics revealed that the hybridizations of the O 2p-Fe 3d and the O 2p-Bi 6sp orbitals decreased with increasing *RE* content [9,13,14]. A recent study showed that atomic hybridization plays an important role in the FeO₆ octahedral distortion, bond covalency, and Fe oxidation state in multiferroic (Bi_{1-x}RE_x)FeO₃ ceramics [9].

The symmetry in the perovskite ABO₃ structure strongly depends on the effective size of the A-site ionic radius resulting from the BO₆ octahedral tilting [15,16]. The decreasing tolerance factor ($t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$) can increase the possibility of octahedral rotation and results in a structural transition from the polar *R3c* to the nonpolar orthorhombic *Pnma* space group [17]. The tolerance factor in (Bi_{1-x}Nd_x)FeO₃ ceramics becomes smaller with increasing content of Nd³⁺, whose radius ($R_A \sim 0.127$ nm) is smaller than that of Bi³⁺ ($R_A \sim 0.14$ nm) [18]. The (Bi_{1-x}RE_x)FeO₃ system exhibits a structural shift from *R3c* toward *Pnma* symmetry as *RE* content increases [19]. In

Fig. 1. SEM grain morphologies from cross-sections of as-sintered ceramics. $\bar{G}$, D_r , $\bar{A}_O$, and $\bar{A}_{Bi}$ are average grain sizes, relative densities, and atomic percentages of oxygen and bismuth, respectively.

$(Bi_{1-x}Nd_x)FeO_3$ ceramics, $R3c$ and nonpolar orthorhombic $PbZrO_3$ -like structures appear respectively in the ranges of $x \leq 0.1$ and $0.15 \leq x \leq 0.2$ [9,20]. The polar $R3c$ space group is characterized by the $a^-a^-a^-$ octahedral rotations and cation displacements [21]. A recent Rietveld-refinement analysis highlighted that oxygen vacancies, bismuth deficiency, and $Bi_2Fe_4O_9$ impurity phase were decreased by A-site Nd substitution in $(Bi_{1-x}Nd_x)FeO_3$ ($x \leq 0.1$) ceramics [9].

Effects of processing atmosphere on defects (such as oxygen vacancies, Bi deficiency, and impurity phases) have been used to tailor electric and magnetic behaviors in Bi-based FE and BFO materials [22,23]. In general, the processing atmosphere plays a key role in microstructure and electric properties [22,23]. In this study, we focus on the influence of processing atmosphere on microstructure, phonon vibrations, atomic hybridization, and PV properties in BFO7Nd ceramics prepared with four different atmosphere ratios (O_2/N_2). A previously developed p - n -junction model was employed to describe the open-circuit voltage and short-circuit current density as functions of irradiation intensity.

2. Experimental procedure

$(Bi_{0.93}Nd_{0.07})FeO_3$ (BFO7Nd) ceramics were synthesized by using the solid-state-reaction technique, in which Bi_2O_3 , Nd_2O_3 , and Fe_2O_3 powders (purity $\geq 99.0\%$) were mixed with stoichiometric ratio of 0.93:0.07:1 in an agate jar with alcohol as milling medium for more than 72 h. The dried mixtures were then calcined (800 °C for 3 h) and sintered (890 °C for 3 h) with four different atmosphere ratios (O_2/N_2) of 1/0, 1/1, $\sim 1/4$ (ambient air), and 0/1. Archimedes' method was used to determine densities, which are about 8.14, 8.27, 8.21, and 7.78 g/cm³ for as-sintered specimens synthesized with O_2/N_2 ratios of 1/0, 1/1, $\sim 1/4$, and 0/1, respectively. The calculated densities for as-sintered specimens processed with O_2/N_2 ratios of 1/0, 1/1, $\sim 1/4$, and 0/1 are respectively about 8.28, 8.34, 8.36, and 8.40 g/cm³ based on

lattice parameters found from X-ray diffraction (XRD).

Grain morphologies and atomic percentages were obtained by using a Hitachi S-3400N scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The X-ray diffraction patterns were obtained using a Rigaku Multiplex Diffractometer. The Rietveld-refinement analysis (with the HighScore Plus software) was employed to determine structural space groups, occupancies of O and Bi atoms, and impurity phases. The back-scattering micro-Raman spectra were obtained using a Nanobase Model XperRam 200 spectrometer equipped with a green laser of $\lambda = 532$ nm. Magnetization hysteresis loops were measured at room temperature by using a LakeShore Model 7407 Vibrating Sample Magnetometer (VSM). The Fe K-edge synchrotron X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were measured in the transmission mode at the 01C1 beamline of the National Synchrotron Radiation Research Center (NSRRC, Taiwan). The soft X-ray absorption spectra were obtained at beamline 20A1 (NSRRC) equipped with a high energy spherical grating monochromator. The Fe $L_{2,3}$ -edge and O K-edge X-ray absorption spectra were recorded in the total electron yield mode. The optical transmission was measured using a Cary 5E UV-vis-NIR spectrometer. For PV studies, ITO (~ 100 nm) and Au (~ 100 nm) thin films were deposited on the surfaces of ceramic specimens (thickness = 0.15 mm) by sputtering deposition. A diode laser with $\lambda = 405$ nm was used as the irradiation source and the irradiated ITO area is ~ 0.15 cm².

3. Results and discussion

Fig. 1 shows SEM grain morphologies of as-sintered ceramics with average grain sizes ($\bar{G}$), relative densities (D_r), and atomic percentages ($\bar{A}_O$ and $\bar{A}_{Bi}$) and of oxygen and bismuth obtained from EDS analysis. The average grain sizes ($\bar{G}$) and vacancy concentrations of oxygen and bismuth increase almost linearly with O_2 concentration in

Fig. 2. XRD patterns and Rietveld refinements from powders of as-sintered specimens. R_{wp} , R_{exp} , and χ^2 are the weighted-profile, statistically expected R value, and goodness-of-fit, respectively. The unit-cell parameters from the Rietveld refinements are given in Table 1.

the specimen processing atmosphere. However, the relative densities are near 100% only in the specimens processed in the normal (ambient air) and the O₂-rich atmospheres (hereafter abbreviated as “O₂-rich-atmosphere specimens”). The XRD patterns obtained from powders of as-sintered specimens are given in Fig. 2 with parameters of Rietveld refinements. The calculated structural space groups, lattice parameters, atomic bond lengths, and occupancies of O and Bi ions are given in Table 1. The Rietveld refinements confirm a predominant rhombohedral R3c phase with minor impurity phase of orthorhombic Pbam Bi₂Fe₄O₉. The R3c lattice parameters of a (from 5.572 to 5.573 Å) and c (from 13.810 to 13.826 Å) increase in the O₂-rich-atmosphere specimens, which are slightly smaller than $a = 5.581$ Å and $c = 13.876$ Å reported in BFO ceramic [24] due to the smaller Nd³⁺ ionic radius ($R_A \sim 0.127$ nm). The Rietveld refinement suggests increasing O and Bi vacancies in the O₂-rich-atmosphere specimens. The increasing average grain sizes in the O₂-rich-atmosphere specimens (Fig. 1) can be explained by increasing O vacancies, which can increase ion migration for grain growth in the high-temperature synthesizing process [25].

Table 1

Space groups, phase ratios, lattice parameters (in the hexagonal unit cell), occupancies and atomic percentages of bismuth (Bi) and oxygen (O) atoms, and bond lengths determined from the Rietveld refinements.

Oxygen: Nitrogen (O ₂ :N ₂)	0:1	~ 1:4 (ambient air)	1:1	1:0
Rhombohedral R3c phase (%)	94.4	96.1	95	95.6
a (Å)	5.572	5.572	5.573	5.573
c (Å)	13.810	13.813	13.819	13.826
α (degrees)	90	90	90	90
γ (degrees)	120	120	120	120
Orthorhombic Pbam Bi ₂ Fe ₄ O ₉ phase (%)	5.6	3.9	5	4.4
Bismuth occupancy (%)	92	90	88	85
Atomic percentage (%) (=occupancy $\times$ 1/5)	18.4	18	17.6	17
Oxygen occupancy (%)	99	98	96	93
Atomic percentage (%) (=occupancy $\times$ 3/5)	59.4	58.8	57.6	55.8
Fe–O(1) bonding length (Å)	2.072	2.092	2.228	2.531
Fe–O(2) bond length (Å)	1.981	1.965	1.879	1.756
Bi/Nd–O(1) bond length (Å)	2.472	2.494	2.525	2.567
Bi/Nd–O(2) bond length (Å)	2.471	2.442	2.434	2.418
Bi/Nd–Fe(1) bond length (Å)	3.305	3.307	3.311	3.402
Bi/Nd–Fe(2) bond length (Å)	3.082	3.137	3.141	3.206

Fig. 3(a) shows bond lengths of Fe–O, Bi/Nd–O, and Bi/Nd–Fe as functions of O₂ concentration as given in Table 1. The deviation between the Fe–O(1) and Fe–O(2) bond lengths increases in the O₂-rich-atmosphere specimens, suggesting increasing ion displacements in the FeO₆ octahedral structure. Similar increasing deviation occurs between

Fig. 3. (a) Atomic bond lengths of Fe–O(1)(2), Bi/Nd–O(1)(2), and Bi/Nd–Fe(1)(2) from Rietveld refinements as shown in Table 1. (b) Calculated lattice parameters of a and α based on the rhombohedral unit cell. Solid lines are guides for the eye.

Fig. 4. XRD patterns and Rietveld refinements from bulk surfaces of as-sintered specimens prepared with all-N₂ and all-O₂ atmospheres.

Bi/Nd–O(1) and Bi/Nd–O(2) bond lengths in the O₂-rich-atmosphere specimens. The increasing Fe–Bi/Nd bond lengths suggest a reduced covalency between Fe and Bi/Nd ions in the O₂-rich-atmosphere specimens. Fig. 3(b) gives the calculated lattice parameters (*a* and *α*) based on the rhombohedral unit cell, indicating a structural shift away from pseudo-cubic symmetry as oxygen concentration is increased in the atmosphere. In brief, the XRD refinement suggests an increased distortion in the FeO₆ octahedral structure and a reduced bond covalency as O₂ concentration is increased.

To understand the origin of O and Bi vacancies in the specimens, the wide-angle X-ray diffraction patterns were obtained from bulk surfaces of as-sintered specimens processed with O₂/N₂ ratios of 0:1 (all N₂) and 1:0 (all O₂) as shown in Fig. 4. The Rietveld refinement confirms formation of minor Bi₂O₃ impurity phases in the O₂-rich-atmosphere specimen. According to the Gibbs free energies, the bismuth oxidation reaction is thermodynamically spontaneous in the range of 200–1600 K [26,27]. The formation of Bi₂O₃ phases can result in Bi deficiency and thus enhances O₂ vacancies in the high-temperature synthesizing processes. The formation of minor Bi₂O₃ phases is consistent with the increased O and Bi vacancies in the O₂-rich-atmosphere specimens as shown in Fig. 1 and Table 1.

Fig. 5(a) shows the normalized Fe K-edge synchrotron X-ray absorptions, including the reference FeO and Fe₂O₃ powders. The pre-edge peak A (as enlarged in the inset) at ~7113 eV can be attributed to the forbidden quadrupole-coupling 1s → 3d transition ($\Delta l = \pm 2$) in conjunction with the Fe 3d-4p orbital hybridization [28]. The pre-edge peak A is sensitive to atomic bonding covalency, cation valence, and electronic configuration [29]. The O₂-rich-atmosphere specimens exhibit slightly stronger pre-edge absorption, suggesting a stronger Fe 3d-4p orbital hybridization. The Fe K-edge absorption (peak B)

Fig. 5. (a) Fe K-edge XANES spectra and (b) Fe L_{2,3}-edge X-ray absorption spectra.

corresponds to the electric-dipole coupling 1s → 4p transition ($\Delta l = \pm 1$) [30]. As enlarged in the inset, the maximum of peak B shows a slight shift toward higher energies with lower O₂ concentration, implying a minor Fe⁴⁺ concentration in the predominantly Fe³⁺ matrix. Fe⁴⁺ cations were also identified in the predominantly Fe³⁺ matrix in atmosphere-controlled polycrystalline BFO [22]. Fig. 5(b) shows the Fe L_{2,3}-edge synchrotron X-ray absorption, corresponding to the transition from the Fe 2p (2p_{1/2} and 2p_{3/2}) to the unoccupied Fe 3d orbitals [31]. The energy splitting in the L₂ and L₃ bands is primarily associated with the t_{2g} and e_g orbitals [32,33]. The coupling between the Fe 3d and the O 2p orbitals in the FeO₆ octahedron causes the ligand-field (LF) splitting from the five-fold-degenerate 3d to the triple-degenerate t_{2g} orbitals and doubly-degenerate e_g orbitals [33]. The energy gaps between the t_{2g} and e_g bands are ~1.5 eV, which is between ~1.4 eV (BFO ceramic) [34] and ~1.8 eV (NdFeO₃ ceramic) [35]. The peak intensity ratio of the e_g and t_{2g} bands decreases in the O₂-rich specimens, implying that the number of unoccupied Fe 3d orbitals is reduced in the O₂-rich-atmosphere specimens. The Fe L₃-edge peak exhibits a slight shift toward higher energy with lower O₂ concentration as indicated by the dashed line in the inset of Fig. 5(b). These results suggest a partial valence shift of Fe³⁺ → Fe⁴⁺ with decreasing O₂ concentration in the atmosphere and are consistent with the Fe K-edge absorption. The Fe³⁺ → Fe⁴⁺ shift may play an electron-donor role to reduce oxygen vacancies as suggested in Table 1.

Fig. 6 gives normalized oxygen K-edge synchrotron X-ray absorptions from the O 1s → O 2p transition hybridized with the unoccupied Fe 3d orbitals [36,37]. Three major absorption bands (A, B, and C) are identified in the region of 528–535 eV as shown by the Gaussian curves.

Fig. 6. Oxygen K-edge synchrotron X-ray absorption spectra. The solid lines are fits of the A, B, and C bands with peak energies. The red line is the sum of fitting lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

A and B bands correspond to the low-spin t_{2g} and high-spin e_g orbitals resulting from the hybridization with unoccupied Fe 3d orbitals [38–40]. The LF splitting gaps between the t_{2g} and e_g bands are about ~ 1.6 – 1.7 eV, which are close to ~ 1.5 eV observed in the Fe L_{3} -edge absorption bands in Fig. 5(b). The peak-intensity ratio (I_B/I_A) of the e_g and t_{2g} bands increases with increasing O_2/N_2 atmosphere ratio, suggesting an increasing number of unoccupied e_g orbitals in the O_2 -rich-atmosphere specimens. This evolution reveals that the hybridization (or covalency degree) between the O 2p and the unoccupied Fe 3d e_g orbitals was reduced in the O_2 -rich-atmosphere specimens.

The C band at ~ 533 eV in Fig. 6 can be attributed to the hybridization between the O 2p and the unoccupied Bi 6sp orbitals [34]. The D band near ~ 534 eV is likely associated with hybridization with the high-level unoccupied Bi 6sp [41] and Nd 4f orbitals. The peak intensity ratio (I_C/I_A) of the A and C bands increases with increasing O_2/N_2 atmosphere ratio, suggesting that the number of unoccupied Bi 6sp orbitals was increased in the O_2 -rich-atmosphere specimens. This result suggests that the O 2p–Bi 6sp orbital hybridization and the Bi–O bond covalency decrease in the O_2 -rich-atmosphere specimens. A first-principles calculation predicted that the O 2p–Bi 6s hybridization is responsible for the structure distortion [42]. The broad E and F absorption bands centered at ~ 537.5 eV and ~ 541 eV respectively are combinations of hybridizations with the unoccupied Fe 4s/4p, Nd 4f/5d, and Bi 6d orbitals [35,40,41,43–48]. Both E and F bands do not show clear dependence on processing atmosphere.

Fig. 7 shows Raman modes with remarkable shifts toward lower frequencies in the O_2 -rich-atmosphere specimens as indicated by the dashed lines. In the $R3c$ space group with $Z = 2$, the total irreducible representation can be expressed as $\Gamma_{\text{total}} = 5A_1 + 5A_2 + 10E$, which includes 13 Raman-active modes, i.e. $4A_1 + 9E$ [49–51]. The low-

Fig. 7. Back-scattering Raman spectra of as-sintered specimens.

Fig. 8. Hysteresis loops of magnetization vs. magnetic field at room temperature. The inset includes enlargements for specimens prepared with all- O_2 and all- N_2 atmospheres.

frequency modes ($< \sim 250$ cm^{-1}) are associated with the A-site Bi (or Nd) and B-site Fe ions [9]. Four predominant vibration modes, $E(1)$, $E(2)$, $A_1(1)$, and $A_1(2)$, can be identified in the regions of ~ 65 – 80 , ~ 120 – 140 , ~ 165 – 170 , and ~ 215 – 230 cm^{-1} , respectively. The frequencies of Raman modes mainly depend on bonding strength and atomic masses in the specimens. The decreasing frequency in the O_2 -rich-atmosphere specimens could result from decreased bonding strengths or/and increasing effective masses of the atoms. As shown in Table 1, the O_2 -rich-atmosphere specimens show more O and Bi vacancies. Thus, Raman spectra suggest decreased atomic bonding strengths in the O_2 -rich-atmosphere specimens. This confirms reduced O 2p–Fe 3d and O 2p–Bi 6sp orbital hybridizations in the O_2 -rich-atmosphere specimens as shown in Fig. 6.

Fig. 8 shows magnetization hysteresis loops at room temperature. Very thin and almost linear antiferromagnetic hysteresis loops were

Fig. 9. (a) Optical transmission and (b) $(\alpha h\nu)^2$ vs. photon energy.

observed with decreased magnetic susceptibilities in the O₂-rich-atmosphere specimens. The magnetization hysteresis loop was slightly enhanced in the O₂-free-atmosphere specimen as shown in the inset. This weak magnetization in the O₂-free-atmosphere specimens may be associated with fewer oxygen vacancies as shown in Fig. 1. A first-principles calculation predicted that enhanced magnetization can occur in specimens with fewer oxygen vacancies [52]. Another possible contribution for this weak magnetization is the Fe–O–Fe superexchange interaction [53]. The Fe K-edge synchrotron absorption (Fig. 5) suggests the existence of Fe⁴⁺ cations in the matrix, in which Fe³⁺ predominates. Ferromagnetic ordering can occur through the super-exchanges of Fe⁴⁺(*t*_{2g}³*e*_g¹) – O – Fe³⁺(*t*_{2g}³*e*_g²) and Fe⁴⁺(*t*_{2g}³*e*_g¹) – O – Fe⁴⁺(*t*_{2g}³*e*_g¹). [53].

Fig. 9 shows plots of optical transmission and $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for the specimens prepared with O₂/N₂ ratios of 1:0, ~1:4 (ambient air), and 0:1. h and ν are Planck's constant and photon frequency. The optical absorption coefficient α can be calculated by using the relation, $T = (1 - R^2)e^{-\alpha d}$, where T , R , and d are the optical transmittance, reflectivity, and sample thickness. Here, we assume that the reflectivity is negligible, i.e. $\alpha = -\ln(T)/d$. The direct optical band gap (E_g) can be estimated using the Tauc relation [54], $(\alpha h\nu)^2 = A(h\nu - E_g)$, by extrapolating the straight line portion of the curve of $(\alpha h\nu)^2$ vs. $h\nu$ as indicated in Fig. 9(b). The band gap increases in the O₂-rich-atmosphere specimens as indicated in Fig. 9(b). The band gap depends on electronic band structure, oxygen vacancies, grain size, and

Fig. 10. (a) Open-circuit voltage (V_{oc}) and (b) short-circuit current density (J_{sc}) as irradiation was switched ON and OFF with increasing intensity. The labeled numbers are irradiation intensities in W/m². The insets are V_{oc} and J_{sc} measured with longer ON/OFF switching time for two illumination intensities in the all-O₂-atmosphere specimen.

defect states [54,55]. The larger band gaps in the O₂-rich-atmosphere specimens possibly result from the decreased O 2p–Fe 3d orbital hybridizations as evidenced in the oxygen K-edge synchrotron XAS (Fig. 6).

Fig. 10 shows open-circuit voltages (V_{oc}) and short-circuit current densities ($J_{sc} = i_{sc}/S$) measured from the heterostructures of ITO tin film/BFO7Nd ceramics/Au thin film as the laser irradiation ($\lambda = 405$ nm) was switched on and off in sequence with increasing irradiation intensity. As illustrated in the insets, V_{oc} and J_{sc} curves with longer ON/OFF switching time for two illumination intensities in the all-O₂-atmosphere specimen exhibit step-like behaviors, suggesting that the photovoltaic responses are not associated with the Maxwell-Wagner charging/discharging mechanism, which could occur in layered dielectrics [56]. The curves of V_{oc} and J_{sc} vs. irradiation intensity are plotted in Fig. 11, which reveal rapidly increasing PV responses below 100 W/m². To characterize the correlation between PV effects and irradiation intensity, a previously developed *p-n*-junction-like model was used to describe the irradiation intensity-dependent V_{oc} and J_{sc} [57]. The photodiode current i_d under a bias voltage V can be expressed as [58]

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

where i_0 , R_s , and ξ are respectively dark current (without irradiation),

Fig. 11. Irradiation intensity-dependent (a) V_{oc} and (b) J_{sc} . The solid lines in (a) and (b) are fits of Eqs. (3) and (4) with parameters in Table 2.

Fig. 12. Characteristic curves of current vs. bias voltage without irradiation. The solid lines are fits of Eq. (1) with parameters in Table 2.

Table 2
Calculated parameters from theoretical fits of the p - n -junction model.

Calculated photovoltaic parameters	O ₂ :N ₂ = 0:1	O ₂ :N ₂ ~1:4 (ambient air)	O ₂ :N ₂ = 1:1	O ₂ :N ₂ = 1:0
Dark current, i_0 (μ A)	0.1	0.1	0.1	0.1
Source resistance, R_s (ohm)	9000	5200	9800	33,000
Diode-quality factor, ξ	10.5	9.5	11.5	13
Voltage across the depletion region in the dark, U_0 (V)	0.80	0.78	0.76	0.72
B ($\times 10^{13}$ V/m ²)	1	0.3	0.8	6
p - n junction widths in the dark, $d_0 \sim (U_0/B)^{1/2}$ (nm)	283	510	308	110
Carrier density, n_p ($\times 10^{23}$ m ⁻³)	1.1	0.4	1.5	12.6

source resistance, and diode-quality factor. Fig. 12 shows the experimental characteristic curves of current vs. voltage without irradiation. The solid curves are fits of Eq. (1) with parameters of i_0 , R_s , and ξ as shown in Fig. 12 and Table 2. In this work, the electron charge $q = 1.6 \times 10^{-19}$ C and $T = 300$ K were chosen for simplicity though irradiation may increase temperature. According to Eq. (1), the current i under irradiation can be written as [57]

$$i = i_p - i_d = i_p - i_0 \{ \exp \{ [V - (i_d - i_p) R_s] q / \xi k T \} - 1 \} \quad (2)$$

where i_p , i_d , and V are the photovoltaic current, diode current, and measured voltage. As derived in the previous work [57], the irradiation intensity-dependent open-circuit voltage (V_{oc}) and short-circuit current (i_{sc}) can be expressed as [57]

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

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

$$B = (q n_p / 2 \epsilon_0 \epsilon_p) (1 + n_p \epsilon_p / \epsilon_n n_n) \quad (5)$$

where S , λ , h , c , and I are irradiated area, irradiation wavelength, Planck constant, light speed, and irradiation intensity. U_0 is the voltage barrier across the depletion region in the dark. β is the optical attenuation length and can be determined from transmission in Fig. 9(a), i.e. $\beta = -d / \ln(T)$. The measured attenuation lengths (β) are respectively about 6.4, 8.7, and 7.8 μ m at wavelength $\lambda = 405$ nm for the specimens synthesized with O₂/N₂ ratios of 1:0 (all O₂), ~1:4 (ambient air), and 0:1 (all N₂). n_p and n_n are carrier densities of p -type BFO7Nd ceramics and n -type ITO thin film. ϵ_p and ϵ_n are dielectric permittivities of BFO7Nd ceramics and ITO thin film. The room-temperature ϵ_p of BFO7Nd ceramics are about 189, 174, 130, and 97 at frequency $f = 1$ MHz for specimens processed respectively with O₂/N₂ ratios of 1/0, 1/1, ~1/4 (ambient air), and 0/1. The carrier density of the n -type ITO thin film is $\sim 0.6 \times 10^{27}$ m⁻³ determined by a Hall-effect measurement and is consistent with the reported $n_n \sim 10^{27}$ m⁻³ [59]. The permittivity ϵ_n of ITO at low frequency as needed in Eq. (8) has not been reported because of its high conductivity. It is expected that the depletion region of ITO is almost free of charge carriers and the permittivity should be near that of a material with structure close to that of ITO. Indium oxide (In₂O₃) thin film has $\epsilon' \sim 37$ at 300 K and 1 kHz [60]. Thus, from Eq. (5) the carrier densities n_p can be calculated by the approximate relation, $n_p \sim 2 B \epsilon_0 \epsilon_p / q$. The calculated carrier densities n_p are given in Table 2 and are close to $\sim 10^{23}$ m⁻³ reported in BFO thin film [61]. The junction width in the dark can be calculated by using the relation, $d_0 \sim (U_0 / B)^{1/2}$ [57]. As shown in Table 2, the calculated junction widths d_0 are consistent with the depletion-layer width between ITO and BFO thin films, which was estimated to be a few hundred nanometers [61].

The solid lines in Fig. 11 are theoretical fits by using Eqs. (3) and (4) with parameters in Table 2. In the theoretical fits, the attenuation length (at $\lambda = 405$ nm) of the specimen synthesized with O₂:N₂ ratio of 1:1 is estimated from the average of all-O₂ and all-N₂ specimens, i.e. $\beta = 7.1$ μ m. The calculated curves of V_{oc} and J_{sc} agree well quantitatively with experimental data at lower irradiation intensities (< 20 W/m²) as enlarged in the insets. The discrepancies between the experimental and calculated V_{oc} at higher irradiation intensities mainly result

Fig. 13. Power-conversion efficiency (η) vs. load voltage for various irradiation intensities. Solid lines are guides for the eye.

Fig. 14. Irradiation intensity-dependent external quantum efficiencies (EQE). Solid lines are guides for the eye.

from increasing intrinsic carrier density. As irradiation intensity increases, the fermi level can be pushed higher because intrinsic carrier density can be increased due to thermal energy from irradiation. The built-in potential barrier in a p - n junction is mainly caused by the difference in fermi levels between p -type and n -type regions. The built-in potential is expected to decrease as the band gap between fermi levels decreases by irradiation. In addition, the lower V_{oc} in the O_2 -rich-atmosphere specimens is likely also associated with higher oxygen vacancies. According to a first-principles calculation, oxygen vacancies can give rise to defect states in BFO below the conduction band and shift the absorption edge to lower energy [62,63]. The built-in potential in the p - n junction decreases as oxygen vacancies increase [62,63].

The discrepancies between the experimental and calculated J_{sc} at higher irradiation intensities in Fig. 11(b) can be mainly attributed to the recombination of charged carriers, which often occurs at the surface or in the bulk of the cell. The p - n -junction-like model used in this study only considers the electron-hole generation by irradiation [57]. As shown in Fig. 1, the increasing oxygen vacancies are likely responsible for the reduced J_{sc} in the O_2 -rich-atmosphere specimens, because oxygen vacancies can increase charge recombination rate at the interface [64]. Other factors, such as microstrain, local domain structure, polarization, and electronic states may also affect the charge conductivity [65,66].

Fig. 13 shows plots of power-conversion efficiency (η) vs. load voltage (V) with increasing irradiation intensity. The power-conversion efficiencies were calculated using $\eta = P_{out}/P_{in}$, where P_{in} and P_{out} are respectively the irradiation power and output electric power calculated from irradiated current and voltage across the load. The maximal PV power-conversion efficiencies (η_{max}) occur at lower intensities and are respectively about 0.09, 0.19, 0.42, and 0.27% for specimens synthesized with O_2/N_2 atmosphere ratios of 1:0, 1:1, ~1:4 (ambient air), and 0:1. Fig. 14 shows the external quantum efficiencies ($EQE = hfJ_{sc}/qI$), which is a conversion from incident photons to conduction electrons in the PV process [57]. The rapid decay with increasing irradiation intensity is mainly caused by charge recombination. The specimen prepared with $O_2/N_2 \sim 1:4$ (ambient air) shows a maximal EQE of ~8%. Table 3 is a brief summary, including previous PV results in BFO materials under ultraviolet-visible irradiations [5,67–70]. The ITO/BFO7Nd ceramic/Au heterostructure has demonstrated comparable photovoltaic V_{oc} , J_{sc} , η , and EQE under ultraviolet irradiation.

4. Conclusions

This work has demonstrated the substantial influence of processing atmosphere on microstructure, O/Bi vacancies, impurity phase, phonon vibration, cation valence, bond strength, band gap, atomic hybridization, and PV properties in $(Bi_{0.93}Nd_{0.07})FeO_3$ ceramics. A decreased FeO_6 octahedral distortion and minor Fe^{4+} cation concentration were identified with decreasing O_2 concentration. The O_2 -rich-atmosphere specimens show decreased O 2p-Fe 3d and O 2p-Bi 6sp hybridizations, which are responsible for the larger band gaps. The PV effects of the ITO/BFO7Nd/Au heterostructure show strong dependence on processing atmosphere and can be quantitatively described by the p - n -junction model.

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Table 3

Comparison of experimental PV parameters in BiFeO₃ thin films, crystals, and ceramics. SRO and ITO represent SrRuO₃ and indium tin oxide, respectively. The BFO7Nd ceramic used in this table was prepared in ambient air (O₂:N₂ ~ 1:4).

PV heterostructure	V _{oc} (V)	J _{sc} (A/m ²)	Irradiation wavelength λ (nm)	Irradiation intensity (W/m ²)	$\eta_{\max}$ (%)	EQE (%)	Ref.
ITO/BFO thin film/SRO	0.3	4×10^{-3}	435	7.5			[67]
Pt/BFO thin film/Pt	20	0.5	375	1000			[68]
Pt/BFO crystal/Pt	13	0.01	405			3×10^{-5}	[69]
Au/BFO crystal/Au		0.075	532	< 200			[70]
ITO/BFO ceramic/Au	0.58	0.05	405	100	0.005	0.16	[5]
ITO/BFO5Sm ceramic/Au	0.7	0.94	405	100	0.25	3	[5]
ITO/BFO7Nd ceramic/Au	0.69	0.75	405	100	0.13	2.4	this work

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