First-principles study of crystal structure, electronic structure, and second-harmonic generation in a polar double perovskite $\text{Bi}_2\text{ZnTiO}_6$

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Within the density functional theory with the generalized gradient approximation, we present a systematic *ab initio* investigation of crystal structure, electronic structure, and linear and nonlinear optical responses in a polar double perovskite $\text{Bi}_2\text{ZnTiO}_6$. The effect of *B*-site ordering is explored by comparing three possible configurations: *A*-type with alternative Zn and Ti layers stacking along the *c* axis; *C*-type with Zn and Ti *c* axis chains; and *G*-type with every Zn(Ti) atoms is surrounded by its nearby six Ti(Zn) atoms. It is found that the system with *G*-type *B*-site ordering is energetically favorable, which is lower in the total energies of 0.055 and 0.133 eV/formula unit than *C*-type and *A*-type, respectively. Optical calculations indicate that all the three configurations show large second-harmonic generation (SHG) coefficients, and the largest static SHG observed in the *C*-type system reaches 123 (10^{-9} esu), the value of which is much larger than ever known polar oxides, e.g., 72 (10^{-9} esu) in LiNbO_3 . The predicted significant nonlinear optical properties are consistent with the calculated high tetragonality as well as the large off-center displacement of Zn, Ti, and Bi atoms. In particular, a large off-center displacement greater than 0.5 Å in Zn atoms is revealed for the first time. A further microscopic picture is presented via the successful connection of the prominent feature of SHG in $\text{Bi}_2\text{ZnTiO}_6$ with that of the linear optical dielectric function in terms of single-photon and double-photon resonances. Our calculations demonstrate the promising application of $\text{Bi}_2\text{ZnTiO}_6$ in optoelectronics. © 2008 American Institute of Physics.

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I. INTRODUCTION

Materials with double perovskite structure have displayed many interesting fundamental physics and technological applications, including colossal low-field magnetoresistance in $\text{Sr}_2\text{FeMoO}_6$,¹ giant magnetocapacitance in $\text{La}_2\text{NiMnO}_6$,² and antiferromagnetic half metals.³ Recently, multiferroic $\text{Bi}_2\text{FeCrO}_6$ (Refs. 4–6 and $\text{Bi}_2\text{NiMnO}_6$ (Refs. 7 and 8) with highly distorted double perovskite structure have drawn great interest due to the coexistence of robust electric polarization *P* and magnetic moment *M* in a single phase. Besides the above mentioned multiferroics, which are composed of magnetic ions, Fe, Cr, Mn, Ni, and Co,⁹ (double) perovskite structures of BiBO_3 or $\text{Bi}_2\text{BB}'\text{O}_6$ with nonmagnetic *B* and *B'* ions (Al, In, Sc, Ga, Zn/Ti, and Mg/Ti) also display interesting physics, including piezoelectricity, ferroelectricity, and nonlinear optical coefficients.^{10–20} They are important as the replacement of lead-free or low lead materials, possessing similar “inert-pair” $6s^2$ electronic configuration with Pb^{2+} , but quite environmentally benign in their oxide form. In particular, a recently synthesized double perovskite $\text{Bi}_2\text{ZnTiO}_6$ is found to have a large *c/a* ratio of 1.2, where *a* and *c* are the lattice constants of a simple ABO_3 perovskite.¹⁹ The calculated ionic polarization in a point charge model reaches as high as $103 \mu\text{C cm}^{-2}$, much larger than ever known polar oxides, e.g., $32 \mu\text{C cm}^{-2}$ in BaTiO_3 ,

$50 \mu\text{C cm}^{-2}$ in PbTiO_3 , $70 \mu\text{C cm}^{-2}$ in LiNbO_3 , or $90 \mu\text{C cm}^{-2}$ in multiferroic BiFeO_3 . On the other hand, experiment on the solid solutions of $[\text{Bi}_2\text{ZnTiO}_6]_x[\text{PbTiO}_3]_{1-x}$ with $1-x \leq 0.6$ also exhibits a significant increase in the tetragonal distortion and T_C . In particular, the tetragonal *c/a* ratio of 1.11 and Curie temperature T_C in excess of 700 °C are found when $x=0.40$.²⁰

It is noted that polar oxides BiAlO_3 and BiInO_3 exhibit large second-harmonic generation (SHG) signals, about 150–170 times larger than that in quartz.^{13,14} Therefore, it is natural to study the nonlinear optical response in $\text{Bi}_2\text{ZnTiO}_6$, which might be significant for its unusual polar structure. In fact, for ferroelectrics, the free energy can be written as

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 - PE, \quad (1)$$

where $P = P_0 + p$. With a given electric field *E*, it is assumed that *P* is one dimensional and along electric field direction. Following the conventional form of nonlinear optics, we express the electric field response *p* as a power series in *E*, $\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots$, with disregard of tensor suffices for now. Here, $\chi^{(2)}$ appears only in the system lacking inversion symmetry. According to the condition of steady state $\partial F / \partial P = 0$, *P* is determined by

$$bP^3 + aP - E = 0. \quad (2)$$

If the contribution of nonlinear part to the electric polarization is small,

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$$\chi^{(1)} = \frac{1}{a + 3bP_0^2} \quad (3)$$

and

$$\chi^{(2)} = \frac{-3bP_0}{(a + 3bP_0^2)^3} = \frac{3bP_0}{8a^3} \propto P_0. \quad (4)$$

Therefore, the larger spontaneous electric polarization P_0 , the stronger nonlinear susceptibilities $\chi^{(2)}$. The significant electric polarization of $103 \mu\text{C cm}^{-2}$ found in $\text{Bi}_2\text{ZnTiO}_6$ (Ref. 19) indicates that the nonlinear optical coefficients should be significant.

The density functional theory with modern theory of electric polarization^{21,22} has been successfully applied in predicting crystal structures and electric polarizations in polar $\text{Bi}_2\text{FeCrO}_6$,²³ $\text{Bi}_2\text{NiMnO}_6$,²⁴ BiFeO_3 ,²⁵ BiAlO_3 ,²⁶ and alloys of $(\text{BiScO}_3)_{1-x}(\text{PbTiO}_3)_x$ as well as $[\text{Bi}_2\text{ZnTiO}_6]_x[\text{PbTiO}_3]_{1-x}$ (with $x=0.25$ and 0.5),²⁷ but the *ab initio* study of crystal structure and electronic structure of pure $\text{Bi}_2\text{ZnTiO}_6$ is still absent, not mentioning its nonlinear optical response. In this paper, within the density functional theory with the generalized gradient approximation (GGA), we have performed a systematic *ab initio* investigation of crystal structure, electronic structure, and nonlinear optical properties of $\text{Bi}_2\text{ZnTiO}_6$. In particular, since current experimental technique could not determine the long-range or short-range orderings of Zn and Ti cations over *B*-site, which is the important information for the discussion on the structure in terms of the *B*-site environment, we explore the effect of *B*-site ordering on the crystal structure and corresponding electronic and optical properties. As shown in Figs. 1(a)–1(c), we consider three types of *B*-site ordering: alternative Zn and Ti layers along *c* the axis (A-type ordering); Zn and Ti atoms chains along the *c* axis (C-type ordering); and every Zn(Ti) atoms is surrounded by its nearby six Ti(Zn) atoms (*G*-type ordering). In the practical calculations, $\sqrt{2}a \times \sqrt{2}a \times 2c$ supercells are adopted to account for all three possible *B*-site ordering structures. The detailed full-relaxed lattice parameters and ionic positions are displayed in Table I. Our calculations presented below will give strong evidence on the correlation between the highly distorted structures and significantly large SHG coefficients in $\text{Bi}_2\text{ZnTiO}_6$. Furthermore, by connecting the nonlinear optical response with linear part, we also present a microscopic picture of SHG in $\text{Bi}_2\text{ZnTiO}_6$. Our calculations suggest the promising application of $\text{Bi}_2\text{ZnTiO}_6$ in future optoelectronics.

II. COMPUTATIONAL METHOD

Our *ab initio* calculations for $\text{Bi}_2\text{ZnTiO}_6$ are performed using the highly accurate full-potential projector augmented wave (PAW) method,²⁸ as implemented in the Vienna *ab initio* Simulation Package (VASP) package.²⁹ They are based on density functional theory with GGA. A large plane-wave cutoff of 500 eV is used throughout. PAW potentials are used to describe the electron-ion interaction, with 15 valence electrons for Bi ($5d^{10}6s^26p^3$), 12 for Zn ($3d^{10}4s^2$), 10 for Ti ($3p^63d^24s^2$), and 6 for O ($2s^22p^4$). Brillouin zone integra-

FIG. 1. (Color online) Crystal structure of $\text{Bi}_2\text{ZnTiO}_6$. (a) A-type. (b) C-type. (c) G-type.

tions are performed with tetrahedron method in a $8 \times 8 \times 4$ Monkhorst–Pack *k*-point mesh centered at Γ . The convergence criterion for the electronic energy is 10^{-6} eV. The atomic positions and lattice constants were fully relaxed by a conjugate gradient technique. The final theoretical structures were obtained when the maximum atomic force and maximum stress is less than $0.004 \text{ eV/\AA}$ and 0.04 kbar , respectively. In the self-consistent band structure and following optical properties calculations, a much denser *k*-points grid $16 \times 16 \times 8$ is adopted with 225 *k*-points in the irreducible Brillouin zone. Also 20 bands per atom are adopted in the optical calculations. The density of states (DOS) is evaluated

TABLE I. Structure parameters of the experimental (Ref. 19), and calculated A-type, C-type, and G-type Bi₂ZnTiO₆. The space group is *P4mm*.

		Expt. (<i>a</i> × <i>a</i> × <i>c</i>)	A-type (<i>a</i> × <i>a</i> × 2 <i>c</i>)	C-type (√2 <i>a</i> × √2 <i>a</i> × <i>c</i>)	G-type (√2 <i>a</i> × √2 <i>a</i> × 2 <i>c</i>)
(i) Lattice constants					
√2 <i>a</i>	(nm)	0.5405	0.5353	0.5306	0.5327
2 <i>c</i>	(nm)	0.9256	0.9955	0.9985	0.9822
(ii) Atomic positions					
Bi	1 <i>a</i>	(0,0,0)	(0,0,0)	(0,0.5,0)	(0,0.5,0)
	1 <i>a</i>		(0,0,0.4677)		
Zn	1 <i>b</i>	(0.5,0.5,0.5662)	(0.5,0.5,0.261)	(0,0,0.553)	(0,0,0.269)
Ti	1 <i>b</i>	(0.5,0.5,0.5662)	(0.5,0.5,0.788)	(0.5,0.5,0.586)	(0.5,0.5,0.302)
O	2 <i>c</i>	(0.5,0,0.692)	(0,0.5,0.348)		
	2 <i>c</i>		(0,0.5,0.849)		
	2 <i>b</i>			(0.257,0.257,0.727)	(0.251,0.251,0.362)
O _⊥	2 <i>c</i>	(0.5,0.5,0.184)	(0.5,0.5,0.064)	(0,0,0.171)	(0,0,0.075)
	2 <i>c</i>		(0.5,0.5,0.616)	(0.5,0.5,0.229)	(0.5,0.5,0.120)

from the self-consistent band structure by tetrahedral method.³⁰

The optical properties are calculated based on the independent-particle approximation, i.e., the excitonic effects and the local-field corrections are neglected.^{31–33} The imaginary part of the dielectric function due to direction interband transitions is given by the Fermi golden rule, i.e.,³¹

$$\varepsilon''_{aa} = \frac{4\pi^2}{\Omega\omega^2} \sum_{i \in VB, j \in CB} \sum_{\mathbf{k}} w_{\mathbf{k}} |p_{ij}^a|^2 \delta(\varepsilon_{\mathbf{k}_j} - \varepsilon_{\mathbf{k}_i} - \omega), \quad (5)$$

where Ω is the unit-cell volume and ω is the photon energy. VB and CB denote the conduction and valence bands, respectively. The dipolar transition matrix elements $p_{ij}^a = \langle \mathbf{k}_j | p_a | \mathbf{k}_i \rangle$ are obtained from the self-consistent band structures within the PAW formalism. Here $|\mathbf{k}_n\rangle$ is the n th Bloch state wave function with crystal momentum $\mathbf{k}$ and a denotes the Cartesian component. The real part of the dielectric function is obtained from ε'' by a Kramers–Kronig transformation³¹

$$\varepsilon'(\omega) = 1 + \frac{2}{\pi} \mathbf{P} \int_0^\infty d\omega' \frac{\omega' \varepsilon''(\omega')}{\omega'^2 - \omega^2}. \quad (6)$$

Here $\mathbf{P}$ is the principle value of the integral.

Given the complex dielectric function $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, all the other linear optical properties can be calculated, e.g., linear refractive index

$$n(\omega) = \left(\frac{\sqrt{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)} + \varepsilon'(\omega)}{2} \right)^{1/2}, \quad (7)$$

and the linear absorption coefficient is related to ε'' by $\alpha = \varepsilon''\omega/(nc)$, where c is the velocity of light in the vacuum. The electron energy-loss function is given by $\text{Im}(-1/\varepsilon)$.

The imaginary part of the second-order optical susceptibility due to the direct interband transitions is given by³³

$$\chi_{abc}^{(2)}(-2\omega, \omega, \omega) = \chi_{abc, \text{VE}}^{(2)}(-2\omega, \omega, \omega) + \chi_{abc, \text{VH}}^{(2)}(-2\omega, \omega, \omega), \quad (8)$$

where the contribution due to the so-called virtual-electron (VE) process is³³

$$\begin{aligned} \chi_{abc, \text{VE}}^{(2)}(-2\omega, \omega, \omega) &= -\frac{\pi}{2\Omega} \sum_{i \in VB} \sum_{j \in CB} \sum_{\mathbf{k}} w_{\mathbf{k}} \left\{ \frac{\text{Im}[p_{ji}^a \langle p_{li}^b p_{li}^c \rangle]}{\varepsilon_{li}^3 (\varepsilon_{li} + \varepsilon_{ji})} \delta(\varepsilon_{li} - \varepsilon) \right. \\ &\quad - \frac{\text{Im}[p_{ji}^a \langle p_{li}^b p_{li}^c \rangle]}{\varepsilon_{li}^3 (2\varepsilon_{li} - \varepsilon_{ji})} \delta(\varepsilon_{li} - \omega) \\ &\quad \left. + \frac{16 \text{Im}[p_{ji}^b \langle p_{li}^a p_{li}^c \rangle]}{\varepsilon_{ji}^3 (2\varepsilon_{li}^3 - \varepsilon_{ji}^3)} \delta(\varepsilon_{ji} - 2\omega) \right\}, \end{aligned} \quad (9)$$

and that due to the virtual-hole (VH) process is³³

$$\begin{aligned} \chi_{abc, \text{VH}}^{(2)}(-2\omega, \omega, \omega) &= -\frac{\pi}{2\Omega} \sum_{i \in VB} \sum_{j \in CB} \sum_{\mathbf{k}} w_{\mathbf{k}} \left\{ \frac{\text{Im}[p_{ji}^a \langle p_{li}^b p_{li}^c \rangle]}{\varepsilon_{li}^3 (\varepsilon_{li} + \varepsilon_{ji})} \delta(\varepsilon_{li} - \omega) \right. \\ &\quad - \frac{\text{Im}[p_{ji}^a \langle p_{li}^b p_{li}^c \rangle]}{\varepsilon_{li}^3 (2\varepsilon_{li} - \varepsilon_{ji})} \delta(\varepsilon_{li} - \omega) \\ &\quad \left. + \frac{16 \text{Im}[p_{ji}^b \langle p_{li}^a p_{li}^c \rangle]}{\varepsilon_{ji}^3 (2\varepsilon_{li}^3 - \varepsilon_{ji}^3)} \delta(\varepsilon_{ji} - 2\omega) \right\}. \end{aligned} \quad (10)$$

Here $\varepsilon_{ji} = \varepsilon_{\mathbf{k}_i} - \varepsilon_{\mathbf{k}_j}$ and $\langle p_{ji}^b p_{li}^c \rangle = \frac{1}{2}(p_{ji}^b p_{li}^c + p_{ji}^c p_{li}^b)$. The real part of the second-order optical susceptibility is then obtained from the imaginary part by a Kramers–Kronig transformation³³

$$\chi'^{(2)}(-2\omega, \omega, \omega) = \frac{2}{\pi} \mathbf{P} \int_0^\infty d\omega' \frac{\omega' \chi''^{(2)}(2\omega', \omega', \omega')}{\omega'^2 - \omega^2}. \quad (11)$$

The electronic part of linear electro-optical coefficient is $r_{abc}^e(\omega)$, which is connected to the second-order optical susceptibility $\chi_{abc}^{(2)}(-2\omega, \omega, \omega)$ through the relation³³

FIG. 2. (Color online) SHG susceptibilities. From top to bottom are the components $\chi_{xxz}^{(2)}$, $\chi_{zxx}^{(2)}$, and $\chi_{zzz}^{(2)}$ respectively. From left to right are A-type, C-type, and G-type, respectively. Blue solid line is for real part and red dotted line is for imaginary part.

$$\chi_{abc}^{(2)}(-\omega, \omega, 0) = -\frac{1}{2}n_a^2(\omega)n_b^2(\omega)r_{abc}^e(\omega), \quad (12)$$

where $n(\omega) = \sqrt{\varepsilon(\omega)}$ is the refractive index in the a direction. In the low frequency limit,

$$\lim_{\omega \rightarrow 0} \chi_{abc}^{(2)}(-2\omega, \omega, \omega) = \lim_{\omega \rightarrow 0} \chi_{abc}^{(2)}(-\omega, \omega, 0). \quad (13)$$

Therefore,

$$r_{abc}^e(0) = -\frac{2}{n_a^2(0)n_b^2(0)} \lim_{\omega \rightarrow 0} \chi_{abc}^{(2)}(-2\omega, \omega, \omega). \quad (14)$$

It is noted that for the photon energy $\hbar\omega$ well below the band gap, the linear electro-optical coefficient $r_{abc}^e(\omega) \approx r_{abc}^e(0)$, which is due to the fact that both the $\chi^{(2)}(-2\omega, \omega, \omega)$ and $n(\omega)$ are nearly constant in this low frequency region. In the present calculations, the δ functions in Eqs. (5), (8), and (9) are approximated by a Gaussian function with $\Gamma=0.1$ eV. The maximum energy in Eqs. (6) and (10) is set as 50 eV to ensure completeness of the real part of ε and $\chi^{(2)}$ in the integrals.

III. RESULTS AND DISCUSSION

First, let us consider the SHG directly. It is noted that the $P4mm$ symmetry of $\text{Bi}_2\text{ZnTiO}_6$ allows five nonvanishing components, i.e., $\chi_{xxz}^{(2)}$, $\chi_{yyz}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{zyy}^{(2)}$, and $\chi_{zzz}^{(2)}$, with $\chi_{xxz}^{(2)} = \chi_{yyz}^{(2)}$ and $\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)}$.³⁴ In Fig. 2, SHG susceptibilities are plotted and compared. From top to bottom are the components $\chi_{xxz}^{(2)}$, $\chi_{zxx}^{(2)}$, and $\chi_{zzz}^{(2)}$, respectively. From left to right, we present the results of A-type, C-type, and G-type, respectively. It is clear that all the systems show significantly large SHG coefficients. Furthermore, for the photon energy smaller than 0.78 eV (A-type), 1.0 eV (C-type), and 1.16 eV (G-type), $\chi^{(2)}$ is purely dispersive, i.e., real and lossless, suggesting that $\text{Bi}_2\text{ZnTiO}_6$ has potential application in nonlinear

optical devices. The real part remains nearly constant at first, then increases steadily as the increase of photon energy, and finally peaks at the absorption edge. At low energy, C-type system shows much larger signals, e.g., at 1 eV, $\chi_{zxx}^{(2)}$ has reached 0.75×10^{-6} esu. As the photon energy increases, G-type system, i.e., energetically favorable case, exhibits much larger SHG signals, e.g., at 3 eV, $\chi_{xxz}^{(2)}$ has surpassed 1×10^{-6} esu, and at 4 eV, $\chi_{zzz}^{(2)}$ is near 1×10^{-6} esu. When the energy is further increased, all the systems show the decreased SHG coefficients. From the above consideration, we can find that the energetically favorable G-type $\text{Bi}_2\text{ZnTiO}_6$ has a large second-order nonlinear optical response. Interestingly, these large SHG spectra can be comparable with the responses in GaAs and zigzag BN nanotubes.³³ The imaginary part of SHG is displayed in Figs. 3–5.

The static SHG susceptibilities, dielectric constant, and corresponding linear electro-optic coefficients are listed in Table II. It is noted that all the components of three systems show large magnitudes ($\geq 50 \times 10^{-9}$ esu). For comparison, it is noted that in LiNbO_3 , which is the popular nonlinear optic

TABLE II. Static dielectric constant (ϵ), second-order susceptibility ($\chi^{(2)}$) (10^{-8} esu), and linear electro-optical coefficient (electronic part r^e) (10^{-8} esu) of three types of $\text{Bi}_2\text{ZnTiO}_6$.

	A-type	C-type	G-type
ϵ_{xx}	6.55	6.62	6.62
ϵ_{zz}	5.69	5.75	5.75
$\chi_{xxz}^{(2)}$	4.86	9.15	7.82
$\chi_{zxx}^{(2)}$	6.24	12.28	9.84
$\chi_{zzz}^{(2)}$	-7.18	-4.99	-4.91
r_{xxz}^e	-0.23	-0.42	-0.36
r_{zxx}^e	-0.33	-0.65	-0.52
r_{zzz}^e	0.44	0.30	0.30

TABLE III. Total energy (eV/f.u.), c/a ratio, bond length (Å), and off-center displacement (Å) in three types of Bi₂ZnTiO₆.

	A-type	C-type	G-type
Total energy	0.133	0.055	0
c/a	1.315	1.331	1.304
Bi–O (1)	2.2370/2.4144	2.3194	2.3211/2.3211
Bi–O (2)	3.0568/2.7519	2.7867/2.8881	2.9141/2.7648
Bi–O (3)	4.2449/3.9470	4.0864	4.9485/4.5831
Bi off-center displacement	0.9821/1.3036	1.13	1.10
Zn–O (1)	2.0778	2.1175	2.0987
Zn–O (2)	1.9667	1.9070	1.9033
Zn–O (3)	3.5265	3.0856	3.4488
Zn off-center displacement	0.7799	0.5893	0.7725
Ti–O (1)	1.9895	1.9535	1.9674
Ti–O (2)	1.7099	1.7836	1.7816
Ti–O (3)	2.7519	3.2090	2.6887
Ti off-center displacement	0.5210	0.7127	0.45355

crystal, the experimental data of $\chi_{zzz}^{(2)}$ are 72 (10^{-9} esu), $\chi_{zzx}^{(2)}$ are 12 (10^{-9} esu), and $\chi_{xxx}^{(2)}$ are 6 (10^{-9} esu),³⁵ while in KNbO₃, $\chi_{zzz}^{(2)}$ are 53 (10^{-9} esu), $\chi_{zzx}^{(2)}$ are 30 (10^{-9} esu), $\chi_{zyy}^{(2)}$ are 35 (10^{-9} esu), $\chi_{xxz}^{(2)}$ are 32 (10^{-9} esu), and $\chi_{yyz}^{(2)}$ are 33 (10^{-9} esu).³⁵ In the mean time, for their large SHG, the linear electro-optic coefficients are also very significant. These linear electro-optic coefficients indicate that when an electric field is applied, a large change of refraction can be observed in Bi₂ZnTiO₆.

Optical calculations based on the local density approximation (LDA) or GGA might overestimate the SHG coefficients mainly because of their underestimation of the band gap. Therefore, to confirm the large SHG in Bi₂ZnTiO₆ mentioned above, we have further performed the *ab initio* calculations of the SHG in LiNbO₃ by using the same computational method described in Sec. II. The PAW potentials used are with three valence electrons for Li ($1s^2 2s^1$) and 13 for Nb ($4s^2 4p^6 4d^4 5s^1$). In the self-consistent band structure and optical properties calculations, a dense k -point grid $16 \times 16 \times 16$ is adopted with 417 k -points in the irreducible Brillouin zone. The calculated largest static component of $\chi^{(2)}$ is 62×10^{-9} esu, which is consistent with experimental data (72×10^{-9} esu). This lends support to our finding of the large SHG in Bi₂ZnTiO₆ reported above. Moreover, we have also performed the LDA optical calculations for Bi₂ZnTiO₆ in the different B -site orderings, and found that the calculated dielectric functions and SHG coefficients (not shown here) are very similar to the corresponding GGA results displayed in Figs. 2 and 9. Therefore, we may conclude that Bi₂ZnTiO₆ possesses the largest static SHG coefficients than other known ferroelectric oxides. Furthermore, such large static nonlinear optic coefficients are found in all types of B -site ordering, thus being almost independent of B -site ordering.

As indicated in Eq. (4), the larger electric polarization, the larger nonlinear optical susceptibilities. In these highly distorted perovskite systems, the electric polarization is directly related to the tetragonality c/a as well as the displacement of ferroelectric atoms away from their centrosymmetric positions. To have a picture of the relationship between the polar structure and large nonlinear optical responses, we list

the exact value of c/a ratio, bonding lengths, and the off-center displacement of Bi, Zn, and Ti atoms in Table III. It is found that the largest c/a is found in C -type system, which reaches 1.331, while the energetically favorable G -type has a c/a ratio of 1.304, and A -type system of 1.315. Such kind of large tetragonality is rare (PbTiO₃ has c/a ratio of 1.06), and only two antiferromagnetic BiCoO₃ and PbVO₃ exhibit similar large polar distortions which are 1.27 and 1.23, respectively. The large c/a ratio in perovskite is produced by a distortion of the B -site coordination geometry from tetragonally elongated octahedral to square based pyramidal, coupled with an A -site bismuth environment also considerable more distorted than that of PbTiO₃, reflecting a more pronounced influence of the $6s^2$ lone pair. As for the bonding lengths, the longest Ti–O bond (3.2090 Å) is found in the C -type system. The longest Zn–O bond (3.5265 Å) is found in the A -type system. For Bi ions, the largest bond length appears in the G -type system. Consequently, significant off-center displacements of Zn, Ti, and Bi atoms are found. In particular, a large off-center displacement is found in Zn atoms for the first time. This finding is much larger than previous *ab initio* results performed in [Bi₂ZnTiO₆]_{1-x}[PbTiO₃]_x alloys, which shows an increase in c/a and off-center displacement as the increase in x .²⁷ In PbTiO₃, the off-center of Ti atom is 0.32 Å and that of Pb is 0.48 Å, much smaller than Bi₂ZnTiO₆ as revealed here. In the mean time, it is noted that in both G -type and A -type systems, the off-center displacement of Zn atom is larger than that of atom Ti, indicating an enhanced ferroelectric driving force from the Zn site. These calculated structure data have supplemented current experimental data,¹⁹ which could not give ample information on the Zn, Ti, as well as Bi environments.

It is noted that there is no direct evidence of ferroelectric behavior in Bi₂ZnTiO₆ from current experiment.¹⁹ This is similar with PbVO₃ and BiCoO₃, which also exhibit very large polar distortion. In such materials, exceptionally large electric field required for switching makes it very difficult to obtain a P - E hysteresis loop. This point is verified by our total energy calculations of Bi₂ZnTiO₆ in centrosymmetric

FIG. 3. (Color online) Absolute value of the imaginary part of $\chi^{(2)}$ as well as imaginary part of dielectric functions $\varepsilon(\omega)$ and $\varepsilon(\omega/2)$ of A-type system.

cubic phase, which shows almost 5 eV higher per formula unit than their polar structures. Nevertheless the nonlinear optical properties as revealed above provide a direction of its potential application.

It is generally believed that the driving force of such unusual polar structure in the A-site driven ferroelectrics, such as BiFeO_3 , BiAlO_3 , BiInO_3 , and present $\text{Bi}_2\text{ZnTiO}_6$ is due to the Bi $6s^2$ lone pair, which can be regarded as $6p^0$ -ness. Therefore, the electron localized function³⁶ is displayed for visualizing localized Bi $6s^2$ lone pair (see Fig. 6). Similar with other bismuth based polar oxides, the lobe shaped electrons lead to anisotropic bondings between surrounding oxygen atoms. In fact, the Bi $6p^0$ -ness is also strengthened by the presence of B-site Ti and Zn off-center displacements, which are due to the hybridization between Ti and O ($3d^0$ -ness), and the strong hybridization of Zn ($4s$ and $4p$) and O, respectively. This point will be evaluated from the local DOS displayed below. Therefore, from the above analysis, the highly distorted structure in $\text{Bi}_2\text{ZnTiO}_6$ arises from both A-site and B-site.

It is clear from Eqs. (9) and (10) that the SHG coefficients can have pronounced features due to both single- and double-frequency resonant terms. To further understand the microscopic origin of such large SHG, here we plot the absolute value of imaginary part of $\chi^{(2)}$ in comparison with the imaginary part of $\varepsilon''(\omega)$ and $\varepsilon''(\omega/2)$. The $P4mm$ symmetry of $\text{Bi}_2\text{ZnTiO}_6$ allows $\varepsilon_{xx} = \varepsilon_{yy}$. For the A-type system (Fig. 3),

FIG. 4. (Color online) Absolute value of the imaginary part of $\chi^{(2)}$ as well as imaginary part of dielectric functions $\varepsilon(\omega)$ and $\varepsilon(\omega/2)$ of C-type system.

the first peak observed around 1.5 eV in $\chi_{xxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ are almost identical to the first peak in $\varepsilon''(\omega/2)_{xx}$. The second peak around 2.1 eV in $\chi_{xxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ is also similar with the second peak in $\varepsilon''(\omega/2)_{xx}$. The third peak in $\chi_{xxz}^{(2)}$ around 2.6 eV is consistent with a broad peak in this range of $\varepsilon''(\omega/2)_{xx}$. All these can be regarded as two-photon resonances, while the third peak in $\chi_{zxx}^{(2)}$ around 2.9 eV is consistent with the first peak in $\varepsilon''(\omega)_{xx}$, indicating single-photon resonances. When the energy is higher than 3 eV, SHG decreased and exhibit obscure peaks. For the C-type system (Fig. 4), almost the same trend in A-type is found, i.e., for the low energy photon (less than 3 eV), $\chi^{(2)}$ is directly related to $\varepsilon''(\omega/2)$. For higher energy photon, peaks in $\chi^{(2)}$ are almost the same as that in $\varepsilon''(\omega)$. Again, for the G-type system (Fig. 5), when energy is less than 3 eV, SHG peaks in $\chi_{xxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ are directly related with the four peaks in $\varepsilon''(\omega/2)_{xx}$, indicating two-photon resonances. The same is found in $\chi_{zzz}^{(2)}$ with three dominating peaks in this energy range. When the energy is larger than 3 eV, SHG is related with $\varepsilon''(\omega/2)$, which indicates single-photon resonance. Therefore, the successful connection of the prominent feature of SHG in $\text{Bi}_2\text{ZnTiO}_6$ with that of the linear optical dielectric function in terms of single-photon and double-photon resonances indicates the source of large SHG in $\text{Bi}_2\text{ZnTiO}_6$.

The optical properties can be analyzed further from DOS. In Fig. 7, we have shown the total and partial DOSs. The basic shape is the same for three types of B-site order-

FIG. 5. (Color online) Absolute value of the imaginary part of $\chi^{(2)}$ as well as imaginary part of dielectric functions $\epsilon(\omega)$ and $\epsilon(\omega/2)$ of G-type system.

ing, but with different bandgaps. From A-type to G-type, the band gap increases from around 1 to 1.5 eV. In all three types of ordering, the lowest bands at -10 eV are mainly from Bi $6s$ states. Above these bands are the bands of the hybridized O p , Ti p , and Zn $4p$, $4s$ states. The conduction band is of Ti d states as well as the band of the Bi $6p$ states at higher energy. The hybridization between Bi and O, Ti and

FIG. 7. (Color online) Total and partial density of states of three types of $\text{Bi}_2\text{ZnTiO}_6$. (i) A-type. (ii) C-type. (iii) G-type.

O ($3d^0$ -ness), and Zn ($4s$ and $4p$) and O are the driving forces of the polar structures. The detailed band structure is plotted in Fig. 8. It is noted that A-type has a direct band gap on Γ point, while the other two types have indirect band gap.

Finally, we display in Fig. 9 the linear optical responses which can be easily accessible in experiments and will verify our theoretical prediction in turn. In Fig. 9, from left to right, we present the results of A-type, C-type, and G-type, respectively. Both xx and zz components are displayed. The difference between the three types of B -site ordering is not as obvious as SHG. The imaginary part of dielectric function in Fig. 9(b) shows the interband transition peaks. The detailed refraction function is displayed in Fig. 9(c) and the static refraction indices for A-type are 2.56 and 2.39 for xx and zz components, respectively. For C-type, they are 2.57 and 2.40, respectively. And for G-type, they are 2.57 and 2.40, respectively. As expected from the imaginary part of ϵ , the absorption spectrum in Fig. 9(d) shows the two broad peaks

FIG. 6. (Color online) Illustration of electron localization function. (a) A-type. (b) C-type. (c) G-type.

FIG. 8. Band structure of three types of $\text{Bi}_2\text{ZnTiO}_6$. (a) A-type. (b) C-type. (c) G-type.

(around 7.5 and 17.5 eV) and a sharp one (27.5 eV). The energy-loss function describes the energy loss of a fast electron traversing in a material and is large at the plasmon energy. The energy-loss function shown in Fig. 9(e) displays two broad peaks and a sharp one, located around 10, 20, and 28 eV, respectively, which are consistent with the roots of $\varepsilon'(\omega)$. These linear optical results will provide useful information for experimentalists.

IV. SUMMARY

In summary, we have made a systematic *ab initio* investigation of crystal structure, electronic structure, linear optical, and SHG in $\text{Bi}_2\text{ZnTiO}_6$. By comparing three possible *B*-site ordering configurations, we have found the following: (i) *G*-type *B*-site ordering is energetically favorable, (ii) all the three types of ordering show large SHG coefficients, and (iii) the largest static SHG appears in *C*-type $\text{Bi}_2\text{ZnTiO}_6$ with the value of 123×10^{-9} esu, almost two times larger than 72×10^{-9} esu in LiNbO_3 . The significant SHG coefficients are consistent with the calculated unusual polar structures, i.e., large *c/a* ratio and off-center displacements, and are further related to the linear part of optical dielectric function in terms of single-photon and double-photon resonances. These results have demonstrated the potential application of $\text{Bi}_2\text{ZnTiO}_6$ in future optoelectronics. We hope our calculations will stimulate further experiments on the SHG measurements in this unusual polar double perovskite oxide.

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FIG. 9. (Color online) Linear optical properties. From left to right are A-type, C-type, and G-type, respectively. (a) Real part of ε . (b) Imaginary part of ε . (c) Refraction spectrum. (d) Absorption spectrum. (e) EELS function. Blue solid line is for ε_{xx} and red dashed line is ε_{zz} . For the $P4mm$ symmetry, $\varepsilon_{xx} = \varepsilon_{yy}$.

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