Inorganic photovoltaic cells based on BiFeO$_3$: spontaneous polarization, lattice matching, light polarization and their relationship to photovoltaic performance

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ABSTRACT

Inorganic ferroelectric perovskite oxides are more stable than hybrid perovskites. However, their solar energy harvest efficiency is not so good. Here, by constructing a series of BiFeO$_3$ based devices (solar cells), we investigated three factors that influence the photovoltaic performance, including spontaneous polarization, terminated ions species in the interface between BiFeO$_3$ and the electrode, and polarized light irradiation. This work was carried out in the framework of density functional theory combined with non-equilibrium Green’s function theory under built-in electric field or finite bias. The results showed that 1) the photocurrent is larger only under a suitable electronic band gap rather than larger spontaneous polarization; 2) the photocurrent reaches the largest in Bi$^{3+}$ ions terminated interface than in the case of Fe$^{3+}$ or O$^2-$ with SrTiO$_3$ electrode; 3) the photocurrent could be largely enhanced if the polarized direction of the monochromatic light is perpendicular to the spontaneous polarization direction. The results would deepen the understanding of some experimental results of BiFeO$_3$ based solar cells.

Keywords: Ferroelectrics; DFT+NEGF; spontaneous polarization; interfaces; polarized light; photovoltaics

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1. INTRODUCTION

Since the energy crisis is now a worldwide problem\cite{1-4}, researchers have begun to
investigate the renewable energy materials, especially the solar energy harvest
materials, such as solar cells. Efforts in the energy conversion efficiency
improvement of silicon p-n junction solar cells are now loss of interest, because the
cost is high and the efficiency could not exceed Shockley-Queisser limit\cite{5, 6}.
However, the recently widely studied perovskite materials do not encounter these
problems. Theoretically, the open circuit voltage could exceed the band gap of the
material and sometimes reached several dozens of volts\cite{7}, thus the energy conversion
efficiency could exceed the Shockley-Queisser limit\cite{8, 9}. Some of these perovskites
were the widely studied organic-inorganic hybrid halides perovskites. The energy
conversion efficiency has reached to 22\%. However, they have encountered
stability problem and may pollute environment\cite{10-12}.

Inorganic ferroelectric perovskites rarely encountered stability problems. Unlike
the p-n junction based solar cells, where the photo excited excitons are separated by
the built-in electric field in the depletion layer, excitons in ferroelectric perovskites
are separated under the built-in electric field. This electric field is mainly originated
from the regular arrangement dipoles. The photovoltaic phenomenon in the
ferroelectric perovskites is usually called bulk photovoltaic phenomenon (BPV)\cite{13}.
One of the most accepted theories for the origin of photovoltaic phenomenon is
depolarization theory\cite{14-17}. The built-in electric field originates from the extra
positive and negative charge in the two interfaces with the electrodes of the cell.
This built-in electric field is also called depolarization field. In addition, the
depolarization field is anti-correlation with the thickness of the cell.

One of the candidate inorganic materials of the BPV effect perovskites is Bismuth
Ferrite\cite{1, 7, 18-30} (BiFeO$_3$, or BFO). The extensively studied BFO is a multiferroic
material which has the multiple properties of ferroelectric, anti-ferromagnetic, and
ferroelastic\cite{31}. Theoretically, the larger spontaneous polarization ($P_s$), the larger
open circuit voltage in ferroelectrics based solar cell. This is because the electric
field ($E$) is proportional to the spontaneous polarization value $P_s$, ($P_s = \chi E_0$),
and the open voltage ($U_o$) is proportional to $E$ ($U_o = cE$). For example, Bhatnagar et al.\cite{29}
found that the open circuit voltage of BiFeO$_3$ ($P_s = 80.2$ μC/cm$^2$) could exceed 15
V, while Spanier’s work\cite{32} indicates that the open circuit voltage of BaTiO$_3$ ($P_s = 26$
μC/cm$^2$) is about 4.8V. The ratio of open circuit voltage is consistent with their ratio
of spontaneous polarization. The spontaneous polarization ($P_s$) in the hexagonal or
rhombohedral BFO is about 80 μC/cm$^2$, which is nearly the largest room
temperature value in the known perovskites\cite{33}. However, larger band gap means
lower current density. So, the actual energy conversion efficiency is still too low
(<2)\%\). Consequently, some experimental works are reported to enhance the
photovoltaic performance of BFO based solar cells\cite{8, 17, 24, 25, 29}. For example, Choi
et al.\cite{20, 26} have studied the relationship between electronic transport characteristics
and the direction of spontaneous polarization by experimental methods. In addition,
they have also studied the relationship between the photocurrent densities and
polarized light. Interface effect is also a very key factor that influences the
photovoltaic performance. However, systematical theoretical works that uncover the mechanism of photovoltaic properties of BFO, especially the electrons transport properties based on the above three factors under sun illumination, are still rare.

In this work, we have done systematic first principles studies of BFO as a photovoltaic solar cell device to investigate the effect of $P_s$, terminated ions with electrode in the device, and directions of polarized light on the photovoltaic performance. With the help of density functional theory (DFT) combined with non-equilibrium Green’s function (NEGF), the electronic states under bias or built-in electric field could be obtained. So, we could investigate how the photovoltaic performance changes by adjusting one main factor, whereas keeping other factors fixed as much as possible. The results may be helpful for the experiments to enhance the power conversion efficiency.

2. COMPUTATIONAL DETAILS

We adopted the linear combination of atomic orbitals (LCAO) method, and the interactions between ion cores and valence electrons was treated with OMX pseudo potential, which is suitable to treat large systems with high accuracy. The exchange and correlation effects were considered by generalized gradient approximation (GGA) which is on the third order of Jacob’s ladder. The room temperature rhombohedral BFO is a G-type antiferromagnetic spin structure with ferroelectric Curie temperature 1103 K, Neel temperature 643 K. Although the spin direction is a little tilted in adjacent, we only considered a collinear G-type antiferromagnetic model as other first-principles works to reduce the computational cost. The easy polarization direction is along [1 1 1] for the room temperature BFO. The $P_s$ is obtained with the theoretical framework of Berry phase, which is the modern theory of polarization. In this method, the charge centers of dipoles in ferroelectrics are obtained by calculating the real space localized Wannier functions. For BFO, the strong correlation effect of Fe 3$d$ electrons is treated with SGGA $+ U$ (the Coulomb repulsive energy of 3$d$ electrons is $U_{eff} = 5$ eV). This is the relatively computing resources inexpensive and suitable method, and it is widely adopted to deal with BFO rather than hybrid functional or GW. As for the built-in or applied electric field, the electron density in the device could not be obtained merely by DFT, so we adopted the DFT combined with NEGF method to get the nonequilibrium transport electronic states (DFT + NEGF). This method, nonequilibrium electron density is obtained by NEGF method (it is realized in real space), then the Hamiltonian is obtained by DFT method (it is realized in reciprocal space), the newly constructed Hamiltonian will then be put into the next NEGF calculations until the input and output charge densities are self-consistent. Because the central scattering region is non-periodic, we need more k points than in periodic lattice. Then, the related properties, such as, IV curve, photocurrent, transmission spectrum and transmission eigenstates will be obtained. This theoretical method has also been successfully applied to p-n junction solar cell. In the entire device calculations above all, when the k point’s mesh is set to $2 \times 2 \times 100$, the convergence
is to be $1 \times 10^{-6}$ eV/atom. Our calculations were performed with Atomistix ToolKit (ATK) package\(^4\). Cell optimizations were done within GGA - PBE by Vienna Ab-initio Simulation Package (VASP)\(^{38, 50-52}\).

In terms of the photocurrent calculations, the electron-photon interaction is given by the Hamiltonian\(^{53-56}\):

$$H' = \frac{e}{m_0} A \cdot P$$

where \(A\) is the vector potential and \(P\) is the momentum operator. For a monochromatic light source, we have:

$$A = e \left( \frac{\hbar \sqrt{\mu_r \varepsilon_r}}{4\pi N \omega c \tilde{\varepsilon}} F \right)^{1/2} \left( b e^{i\omega t} + b' e^{-i\omega t} \right)$$

Here, \(A\) is related to relative permeability \(\mu_r\), relative permittivity \(\varepsilon_r\), permittivity \(\tilde{\varepsilon}\) of the material, and to the frequency \(\omega\), photon flux \(F\), number of photons \(N\) and polarized direction of the light. In this paper, we adopted \(\mu_r = 3.2\), \(\varepsilon_r = 53\) obtained from experiments\(^{57-59}\), the photon flux \(F = 1 s^{-1} \AA^{-2}\), and the polar light energy is ranged from 0 to 3.6 eV.

We divide the device Hamiltonian into left part \(H_L\) (corresponding to left electrode), central part \(H_{CR}\) (corresponding to central region), and right part \(H_R\) \(^{45}\)(corresponding to right electrode). The architecture of the devices is shown in Fig. S1. The electron-photon interaction \(H'\) is included in \(H_{CR}\). \(H_L\) and \(H_R\) are calculated under periodic boundary conditions. The electron density of these two parts could be obtained by DFT. As for the central region, \(H_{CR}\) is evaluated with open boundary conditions. The corresponding spectral density matrix could be obtained by NEGF:

$$\rho(E)^{L(R)} = \frac{1}{2\pi} G(E) \Gamma(E)^{L(R)} G^+(E)$$

\(\rho(E)^{L(R)}\) is the spectral density matrix of the central region. It contains the contributions from the left and right parts of the electrode. \(G(E)\) is the retarded Green’s function matrix, and it contains the effect of the electrode states on the electronic structure of the central region, named self-energy\(^{45}\) \(\Sigma^{L(R)}\):

$$G(E) = [(E + i \delta_+) S - H_{CR} - \Sigma(E)^L - \Sigma(E)^R]^{-1}$$

Here, \(\delta_+\) is an infinitesimal positive number, \(S\) and \(H_{CR}\) are the overlap and Hamiltonian matrices of the central region. The broadening function of the left (right) electrode is:

$$\Gamma(E)^{L(R)} = i[\Sigma(E)^{L(R)} - \Sigma(E)^{L(R)}^+]$$

The calculation of the self-energy needs more k points in C direction\(^{60}\), and 100 k points are enough in this work.

Once the electron density is obtained, the new Hamiltonian \(H_{CR}\) could be obtained by Kohn-Sham method (DFT). The final electron density could be obtained until the loop is self-consistent.

So, we get the photocurrent of one electrode in the solar device (where \(T_{a\beta}^{\pm}\) is
the transmission coefficient of the two electrodes in opposite direction):

\[
I_{\alpha} = \frac{e}{\hbar} \int_{-\infty}^{+\infty} \sum_{\alpha, \beta = L, R} \left[ 1 - f_{\alpha}(E) \right] f_{\beta}(E - \hbar \omega) T^{-}_{\alpha, \beta}(E) \]

\[
- f_{\alpha}(E) \left[ 1 - f_{\beta}(E + \hbar \omega) \right] T^{+}_{\alpha, \beta}(E) dE
\]

The electron-photon coupling matrix is contained in the above expression. Finally, the photocurrent formula is

\[
I_{\text{ph}} = I_L - I_R.
\]

As for the finite bias IV curve, we adopted the Landauer-Büttiker formula:

\[
I(V_b) = \frac{2e}{\hbar} \int_{-\infty}^{+\infty} T(E, V_b) \left[ f_l(E - \mu_l) - f_r(E - \mu_r) \right] dE
\]

where \( T(E, V_b) \) is the transmission coefficients, \( \mu_l, \mu_r \) are the electrochemical potential of left and right electrodes, and \( f_l, f_r \) are the corresponding Fermi distribution function. \( V_b \) is the bias between the left and right electrodes.

3. RESULTS AND DISCUSSIONS

The room temperature BFO is not a standard cubic perovskite structure. It tilts from a structure with \( Fm\bar{3}m \) cubic space group, and leads to \( R3c \) hexagonal (\( R3cH \)) or rhombohedral (\( R3cR \)) crystal structure with Glazer notation as shown in Fig. 1a. The driving force of structure distortion originates from the hybridization of \( \text{O} \, 2p \) orbitals and \( \text{Fe} \, 3d \) orbitals under the repulsive force of stereochemical active \( \text{Bi}^{3+} \) 6s lone pairs. We adopted the room temperature BFO as a prototype to construct the pure BFO solar cell devices, the Mn and Cr elements modulated \( P \) solar cell devices (see Fig. 2a and 2b), and the SrTiO\(_3\) (or STO) lattice matched solar
cell devices (see Fig. 3a, 3b and 3c).

The device is composed of left electrode, left electrode extension region, scattering region, right electrode extension region, right electrode. The architecture of the devices is shown in Fig. S1. Due to the large computing resource consumption, the central region here is relatively smaller than the one in real device.

In this paper, central region is mainly composed of BFO, while the electrodes are composed of BFO or STO. As we known, STO is a perovskite oxide with the band gap of 3.25 eV\textsuperscript{64}, and the gap is smaller than the widely known wide band gap semiconductor GaN (3.4 eV)\textsuperscript{65}. So, the conductivity is higher than GaN. In addition, the lattice mismatch with BFO is smaller than other materials\textsuperscript{66, 67}, such as metal. If we use metal as electrode, many other factors that influent the photovoltaic performance would occur. And these factors are rather complex to be decoupled, such as lattice mismatch between BFO and metal, Coulomb screening at the interface of BFO and metal. So, we used STO as an electrode material.

To check the rationality of our theoretical methods adopted in this work, we computed the band gap and $P_s$ of bulk BFO, and the gap is 2.41 eV while the $P_s$ along [1 1 1] direction is 80.19 $\mu$C/cm$^2$. The results are consistent with previous theoretical work\textsuperscript{41}. The calculated electrostatic potential difference in the c direction of the perfect $R3c$ BFO cell is 0.976 V (This could be the open circuit voltage of the device, and consistent with the experimental results\textsuperscript{68} at 0 K). Here, the lattice length in c direction is $1.37 \times 10^{-9}$m. So, the calculated depolarization field is about $7.06 \times 10^8$ V/m, a little larger than experimental value $5 \times 10^7$ V/m\textsuperscript{69}, as is shown in Fig. 1d and lower panel of Fig. 1e. This may originate from the impurities or complex domain structures in experimental samples\textsuperscript{70-75}, and the different directions of depolarization field in these domain walls could cancel out some components in c direction overall. The depolarization field is the main origin of internal built-in electric field in this Nano device\textsuperscript{16}.

3.1 Polarization effects on the photocurrent

In order to get different $P_s$ in BFO while keeping the corresponding crystal structures nearly unchanged, we replaced two adjacent Fe ions with Cr and Mn (BF(Cr,Mn)O) or Mn and Cr (BF(Mn,Cr)O) in two BFO cells ($R3c$H) separately as shown in Fig. 1f and 1g on the upper panels. Thus, the concentrations of Cr or Mn in the above two structures are all 3.3%. The valence states of Cr and Mn are all +3. Because the ions radius of Mn and Cr are similar to Fe, while the electron affinity is different with Fe, we could modulate the $P_s$ of BFO by the element substitution in the above two cases. The two cell structures are not the same. This is because the bond length and bond angle of Cr (Mn) with the nearest O are different in the two cells (see Fig. S2 and Tab. S2). Finally, two devices are constructed based on the above substituted hexagonal BFO structures. And the corresponding devices of the substituted cells of BFO are shown in the upper panel of Fig. 2b and 2a separately.

Due to the different electron affinity of Cr and Mn ions, the oppositely substituted direction will lead to different $P_s$ or depolarization electric fields in the cells. Because the electron affinity of Cr ion is larger than Mn ion, the total depolarization field in
BF(Cr,Mn)O should be smaller than the one in BF(Mn,Cr)O, as shown in the lower panel of Fig. 1f and 1g. Thus, the $P_s$ in BF(Cr,Mn)O is smaller than the one in BF(Mn,Cr)O. The calculated $P_s$ and band gap are 78.47 μC/cm$^2$, 1.37 eV for BF(Cr,Mn)O, and 87.12 μC/cm$^2$, 1.41 eV for BF(Mn,Cr)O as shown in Tab. 1. Both the $P_s$ and electronic band gap in BF(Cr,Mn)O are smaller than the one of BF(Mn,Cr)O.

The depolarization field in the two substituted cells are also different. The field in BF(Cr,Mn)O should be smaller than the one in BF(Mn,Cr)O, because the electrostatic potential difference in BF(Cr,Mn)O is smaller than the one in BF(Mn,Cr)O, as shown in Fig. 1d. Although larger depolarization field should lead to larger electric current, the current is also relevant to the carrier’s density. If the carrier’s density is small, the current is also small under larger depolarization field. So, smaller depolarization field might lead to larger electric current because the carrier’s density may be larger. Here, as the excitons’ binding energy is always correlated with band gap, the excitons in crystals with narrower band gap (BF(Cr,Mn)O) are easier to be formed and be separated by the depolarization electric field in the device. Thus, the photovoltaic performance of BF(Cr,Mn)O based solar cell should be better than the one of BF(Mn,Cr)O based solar cell.

In order to illustrate this opinion, we calculated the photocurrent under AM1.5 (defined as the ratio between the length of sunlight propagation in the atmosphere $d$ and the atmosphere thickness $D$, here the ratio is 1.5) solar spectrum as shown in Fig. 2d. The photocurrent with BF(Cr,Mn)O based device presented in solid black line is larger than BF(Mn,Cr)O based one. The photocurrent density in BF(Cr,Mn)O based device under no bias voltage is $4.98 \times 10^1$ μA/cm$^2$, larger than $2.04 \times 10^1$ μA/cm$^2$ in BF(Mn,Cr)O based device as shown in Tab. 1. Although the device is under AM1.5 solar spectrum, only photons with energy larger than the band gap could be absorbed. This is because the electron hoping from valence band maximum (VBM) to conduction band minimum (CBM) needs to absorb photon energy larger than the band gap. The onset of the photocurrent is about 2.5 eV, smaller than the corresponding band gap. Here, the band gap was calculated by the method of DFT, while the photocurrent was calculated mainly by NEGF. Both DFT and NEGF are the methods for solving the many-body Schrödinger equation. NEGF could give the results more precise than DFT$^{76}$. DFT is well known for its underestimation of the band gap, as the exchange and correlation effects are not exact. So, the starting value of photocurrent is smaller than the band gap, as shown in Fig. 2d. Here, we only care for the relative band gap, rather than the absolute one. Because the photocurrent calculations are rather time-consuming, we took only 12 points in the photon energy range. There exist some abrupt changes in the photocurrent curve.

To uncover the reason why the $P_s$ value is not a key factor for the solar cell performance, we calculated the transmission eigenstates under finite bias (-1 ~ 1 volt) as shown in Fig. 2a and 2b on the lower panels. Obviously, the transmission eigenstates in BF(Cr,Mn)O based device spread nearly over the whole scattering region, see the lower panel in Fig. 2b, while they only gather in the extension region of the left electrode in BF(Mn,Cr)O based device, see the lower panel in Fig. 2a.
From the perspective of effective potential, there exists a valley in the potential curve for the BF(Cr,Mn)O based device while there exists a peak for the one in BF(Mn,Cr)O based device as shown in Fig. 2c. The electrons could easily transport in the former one than the latter. So, the conductance in former device is better than the last one, because the excitons are easier to be formed and separated in the lower band gap materials. So, our result is similar to the case of organic-inorganic hybrid perovskites\textsuperscript{77}. Our calculated photocurrent density is larger than experiments by Choi et al.\textsuperscript{26}. This is because their experiments were adopted with only green light irradiation, while the photon energy is ranged from 0 to 3.6 eV in our whole theoretical work.

3.2 Interface atomic layer on the photocurrent density

In order to investigate the Bi, Fe and O terminated heterogeneous structure on the photovoltaic performance, we constructed a series of devices with different terminated ions for the right part of the device, where the interfaces are formed by (1 1 1) surface of BFO and (1 1 1) surface of STO, as shown in Fig. 3a, 3b and 3c. At the same time, we kept the left part of the device unchanged. The reason why we choose STO as electrode has been given above. The heterogeneous structure was constructed when the average stress $\epsilon^{av}$ is less than 0.65%. Here $\epsilon^{av}$ is defined as the average stress of the three directions of the heterogeneous structure\textsuperscript{78}. The stress in each direction is related to the rotation angle of the BFO and STO interface. At last, we choose the structure with the relatively lower average stress and strain energy. Thus, three devices with Bi, Fe, and O terminated ions were obtained. In addition, we kept the terminated ions of STO on the right part of the electrode unchanged in the above three cases.

In Bi terminated device (Device 1), the photocurrent density under no bias is larger than the one in O terminated device (Device 3), which is also larger than Fe terminated one (Device 2) as shown in Fig. 3e and Tab. 2. In order to find the reason, we firstly calculated the transmission eigenstates of the three devices as shown in Fig. 3a, 3b, and 3c. The transmission eigenstates in Device 1 spread almost over the whole device (see the lower panel of in Fig. 3a), while the states in Device 2 and 3 mainly focus on the edge of the BFO scattering region (see the lower panel in Fig. 3b and 3c). The results implicated that the conductance in the latter two devices are not so well compared to the first device. To uncover the origin of the phenomenon, we calculated the effective potential of electrons at finite bias, ranging from -1 to 1 volt as shown in Fig. 3d. Obviously, the potential barrier in Device 1 (blue dotted line) is lower than the one in Device 2, so the electrons could easily pass through it. For Device 2 (red dashed line) and Device 3 (green solid line), the potential barriers are all higher than the one of Device 1. Obviously, the electrons are easier to pass through Device 1 than Device 2 and Device 3. Due to the dramatic potential energy change near the right electrode in Device 2 (about 38 Å in c direction), the resistant force on the electrons ($F = -\partial V_{\text{eff}}/\partial z$) is larger than the one in Device 3. So, the conductance is not so well compared with Device 3, because the electrons are blocked on the left interface (see the lower panel in Fig. 3b). The large potential energy difference near
the right electrode in Device 2 mainly originates from the big electronegativity difference between Fe$^{3+}$ in BFO and O$^{2-}$ in STO. At the same time, the photocurrent shows the similar tendency to the conductance of the devices. The different feature of these three devices is the different terminated ion species with the same STO electrode on the right part of these devices. Thus, the terminated ions of BFO have a great impact on the photovoltaic performance. We also deduced that the possible reason for the photovoltaic difference is the local dipole difference in the interfaces of the three devices. Although the devices in the above conditions may be difficult to control exactly experimentally under current conditions, our work could be meaningful because it makes up for the inadequacies of the experiments.

3.3 Polarized light on the solar cell performance

For the anisotropic BFO ferroelectric materials, the polarized light should have an important impact on the excitons formation. In order to explain this phenomenon, two kinds of polarized light, which are $x$ direction polarized and $z$ direction polarized, were imposed on Device 2, and then corresponding transmission eigenstates and photocurrent were calculated as shown in Fig. 3b, 3e separately. The absolute value of photocurrent density was calculated and shown in Tab. 2. Obviously, the photocurrent density under no bias in the $x$ direction polarized light device is almost 10 times larger than the one in the $z$ direction polarized light device.

In order to explain this phenomenon, we calculated the projected band structure of bulk BFO along the high symmetry points in the Brillouin zone as shown in Fig. 1c and 1b separately. We found that the O 2$p$ orbitals dominate the VBM while Fe 3$d$ orbitals dominate the CBM and the effective mass of electrons (related to the curvature radius of the $E - k$ curve) in valance band along $z$ direction ($A \rightarrow \Gamma, M \rightarrow L$) is larger than the one in $x$ direction ($\Gamma \rightarrow K, H \rightarrow A$). The electrons under polarized light could easily hop from O 2$p$ orbitals to Fe 3$d$ orbitals in $x$ direction polarized case, because the electronic component in the electromagnetic wave is the main driving force to excite the electrons hoping from valence band to conduction band. Consequently, the photocurrent is larger in device under $x$ direction polarized light. Our theoretical work deepened the understanding of the experimental results by Choi et al.

4. CONCLUSIONS

In this article, we mainly investigated three key factors that influence the photovoltaic performance as solar cell by constructing a series of devices based on BFO. Firstly, although the photocurrent originates from the built-in electric field formed by electric dipoles, the larger $P_s$ is not the main factor that induces larger photocurrent, because the gap is another key factor for the carriers’ formation. Smaller band gap usually corresponds to smaller exciton bonding energy, thus leading to larger photocurrent under the same solar illumination. Secondly, the interface ions of BFO have an important influence on the photocurrent when BFO is made into a heterogeneous solar cell, because the local electric field formed by interface ions could impact the electronic transport properties. This discovery inspired us that the
photovoltaic performance could be enhanced not only by controlling the terminated ion species but also by contacting with electrode with different chemical potential. Thirdly, the energy conversion efficiency could be enhanced if the incident monochromatic light is polarized along a special direction. This phenomenon may originate from the anisotropy of carrier effective mass in the lattice of BFO. The results will deepen the understanding of some experimental results of BFO based solar cells.

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Tables:

**Tab. 1.** The electronic band gap, spontaneous polarization, total photocurrent, cross-sectional area, and photocurrent density of BF(Cr,Mn)O and BF(Mn,Cr)O based solar cell devices.

| Device          | \( E_g \) (eV) | \( P_s \) (\( \mu \)C/cm\(^2\)) | \(|I_{\text{tot}}|\) (A) | \( S \) (cm\(^2\)) | \(|j|\) (\( \mu \)A/cm\(^2\)) |
|-----------------|----------------|-------------------------------|--------------------------|--------------------|---------------------|
| BF(Cr, Mn)O     | 1.38           | 78.4                          | 1.34\( \times \)10\(^{-19} \) | 2.69\( \times \)10\(^{-15} \) | 4.98\( \times \)10\(^1 \) |
| BF(Mn, Cr)O     | 1.41           | 87.1                          | 5.49\( \times \)10\(^{-20} \) | 2.69\( \times \)10\(^{-15} \) | 2.04\( \times \)10\(^1 \) |

**Tab. 2.** The total photocurrent, cross-sectional area, and current density of Device 1 (Bi terminated), Device 2 (Fe terminated) and Device 3 (O terminated) in the case of \( z \) polarized polar light, and the corresponding parameters of Device 2 under \( x \) direction polarized polar light.

| Device       | \(|I_{\text{tot}}|\) (A) | \( S \) (cm\(^2\)) | \(|j|\) (\( \mu \)A/cm\(^2\)) |
|--------------|----------------|-----------------|----------------|
| Device 1-z   | 2.77\( \times \)10\(^{-20} \) | 5.28\( \times \)10\(^{15} \) | 5.26                      |
| Device 2-z   | 2.68\( \times \)10\(^{-21} \) | 5.28\( \times \)10\(^{15} \) | 5.08\( \times \)10\(^{-1} \) |
| Device 2-x   | 2.96\( \times \)10\(^{-20} \) | 5.28\( \times \)10\(^{15} \) | 5.61                      |
| Device 3-z   | 9.27\( \times \)10\(^{-21} \) | 5.28\( \times \)10\(^{15} \) | 1.76                      |
Fig. 1: Structure of perfect cubic BFO structure and rhombohedral distorted one with Glazer notation $a'a'a'$ (a), Brillouin zone of $R3cH$ lattice, (b) the projected band structure (dark green lines mean Fe 3$d$ orbitals, red lines mean O 2$p$ orbitals) (c), the electrostatic potential of perfect BFO (solid blue line), BF(Mn,Cr)O (dashed red line), BF(Cr,Mn)O (dotted black line) based devices with no bias (d), unit cell of BFO (upper panel) and its depolarization model (lower panel) (e), unit cell of BF(Cr,Mn)O (upper panel) and its depolarization model (lower panel) (f), unit cell of BF(Mn,Cr)O (upper panel) and its depolarization model (lower panel) (g).
Fig. 2: The Mn, Cr substituted devices (BF(Mn,Cr)O) and related transmission eigenstates (a) Cr, Mn substituted devices (BF(Cr,Mn)O) and related transmission eigenstates (b), the effective potential of BF(Mn,Cr)O with blue solid line and BF(Cr,Mn)O with dotted red line under finite bias (c), and related spin resolved photocurrent under AM1.5 solar spectrum with photon energy from 1.5 to 3.6 eV (d).
Fig. 3: Devices with Bi terminated (Device 1) and corresponding transmission eigenstates (a), Fe terminated (Device 2) and corresponding transmission eigenstates (b), O terminated (Device 3) and corresponding transmission eigenstates (c), the corresponding effective potential under finite bias (d), and the spin resolved photocurrent with $z$ polarized light and $x$ polarized light (e).