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Determination of the electronic, dielectric, and optical properties of sillenite $\text{Bi}_{12}\text{TiO}_{20}$ and perovskite-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ materials from hybrid first-principle calculations

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Density functional theory calculation was conducted to determine the optoelectronic properties of bismuth titanate sillenite ($\text{Bi}_{12}\text{TiO}_{20}$) and perovskite-like ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) structures. The lattice parameters were experimentally obtained from Rietveld analysis. The density functional perturbation theory approach was used with the standard Perdew–Burke–Ernzerhof functional and screened Coulomb hybrid Heyd–Scuseria–Ernzerhof functional to investigate the electronic structure and absorption coefficient. Both compounds have good carrier transport properties, low effective hole and electron masses, high dielectric constant, and low exciton binding energy. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4945344>]

I. INTRODUCTION

Producing a successful semiconductor material involves associating the intrinsic photophysical properties with the chemical compositions and/or electronic structures.^{1–5} This is particularly relevant in the case of semiconductor materials for solar applications,^{6–10} where the capability of the semiconductor to use effectively solar light depends on combination of a series of properties.² Thus, the efforts devoted to the accurate theoretical and experimental characterization of a large variety of semiconductor materials aimed to elucidate fundamental properties, such as band gap, optical absorption coefficient, dielectric constant, and charge carrier effective masses.

In this context, bismuth titanates, such as $\text{Bi}_2\text{Ti}_4\text{O}_{11}$,¹¹ $\text{Bi}_8\text{TiO}_{14}$,¹² $\text{Bi}_2\text{Ti}_2\text{O}_7$,¹³ $\text{Bi}_{12}\text{TiO}_{20}$, and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$,¹⁴ received great interest because of their promising optoelectronic properties, which can be tuned through site substitution with different elements.¹⁵ For example, sillenite $\text{Bi}_{12}\text{TiO}_{20}$ and perovskite-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystal structures are of particular interest because they are used in photocatalysis to degrade organic pollutants.^{16–19} In addition, they are used in optoelectronic devices because of their photorefractive properties, and their high electro-optical coefficients make them applicable in the field of holographic interferometry.²⁰ On the other hand, perovskite-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been used as a promising material for nonvolatile ferroelectric random access memories (FRAMs) because of its excellent fatigue resistance during repeated polarization reversals with an electric field.²¹

The synthesis of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is extensively explored using many methods,^{22–25} and several morphologies, such as nanowires,²⁶ nanotubes,²⁷ and hierarchical assemblies, have been reported as photoactive materials.^{28,29} Although these structures were experimentally investigated, the intrinsic

electronic structure and band gap, which govern the photo-conversion process, have not been well characterized.^{17,30–33} In the literature, their band gaps remain controversial, as they have been reported whether there is the presence^{18,19} or absence¹⁶ of a visible response. Furthermore, important characteristics such as the dielectric constant, charge carrier effective masses, and band edges have not been reported for these materials.

As we reported for $\text{Bi}_2\text{Ti}_2\text{O}_7$, the pyrochlore structure has extended photophysical properties that can be applied in various potential applications in substitution or mixture with TiO_2 in dye-sensitized solar cells and photocatalytic applications.³⁴ The consistency between the measured and calculated properties for this material encouraged us to apply this methodology to other bismuth titanate structures.

To clarify the inconsistencies in the reported values of optoelectronic properties for both sillenite and perovskite-like bismuth titanate structures, we conducted a synergic experimental and theoretical characterization of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ materials. In the experimental approach, the pure phase was carefully synthesized. For the calculation, the density functional theory (DFT) and density functional perturbation theory (DFPT) with both the standard Perdew–Burke–Ernzerhof (PBE) functional and the more accurate screened Coulomb hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional were used.^{7–10} Our choice of HSE06 was based on the previous reports of the widely used semiconductors in the fields of photocatalysis and photovoltaics, which showed high accuracy in predicting these photophysical properties compared with experimental data.^{7–10,34–36} This result is distinctive from the small band gaps that were calculated using the standard PBE functional.^{30,31,37} We emphasize here that our highly accurate characterization of these bismuth titanate compounds indicates that this material has remarkable photophysical properties, making it a promising material to be used in optoelectronic devices.

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II. EXPERIMENTAL AND THEORITICAL METHODS

A. Chemicals

The following chemicals were used: bismuth nitrate pentahydrate (Aldrich, purity 99.999%), titanium isopropoxide (Aldrich, purity 99.999%), glacial acetic acid (Fisher Scientific, purity 99.8%), and ammonium hydroxide (Fisher Scientific, 29.44%).

B. Synthesis of bismuth titanate powders and films

Bismuth titanate powders were synthesized using the co-precipitation method.³⁴ $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (6 mmol) was dissolved in 25 ml of glacial acetic acid under stirring at room temperature for 3 h until the solution became clear. Then, titanium isopropoxide was added (0.5 mmol) for the sillenite structure with different Bi/Ti ratios and (4.5 mmol) for perovskite-like structure. After 5 min of stirring, 33 ml of cold ammonium hydroxide was slowly added. When the pH became ~ 7 , a white precipitate was formed, which was filtered and extensively washed with Milli-Q water ($>18 \text{ M}\Omega$). After drying at 90°C for 24 h, the obtained mixture was ground and heat-treated for 16 h at 600°C for sillenite and 700°C for perovskite-like in a static furnace.

C. Structural and optical characterization

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advanced A25 diffractometer equipped with a Cu X-ray tube ($\text{Cu-K}\alpha$; $\lambda = 0.15418 \text{ nm}$), which was operated at 40 kV and 40 mA in the Bragg-Brentano geometry using a linear position-sensitive detector with an opening of 2.9° . The diffractometer was configured with a 0.44° divergence slit, a 2.9° anti-scatter slit, 2.5° Soller slits, and a nickel filter to attenuate contributions from the $\text{Cu-K}\beta$ fluorescence. The XRD data were analyzed via Rietveld method using the fundamental-parameter approach, as implemented in the software TOPAS V4.2 (Bruker-AXS). The XRD patterns of sillenite and perovskite-like bismuth titanate were refined using the cubic structure, which were obtained from JCPDS Nos. 00-034-0097 and 00-035-0795, respectively. The profile parameters included the scale factor, a sample displacement parameter, and a three-term polynomial for the background. The fundamental-parameter approach involves analytically calculating the instrumental broadening in the peak profile.

The absorption properties of the final powder samples were measured using diffuse reflectance ultraviolet-visible (UV-Vis) spectrometry, which was collected using a JASCO model V-670 spectrophotometer equipped with an integrating sphere. The spectra were scanned from 200 to 700 nm using halogen and deuterium lamps as the light sources, and the data were processed using Kubelka-Munk function.

D. Computational methods

The sillenite $\text{Bi}_{12}\text{TiO}_{20}$ and perovskite-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures were optimized using periodic DFT, as implemented

in the VASP program,^{38–41} with the PBE exchange-correlation functional⁴² and projected-augmented plane wave (PAW) approach.⁴³ The configurations of the valence electrons in the PAW potentials were $6s^2 6p^3$ for Bi, $3d^3 4s^1$ for Ti, and $2s^2 2p^4$ for O. The oxidation states of the examined elements in our structural models were Bi^{3+} , Ti^{4+} , and O^{2-} . Cutoff energies of 500 and 610 eV were used for the wave functions and the charge augmentations, respectively. The convergence criterion for the self-consistent-field (SCF) cycles was set to 10^{-5} eV per cell. The atomic positions and cell parameters were fully relaxed until the Hellmann–Feynman forces on each atom were less than $0.01 \text{ eV } \text{\AA}^{-1}$. The first Brillouin zones were sampled using $5 \times 5 \times 5$ and $6 \times 6 \times 2$ Monkhorst-Pack k-point meshes⁴⁴ for sillenite and perovskite-like structures, respectively.

The electronic structure of these materials was calculated using the DFT with the screened coulomb hybrid HSE06 exchange-correlation functional,^{45–47} as implemented in the VASP, based on the optimized geometries obtained at the PBE level.^{38–41} The tetrahedron method with Blöchl corrections was used for the Brillouin-zone integration. In k -space band structure calculations, the Gaussian smearing method was used for the energy dispersion curves. A convergence test made on the two materials with increased cutoff energy up to 580 eV revealed identical electronic structure results showing exactly the same band gap values as those obtained with 500 eV (see Fig. S1).⁴⁸ It is well-known that the GGA functional limitation (underestimated band gaps) should be considerably alleviated by using HSE06.^{8–10,49–54}

The UV-Vis optical absorption of these materials was calculated by applying the sum-over-state method implemented in VASP along with HSE06 formalism. The optical properties were obtained from the frequency-dependent complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ following a methodology described in the literature.⁵⁵ The real part $\epsilon_1(\omega)$ was obtained using Kramers-Kronig relation and is defined as the electronic contribution to the dielectric constant (ϵ_∞). The imaginary part $\epsilon_2(\omega)$ was calculated by summing all possible transitions from occupied to unoccupied states in the Brillouin zone, which was weighted with the matrix elements that describe the probabilities of transition. To determine the fraction of light absorbed in these materials, we calculated the optical absorption coefficient ω (in cm^{-1}) for each compound as a function of the wavelength of the incident light using the following equations:

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} \quad (1)$$

$$k(\omega) = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2} \right)^{\frac{1}{2}}, \quad (2)$$

where λ and ω are the wavelength and frequency of the incident light, respectively, and $k(\omega)$ is the extinction coefficient or the imaginary part of the complex refractive index. The convergence test made on the two materials with increased cutoff energy up to 580 eV also showed very similar optical results as those obtained with 500 eV (see Figs. S2 and S3⁴⁸).

The ionic contributions to the dielectric constant tensors (ϵ_{vib}) of these materials were obtained by computing the full phonon spectrum of the crystal using the DFPT and PBE functional in the framework of the linear response method, which was implemented in VASP.

The effective mass tensors of photogenerated holes (m_h^*) and electrons (m_e^*) at the band edges of these compounds were computed based on their k -space band structures, which were obtained from the DFT/PBE method, using the following expression:

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(k)}{\partial k_i \partial k_j} \quad (i, j = x, y, z), \quad (3)$$

where i and j denote reciprocal components and $E_n(k)$ is the dispersion relation for the n -band with step size h of 0.01 bohr^{-1} ($1 \text{ bohr} = 0.529 \text{ \AA}$). The second derivatives of the band energy with respect to the wave vector were numerically evaluated using the finite difference method.⁵⁶

The exciton binding energy was calculated based on the hydrogenic model as follows:

$$E_b = \frac{\mu}{m_0 \epsilon_r^2} R_H, \quad (4)$$

where m_0 is the free electron mass, R_H is the Rydberg constant of the hydrogen atom (13.6 eV), ϵ_r is the average macroscopic (including electronic and ionic contributions) dielectric constant, and μ is the effective reduced mass of the exciton, which is given as follows:

$$\frac{1}{\mu} = \frac{1}{m_h^*} + \frac{1}{m_e^*}. \quad (5)$$

Note that for $\text{Bi}_{12}\text{TiO}_{20}$ (cubic crystal structure), the effective masses of the hole (m_h^*) and the electron (m_e^*) were obtained from the arithmetic mean of the components in three crystallographic directions, whereas the geometric mean was considered for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (non-cubic crystal structure). In both materials, the macroscopic dielectric constant (ϵ_r) was obtained from the arithmetic average of the components in three crystallographic directions.

III. RESULTS AND DISCUSSION

A. Structural properties

The structural properties of the synthesized powders were determined using XRD measurement and Rietveld refinement. Fig. 1 shows the XRD patterns of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders that were synthesized using the co-precipitation method. The detailed Rietveld refinement fit is shown in Fig. S4.⁴⁸ The XRD patterns show that both structures are single phase. All peaks were indexed according to JCPDS Nos. 00-034-0097 and 00-035-0795 for $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, respectively.

Based on the Rietveld refinement of the two crystal structures, we systematically modeled the refined structures using the DFT/PBE computational method. $\text{Bi}_{12}\text{TiO}_{20}$ was modeled as a cubic crystal structure in a sillenite family. Our model contains 2 functional units ($\text{Bi}_{24}\text{Ti}_{12}\text{O}_{40}$) or 66 atoms (see Fig. 2(a)). The least symmetrical phase of bismuth titanate

FIG. 1. XRD patterns of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders that were synthesized using the co-precipitation method.

is $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with a pseudo-orthorhombic crystal structure. Its model contains four functional units ($\text{Bi}_{16}\text{Ti}_{12}\text{O}_{48}$) with 76 atoms as shown in Fig. 2(b).

The measured and calculated lattice parameters are summarized in Table I. Fig. 2(a) shows the most relaxed crystal structure of the $\text{Bi}_{12}\text{TiO}_{20}$. The optimized bond lengths

FIG. 2. Optimized crystal structures using the DFT/PBE method of (a) $\text{Bi}_{12}\text{TiO}_{20}$ and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Color legend: Bi in purple, Ti in gray, and O in red.

TABLE I. Lattice parameters measured by the Rietveld refinement (Expt.) and DFT/PBE (DFT) of sillenite $\text{Bi}_{12}\text{TiO}_{20}$ and perovskite-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Solid	Lattice parameters (Å)		
	<i>a</i>	<i>b</i>	<i>c</i>
$\text{Bi}_{12}\text{TiO}_{20}$ (Expt.)	10.171	...	...
$\text{Bi}_{12}\text{TiO}_{20}$ (DFT)	10.142	...	...
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Expt.)	5.407	5.443	32.825
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (DFT)	5.442	5.421	32.713

are summarized in Table SI.⁴⁸ The sillenite structure has a cubic symmetry of the $I23$ space group. It has a general formula of $\text{Bi}_{12}\text{MO}_{20}$, where M is the tetravalent transition metal (Ti^{4+}) that forms the TiO_4 tetrahedra. Bismuth (Bi^{3+}) is penta coordinated to three types of oxygen atoms forming a distorted polyhedra and a stereochemically active $6s^2$ lone electron pair. The Ti–O bond length is experimentally found to be 1.72 Å, and the five Bi–O bonds are 2.65, 2.62, 2.21, 2.19, and 2.07 Å with $\pm 0.01\%$ error. The TiO_4 tetrahedra occupy the corners and the center of the cell lattice. The Bi–O polyhedron network connects to the geometrically regular TiO_4 tetrahedra. Yao *et al.* claimed that this Bi–O polyhedral facilitated the photocatalytic activity in photodegrading organic pollutants.¹⁹ Relaxation of the lattice parameter yields $a = 10.142$ Å, which is consistent with the measured value of $a = 10.171$ Å and previously reported values.^{57,58} A similar trend between measured and calculated values was obtained for the bond lengths, as listed in Table SI.⁴⁸ The calculated single Ti–O bond length was 1.849 Å; the five Bi–O bond lengths were 2.59, 2.56, 2.25, 2.24, and 2.12 Å with $\pm 0.01\%$ error.

The refined $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ aurivillius (perovskite-like) structure is shown in Fig. 2(b). The model contains four functional units ($\text{Bi}_{16}\text{Ti}_{12}\text{O}_{48}$) with 76 atoms. It shows a pseudo-orthorhombic crystal structure in the $Aba2$ space group. The experimental lattice parameters shown in Table I are consistent with the calculated values and the literature.^{59–61} The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structure is composed of fluorite bismuth-oxide (Bi_2O_2)²⁺ layers between perovskite-like ($\text{Bi}_2\text{Ti}_3\text{O}_{10}$)²⁻ layers along the *c*-axis, as shown in Fig. 2(b). There are two types of Ti atoms, Ti(1) in the middle of the perovskite-like layer and Ti(2) at the connection between the perovskite-like and the bismuth-oxide layers, both of them octahedrally coordinated. The bond lengths from Rietveld refinement were 1.74, 1.96, and 2.20 Å for Ti (1) in the octahedral configuration. The second titanium, Ti (2), is in a distorted octahedra with Ti–O bond lengths of 1.72, 1.85, 2.10, and 2.27 Å. These values are notably consistent with those obtained from the most relaxed calculated values with 3 bond lengths: for Ti (1)–O: 1.87, 1.99, and 2.03 Å; for Ti (2)–O: 1.78, 1.91, 2.09, and 2.31 Å. The Bi atom in the $\text{Bi}_2\text{O}_2^{2+}$ layer has three Bi–O bonds of lengths 2.32, 2.41, and 3.02 Å. Bi (2) in ($\text{Bi}_2\text{Ti}_3\text{O}_{10}$)²⁻ has four different Bi–O bonds of 2.33, 2.41, 2.51, and 2.83 Å. Similar values were obtained from the relaxed structure with 2.34, 2.47, and 3.20 Å for Bi (1) and 2.23, 2.29, 2.39, and 2.86 Å for Bi (2).

It is worth mentioning that several synthesis instances reported a phase transition at different temperatures.^{62,63} For example, at the Curie temperature of 675 °C, it

transforms into a paraelectric phase with a centro-symmetric tetragonal structure. Our calculated and measured lattice parameters are fairly consistent at ambient temperature. The non-centrosymmetric structure of those compounds at room temperature highlights interesting anisotropic physical properties, which are discussed in Secs. III B–III D.

B. Electronic structure

Fig. 3 shows the diffuse reflectance UV-Vis spectra of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders. The spectrum of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ material shows an absorption edge at 380 nm. In contrast, the absorption edge of $\text{Bi}_{12}\text{TiO}_{20}$ is shifted to the visible region probably because of defects in the structure.⁶⁴ Tauc plots corresponding to the obtained spectra (Fig. S5⁴⁸) show measured band gaps of 3.0 and 3.3 eV for $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, respectively. Detailed investigation for $\text{Bi}_{12}\text{TiO}_{20}$ structure was carried out to identify the crucial effects of the Bi/Ti stoichiometry on the absorption edge. The stoichiometry of the compounds was confirmed by combining ICP result and the Rietveld analysis. In Fig. S6,⁴⁸ absorption edge of the sample with Bi/Ti ratio of 4.7 shows a blue shift in comparison to the sample with 12:1, whereas the sample with excess bismuth of Bi: Ti = 14:1 shows a red shift. These results confirm that, although the XRD patterns appear identical, non-stoichiometry of the structure causes varied information of the band edges. Previous experimental studies indeed reported inconsistent band gap values: 2.4 eV,¹⁹ 2.78 eV,⁶⁵ 2.75 eV,¹⁸ 2.94 eV,⁶⁶ 3.1 eV,⁶⁷ and 3.2 eV⁶⁸ for $\text{Bi}_{12}\text{TiO}_{20}$, while band gap values of 3.27 eV and 3.6 eV were reported for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.^{69,70}

The calculated electronic density of states (DOS) for the sillenite $\text{Bi}_{12}\text{TiO}_{20}$ and perovskite-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures using the DFT/HSE06 method are shown in Fig. 4. Their calculated energy dispersion curves using the DFT/PBE method are provided in Fig. 5. These values include spin-orbit coupling consideration using single-point calculations with VASP adding to the Hamiltonian with the non-collinear formalism and using the DFT/PBE and DFT/HSE06 methods. For $\text{Bi}_{12}\text{TiO}_{20}$, the valence-band states in a wide energy range below the Fermi level are formed by occupied O 2p

FIG. 3. Diffuse reflectance UV-Vis spectra of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders, which were synthesized using the co-precipitation method.

FIG. 4. DOS of (a) $\text{Bi}_{12}\text{TiO}_{20}$ and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures obtained using the DFT/HSE06 method applying spin-orbit coupling. Total DOS in black; projected DOS on Bi, Ti, and O in red, blue, and green, respectively. Fermi levels (E_f) are set at 0 eV.

orbitals and weak contribution from Bi 6s orbitals, whereas the conduction-band states in the 1 eV range above the bottom part are mainly composed of empty Bi 6s orbitals (Fig. 4(a)). Our calculations predict a direct band gap (at the Γ or H point) semiconductor (Fig. 5(a)) with a band gap energy of 3.1 eV. The lowest-energy band gap of this material originates from the direct O $2p^6$ –Bi $6p^0$ orbital transitions. For $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, the electronic analysis reveals that valence-band states in a wide energy range below the Fermi level are dominated by O 2p orbitals with negligible contributions from Bi 6s orbitals, whereas the conduction-band states primarily consist of empty Ti 3d orbitals (Fig. 4(b)). This material is predicted as an indirect (from T to X or Γ points) semiconductor (Fig. 5(b)) with a larger band gap of 3.6 eV, characterized by indirect transitions from O $2p^6$ to Ti $3d^0$ orbitals. Our calculated DOS of these materials using the DFT/PBE method revealed much smaller band gap

energies (2.2 eV for $\text{Bi}_{12}\text{TiO}_{20}$ and 2.3 eV for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$) (Fig. S7),⁴⁸ which were similarly reported in previous theoretical studies.^{30,31,37} Alternatively, small increments in band gap by 0.2 and 0.04 eV for sillenite and perovskite-like structures, respectively, were obtained without taking spin-orbit coupling into consideration (Figs. S8 and S9).⁴⁸ These results confirm once again the crucial requirement of using the HSE06 exchange-correlation functional instead of standard GGA functionals, such as PBE, as well as inclusion of spin-orbit coupling effect, to accurately predict the experimental band gap of semiconductor compounds.

C. Dielectric and optical properties

The dielectric constant is an important parameter that represents the ability of a dielectric material to screen the external electric field by polarization. Two contributions are present in the dielectric constant: the electronic one, which is linked to polarization from reorganization of the electronic density (optical), and the vibrational one, which involves ionic motion. Previous experimental work on typical semiconductors used in photovoltaic devices showed that a value greater than 10 for the macroscopic dielectric constant (electronic and ionic contributions) is sufficient to obtain good exciton dissociation into free charge carriers.^{71,72}

We calculated the optical (ϵ_∞) and macroscopic (ϵ_f) dielectric constant tensors of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystals using the PBE and HSE06 exchange-correlation functionals. Table II summarizes the obtained components in the three principle crystallographic directions. The real part of the dielectric function (ϵ_1) as a function of the incident radiation energy in the range of 0–8 eV is shown in Fig. 6. Because of the cubic symmetry of sillenite, the dielectric tensor is isotropic with $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$. Both compounds have similar curvatures, although starting edges are dislocated because of different band gaps. Such similarities arise from the similarity in band structure and electrons transitions. The real part (ϵ_1) describes the electronic part (ϵ_∞) of the dielectric constant of the materials at the band gap energy.

FIG. 5. Electronic band dispersions along the high-symmetry k -points of (a) $\text{Bi}_{12}\text{TiO}_{20}$ and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures, which were obtained using the DFPT/PBE method applying spin-orbit coupling. E_f is set at 0 eV.

TABLE II. Optical (ϵ_∞), vibrational (ϵ_{vib}), and macroscopic (ϵ_r) dielectric constant components in three principal directions of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures obtained using PBE for (ϵ_{vib}) and HSE06 for (ϵ_∞), respectively.

	Direction	ϵ_∞	ϵ_{vib}	ϵ_r
$\text{Bi}_{12}\text{TiO}_{20}$	$xx = yy = zz$	6.26	25.0	31.2
	xx	4.88	51.9	56.8
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	yy	5.29	62.1	67.3
	zz	7.00	40.4	47.4

The electronic part of the dielectric constant tensor was deduced from ϵ_1 computed using HSE06 as shown in Fig. 6, while the ionic component tensors for both components were computed using PBE functional following the methodology described in Computational Methods. For sillenite, a high dielectric constant ϵ_r of 31.2 was found along the three principal directions with $\epsilon_\infty = 6.26$ (Fig. 6(a)) and $\epsilon_{\text{vib}} = 25.0$ as shown in Table II. Our calculated macroscopic dielectric constant is consistent with the reported experimental one of 41 using the dielectric resonator technique.^{58,73} The perovskite-like structure retains higher macroscopic dielectric constant than sillenite,⁷⁴ with values of 56.8, 67.3, and 47.4 along the xx , yy , zz directions, respectively, and 57.2 as an average value. The vibrational component values are 51.9, 62.1, and 40.4 along the principle directions. The average electronic contribution is 5.72 deduced from the xx , yy , and zz direction values interpreted from Fig. 6(b). The dielectric constant of the perovskite-like structure is reported to be temperature-dependent and increases with increasing temperature.⁷⁵ At the relaxing frequency, the major contribution of the total dielectric constant in both crystals comes from the ionic part because of the high electronegativity of oxygen.⁷⁶ The ionic

contribution is proportional to the oxide (TiO) large Born effective charges and inversely proportional to the photon frequency. At very high frequencies ($>10^{12}$ Hz), the ionic contribution tends to decrease because the ions respond more slowly than the electrons to an applied field, which results in a larger contribution from the electronic part. A dielectric constant tensor can also help characterizing optically active materials when small non-diagonal components appear, even if the crystal structure is cubic.³²

An optical band gap can be extracted from the frequency dependence of the imaginary part of the dielectric constant by looking at the adjacent slope of the first local maximum (peak) of the imaginary part (ϵ_2) or the threshold energy. The major peak in Fig. 7 is attributed to the interband direct (or indirect) optical transitions from O 2p valence band orbitals to Bi 6p conduction band orbitals for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (or to Ti 3d conduction band empty orbitals for $\text{Bi}_{12}\text{TiO}_{20}$). The curves of ϵ_2 in Figs. 7(a) and 7(b) show that the critical point occurs at approximately 3.2 eV and 3.6 eV for sillenite and perovskite-like structures, respectively. Thus, the absorption energy edge, which is plotted with the imaginary part in Fig. 8, proves the obtained band gap in the DOS calculations using the HSE06 functional.

The calculated optical absorption coefficient spectra, presented in Fig. 8, were obtained by averaging the imaginary and real parts of the dielectric function, computed using HSE06 over three polarization vectors as a function of the wavelength of the incident light. Generally, both compounds exhibit low absorbance in the visible-light range. For the perovskite-like structure, the principal absorption edge is located at 340 nm, which mainly originates from the electronic transitions from O 2p-to Bi 6p-states. There is a significant optical anisotropy near the absorption edge as shown in

FIG. 6. Real part of the frequency-dependent dielectric function along three principal light polarization vectors of (a) $\text{Bi}_{12}\text{TiO}_{20}$ and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures, which were obtained using HSE06.

FIG. 7. Imaginary part of the frequency-dependent dielectric function along three principal light polarization vectors of (a) $\text{Bi}_{12}\text{TiO}_{20}$ and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures, which were obtained using HSE06.

FIG. 8. Optical absorption coefficient spectra of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures, which were obtained using HSE06.

Figs. 6 and 7, which results from its special crystal structure and electronic structure. This result obviously shows that the bismuth titanate sillenite structure is a better photon absorber than the perovskite-like one.

D. Exciton dissociation and charge carrier transport properties

The effective mass of holes and electrons is an excellent descriptor of the charge carrier transport properties of the crystal. They are related to the curvature of the valence band (for the holes) or conduction band (for the electrons) around the extremum of the band. The determination of the charge carrier effective masses along different crystallographic directions provides access to the possible anisotropy of charge carriers through the crystal structure of the material. As experimentally demonstrated, the effective mass of both holes and electrons should be smaller than $0.5 m_0$ at least in one crystallographic direction to obtain good charge carrier transport properties.^{71,77,78}

We computed the effective mass tensors of the photogenerated holes (m_h^*) and electrons (m_e^*) at the band edges of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystals using their electronic band structure, which were obtained from the PBE exchange-correlation functional. Table III reports the obtained values in the transverse and longitudinal crystallographic directions and the available experimental data. For sillenite, the smallest electron and hole effective mass was found along the zz direction with a value of $0.05 m_0$ (units of the electron mass). This result guarantees notably high hole and

electron mobility and good charge carrier transport properties because it is less than $0.5 m_0$.³⁵ However, the migration of the electron and hole in identical directions may result in a poor charge separation at the surface of the material. For efficient separation, the charges must travel in two different crystallographic directions. The bismuth titanate perovskite-like structure has high electron mobility ($0.14 m_0$) in the xx and zz directions and higher hole mobility by one order of magnitude ($0.014 m_0$) in the zz direction. The notably small hole and electron effective masses in two different directions prove that charge carriers in the perovskite-like structure are separated by a single-phase material, known as the bulk photovoltaic effect, which is interesting for ferroelectric properties.⁷⁹ A similar behavior was observed in the pyrochlore phase of bismuth titanate.³⁴ Generally, because of the high electronic carrier mobility, these compounds may act as promising electronic materials.

As previously mentioned, the binding energy of the exciton (E_b) should be lower than the thermal energy (25 meV at room temperature) to efficiently dissociate this photogenerated exciton into free charge carriers.⁸⁰⁻⁸³ Experimentally, the exciton generation is faster than atomic motions in the crystal. This principle is the vertical transition principle, which implies that the charge-screening felt by the exciton when it is generated only comes from ϵ_∞ because only the electronic density can reorganize at this time scale. This particle is the unrelaxed exciton. Then, the atoms move to adapt to the exciton. At that time, the charge screening is governed by ϵ_r and produces the relaxed exciton. The present study assumes that for photovoltaic devices, the exciton dissociation has a longer time scale than the atomic motions; consequently, E_b corresponds to the binding energy of the relaxed exciton.

We calculated the exciton binding energy E_b of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystals using the hydrogenic model and the HSE06 functional as described in our methodology. We found that sillenite and perovskite-like structures have low values of 2.1 and 0.9 meV, respectively. These values are much lower than the thermal energy at room temperature (25 meV), which assumed to dissociate the exciton. Thus, both compounds provide Mott-Wannier excitons with easy and efficient exciton dissociation into free charge carriers compared to other well-known semiconductors, e.g., ZnO and CdSe.³⁵

IV. CONCLUSION

In summary, sillenite and perovskite-like crystalline phases of bismuth titanate compounds ($\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$) have been synthesized and characterized with a synergic experimental and computational approach. Using the accurate HSE06 functional and taking spin-orbit coupling effect into account, both compounds exhibit relatively large optical band gaps: 3.1 eV for sillenite and 3.6 eV for perovskite-like structures, respectively. $\text{Bi}_{12}\text{TiO}_{20}$ has larger absorption coefficient and band edge than $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and provides lower effective masses, which ensures better transport properties for charge carriers. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has higher dielectric constant and notably small effective mass in the z direction.

TABLE III. Effective masses of holes (m_h^*/m_0) and electrons (m_e^*/m_0) in three principal directions of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structures, which were obtained using the DFT/PBE method. m_0 is the free electron mass.

	m_h^*/m_0			m_e^*/m_0		
	xx	yy	zz	xx	yy	zz
$\text{Bi}_{12}\text{TiO}_{20}$	0.52	0.09	0.05	1.27	0.14	0.05
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	0.14	8.64	0.14	4.41	0.74	0.014

The good optoelectronic properties for titanate were identified which should be utilized to design photovoltaic perovskite-like ferroelectrics or photocatalytic applications.

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