Dopant size effect on BiFeO$_3$ perovskite structure for enhanced photovoltaic activity

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Abstract

This study is carried out using first principles density functional theory calculations within gpaw code. Atomic size effect is analyzed and investigated by doping either Li, Cs or both on Barium doped BiFeO$_3$ (BFO) which belongs to monoclinic $P2_1/m$ space group. The calculated results reveal that Cs doped BFO had significantly improved photocurrent density seemingly due to broadened absorption peaks & plasmons generation. Co-doping two atoms with large size difference have a significant effect on plasmon width & peak than doping with a single & small sized atom. At higher photon energy realms of the order 10 eV, the index of refraction reduces to $n(\omega) \to 1$ implying that light wave can tunnel through the pristine & doped BFO without any phase change, thus indicating its potential as an efficient candidate for a photonic application. In addition, doped BFO shows abundant photocurrent generation properties which would be important in solar cell & photovoltaic applications.

Keywords: Bismuth ferrite, Density functional theory, Photoelectron, Photovoltaic, Multiferroic, Optical band gap.

1. Introduction

BiFeO$_3$ (BFO) is multiferroic perovskite crystal structure, which permits coexistence of various orders at room temperature. Doping fine or large sized atoms further improves simultaneous coexistence of different orders in single phase resulting in enhanced structural, optical and electronic properties of materials [1].

Several attempts have been done in advancement of the ferromagnetic properties of BFO & for improvements in leakage current amount decrement by doping either in A-site or B-site or both sites [2]. Shaan Ameer et al [3] reported that doping Li on BFO reduces ferromagnetism. However, optical property enhanced due to small optical band gap energy. Moreover, Aungkan Sen et al [4] suggested proportional doping of Ba & Li in BFO result in improved optical absorbance and dielectric property.

Highest level of doping not only alter the properties of the materials, but had remarkable impact on the crystal structure as well. For instance, La-doped BFO structure is transformed from rhombohedral to triclinic or orthorhombic around 10 mol %, and a smaller ionic radius rare-earth doping at the B-site causes structural distortion, and brought forth antiferroelectric-like double-hysteresis P-E loops. Moreover, rare-earth elements with a smaller ion radius, because of a geometrical & magnetic moments factor, are forced to align themselves either in symmetrical or antisymmetrical orientation, resulting in various magnetic order phases. Arnold et al [5] also ascertained that rare-earth doped BFO materials’ ionic radii at B-site are the prominent source for phase transitions and structural phase transitions, which is also supported by other literatures [6–8].

Besides phase, structural and property alteration, chemical strain forces can be exhibited among atoms because of short and long range interactions. J.A. Schiemer et al [9] studied significance of strain in coupling phase orders with effect on elastic response of either in high or low level doped crystals in relation to magnetic order, oxygen vacancy dynamics, and conductivity. It is also inferred that important transformation in multiferroic properties are highly correlated to structural changes. It has been well understood that applied strain on BFO scales up the magnetic, piezoelectric, ferroelectric, and optical properties [10].

Liang Bai et al [11] also experimented and observed that doping Co$^{3+}$ ions knocks out Fe$^{3+}$ ions from B-sites and opens up for random substitute. Consequently, a spirally arranged spin becomes disrupted and chemical strain is grown because of uneven size of the two B-site cations (Co$^{3+}$ and Fe$^{3+}$ ions). In spite of the previous efforts, strain evolution due to dopant size & its facilitation for coupling of multiferroic orders still remains debatable. Here we considered perovskite monoclinic BFO ($P2_1/m$) phase & the experimentally synthesized counterpart as heated over a range of high temperature during sintering processes, is evidenced with appearance of several phases plus parasitic phase (Bi$_2$Fe$_4$O$_9$) [12].

In the course of sintering process, various transformation is undergone as function of temperature leading to bismuth precipitated, due to its volatility resulting in impure BFO phases, which is often called secondary phase of the cubic structure. However, these phases are further purified by proportional addition of Bi$_2$O$_3$ and Fe$_2$O$_3$ [13], see Eq. (1).

$$\text{Bi}_2\text{Fe}_2\text{O}_9 + \text{Bi}_2\text{O}_3 \rightarrow 4\text{BiFeO}_3$$ (1)
We considered perovskite monoclinic BFO (P21/m) phase because one could easily understand doping effect. Therefore, this work explores cesium (Cs) and lithium (Li) size effect on barium (Ba) doped BiFeO3. It results in structural phase transition due to strain created because of size of substitute atoms (Fig. 1).

2. Computational method

Ab initio calculations were performed using the projector augmented wave (PAW) method as implemented in gpaw code [14]. The electron wave-function is approximated using the implementation of a projector augmented wave method [15] & the Schrödinger equation applied to total energy functions are solved self-consistently using the Kohn-Sham scheme [16]. All electron waves are expanded over periodic potential plane with a method of P.E. Blöchl [17] having a, k-points, and a reciprocal lattice grid indices. A plane wave cut-off energy used is 520 eV. The k-points within Brillouin zone (BZ) is chosen according to Monkhorst-Pack scheme [18], where a k-mesh of 8x8x8 is used.

The interactions of the valence electrons with the core electrons and nuclei is treated within a projector augmented wave (paw) data sets [14, 15]. The number of valence electrons considered for each element within the paw data sets is Bi (5d106s26p2), Fe (3d64s2), O (2s22p4), Cs (5s25p66s1), Li (2s1), & Ba (5s25p66s2). Geometry relaxations are carried out using BFGS minimizer [19], where optimizations of the atomic coordinates and the unit cell degrees of freedom is done within the concept of the Hellmann-Feynman forces and stresses [20, 21] calculated on the Born-Oppenheimer (BO) surface [22]. The convergence criteria for the forces were set at 0.05 eV/Å. The exchange-correlation energies are approximated within the generalized gradient approximation of PBE [23] & a k-mesh of 8x8x8 is used in a geometry relaxation calculations. The strongly correlated nature of d electrons of Fe were treated using Hubbard-like model which is introduced into the Gpaw code according to [24, 25], where U-J=7.5 eV.

Brillouin zone integration were performed with the tetrahedron method which is proved efficient especially for excited states & magnetically induced dielectric function calculation [26]. Ground state calculation is performed with k-point density of 5 points per Å⁻¹ with Γ-point inclusion. A restarted calculations were done with a fixed density of 7.5 points per Å⁻¹ over densely sampled k-points grid. The k-point density is calculated as:

\[ N = \frac{a^*}{2\pi} \]  

where N is the number of k-points and a* is the reciprocal of a lattice vector a of the unit-cell. One can analyse and understand material’s optical response property once incident photon energy is imparted to the electron, where the material’s response or dielectric function is given as

\[ \varepsilon (\omega) = \varepsilon_1 (\omega) + i\varepsilon_2 (\omega) \]  

The imaginary part \( \varepsilon_2 (\omega) \) is calculated from the density matrix of the electronic structure [27] according to the implementations by the group of G. Kresse [28, 29], & given by

\[ \varepsilon_2 (\omega) = \frac{2e^2}{\Omega \omega^2} \sum_{\mathbf{k},\mathbf{c}} w_\mathbf{k} |\langle \mathbf{r} | \mathbf{r} \rangle \mathbf{c} |^2 \delta (\mathbf{E}_\mathbf{k} - \mathbf{E}_\mathbf{c} - \hbar \omega) \]  

where \( e \) is the electronic charge, and \( \psi_\mathbf{k}^c \) and \( \psi_\mathbf{k}^c \) are the conduction band (CB) and valence band (VB) wave functions at \( \mathbf{k} \), respectively, \( \hbar \omega \) is the energy of the incident phonon, \( \mathbf{u} \mathbf{r} \) is the momentum operator, \( w_\mathbf{k} \) is a joint density of states, & \( \Omega \) is the volume of the primitive cell.

The Real part \( \varepsilon_1 (\omega) \) of the dielectric function can be found from the Kramer-Kronig equation [30].

\[ \varepsilon_1 (\omega) = 1 + \frac{2P}{\pi} \sum_{\omega'} \frac{\omega' \varepsilon_2 (\omega') d\omega'}{\omega' - \omega^2} \]  

where, P stands for the principal value of the integral.

The optical absorption coefficient was obtained by using Eq. (6).

\[ \alpha = \sqrt{\frac{2\omega}{c}} \sqrt{\frac{\varepsilon_1^2 (\omega) + \varepsilon_2^2 (\omega) - \varepsilon_1 (\omega)}{\varepsilon_1 (\omega)}} \]  

where \( \omega \) is photon frequency, \( c \) is speed of light, \( \varepsilon_1 \) & \( \varepsilon_2 \) are frequency dependent real and imaginary parts of dielectric function as stated in Eq. (3). For photovoltaic applications, the BFO should be able to absorb as much light as possible to generate a photocurrent, which requires a lower band gap and a large absorption coefficient.

The photocurrent density under irradiation with a certain wavelength can be described by an empirical Glass Law [31].

\[ J_{ph} = \alpha \varepsilon I \]  

where \( \alpha \) is the optical absorption coefficient, \( \varepsilon \) is a material-dependent Glass coefficient, and I is irradiation intensity. The photocurrent density \( J_{ph} \) is linearly proportional to the absorption coefficient. The relation between \( \alpha \) and an optical band gap \( E_g^* \) can be estimated using the Tauc relation [32].

\[ \alpha (h\omega) \sim A (h\omega - E_g^*)^{1/2} \]  

where A is a material dependent constant and \( h\omega \) is the incident photon energy. According to Eq. (7) & Eq. (8), one can extrapolate a larger photocurrent density by increasing the absorption coefficient with a small band gap.

From dielectric function, all the other optical properties such as, reflectivity \( R \), refractive index \( n_0 \), & extinction coefficient \( \kappa \) is also obtained [33–35], & given as follows.

\[ n(\omega) = \frac{1}{\sqrt{2}} \sqrt{\frac{\varepsilon_1^2 (\omega) + \varepsilon_2^2 (\omega) + \varepsilon_1 (\omega)}{\varepsilon_1 (\omega)}} \]  

In addition, reflectivity \( R(\omega) \), & energy loss function \( \epsilon (\omega) \) is calculated as

\[ R(\omega) = \left| \frac{\sqrt{n^2 (\omega) - 1}}{\sqrt{n^2 (\omega) + 1}} \right|^2 \]  

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(a) Pristine BiFeO$_3$ (P2$_1$/m)
(b) Li, Cs co-doped BiFeO$_3$ (P2$_1$/m)
(c) Li doped BiFeO$_3$ (P2$_1$/m)
(d) Cs doped BiFeO$_3$ (P2$_1$/m)

Figure 1: Color online. Crystal structure of bulk pristine BiFeO$_3$ in comparison with doped BiFeO$_3$ illustrating the structural tilting of BiO$_6$ polyhedra relative to neighbouring polyhedrons.

\[ \epsilon(\omega) = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)}, \]  
(11)

respectively.

The spin-orbit module calculates spin-orbit band structures non-self consistently. The input is a standard converged GPAW calculation and the module diagonalizes the spin-orbit Hamiltonian in a basis of scalar-relativistic Kohn-Sham eigenstates. Since the spin-orbit coupling is largest close to the nuclei, we only consider contributions from inside the PAW augmentation spheres where the all-electron states can be expanded as

\[ |\psi_{nk}\rangle = \sum_i a_i |\tilde{p}_a i\rangle |\psi_{nk}\rangle |\phi_a\rangle \]  
(12)

The full Bloch Hamiltonian in a basis of scalar relativistic states becomes

\[ H_{\text{int/\sigma\sigma'}}(k) = \epsilon_{\text{int/\sigma\sigma'}}(\omega) + \langle \tilde{p}_a k | H^{\text{SO}}(k) | \tilde{p}_a k' \rangle \delta_{\text{int/\sigma\sigma'}} + \sum_{n'k} \langle \tilde{p}_a n | H^{\text{SO}}(k) | \tilde{p}_a n' \rangle \delta_{\text{int/\sigma\sigma'}} (\phi_{nk}\langle \phi_{n'k'}| \psi_{nk} \rangle \langle \phi_{n'k'}| \phi_{nk}\rangle) \]  
(13)

where the spinors are chosen along the z-axis as default. It is also possible to obtain the eigenstates of the full spin-orbit Hamiltonian as well as the spin character along the z-axis. The spin character is defined as

\[ s_{mk} \equiv \langle mk | \sigma_z | mk \rangle \]  
(14)

and is useful for analysing the degree of spin-orbit induced hybridization between spin up and spin down states [36].
3. Results and Discussion

Experimental refined x-ray diffraction structural positions were obtained from Inorganic Crystal Structure Database (ICSD) [37]. Structural volume optimization made over lattice range 5.0 Å to 6.0 Å, and obtained $a(\AA) = 5.5803663$, $b(\AA) = 7.9236074$, & $c(\AA) = 5.6120707$, and $\alpha(\text{}) = 90. \beta(\text{}) = 90. \& \gamma(\text{}) = 90.015$ which are in close agreement to experimental parameters. The bulk modulus at monoclinic $P2_1/m$ space group (Fig. 1) is found to be $B = 161.582$ GPa, & also shown weak ferromagnetism with average a remnant magnetization of $3.5\times10^{-6} \mu_B$/Fe. This value is close to literature value $4\times10^{-6} \mu_B$/Fe [38].

Band structure is calculated in Fig. 2 using spin-orbit coupling module as implemented in the Gpaw electronic structure code, & plotted over special k-points which were exported online according to a literature [39] by inputting the crystallographic information file of $P2_1/m$ space group.

The calculated absorption coefficient $\alpha(\omega)$ of pristine compared with doped bismuth ferrite are shown in Fig. 3. The absorption ability seems to be reduced for all doped systems compared to pristine BFO in low energy-loss region. In addition, the optical bandgap is significantly decreased as illustrated in the Table. 1, but a dopant size also seems to have an effect on the optical gap (Fig. 2).

The imaginary part, $\varepsilon_2(\omega)$ (Fig. 3) shows absorption peaks in a photon energies range of 0.0-10.0 eV. The imaginary part is associated with only inter-band transition, and the real part $\varepsilon_1(\omega)$ approaches to zero at certain realms of photon energies, signaling a resonance at which collective electrons start to excite at plasma frequency. It looks from Fig. 2 that a congested bound of bands near the Fermi level of valence band seems to oscillate with plasma frequency. From Fig. 4, the optical bandgaps presented in the Table 1 are calculated using Tauc relation (Eq. (8)), & according to a tangent line curve fitting approach adopted from a literature [40].

We also notice from Figs. 4 & 5 that absorption peaks occur over a wider ranges of photon energies by doping the BFO, & that a decrease in the imaginary part $\varepsilon_2(\omega)$ at higher photon energy potentially indicates a decline in absorption of photon energy to bound electron of valance band. Thus, the excitation of the plasmons by light is demonstrated by a decrease of the reflectivity $R(\omega)$ of the light at plasma frequency because of photon energy is consumed up by oscillating bound electrons. The refractive index as indicated in Fig. 5 shows that $n(\omega) \rightarrow 1$, at high photon energies ($\sim 10-15$ eV). This could potentially imply that light can pass through the material without a phase change, which is a novel characteristics of photonic crystals. Such a claim also agrees with experimental & theoretical concepts explained in literature [41, 42].

As shown in Fig. 6, plasmons move in a periodic potential and unlike ideal plasmons, and pristine BFO, had three peaks at 10 eV, 19 eV & 27 eV. Li & Cs co-doped BFO had three peaks at 21 eV, 24 eV, & 27 eV. Li doped BFO had two peaks at 21 eV, & 28 eV. Cs doped BFO had three peaks at 15 eV, 26 eV, & 28 eV. The energy-loss may show plasmon excitation in region of about 10-30 eV often during inter-band transition of

Figure 2: Scatter spin-orbit coupled band structure calculated using Eq. (14). The colors show the spin character: blue designated as spin down, red as spin up and dashed gray lines as bands without spin-orbit coupling respectively. (For color online, the reader is referred to the web version of this article).
Table 1: Calculations of magnetization, optical band gap energy, & magnetic moment contribution per Fe atom, is given. Wherever it applies in this paper, BFO means pristine BiFeO$_3$, LiCs-BFO means Li & Cs co-doped BFO, Li-BFO means Li doped BFO, & Cs-BFO means Cs doped BFO.

| System       | Magnetization [$\mu_B$] | Optical band gap [eV] | Moment per Fe-atom [$\mu_B$/Fe] |
|--------------|-------------------------|-----------------------|---------------------------------|
| BFO          | $1.5 \times 10^{-6}$    | 2.13275               | $4 \times 10^{-6}$              |
| LiCs-BFO     | 0.000                   | 0.6855                | 0.000                           |
| Li-BFO       | $2 \times 10^{-6}$      | 0.7125                | $1 \times 10^{-6}$              |
| Cs-BFO       | 1.532450                | 0.6746                | 0.71731                         |

Figure 3: The absorption coefficient $\alpha(\omega)$ for pristine BiFeO$_3$ in comparison to doped BiFeO$_3$. (For color online, the reader is referred to the web version of this article).

single electron. However, high energy-loss region is highly associated with excitation of bound electron with multiple peaks. These bound electron significantly increase photocurrent generation which enormously enhance photovoltaic effect. It is been noted that two plasmons of pristine BFO interact via electron-hole pair resulting in biplasmons generation due to Cs doping. However, Li doping affected the amount of energy of the two peak points plus a very small peak at 30 eV. Therefore, Cs size had effect on biplasmons generation in comparison to the Li size. In some cases, plasmons width & peak explain the phase changes. We can infer that size of the dopant atom has remarkable impact on both number & width of plasmons resulting in enhanced photovoltaic property. Hence, co-doping of Li & Cs in a Barium doped bismuth ferrite seems to have a potential for improved efficiency as a photoelectron capturing device.

4. Conclusion

The investigations can be summarized as follows.

- With doping, absorption coefficient has widened resulting to a decreased optical bandgap & hence shows a potential for an increased solar cell property.
- A squared absorption coefficient peak shows an increase in width of by about 4 eV towards a realm of higher photon energies in the case of doped BFO. This is believed to be a sign of an increased solar cell activity.
- Dielectric functions seem to have large values at zero pho-

Figure 4: Tauc plots ($\alpha h\omega$)$^2$ vs. photon energy $h\omega$ for direct band gap $E_g$ extrapolation or estimation of pristine BFO, Li & Cs co-doped BFO, Li doped BFO, & Cs doped BFO in respective order of from top to bottom.
ton energies, but these values seem to be reduced significantly by an introduction of a series of photon energies of up to $\hbar \omega = 10$ eV. For photon energies of 10-15 eV, $n(\omega) \rightarrow 1$.

- The crossing of the imaginary part of the dielectric function $\varepsilon_2(\omega)$ of a zero values at multiple realms of the photon energies $\hbar \omega$ indicates a potential importance of the system in applications based on photonic conductivity.

- The systems’ $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$, & $n(\omega)$ seem to be reduced rapidly with introduction of photon energies, while a major contributor to the magnitude of $n(\omega)$ seems to be $\varepsilon_2(\omega)$.

- Expanded width of energy loss peaks happen with doping & an occurrence of such peaks at higher photon energies indicates a potential importance for applications in a plasmonic effect.

Disclosure statement

The authors declare that there is no conflict of interest.

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