Insights into the Impact of Yttrium Doping at the Ba and Ti Sites of BaTiO₃ on the Electronic Structures and Optical Properties: A First-Principles Study

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1. INTRODUCTION

Barium titanate materials have received much attention because of the scientific interest related to exceptional and multiple meaningful properties such as high dielectric permittivity, positive temperature coefficient of resistivity, high-voltage tunability, ferroelectricity, pyroelectricity, and piezoelectricity.¹⁻⁶ These characteristics have contributed the use of barium titanate ceramics in various applications including multilayer ceramic capacitors, piezoelectric and ultrasonic actuators, pyroelectric detectors, temperature sensors and controllers, and microwave devices for telecommunications.⁷⁻¹³ Barium titanate (BaTiO₃) has its structure based on ABO₃ general formula in which A is the larger cation located in eight corners and six oxygen atoms located in the middle of surfaces, while B is the smaller cation located in the center of the unit cells.⁵⁻⁸ BaTiO₃ is composed of perovskite-based metal oxide materials that can be crystallized in cubic (Pn̅3m) and tetragonal (P4mm) crystal structures at room temperature,¹⁴ which are the most investigated structures.¹⁵ However, the tetragonal structure shows the most stable structure at ambient conditions. Despite their wide potential of applications, BaTiO₃-based materials have been faced with certain practical limitations because of the narrow range of tetragonal stability and lower piezoelectric coefficient¹⁶. To further improve the ferroelectric and dielectric properties of BaTiO₃, the current research strategy is driven by the prospects of synthesizing new systems, by means of replacing Ba²⁺ or Ti⁴⁺ by other ions of comparable ionic sizes. In fact, the perovskite structures show high flexibility and intrinsic capacity to host ions of different sizes, and a large number of different dopants can be incorporated at the Ba sites or at the Ti sites in perovskite-based metal oxide materials.¹⁷⁻²⁰ In particular, trivalent rare-earth dopants have attracted wide attention because of their ability to act as a donor or an acceptor. It is reported that doping a small amount of rare-earth dopants into BaTiO₃ systems can greatly improve the microstructure of ceramic materials, phase composition, sintering properties, mechanical properties, physical and chemical properties, and dielectric properties.⁷

In consideration of their obvious importance, many experimental and theoretical works based on BaTiO₃ materials with tailoring the physical—chemical properties and electrical properties through different dopants have been achieved. On the experimental side, Ren et al.²¹ have synthesized Ba₁₋ₓYₓTiO₃ solubility associating with the electron compen-
sation prepared by using a solid-state reaction method. They reported that doping Y at A site can lead to high conductivity, appended by a giant permittivity and large dielectric loss. Also, the effects of rare-earth doping in BaTiO3 were experimentally prepared using a conventional powder sintering technique.17 Hence, it was observed that the different rare-earth element possessed a critical effect on dielectric properties, where Y-doping showed the largest leakage current compared with that of other rare-earth elements. Recently, Liu et al.22 have investigated the experimental synthesis of Y-doped BaTiO3 ceramics by using the sol–gel technique. They proposed a new method to evaluate the depletion layer width of Y-doped BaTiO3 grains. On the theoretical side, it has been suggested from interatomic potential-based defect calculations that defect clustering in rare-earth-doped BaTiO3 can introduce a significant strain on the lattice, resulting in positive binding energy.18 So far, to the best of our knowledge, there is no theoretical investigation on optoelectronics properties of rare-earth-doped BaTiO3.

In this contribution, we intend to present a theoretical study of the structural, electronic, optical, and piezoelectric properties of rare-earth-doped BaTiO3. The first-principles methods we use for simulations are based on density functional theory accompanied by Tran–Blaha-modified Becke–Johnson (TB–mBJ) with generalized gradient approximation (GGA) + U approaches. To get a better understanding of the mechanism, the doping implications on the properties of BaTiO3, it is necessary to contrast the doping effects at both A and B sites of BaTiO3. Herein, Y is doped at both A and B sites of BaTiO3, and their effects on the crystal structures and the electronic and optical properties of BaTiO3 are compared. Their bonding characteristics are also shown. In addition, the Born effective charges and piezoelectric properties are investigated in detail.

2. RESULTS AND DISCUSSION

The crystal structure of pristine BaTiO3 is tetragonal (the space group is P4mm) with Ti atoms positioned at the cube center, Ba atoms located at the cube corner, and O atoms located at the face centers. The optimized lattice parameter values and the average bond length between the neighboring elements for pristine BaTiO3 are gathered in Table 1 as well as the experimental data23 and theoretical works for comparison. Our calculated lattice parameters well reproduced the measured X-ray diffraction values.23 In the optimized geometry of Y doping at the Ba site (Ti site) in BaTiO3, it is found that a- and c-lattice parameters change slightly with respect to those of pristine BaTiO3. This variation results from distortion of the tetragonal crystalline structure after Y doping. The optimized structures of pristine BaTiO3 and Y-doped BaTiO3 at both Ba and Ti sites are depicted in Figure 1.

The calculated lattice constants of Y doping at both Ba and Ti sites are also listed in Table 1, where a fair agreement is observed from the experimental values published by Ren et al.23,24 Our results show that the lattice parameters of pristine BaTiO3 are 2.914 and 2.072 Å, respectively, which are in excellent accord with the experimental data23 and previous theoretical results.24,25 For Y doping at both Ba and Ti sites, the process reduces the Ti–O bond lengths because of the lattice distortion. Our findings indicate that Y doping has long-range effects on the crystalline structure in which all interatomic bond lengths are modified.

The electronic band structures of pristine BaTiO3 and Y-doped BaTiO3 at both Ba and Ti sites are calculated by using TB–mBJ and TB–mBJ with GGA + U approaches, as shown in Figure 2. The electronic band structure of pristine BaTiO3 determined with TB–mBJ exchange potentials exhibited the valence band maximum (VBM) simultaneously at R- and M-points and conduction band minimum (CBM) at Γ-point. Such arrangement of valence and conduction band edges makes it an indirect band gap semiconductor of magnitude 2.78 eV, which is more consistent with the experimental band

| Table 1. Lattice Parameters, a, c (Å), Volume, V (Å³), and Bond Length (Å) Results for Pure and Doped BaTiO3 |
|---------------------------------------------------------|
| BaTiO3 | a (Å) | c (Å) | V (Å³) | Ti–O (Å) | Ba–O (Å) | Y–O (Å) |
|---------|-------|-------|--------|----------|----------|--------|
| BaTiO3  | 3.999 | 4.208 | 67.30  | 2.072    | 2.914    |        |
|         | 4.00023 | 4.02423 | 64.384923 |          |          |        |
|         | 4.02523 | 4.66225 | 65.398925 |          |          |        |
|         | 3.98424 | 4.06644 | 64.53724 |          |          |        |
| Ba0.875Y0.125TiO3 | 3.967 | 4.063 | 63.94 | 2.017 | 2.845 | 2.526 |
| BaTi0.875Y0.125O3 | 4.021 | 4.122 | 66.66 | 2.023 | 2.676 | 2.179 |

Figure 1. Optimized crystal structures of (a) pristine BaTiO3, (b) Ba0.875Y0.125TiO3, and (c) BaTi0.875Y0.125O3. Ba is shown in green, Ti in gray, O in red, and Y in cyan.
gap value (3.2 eV)\textsuperscript{26} and theoretical works.\textsuperscript{24,25,27} The substitution of Y in BaTiO\textsubscript{3} at the Ba and Ti sites has significantly restructured its electronic band structure. As shown in Figure 2, the VBM of Y doping at the Ba site has been driven to lower energies in the valence band, while the VBM of Y doping at the Ti site moves to the higher energy situation. In contrast to the band structure of pure BaTiO\textsubscript{3}, the VBM in the case of Y doping at both sites appeared at $\Gamma$-point. Similarly, the conduction band has been altered significantly and shifted to lower energies for the Ba site and higher energies for the Ti site. The CBM in Ba\textsubscript{0.875}Y\textsubscript{0.125}TiO\textsubscript{3} and BaTiO\textsubscript{3} appeared at $\Gamma$-point in the BZ. Moreover, Y-originated impurity bands have been over the Fermi level for Ba\textsubscript{0.875}Y\textsubscript{0.125}TiO\textsubscript{3}. A larger energy gap has been seen between the conduction band edges and the valence band edges. The energy separation between the VBM and CBM at $\Gamma$-point in BZ amounts to 2.91 and 2.85 eV for Ba\textsubscript{0.875}Y\textsubscript{0.125}TiO\textsubscript{3} and BaTi\textsubscript{0.875}Y\textsubscript{0.125}O\textsubscript{3} respectively. We further investigated the electronic band structures of these materials by applying the Hubbard $U$-parameter to the d-band of Y and Ti elements. This has shown important effects on the electronic band structures of these materials. As shown by green-colored bands in Figure 2, the electronic band structure obtained with GGA + $U$ has qualitatively similar dispersion to that determined only with TB–mBJ; however, the separation between valence and conduction band edges has been significantly reduced. For pristine BaTiO\textsubscript{3}, the GGA + $U$ approach leads to a band gap of 1.69 eV, which is much smaller than the band gap value obtained with TB–mBJ as well as the experimental value. We can conclude that TB–mBJ provides an efficient framework for band gap prediction. Similarly, the separation between the valence band and the conduction band in the band structure determined with GGA + $U$ has been recorded as 1.40 and 2.2 eV for Y doping at the Ba and Ti sites, respectively.

To obtain a deeper insight into the changes in the electronic structure, we analyzed the density of states of the pure and Y-doped perovskite, as shown in Figure 3. The total and partial DOSs showed that the upper region of the valence band is mainly due to Ti 3d states mixed with 2p states. The minimum of the conduction band is dominated by unoccupied Ti 3d transition-metal states. However, all occupied Ti 3d states are strongly hybridized with the nearby O 2p states. It can be observed that Ba does not contribute to VBM and CBM, although it does provide electrons to balance the system charge.\textsuperscript{25} Therefore, the band gap value of BaTiO\textsubscript{3} depends on the relative energy positions of Ti 3d and O 2p states. With regard to the Y doping at both sites, the main feature of the VBM and CBM is similar to that of the archetype BaTiO\textsubscript{3}, indicating no evident change of the distribution of the VBM and CBM except for the band gap. It can be seen for Y doping that the VBM is mainly occupied by the Ti 3d states and 2p states, as shown in Figure 3b,c. Then, the CBM principally abides of the Ti 3d states with the presence of Y 4d states. The appearance of impurity bands is believed to result in the charge spillage across the Fermi level, which is likely to cause metallization of the BaTiO\textsubscript{3} by substituting Y over Ba sites. The charge compensation in BaTiO\textsubscript{3} by doping Y has also been reported experimentally by Ren et al.\textsuperscript{21}

In order to get insight into the chemical bonding nature, the contour plots for the electron charge density of BaTiO\textsubscript{3}, Ba\textsubscript{0.875}Y\textsubscript{0.125}TiO\textsubscript{3} and BaTi\textsubscript{0.875}Y\textsubscript{0.125}O\textsubscript{3} are calculated and reported in Figure 4a–c. Analysis of Figure 4a–c indicates that the bonding between Ti and O atoms is characterized by a weak covalent character as a result of hybridization between the O 2p and the Ti 3d states, while the Ba–O bonding exhibits an ionic nature. In the case of Y doping at the Ba and Ti sites, the plot of Figure 4b reveals that a similar chemical bonding characteristic is observed between Y and O atoms. It can be shown that mixed covalent and ionic bonding is revealed for all materials.

Next, we present the optical spectra of pure and Y-doped BaTiO\textsubscript{3} determined with the TB–mBJ exchange potential in the following. Figure 5 represents the real and dielectric functions determined along the x- and z-axes. Because these materials have different lattice parameters along the x- and z-axes.

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c01638)  
Figure 2. Electronic band structures of (a) BaTiO\textsubscript{3}, (b) Ba\textsubscript{0.875}Y\textsubscript{0.125}TiO\textsubscript{3}, and (c) BaTi\textsubscript{0.875}Y\textsubscript{0.125}O\textsubscript{3} calculated with TB–mBJ and GGA + $U$.

![Figure 3](https://dx.doi.org/10.1021/acsomega.0c01638)  
Figure 3. Density of states of (a) pure BaTiO\textsubscript{3}, (b) Ba\textsubscript{0.875}Y\textsubscript{0.125}TiO\textsubscript{3}, and (c) BaTi\textsubscript{0.875}Y\textsubscript{0.125}O\textsubscript{3} using the TB–mBJ approach.
directions, the dielectric functions and the subsequent optical coefficient showed a considerable degree of anisotropy along the x- and z-directions. On the other hand, the optical spectra for these materials have been found isotropic because of similar lattice parameters along the x- and y-axes. Therefore, the optical spectra along the x- and z-directions have been shown in the present work.

The static dielectric constants ($\varepsilon_0$) obtained from the real part of the dielectric function of pure BaTiO$_3$ shown in Figure 5a have been found to be $\varepsilon_0 \approx 4.67$ and $\varepsilon_0 \approx 4.34$ along the x- and z-axes, respectively. Similarly, the static dielectric constants obtained for Ba$_{0.875}$Y$_{0.125}$TiO$_3$ and BaTi$_{0.875}$Y$_{0.125}$O$_3$ are found at the x-axis of $\varepsilon_0 \approx 14.01$ and 9.78 at the z-axis of 6.04 and 9.66 at the x-axis, respectively. In this context, the incorporation of Y into BaTiO$_3$ has been demonstrated to increase the static dielectric constants, which exhibited higher dielectric properties compared to that of pristine BaTiO$_3$. Note that $\varepsilon_0$ characterizes the electronic polarization features of an optical material. The large values $\varepsilon_0$ determined for BaTiO$_3$ and Y-doped BaTiO$_3$ demonstrate the large electronic polarizability features of these materials. Moreover, Ba$_{0.875}$Y$_{0.125}$TiO$_3$ shows higher dielectric constant than BaTi$_{0.875}$Y$_{0.125}$O$_3$. $\varepsilon_R$ achieves maximum values in the lower part of ultraviolet (UV) range of light at 4.22, 5.18 eV, and 4.75 for BaTiO$_3$, Ba$_{0.875}$Y$_{0.125}$TiO$_3$, and BaTi$_{0.875}$Y$_{0.125}$O$_3$, respectively. With further increase in the photon energies, dispersion of $\varepsilon_R$ goes through an abrupt decrease and achieve negative energies at 11.50 and 12.60 eV for BaTiO$_3$, Ba$_{0.875}$Y$_{0.125}$TiO$_3$, and BaTi$_{0.875}$Y$_{0.125}$O$_3$, respectively. The positive and negative values of $\varepsilon_R$ represent the dielectric and metallic behavior of these materials.

The imaginary part of dielectric function ($\varepsilon_i(\omega)$) for pure and Y-doped BaTiO$_3$ is displayed in Figure 5b,d.f. The peaks in the dispersion of $\varepsilon_i$ represent the optical transition taking place, inter- and intra-band optical transition. Hence, the optical transition taking place between the occupied states in the valence band to the unoccupied states in the conduction band is encountered by peaks in the dispersion of $\varepsilon_i$. The sharp peaks in the x- and z-components of $\varepsilon_i$ for BaTiO$_3$ shown in Figure 5c are therefore believed to be originated from the optical transition taking place from the occupied states in the VBM located simultaneously at the R- and M-points in the BZ to CBM appeared at the G-point. Several peaks of low intensity have also been seen in the dispersion of $\varepsilon_i$ determined for BaTiO$_3$ at high photon energies. They are expected to take place between the occupied states in the deep valence band to the empty states in the conduction band. Moreover, the x-component of $\varepsilon_i$ determined for Y doping at Ba and Ti sites exhibited a sharp peak at low photon energy of magnitude 0.21 and 0.15 eV, respectively. The observed peak is likely caused by the optical transition between the impurity band appeared in the vicinity of the Fermi level seen in Figure 5d.f.

Figure 6 summarizes the calculated absorption coefficients of pure and Y-doped BaTiO$_3$ along the x- and z-axes. As seen, these materials showed an exceptionally larger absorption of incident light. They showed moderate absorption in the lower part of UV range (below 15 eV). The absorption spectra of the investigated materials have experienced an abrupt increase with increase in photon energy beyond 15 eV. All materials showed
slightly different optical absorption along the x- and z-directions. The maximum optical absorption for BaTiO$_3$ along the x- and z-directions have been recorded as $3.63 \times 10^6$ cm$^{-1}$ at 19.63 eV and $3.48 \times 10^6$ cm$^{-1}$ at 19.81 eV, respectively. For $\text{Ba}_0.875\text{Y}_{0.125}\text{TiO}_3$, the optical absorption approached as large as $2.71 \times 10^6$ cm$^{-1}$ at 20.13 eV and $2.85 \times 10^6$ cm$^{-1}$ at 19.79 eV along the x- and z-axes. In the case of $\text{BaTi}_{0.875}\text{Y}_{0.125}\text{O}_3$, the optical absorption is found to be $3.39 \times 10^6$ cm$^{-1}$ at 19.73 eV and $3.375 \times 10^6$ cm$^{-1}$ at 19.9 eV along the x- and z-axes.

Figure 7 illustrates the reflectivity spectra against the photon of pure and Y-doped BaTiO$_3$. These materials have shown a moderate reflection in the visible and low UV ranges, and large reflection has been seen in the UV range beyond 20 eV. Figure 6 shows that doping of Y into BaTiO$_3$ has resulted in the reduction of its reflectivity features. These materials exhibited a slightly different reflectivity along the x- and z-directions. It has been found slightly larger along the x-direction for the photon energies below 10 eV; however, the reflectivity along the z-direction is found larger than the x-direction for the photon energies above 10 eV. For BaTiO$_3$, the maximum reflectivity along the x- and y-directions has been recorded as 0.56 at 24.00 eV and 0.57 at 24.97 eV, respectively. Similarly, the maximum reflectivity along the x- and z-axes for $\text{Ba}_0.875\text{Y}_{0.125}\text{TiO}_3$ is evaluated as 0.47 at 26.14 eV and 0.45 at 25.76 eV, respectively. For $\text{BaTi}_{0.875}\text{Y}_{0.125}\text{O}_3$, the maximum reflectivity along the x- and y-axes is found to be 0.49 at 22.55 eV and 0.5 at 22.53 eV along the x- and z-axes, respectively.

To investigate the optical transparency of the considered materials, we determined their refractive indices $n(\omega)$ as shown in Figure 8. As seen, the refractive spectra of these materials exhibited the refractive indices larger than unity in the infrared, visible, and in a larger part of UV range. The optical refraction reduced to less than unity for photon energies beyond 12 eV for investigated materials. Materials exhibiting refractive indices equal to or larger than unity are considered as transparent for the incident light. Therefore, it is reasonable to claim the pure and Y-doped BaTiO$_3$ as transparent for the incident light below 12 eV and as opaque beyond 12 eV. The maximum values of refractive indices are estimated to be 3.08 at 4.41 eV and 2.96 at 4.65 eV along the x- and z-axes, respectively, for BaTiO$_3$. Thus, we obtained that the maximum values for optical refraction are 3.84 at 0.01 eV and 2.99 at 5.44 eV in the case of $\text{Ba}_0.875\text{Y}_{0.125}\text{TiO}_3$ and 2.98 at 0.01 eV and 2.98 at 4.04 eV in the case of $\text{BaTi}_{0.875}\text{Y}_{0.125}\text{O}_3$ along the x- and z-axes, respectively.

![Figure 7](image1.png)

Figure 7. Reflectivity spectra of (a) pure BaTiO$_3$, (b) $\text{Ba}_0.875\text{Y}_{0.125}\text{TiO}_3$, and (c) $\text{BaTi}_{0.875}\text{Y}_{0.125}\text{O}_3$.

![Figure 8](image2.png)

Figure 8. Refraction spectra of (a) pure BaTiO$_3$, (b) $\text{Ba}_0.875\text{Y}_{0.125}\text{TiO}_3$, and (c) $\text{BaTi}_{0.875}\text{Y}_{0.125}\text{O}_3$.

Calculation of Born effective charge ($Z^*$) tensors has been considered as useful for the quantification of the charges associated with atoms/ions. For the present BaTiO$_3$ and doped structure with yttrium, the $Z^*$ values, calculated with density functional theory by respecting charge neutrality sum rule, are gathered in Table 2. For the pure BaTiO$_3$, by considering the ferroelectric direction set as z-axis, only the diagonal charge tensors are nonzero. In Table 2, we listed, however, the trace of the diagonal charges. Furthermore, oxygen sites show two different substitution sites: Ba and Ti. To investigate the optical transparency of the considered materials, we determined their refractive indices $n(\omega)$ as shown in Figure 8. As seen, the refractive spectra of these materials exhibited the refractive indices larger than unity in the infrared, visible, and in a larger part of UV range. The optical refraction reduced to less than unity for photon energies beyond 12.5 eV for investigated materials. Materials exhibiting refractive indices equal to or larger than unity are considered as transparent for the incident light. Therefore, it is reasonable to claim the pure and Y-doped BaTiO$_3$ as transparent for the incident light below 12 eV and as opaque beyond 12 eV. The maximum values of refractive indices are estimated to be 3.08 at 4.41 eV and 2.96 at 4.65 eV along the x- and z-axes, respectively, for BaTiO$_3$. Thus, we obtained that the maximum values for optical refraction are 3.84 at 0.01 eV and 2.99 at 5.44 eV in the case of $\text{Ba}_0.875\text{Y}_{0.125}\text{TiO}_3$ and 2.98 at 0.01 eV and 2.98 at 4.04 eV in the case of $\text{BaTi}_{0.875}\text{Y}_{0.125}\text{O}_3$ along the x- and z-axes, respectively.

![Table 2](image3.png)

Table 2. Calculated Born Effective Charge Tensors (in e) (Trace) and Piezoelectric Constants (in C/m$^2$) of Pure and Doped BaTiO$_3$

| ion/compound | BaTiO$_3$ | $\text{Ba}_0.875\text{Y}_{0.125}\text{TiO}_3$ | $\text{BaTi}_{0.875}\text{Y}_{0.125}\text{O}_3$ |
|--------------|-----------|---------------------------------|---------------------------------|
| Ba           | 2.76      | 1.35 (−51%)                     | 2.56 (−9%)                      |
| Ti           | 6.28      | 4.40 (−29%)                     | 4.70 (−25%)                     |
| O1           | −2.63     | −2.367 (+10%)                   | −2.0 (−23%)                     |
| O2           | −3.20     | −3.25 (+1.5%)                   | −4.5 (+40%)                     |
| O3           | −3.20     | −3.4 (+2%)                      | −4.48 (+40%)                    |
| Y            | 3.18      | 3.70                            |                                 |
| $c_{33}$ (C/m$^2$) | 4.75       | 4.78$^{30,31}$                  |                                 |
When we analyze carefully the values of effective charges in both new doped structures, we might observe that substitution introduces anisotropy in Ba, Ti, and O charge tensors, while tensors for Y and Ba remain diagonal. Also, O atoms show an increase in dynamical charge by +1.0, +1.5, and 2% for the oxygen atoms along the polarization direction. In parallel to this, there is a pronounced decrease of the charge in the case of Ba atoms (51%) and Ti (29%) along the direction of polarization. In the case of Y doping at the Ti site, the trend in the effective charges is almost the same, but with the strong increase of O2 and O3 charges, less loss in effective charge in Ba compared to the former structure. Titanium has lost 25% of its effective charge, while Y increases by 14% compared to its charge when it replaces a Ba atom. The results indicate that the doped BaTiO3 with Y increases the anisotropy of Ti environments and at the same time a slight decrease in Ti–O and Ba–O bond lengths (see Table 1), which leads to the appearance of anisotropy but more stabilized structure. The same behavior was observed in the recent work on Zr/Ca doping BaTiO3, where Born effective charges calculated have shown that doping BaTiO3 with Ca or Zr increases the dynamical charges on Ti as well as on O and decreases the dynamical charge on Ba. Furthermore, it is well known that oxide perovskites produce anomalous Born effective charges values because of the Coulomb interactions and its destabilization that produces ferroelectricity. The pure BaTiO3 well reproduces this anomaly when doped with Y.

Ferroelectric oxides have the ability to not only exhibit a switchable polarization but distinct interesting functional properties for technological applications: the large dielectric and piezoelectric constants which are directly related to their properties for technological applications: the large dielectric constant and related optical coefficients shed more light about the changes in the behavior of the considered compounds. Our findings show that the dielectric constants for different axes have been increased because of the introduction of the Y dopant. We extended our interest to calculate the Born effective charges and piezoelectric properties by using polarization theory, finite difference approach, and Berry-phase approach. Compared to the original pure BaTiO3, Y doping has destroyed the piezoelectricity because they changed to metallic systems for both considered cases.

4. COMPUTATIONAL METHODOLOGY

Our computational calculations were done with the WIEN2K code,37 which is based on the linearized augmented plane wave method.38,39 Exchange and correlation were treated within the GGA in the form of Perdew–Burke–Ernzerhof to express the exchange–correlation energy.35 The TB–mBJ40 method was used for the treatment of exchange–correlation effects. GGA + U methods were applied as well to describe the d states of Ti and the Y dopant. Here, U (equal to what is often called U_{eff} = U − J = 7 (Ti) and 4 (Y) eV) is used as the on-site interaction term, as proposed in refs 37–41. Moreover, the all-electron calculations were performed by combining the TB–mBJ approach with the Hubbard U correction to investigate their suitability in describing electronic structures. The cutoff R_{cut} × K_{max} was set to 7.0 as for basis set. The Monkhorst–Pack special k-point approach35 has been endorsed for the integration of the Brillouin zone (BZ). The integrals over the special points in BZ were performed with 8 × 8 × 2 k-point grid to warranty an acceptable energy convergence. The total energy was converged up to 10−5 Ryd/atom cell in the present self-consistent calculations for well-defined results.

For Y-doped BaTiO3, we carried out ab initio calculations by adopting a 2 × 2 × 2 supercell that contains eight BaTiO3 formula cells. The dopant concentration of 12.5% has been modeled by substituting one Ba (or Ti) atom with one rare-earth Y atom in the 40 atom BaTiO3 supercell. Correspondingly, the concentrations are Ba_{1-x}Y_{x}TiO3 for A site doping and Ba_{y}Ti_{1-y-y}_{O3} for B site doping.

The vibrational properties, mainly Born effective charges and dielectric tensors, were calculated using the DFPT,41 while the piezoelectric constants were calculated using the metric tensor formulation of strain as described in ref 44. For the polar BaTiO3, the piezoelectric responses can be nonzero. We calculated the piezoelectric coefficients as the derivative of the polarization with respect to strain at zero electric field. In fact, for any solid, the total macroscopic polarization P is the sum of the spontaneous polarization P_{sp} (strain independent) of the equilibrium structure in the absence of external fields, which induces piezoelectricity by strain. The total polarization is then P = P_{sp} + P_{p}. The piezoelectric tensor can be expressed as γ_{sp} = \frac{ΔP}{Δε}. For the present perovskite, the γ_{sp} parameters were calculated using the finite difference approach, whereas the polarization was extracted from the Berry-phase approach as implemented in Quantumwise (ATK).29

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Notes
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