

Photovoltaic conversion of rare earth-doped BiFeO₃ multiferroic ceramics

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Large photovoltaic (PV) open-circuit voltage, short-circuit current density, and power-conversion efficiencies under illumination of $\lambda=405$ nm have been observed in the heterostructures of indium tin oxide (ITO)/(Bi_{1-x}R_x)FeO₃ ceramic/Au (R=La, Nd, Sm, Eu, Gd, and Dy) for $x=0.0-0.07$. (Bi_{1-x}R_x)FeO₃ ceramics were prepared by the solid state reaction method. ITO and Au films were deposited using sputtering deposition. The PV effects and power-conversion efficiency strongly depend on doping concentration, illumination intensity, and ceramic thickness. For instance, the maximal open-circuit voltages (V_{oc}) and short-circuit current densities (J_{sc}) in ITO/(Bi_{0.95}Nd_{0.05})FeO₃ ceramic/Au can reach 0.8-0.92 V and 1-5 A/m². The maximal power-conversion efficiency (PCE) and external quantum efficiencies (EQE) in the ITO/(Bi_{0.95}Nd_{0.05})FeO₃/Au structure reach respectively 0.82% and 1.4% under illumination of $\lambda=405$ nm. The light-to-electric PCE is calculated as $PCE=P_{out}/P_{in}$, where $P_{out}=J_L \times V_L$ is the photovoltaic output power density (W/m²) and P_{in} is the illumination intensity. J_L and V_L are respectively load current density and load voltage under illumination. The maximal PCE in the ITO/(Bi_{0.95}Nd_{0.05})FeO₃/Au under standard solar irradiation is about 0.025%, which is larger than 0.005% in (La_{0.7}Sr_{0.3})MnO₃/(Pb_{0.97}La_{0.03})(Zr_{0.52}Ti_{0.48})O₃/Nb-SrTiO₃ films under sunlight [1], 0.0025% in graphene/polycrystalline BFO/Pt films under AM 1.5 irradiation [2], and 0.01% in ITO/BFO/BiCrO₃/CaRuO₃/LaAlO₃ films under a solar simulator [3].

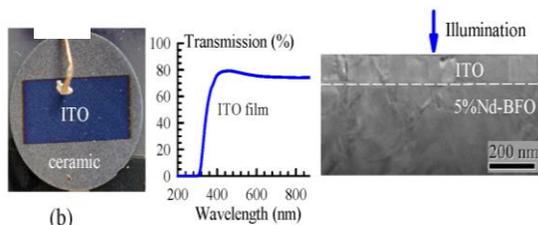


Figure 1 Ceramic disk with ITO electrode, optical transmission of ITO, and TEM image near the interface between ITO and ceramic.

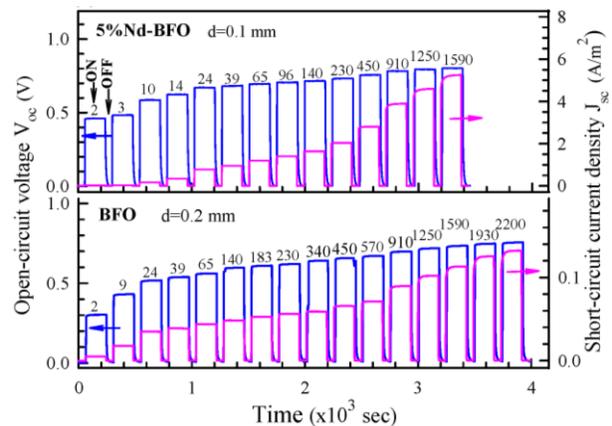


Figure 2 Open-circuit voltage V_{oc} and short-circuit current density J_{sc} as light was switched on and off with increasing incident intensity (in unit of W/m²) labeled above the tops of illumination plateaus.

The characteristic curves (current i vs. voltage V) in the dark can be expressed as

$$i_d = i_o \{ \exp[q(V - i_d R_d) / \zeta kT] - 1 \}. \quad (1)$$

where i_d , R_d and ζ are the diode current, diode resistance, and diode-quality factor. The asymmetrical characteristic curves suggest that the heterojunction between ITO film and $(\text{Bi}_{1-x}\text{R}_x)\text{FeO}_3$ ceramics is responsible for the photovoltaic responses.

To determine the oxidation states of Fe and Bi ions in $(\text{Bi}_{1-x}\text{R}_x)\text{FeO}_3$ perovskite, Fe K-edge and Bi L_{III}-edge X-ray absorption near-edge structure (XANES) spectra were measured. The results reveal that the valences of Fe and Bi ions in BFO and $(\text{Bi}_{1-x}\text{R}_x)\text{FeO}_3$ are +3 and also rules out the presence of the other bismuth ferrite secondary phases. The $k^2\chi(k)$ spectra of BFO and $(\text{Bi}_{1-x}\text{R}_x)\text{FeO}_3$ are similar and suggest that A-site R^{3+} substitution does not affect structural order. The Fourier transforms of extended X-ray absorption fine structure (EXAFS) spectra were also studied to identify interatomic distances of F–O and Bi–O bonds in $(\text{Bi}_{1-x}\text{R}_x)\text{FeO}_3$ compounds.

The micro-Raman spectra were obtained to identify rare earth doped effects of atomic vibrations. The Raman active modes of rhombohedral R3c for BiFeO_3 can be summarized as the following irreducible representation: $\Gamma=4A_1+9E$ [4,5]. Bi atoms participate mainly in the low-frequency modes below 170 cm^{-1} and Fe atoms involve in the vibration modes in the region of $150\text{-}270 \text{ cm}^{-1}$. Oxygen motions strongly dominate in modes above 260 cm^{-1} . The four lowest and strongest vibrations can be attributed to $E(1)$ mode near 67 cm^{-1} , $E(\text{LO}2)$ mode near 130 cm^{-1} , $A_1(\text{LO}1)$ mode near 170 cm^{-1} , and $A_1(\text{LO}2)$ mode near 220 cm^{-1} . The atomic vibrations near 220 cm^{-1} are mainly originated from the A_1 tilt mode of FeO_6 oxygen octahedral.

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