Lanthanum and strontium modified bismuth ferrite based perovskites with ultra-narrow band gaps

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Abstract
The wide optical band gaps of ferroelectric perovskite oxides have restricted their light absorbing capacities in the photovoltaic devices. In this work, an ultra-narrow band gap $E_g$ and wide optical absorption across the ultraviolet-visible-infrared sunlight spectrum was achieved in lanthanum and strontium atoms modified Bi(Fe, Mn)O$_3$ perovskites by chemical substitution and defect engineering. XRD results show that the A and B site co-substituted samples are single phase. The XPS characterizations indicate the Fe ions are in the trivalent state for all the samples. The LM6 and SM6 samples exhibit an ultra-narrow band gap about 1.26 eV and 1.06 eV, respectively. The reduced $E_g$ was due to the defect states produced within the band gap, acting as a scaffold to give electrons to Fe 3d states and receive the electrons from O 2p states. Based on this research, these chemically modified BFO based perovskite could potentially extend its sunlight absorption deep into the infrared region.

Introduction
Ferroelectric photovoltaic (FEPV) effects in perovskite oxides have gained more and more focus in recent years for solar cell applications [1–3]. For conventional p-n junction semiconductor solar cells, photons with energy above the band gap $E_g$ can be absorbed to generate electron–hole (e-h) pairs, which are then separated by the built-in electric field existing only in the p-n junction. For ferroelectric photovoltaic effects, the built-in electric field is derived from the remnant polarization of the ferroelectrics, so the open circuit voltage $V_{oc}$ is not limited by the band gap [4]. Therefore, the power conversion efficiency can potentially exceed the Shockley–Queisser limit, which prevents the single p-n junction solar cell having more than 33.7% of energy conversion efficiency [5]. Besides, the built-in electric field in ferroelectrics is throughout the bulk region, which may facilitate the separation of electron-hole pairs. Another unique advantage of ferroelectrics is their photocurrent direction could be switched by external electrical field via changing the spontaneous polarization direction [5, 6]. Compared with their metal halide perovskite competitors (e.g. CH$_3$NH$_3$PbI$_3$), ferroelectrics oxides are much more stable under severe mechanical, chemical and thermal conditions [7]. Furthermore, they are generally inexpensive and abundant. All these characteristics make ferroelectric oxides good candidates employed in photovoltaic devices.

Nevertheless, the band gap of ABO$_3$ type ferroelectric materials such as BaTiO$_3$, Pb(Zr,Ti)O$_3$, and Bi$_4$Ti$_3$O$_{12}$, is usually very wide (>3 eV), due to the large difference between electro-negativities of oxygen and the B site transition-metal atoms [4]. When used as light absorbing materials, these wide band gap ferroelectrics mainly absorb ultraviolet light, which comprises only about 3.5% of solar irradiation. In contrast, the visible and infrared light, which comprises most of the solar irradiation, could barely be absorbed, resulting in very low power conversion efficiencies and small photocurrent.

In recent years, photovoltaic properties in bismuth ferrite BiFeO$_3$ (BFO) have received immense research attention owing to its large remnant polarization (>60 μC cm$^{-2}$) and small band gap (about 2.7 eV), which is lower than the band gap of many other ferroelectric materials [8]. BFO is a lead-free perovskite material widely known for its outstanding physical properties, e.g. large remnant polarization, high Curie temperature.
Experimental details

The samples with the compositions Bi_{0.96-x}La_{0.04+x}Fe_{1-x}Cr_xO_3 (x = 0.04, 0.06, 0.08) (denoted as BF92-LF4-LM4, BF90-LF4-LM6, BF88-LF4-LM8, respectively) and Bi_{0.90-La_{0.04}Sr_{0.06}}O_3 (denoted as BF90-LF4-SM6) were prepared by the solid state reaction (SSR) method. Undoped BFO samples were also prepared by SSR to make comparisons. The raw materials are Bi_{2}O_{3} (Alfa Aesar, 99%), Fe_{2}O_{3} (Alfa Aesar, 99.945%), La_{2}O_{3} (Sinopharm, 99.99%), SrCO_{3} (Sinopharm, 99.0%), and MnO_{2} (Alfa Aesar, 99%).

The raw oxide powders were weighed according to each desired chemical formula, and then mixed and ground by an agate mortar and pestle with ethanol as the milling medium. The samples were calcined in a chamber furnace at 780 °C for 5 h. After calcination, powders were reground, granulated, and pressed uniaxially into 20 mm diameter green pellets under 200 MPa. The green pellets were then sintered in a chamber furnace in air atmosphere at 990 °C for 3 h for SM6 samples, and 930 °C for 3 h for LM4, LM6 and LM8 samples. Undoped BFO samples were sintered at 890 °C for 3 h. The density of the disk samples were measured by the Archimedes method and it is above 95% and 92% of theoretical density of pure BFO for LM6 and SM6 samples, respectively.
The microstructure was observed with a Field Emission Scanning Electron Microscope (FE-SEM) (Hitachi, S-4800). The crystal structure and phase purity of the samples were examined using an x-ray diffractometer (Rigaku, D/max 2550 V) using CuKα radiation. For the Raman spectroscopic study, the sintered pellets were polished using diamond paste and the Raman spectra were obtained with a Raman instrument (Renishaw, Raman inVia-Reflex) with laser wavelength of 532 nm.

The x-ray photoelectron spectra (XPS) of ceramic samples were taken at room temperature with an x-ray photoelectron microprobe (Thermo Fisher Scientific, Escalab 250Xi). The spectra were excited with a monochromatized AlKα-radiation. The diffuse reflectance and absorbance spectra of the ceramic samples were acquired in the range 200–1400 nm using a UV–vis-NIR Spectrophotometer (Shimadzu, UV-3600) with fine BaSO4 powder as a non-absorbing standard.

For electrical measurements, ceramic pellets were polished and then coated with silver paste and fired at 600 °C for 10 min. The frequency-dependent dielectric properties were measured at room temperature using a precision LCR meter (Tonghui, TH2838).

The temperature dependent dielectric properties were obtained by a dielectric measurement system (TZDM, RT-1000). The electrical resistivity measurement was carried out by a high resistance meter (Keithley, 6517B).

Results and discussions

The microstructure of the fractured surface of LM6 and SM6 ceramic samples were displayed in figure 1. It can be seen that both samples are dense with polyhedral grains, and the grain size is about 2–3 μm. Compared with LM6 sample, the fracture surfaces of SM6 sample are less smooth, and a few pores can be found present at the grain boundaries. The pores may indicate that the volatility was not completely suppressed for SM6 samples. The powder XRD patterns of all the doped and undoped BFO samples are shown in figure 2. These patterns can be indexed as a rhombohedrally distorted perovskite with space group $R3c$. No secondary impurity phase was discernible within the sensitivity of the XRD equipment for all the doped samples. However, for the undoped samples, a small amount of Bi2O3 can be identified, which suggest that in this study doping in BFO could effectively suppress the formation of the secondary phases, as was shown in Zhang’s research [21].

The lattice parameter of all the samples were calculated from the XRD data and shown in table 2. A continuous decease in lattice parameters with increasing doping amount could be observed. Consequently, the volume of one unit cell was also decreased for all the doped samples. This shrinkage of lattice parameters were also observed in La and Ti co-doped BFO samples [21].

To identify the doping effects on atomic vibrations, Raman spectra were measured at room temperature in the range of 100–700 nm$^{-1}$. Figure 3 suggests that all samples exhibit similar Raman vibrations, confirming the same $R3c$ symmetry. Group theory predicts BFO should have four $A_1$ and nine $E$ Raman active modes [22]. The strong peaks at 140, 171, 224, 472 cm$^{-1}$ can be assigned to the four $A_1$ Raman active modes and the remaining peaks can be assigned to the $E$ modes. The $A_1$-3 modes, which was attributed to the tilting of the FeO$_6$ oxygen octahedral [23], was greatly suppressed for SM6 samples. This may imply the different influence of the La and Sr atoms on the tilting of the oxygen octahedral.
The XPS spectra of Bi, O and Fe elements were acquired and plotted in figure 4 to confirm the electronic valence. As can be seen from figure 4(a), the peak binding energy of Bi 4f7/2 and Bi 4f5/2 was 158.8 eV and 164.1 eV, respectively. Therefore, the spin–orbital splitting energy of Bi 4f is 5.3 eV, which confirms the trivalent state of bismuth ions [24]. Energy positions of Fe 2p XPS was known sensitive to the valence of Fe [25]. In figure 4(b), peak A and peak C reflect Fe 2p3/2 and Fe 2p1/2 electron levels, respectively, and they are due to the spin–orbit interaction. Peaks B and D are charge transfer satellites arising from screening of the initial Fe 2p

![Figure 2. Powder XRD patterns of the doped and undoped BFO samples.](image)

**Table 2.** The lattice parameters for the doped and undoped BFO samples.

| Lattice parameter | Sample | a (Å) | c (Å) | Volume Vh (Å³) |
|-------------------|--------|-------|-------|---------------|
|                   | LM4    | 5.57  | 13.82 | 371.31        |
|                   | LM6    | 5.57  | 13.77 | 369.97        |
|                   | LM8    | 5.56  | 13.77 | 368.64        |
|                   | SM6    | 5.55  | 13.63 | 363.58        |
|                   | BFO    | 5.58  | 13.85 | 373.45        |

![Figure 3. Raman spectra of LM series and SM6 samples.](image)

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vacancy by the electron of the neighboring atoms [26]. The asymmetry of the main Fe 2p peaks was attributed to the electrostatic interaction of the 2p vacancy and the open 3d subshell. The energy separation between the main Fe 2p is 13.3 eV. The peak positions and overall profile are characteristic of the spectra of Fe$^{3+}$ with a Fe 2p$_{3/2}$ peak position at about 710.3 eV for both LM6 and SM6 samples. Therefore, it can be confirmed from the XPS studies that Fe mainly exists in the 3$^+$ state. In figure 4(c), the XPS spectra of O 1s show two binding energy peaks at about 529.4 eV and 530.6 eV, respectively. The former can be attributed to the intrinsic oxygen ions at the lattice and the latter was extrapolated to be related to the adsorbed oxygen or surface defects [24, 27].

Figure 5 shows the frequency dependence of dielectric constant and loss at room temperature. For LM samples, both the dielectric constant and loss decrease with increase in frequencies as shown in figure 5(a). This is a normal behavior of a typical dielectric material, as the contribution from interfacial, dipolar, ionic and atomic polarizations decreases with increase in frequency and only electronic polarization contributes at very high frequency [28]. Furthermore, both the dielectric constant and loss increase with increase in Mn doping.
amount. As for the SM6 sample, as shown in figure 5(b), the dielectric constant is much higher than LM series samples. This is probably due to the larger contribution of the conductivity for the SM6 samples, as will be shown in figure 7. On the other hand, the magnitude of dielectric loss of SM6 samples is similar to LM6, but it first drops with increase in frequency up to 5 KHz, and then increase with frequency. The upturn is probably due to the influence of the lattice point defects such as oxygen vacancies, which exist in a larger amount in SM6 samples compared with LM6 samples.

Figure 6 shows the temperature dependence of dielectric constant and loss at four different frequencies (1 KHz, 10 KHz, 100 KHz and 1 MHz). It can be seen that both the dielectric constant and loss of LM6 samples increase with temperature. For SM6 samples, the peak at 180 °C in the dielectric constant plot could be attributed to the oxygen vacancies as well.

In order to identify the defect energy levels, the temperature dependence of electrical resistivity for LM6 and SM6 samples were measured and shown in figure 7(a). The resistivity for both samples are at the same order of magnitude at room temperature ($3 \sim 4 \times 10^5 \Omega \cdot m$). However, with the increase in temperature, the resistivity of SM6 sample decreases more rapidly than LM6 sample. The activation energy $E_a$ in figure 7(b) are obtained according to the relationship:

$$\rho = \rho_0 \exp \left( \frac{E_a}{k_B T} \right),$$

in which $k_B$ is Boltzmann constant and $\rho_0$ is the resistivity at infinite temperature (a constant). $E_a$ was estimated from the slope of $\ln \rho$ versus $1000/T$ plot. For LM6 sample, $E_a$ was derived as 0.44 eV, which could be due to the first ionization of oxygen vacancies [29]. For SM6 sample, there were clearly two regions representing two different activation energy. In the lower temperature region, $E_a$ was calculated as 0.64 eV and in the higher temperature region 0.82 eV, which could be attributed to the contribution from the first and second ionization
of oxygen vacancies, respectively [29, 30]. These oxygen vacancies could give rise to electronic states within the band gaps. Those results are consistent with the dielectric constant measurement in figure 6.

Considering the potential photovoltaic applications of these BFO based materials, the optical absorbance spectra of LM6 and SM6 samples acquired in the range of 200 nm to 1400 nm at room temperature, as shown in figure 8. For LM6 sample, the three absorption peaks observed at 240 nm, 372 nm and 508 nm can be attributed to $p$-$d$ charge-transfer excitations across the band gap [20, 25]. The 650 nm and 880 nm absorption peaks could arise from $^6A_{1g}$ to $^4T_{2g}$ and $^6A_{1g}$ to $^4T_{1g}$ on-site $d$-$d$ crystal-field excitations of the Fe$^{3+}$ ions, respectively [20, 25]. For SM6 sample, the on-site $d$-$d$ crystal-field excitations peaks shown in LM result could not be easily identified, but the absorbance was obviously enhanced at photon wavelength above 700 nm.

The optical band gap $E_g$ was derived using absorbance data and Tauc’s relationship, by extrapolating the linear part of the $(\alpha h\nu)^2$ versus $h\nu$ curves as shown in the inset of figure 8. LM6 and SM6 samples exhibit a band gap about 1.26 eV and 1.06 eV, respectively, which is smaller than the lowest photon energy (1.59 eV) of the visible light spectrum and enables the Sunlight absorption deep into infrared region. The reduced band gap compared with pure BFO was attributed to the new energy states (gap states) introduced between the conduction band and valence band [4, 17, 20, 25, 31]. The gap states could play the role of a scaffold, which gives electrons to Fe 3d states (CBM), and receive the electrons from O 2p states (VBM). These in-gap absorption could arise from the oxygen vacancies created by A and B site substitutions [10, 32].

Conclusions

In summary, we have prepared La and Sr modified Bi(Fe, Mn)O$_3$ single phase ceramic samples. The XRD and Raman spectra reveal that all A and B site modified BFO samples still have a rhombohedral R3c phase. LM6 and SM6 samples exhibit ultra-narrow band gaps about 1.26 eV and 1.06 eV, respectively. The reduced $E_g$ was attributed to the defect states created within the band gap, acting as a scaffold provide electron to Fe 5d and receive the electron from O 2p states. This approach could expand the Sunlight absorption spectrum of BFO based materials, rendering them more potential to be employed in photovoltaic applications.

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