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We report the photovoltaic properties of doped ferroelectric $[Bi_{0.9}La_{0.1}][Fe_{0.97}Ti_{0.02}Zr_{0.01}]O_3$ (BLFTZO) thin films. Polycrystalline BLFTZO films were fabricated on $Pt/TiO_2/SiO_2/Si$ substrates by pulsed laser deposition technique. Al-doped ZnO transparent top electrodes complete the ZnO:Al/BLFTZO/Pt metal-ferroelectric-metal capacitor structures. BLFTZO showed switchable photoresponse in both polarities. The open circuit voltage ($V_{OC}$) and short circuit current ($J_{SC}$) were found to be $\sim 0.022\,V$ and $\sim 650\,\mu A/cm^2$, respectively after positive poling, whereas significant difference in $V_{OC} \sim 0.018V$ and $J_{SC} \sim 700\,\mu A/cm^2$ was observed after negative poling. The observed switchable photocurrent and photovoltage responses are explained on the basis of polarization flipping in BLFTZO due to the applied poling field. © 2014 AIP Publishing LLC.
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Ferroelectric materials are interesting due to their spontaneous polarization which is essential for device applications.[1,2] Moreover, they show an intrinsic photovoltaic (PV) response arising from a strong coupling between light, photocurrents, and atomic-scale degrees of freedom that cause a current-driven modulation of the internal field.[3] PV properties in both bulk and thin ferroelectric films of $BaTiO_3$, $LiNbO_3$ and $Pb(Zr,Ti)O_3$ have been studied.[4] However, the pure single phase $BiFeO_3$ (BFO), due to its superior multiferroic properties and optical bandgap (2.67–2.74 eV) in the visible region,[5] is highly suitable for PV applications compared to many other wide bandgap ferroelectrics.[6] Recently, Ji *et al.*[7] reported PV effect in BFO thin films under visible light illumination with a switchable photocurrent with respect to the direction of the ferroelectric polarization. Also, we recently reported the effect of poling on the photovoltaic properties of highly oriented $BiFeO_3$ thin films.[8] The switchable photocurrent is strongly affected by the electrode interface, as observed by Choi *et al.*[9] in BFO single crystal. It was also reported that the PV current in some BFO thin film samples cannot be switched, which was attributed to the interface depletion layer between BFO and the electrode.[10] They reported that diode-like rectification follows the polarization-dependent interface band bending of BFO single-crystal slabs that are electrically switchable.[11] That is, the open circuit voltage (Voc) and short circuit current density (Jsc) depend upon the remnant polarization direction. Farokhipoor and Noheda[12] recently demonstrated that the PV effect in BFO films originates from the 71° and/or 109° domain walls due to the asymmetry in polarization. Moreover, two mechanisms were proposed for the separation of photo-excited charge carriers, one taking place at the

interfaces and the other attributed to the intrinsic polarization.[6,13]

In BFO-based PV devices, both metallic and conducting oxide top electrodes have been used. Improved PV properties in ferroelectric thin films were obtained when transparent conductive oxide electrodes (TCO), such as indium tin oxide (ITO) and 2% Al doped ZnO, were used as top electrode instead of metal electrodes.[14] Chen *et al.*[15] studied the influence of ITO top electrode on narrow band gap BFO ferroelectric thin films finding that it plays a key role in achieving larger PV effect that is about 25 times higher than values obtained with Au as the top electrode. Further, we studied the photoconductivity as a function of frequency in a BFO wide area capacitor.[16] It was found that conductivity increases as the frequency increases in $La_{0.67}Sr_{0.33}CoO_3/BFO/ZnO:Al$ heterostructures. More recently, Guo *et al.*[17] also reported the switchable PV effect in Sr substituted BFO polycrystalline thin films (with high oxygen vacancy concentrations), whereas they found that it is hard to detect such an effect in the case of pristine BFO thin films (with lower oxygen vacancies) until the polarization flipping occurs.

Co-substitution (A-site and B-site) in the perovskite BFO lattice has been attempted by various researchers to improve the ferroelectric and magnetic properties.[18] In general, co-substitution will suppress oxygen vacancies and reduce the conductivity by means of reducing the $Fe^{2+}$ content, and, therefore, leading to a stoichiometry with no vacancies. Co-doping in BFO substantially improves the saturation polarization ($P_s$) up to $70\,\mu C \cdot cm^{-2}$, and the dielectric and ferromagnetic properties without changing the rhombohedral structure.[19,20] It has been found that the secondary phases were significantly suppressed in Pr and Sc co-substituted BFO ceramics, as compared to pure BFO. Piezoforce Microscopy (PFM) results corroborated the lower

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leakage current behavior and enhanced magnetic properties in Pr and Co co-substituted BFO (BPFCO) thin films.[21] In our previous studies, we reported well defined magnetic hysteresis behavior with high magnetic moment and the strong ferromagnetic properties for Sm and Co co-substituted BFO (BSFCO) ceramics.[22] Yang *et al.*,[23] in their experimental studies on BFO, showed that the specific arrangement of magnetic domains of a ferroelectric material leads to a new PV charge separation mechanism that produces photovoltages higher than the bandgap. Interestingly, common ferromagnetic transition metals, such as Fe, Ni, and Co, possess the characteristic Stoner energy bandgap, 1 eV, which can allow absorption of radiation from the Sun.[24,25]

While numerous studies are available on the structural, dielectric, and multiferroic properties of pure and co-substituted BFO bulk ceramics and thin films, relatively, few studies on the PV behavior of co-substituted BFO are available. Herein, we present our studies of the PV effect with switchable photoresponse in $[Bi_{0.9}La_{0.1}][Fe_{0.97}Ti_{0.02}Zr_{0.01}]O_3$ (BLFTZO) thin films with Al-doped ZnO (ZnO:Al) as the top electrode. The photovoltaic response of the ZnO:Al/BLFTZO/Pt metal-ferroelectric-metal (MFM) capacitor structure was studied under electrical poling treatments.

Co-substituted BLFTZO thin films were grown by utilizing a pulsed laser deposition (PLD) facility. The thin films were grown at ~15 mTorr oxygen pressure, ~740 °C substrate temperature, and ~70 mJ pulse energy at the target with a repetition rate of 10 Hz ($\lambda = 248$ nm). 300-nm thick films were grown on Pt/TiO2/SiO2/Si substrates in ~1600 s. 2% Al-doped ZnO top electrodes (100-nm thick) were deposited with a shadow mask ~200 $\mu$m in diameter. The BLFTZO thin films were characterized by X-ray diffraction (XRD) (Rigaku D/Max Ultima II X-ray diffractometer) using a Cu K$\alpha$ source operating at a scan rate of 0.1°/min over the 2$\theta$ range of 20–80°. Temperature dependent (100–475 K) Raman studies were carried utilizing Horiba T64000 triple monochromator with microprobe consisting of an optical microscope with 50× objective and 514 nm laser radiation of power ~5.5 mW focused to a ~2 $\mu$m spot. Piezoresponse Force Microscopy (PFM) was carried out with a tip voltage of ±10 V (Veeco make). The I-V characteristics of ZnO:Al/BLFTZO/Pt heterostructures were measured in top-bottom electrode configuration using a Keithley model 2401 electrometer. Photovoltaic measurements were obtained with a light source density of ~1 kW/m$^2$ in a ABET Technologies Model 3000 Solar Simulator.
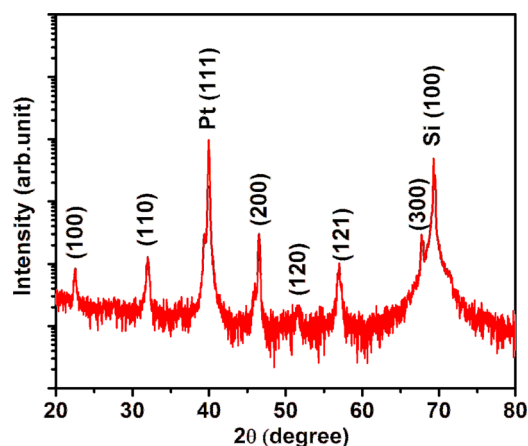


FIG. 1. XRD diffractograms of polycrystalline thin films of BLFTZO.

The phase purity of BLFTZO films was confirmed by X-ray diffraction studies. As shown in Fig. 1, the XRD diffractograms show peaks consistent with a rhombohedral structure of space group [R3c], where the sharpness of the features indicate a high quality polycrystalline films. Further, the single phase formation of BLFTZO was confirmed by Raman spectroscopy, where all modes corresponding to BFO were identified in the 10–1000 cm$^{-1}$ spectral window. Four strong peaks in the low frequency region (50–400 cm$^{-1}$) were identified as first order zone center optical phonons based on the reported peak assignment for single crystal BFO.[26] From group theory mode assignments, the peak at 73 cm$^{-1}$ corresponds to the E mode, whereas, and the peaks at 148, 175, and 227 cm$^{-1}$ were identified as A$_1$ modes. Broad features appearing at higher frequencies remain to be identified. The Raman bands of BLFTZO are somewhat broader than those of BFO due to substitutional disorder. We analyzed the peak positions of the Bi-associated modes at 73, 148, and 175 cm$^{-1}$ as a function of temperature, as presented in Figure 2(b). From earlier reports, the E mode at 73 cm$^{-1}$ is associated with the motion of Bi-O bond and its variation reflects the change in the dielectric constant and, hence, the ferroelectricity.[27] The temperature dependence of the E mode is monotonous in the studied range, thus precluding any ferroelectric transition. Similar linear changes in the peak positions for the two A$_1$ modes were also observed.

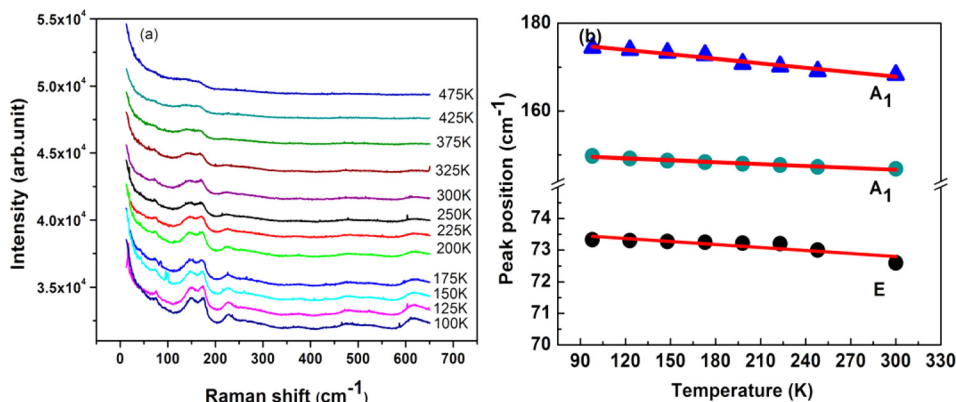Piezoresponse force microscopy (PFM) was deployed to study the ferroelectric response of BLFTZO films (Fig. 3).



FIG. 2. (a) Temperature dependent Raman spectra of BLFTZO thin film in the temperature range of 300–475 K. (b) Frequency of the Raman modes as a function of temperature.
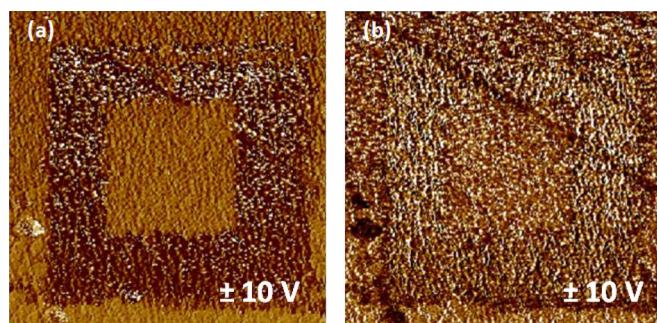
FIG. 3. Switchable ferroelectric effects measured by piezoresponse force microscopy on BLFTZO films with an applied bias voltage of ±10 V over a 5 $\mu m^2$ area: (a) phase; (b) amplitude.



FIG. 4. Current density as a function of applied bias voltage for the ZnO:Al/ BLFTZO/Pt heterostructures obtained under illumination (energy density $\sim$ 1 kW/m$^2$). The inset corresponds to the enlarged region around the origin and identifies the values for $V_{OC}$ and $J_{SC}$ (Legend: red = negative poling, blue = positive poling, black = no poling).

The color contrast demonstrates the switchable ferroelectric response of the BLFTZO films. Furthermore, the out-of-plane PFM phase hysteresis loop and amplitude signals versus voltage curves indicate their ferroelectric nature.

The I-V characteristics of ZnO:Al/BLFTZO/Pt MFM capacitor were obtained under dark and white light illumination, as shown in Fig. 4. Electrical poling of the films was accomplished by applying a bias voltage of ±10 V. The I–V curves exhibit greater current both in reverse and forward bias poling, along with appreciable $J_{SC}$ and $V_{OC}$ values under illumination compared to those obtained in darkness. It can also be seen in the inset of Fig. 4 that the BLFTZO showed switchable $J_{SC}$ and $V_{OC}$ according to poling direction and hence ferroelectric polarization. The $J_{SC}$ measured at zero bias was found to be $\sim$650 $\mu A/cm^2$ for the ferroelectric polarization, while $V_{OC} \sim 0.022$ V was observed when exposed to light in positive polarity. The $J_{SC}$ and $V_{OC}$ were observed to be $\sim$700 $\mu A/cm^2$ and $\sim$0.017 V, respectively, in opposite polarity. These results clearly indicate that the observed photovoltaic effect originates from the ferroelectric polarization of BLFTZO films, where the photo-generated
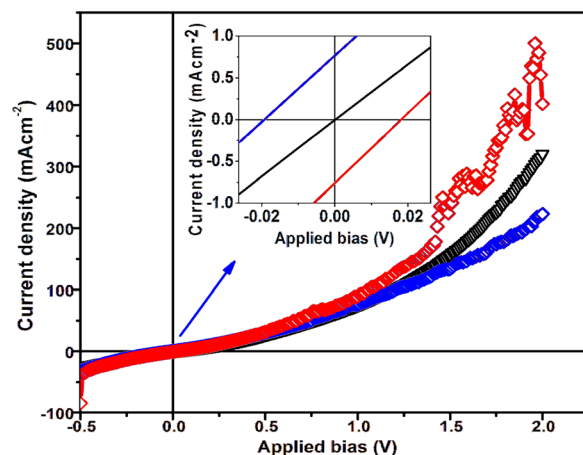
charge carriers are effectively separated by the de-polarization field. The presence of switchable $J_{SC}$ and $V_{OC}$ further supports the de-polarization field induced charge separation in BLFTZO.

The switchable photoresponse of BLFTZO films was also studied as a function of time (Figs. 5(a) and 5(b)). For this study, incident light with intensity of 1 kW/m$^2$ was impinged periodically every 10 s, and the photocurrent at zero bias was measured. It can be seen that $J_{SC}$ increases rapidly to $\sim$700 $\mu A/cm^2$ when exposed to light, followed by an exponential decrease in current density with a delay of $\sim$250 ms calculated from fitted data shown in inset of Fig. 5(a) that stabilizes at $\sim$200 $\mu A/cm^2$. When the light is turned off, $J_{SC}$ decreases rapidly with delay of $\sim$160 ms to reach its original state. Similar trends were observed for the opposite polarization of BLFTZO (Fig. 5(b)) confirming the switchable
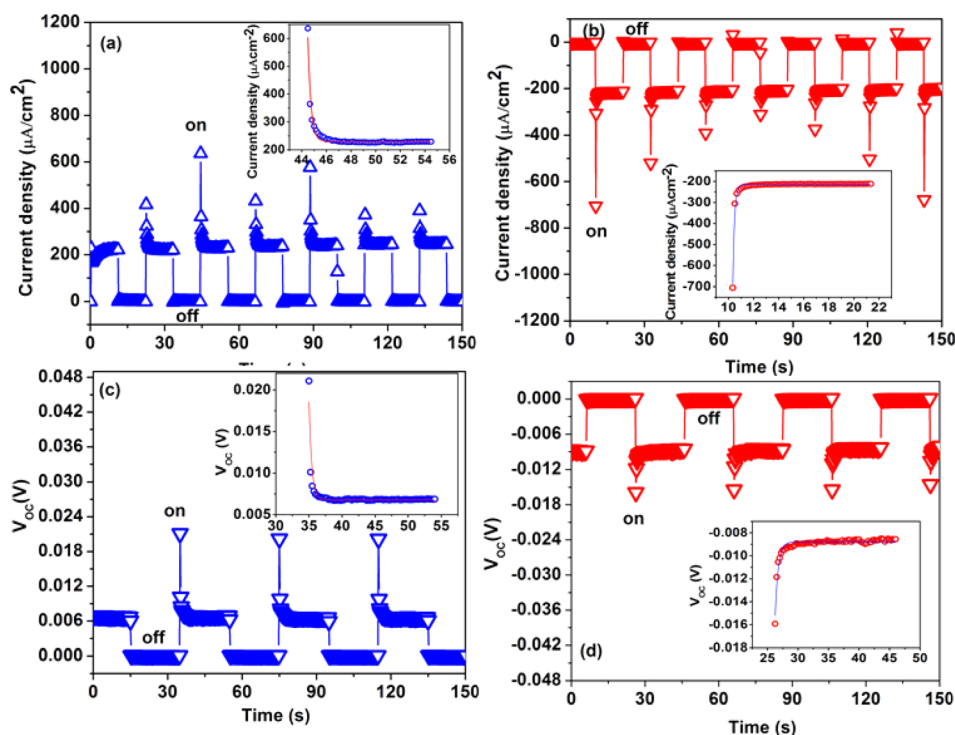


FIG. 5. Switchable $J_{SC}$ and $V_{OC}$ as a function of time in ZnO:Al/ BLFTZO/ Pt heterostructures under illumination (energy density $\sim$ 1 kW/m$^2$): (a) $J_{SC}$ in positive polarity, (b) $J_{SC}$ in negative polarity, (c) $V_{OC}$ in positive polarity, (d) $V_{OC}$ in negative polarity.

photoresponse of the ZnO:Al/BLFTZO/Pt heterostructures.[28] The observed spikes in photocurrent with light illumination can be ascribed to Joule heating, causing the internal resistance to increase and Jsc to decrease until thermal equilibrium is attained. However, the pyroelectric effect cannot be discarded to account for the observed spikes in the photocurrent at zero bias.[29]

Further, the $V_{OC}$ of BLFTZO was studied as a function of time for both polarization directions on periodic exposure of light, and the results are shown in Figures 5(c) and 5(d). Similar spiky behavior was observed in photovoltage transients that probably has the same origin as the photocurrent. It can be seen that $V_{OC}$ increases rapidly on light exposure, followed by a exponential decay of ~250 ms calculated from fitted data shown in inset of Fig. 5(c), that stabilizes at ~0.0120 V. When the light is turned off, the $V_{OC}$ decreases rapidly to reach its original value. Similar trends were observed for the opposite polarization of BLFTZO (Fig. 5(d)).

In summary, we have studied the photovoltaic properties of BLFTZO in ZnO:Al/BLFTZO/Pt metal-ferroelectric-metal capacitor heterostructures. XRD and Raman measurements confirmed the rhombohedral space group [R3c] of BLFTZO. The ferroelectric polarization throughout the BLFTZO films was confirmed by PFM images. I-V measurements show switchable ferroelectric response in ZnO:Al/BLFTZO/Pt heterostructures and a corresponding switchable photovoltaic behavior attributed to polarization flipping upon poling. Measurements of the time dependence of the $V_{OC}$ and $J_{SC}$ in both polarities show a transient spike ascribed to Joule heating.

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