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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 $(Bi_{1-x}Sm_x)FeO_3$ ($x = 0.0, 0.05, 0.10$) ceramics (BFO100*x*Sm) 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 *R*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, $T_N \sim 630$ 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 Bi^{3+} toward O^{2-} [2]. It was reported that the Curie temperature T_C in rare-earth-doped compositions of $(Bi_{1-x}RE_x)FeO_3$ (RE = La, Nd, Sm, Gd) decreases with decreasing average A-site ionic polarizability and tolerance factor [3]. Rhombohedral *R*3c $BiFeO_3$ 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 $(Bi_{1-x}RE_x)FeO_3$ (RE = La, Nd, Sm, Gd) for $x \leq 0.1$ correspond to the perovskite rhombohedral *R*3c phase of $BiFeO_3$ [3]. The $(Bi_{1-x}Sm_x)FeO_3$ 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 $(Bi_{1-x}Sm_x)FeO_3$ 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]. $(Bi_{1-x}Sm_x)FeO_3$ ceramics and thin films show enhanced magnetization with increasing Sm ratio [12–16]. $(Bi_{1-x}Sm_x)FeO_3$ ceramics show a magnetic structure transition from a spin cycloid to a G-type antiferromagnetic behavior at $x \sim 14\%$ [15,16].

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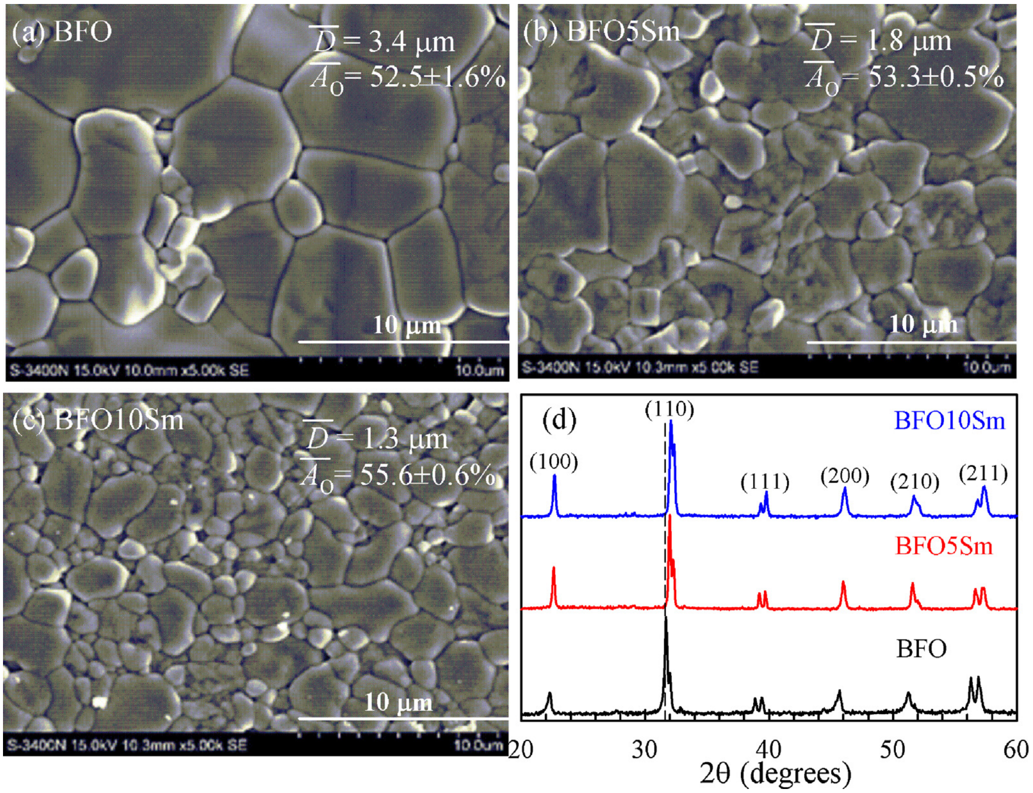

Fig. 1. (a-c) SEM grain morphologies of thermally etched ceramics and (d) XRD spectra of as-sintered samples at room temperature. $\bar{D}$ and $\bar{A}_O$ are average grain size and average oxygen atomic ratio, respectively.

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), $(Bi_{0.95}Sm_{0.05})FeO_3$ (BFO5Sm), and $(Bi_{0.90}Sm_{0.10})FeO_3$ (BFO10Sm) ceramics were prepared by the solid state reaction, in which Bi_2O_3, Sm_2O_3, and Fe_2O_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 $\lambda = 532$ 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 ($\lambda = 405$ 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.