

Influence of complex antisite defects in structural distortion, electrical and optical properties of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3(110)$ surface: A DFT investigation

Vu Tien Lam^{1,2}, Nguyen Huu Lam^{1,3}, Nguyen Hoang Linh¹,
Duong Quoc Van^{4,‡} and Dang Duc Dung^{1,†}

¹Multifunctional Ferroics Materials Lab., Faculty of Engineering Physics,
Hanoi University of Science and Technology, 1 Dai Co Viet Road, Hanoi, Vietnam

²Department of Energy Science, Sungkyunkwan University, Suwon 16419, Republic of Korea

³Department of Physics, University of Ulsan, Ulsan, 44610, Republic of Korea

⁴Faculty of Physics, Hanoi National University of Education, 136 Xuan Thuy Street, Hanoi,
Vietnam

E-mail: [†]dung.dangduc@hust.edu.vn and [‡]q.van@hnue.edu.vn

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Abstract. Bismuth sodium titanate (BNT) is a crucial lead-free multiferroic material whose functional properties are highly sensitive to surface structure and native defects. This study employs first-principles calculations based on Density Functional Theory (DFT) to systematically investigate the structural, electronic, and optical properties of the BNT(110) surface containing complex antisite defects. We first confirm that the pristine BNT(110) surface undergoes significant atomic relaxation and polarization changes compared to the bulk. Subsequent introduction of antisite defects dramatically modifies the local lattice parameters, leading to significant strain and altered coordination polyhedral. As the results, the antisite defects introduce localized deep-level states within the band gap, resulting in a substantial reduction of the band gap energy. Analysis of the projected density of states (PDOS) reveals that these states are predominantly derived from hybridized Ti-3d and O-2p orbitals from atoms adjacent to the defect site. Furthermore, the calculated optical absorption spectra indicate a strong sub-gap absorption in the visible region due to the defect-induced states, suggesting potential for enhanced light absorption. This study provides critical insights into the intrinsic effects of complex antisite defects on the functional surfaces of BNT, which is essential for optimizing defect engineering strategies in BNT-based electronic and photocatalytic devices.

Keywords: $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$; surface; band structure; magnetic properties; optical properties.

Classification numbers: 31.15.E-; 73.20.-r; 61.72.-y; 77.84.-s; 75.50.Dd.

1. Introduction

The growing global emphasis on sustainable and environmentally responsible materials has continually driven research toward developing lead-free ferroelectrics as viable, high-performance replacements for traditional lead-based systems [1–3]. The urgency of the traditional toxic systems is underpinned by the severe health risks associated with lead element, which has been a concern even throughout human history, recently posited to have played a strange role in evolutionary competition due to differential human tolerance [3]. Among lead-free candidates, bismuth sodium titanate (with formula $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, BNT), a complex perovskite oxide, has long been recognized as a promising candidate. Over the past decade, BNT has drawn significant attention to its outstanding ferroelectric and piezoelectric properties, which closely rival those of the widely utilized lead zirconate titanate (PZT) [2]. With its non-toxic composition, strong remnant polarization ($\sim 38 \mu\text{C}/\text{cm}^2$), and high Curie temperature ($\sim 320^\circ\text{C}$) [1,3], BNT offers excellent stability and dependable performance across a broad thermal range. Nonetheless, its relatively high coercive field (around $73 \text{ kV}/\text{cm}$) continues to present a technical challenge, as it demands substantial energy for polarization reversal and may consequently limit the operational lifetime of devices [1,3].

Beyond traditional ferroelectric functionalities, BNT has also become increasingly relevant to the expanding field of multiferroics, which exhibit both ferroelectric and magnetic ordering. These systems are viewed as the foundation for next-generation multifunctional devices, offering the prospect of controlling magnetism via electric fields and vice versa [4]. However, realizing intrinsic multiferroism remains a formidable challenge, as the electronic requirements for ferroelectricity (typically empty d -orbitals) conflict with those necessary for ferromagnetism (partially filled d -orbitals). As a result, genuine single-phase multiferroics are exceptionally rare.

Since intrinsic multiferroism is chemically contraindicated in conventional ferroelectrics due to the exclusive d^0 electronic requirement, defect engineering has emerged as a vital strategy to induce magnetism in otherwise non-magnetic oxides. Recent studies have indicated that defect engineering provides an alternative pathway for inducing magnetism and even modulating optical responses in BNT [4–6]. Both theoretical and experimental investigations have established that room-temperature ferromagnetism in BNT can arise from intrinsic lattice defects, including cation and oxygen vacancies as well as non-stoichiometric configurations [7–9]. These findings have inspired broader efforts to understand how intentional manipulation of such defects might tailor the multifunctional behavior of this material.

Our previous work examined defect-induced phenomena primarily in the bulk phase and on the BNT(100) surface of BNT [7–9], which is often predicted to be energetically favorable in surface energy calculations. Yet, this theoretical preference does not always align with experimental evidence. In practice, the BNT(110) surface orientation has been frequently observed in epitaxially grown thin films and naturally faced single crystals [1, 10–12]. This makes the (110) surface particularly relevant for realistic device modeling and performance optimization. In our recent *ab initio* analyses [8,9], we found preliminary evidence suggesting that complex surface defects in this orientation can generate localized magnetic moments. Among various kinds of defects, antisite defects in which cations exchange lattice positions play a profound role in modifying local symmetry and electronic structure. In complex perovskites like BNT, the similar ionic radii of the A-site cations (Bi^{3+} , Na^+) facilitate the formation of such defects during high-temperature synthesis. Sundheep. R *et al.* [13] found that antisite defects are not stable at perovskite-perovskite

interfaces and relax to form cation interstitial and halide vacancy defects. However, recent experimental reports that antisite defects are prevalent at surfaces of FAPbI₃ compound and other lead perovskites [14, 15]. Prior our theoretical studies have indicated that cation vacancies can induce magnetic moments in BNT [7–9]. However, the impact of complex antisite pairs is less understood, particularly regarding how the charge imbalance introduced by aliovalent substitution drives orbital polarization and band-gap renormalization.

Therefore, the present study focuses on a detailed investigation of the structural, electronic, and optical characteristics of the BNT(110) surface, with particular emphasis on the effects of complex antisite defects. To this end, we also employ Density Functional Theory (DFT) calculations incorporating the Hubbard U correction (DFT+ U) [16], a technique that addresses well-known DFT limitations such as underestimated band gaps and insufficient treatment of localized electronic states. We aim to clarify how antisite defects reshape atomic geometry, modify the electronic band structure, and alter optical absorption characteristics on the BNT (110) surface. These insights are expected to contribute to the rational design and targeted optimization of next-generation lead-free multiferroic and photocatalytic systems.

2. Computational details

All first-principles simulations were carried out DFT as implemented in the CASTEP package [17]. The electron exchange–correlation interactions were treated within the Generalized Gradient Approximation, employing the Perdew–Burke–Ernzerhof functional [18]. A plane-wave basis set with ultrasoft pseudopotentials was adopted, and a kinetic energy cutoff of 500 eV was used throughout. Structural optimizations were considered converged when the total energy change between successive iterations fell below 1×10^{-6} eV/atom and the maximum Hellmann-Feynman force on any atom was smaller than 0.01 eV/Å. The Brillouin zone was sampled using a $1 \times 4 \times 2$ Monkhorst-Pack k -point grid [19]. To achieve a more reliable representation of the localized Ti-3d electronic states, we incorporated an on-site DFT+ U methods using U values of 10 eV to assess the sensitivity of the results to this parameter. The BNT(110) surface was modeled using a periodic slab constructed from the geometry-optimized primitive cell of rhombohedral BNT (space group $R3c$). The initial atomic positions were relaxed within the experimentally reported lattice parameters ($a = b = 5.488$ Å, $c = 13.504$ Å), which are in excellent agreement with previous measurements [20]. Subsequently, a $3 \times 2 \times 1$ supercell was cleaved along the (110) plane, and an initial 10 Å vacuum layer was introduced along the surface normally to eliminate spurious interactions between periodic surfaces [8]. Extending the vacuum beyond this limit was deemed computationally inefficient, as it increases the simulation cell volume and memory requirements without yielding a statistically significant change in the total energy or electronic structure. The optical properties of the relaxed configurations were evaluated using the optical property analysis module within CASTEP.

3. Results and discussion

Figure 1 illustrates the atomic configuration of the optimized BNT(110) perfect surface employed in this study. In Fig. 1(a), the three-dimensional view clearly shows the layered nature of the BNT(110) surface, which includes 6 Na atoms, 6 Bi atoms, 12 Ti atoms and 36 O atoms. The side view in Fig. 1(b) emphasizes the tilting and distortion of TiO₆ octahedra near the surface

region, which slightly differs from the bulk configuration due to atomic relaxation effects [21]. Fig. 1(c) provides the top view of the slab, revealing a periodic TiO_6 octahedra surrounded by Bi and Na cations. A vacuum layer of 10 Å separates adjacent periodic images along the surface, effectively preventing inter-slab interactions.

Figure 2 shows the defect structures and Table 1 summarizes the lattice parameters for the pristine BNT(110) surface and all six complex antisite defect cases after completing structural optimization. The initial dimensions of the pristine surface cell $a = 23.8495$ Å; $b = 11.6537$ Å, and $c = 7.2537$ Å provide a baseline for the structural response to defect incorporation. The introduction of antisite defects causes significant and non-uniform lattice distortions. In general, substitutions on the A-site (B(Na)NT, B(Ti)NT, BN(Bi)T, BN(Ti)T) primarily lead to lattice contraction along all three axes, particularly noticeable in a coordination. For instance, the B(Na)NT defect reduces to 17.5716 Å, indicating a substantial rearrangement of the surface layer atoms to accommodate the localized strain introduced by the defect. In contrast, substitutions on the B-site, BNT(Bi) and BNT(Na), show a more varied response. While a parameter also contracts, the c parameter (which is related to the slab thickness) exhibits a marked expansion. This suggests that the B-site antisite induces a greater perturbation in the octahedral tilting and distortion, leading to significant strain relief along the surface.

It is observed that the defects notably affect the a and c lattice constants, while the b constants remain nearly unchanged. The reason is the b -axis direction aligns with the continuous chains of TiO_6 octahedra [22]. The Ti-O bonds within these octahedra possess strong covalent character and high mechanical stiffness. Consequently, this rigid octahedral “backbone” resists compression or expansion, maintaining the b lattice parameter

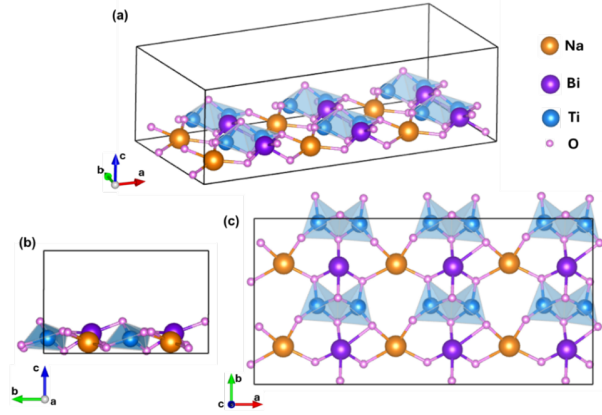


Fig. 1. (Color online) Optimized crystal structure of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3(110)$ surface: (a) 3D-view; (b) side-view; (c) top-view.

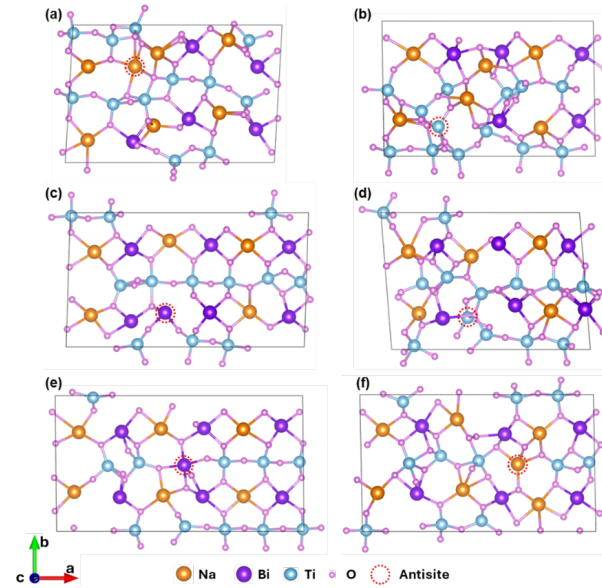


Fig. 2. (Color online) Optimized structure of BNT(110) with various antisite defects: (a) B(Na)NT; (b) B(Ti)NT; (c) BN(Bi)T; (d) BN(Ti)T; (e) BNT(Bi); (f) BNT(Na).

relatively constant despite the introduction of defects. In contrast, the a -axis direction is dominated by the A-site sub-lattice (Bi/Na cations) and the inter-octahedral spacing. The bonding in this direction is more ionic and structurally compliant. When antisite defects introduce local strain or volume changes, the lattice preferentially relaxes along a -axis, leading to the significant contraction observed in Table 1. These structural changes are critical as they directly influence the electronic band structure, magnetic properties, and ultimately, the optical characteristics of the surface with defects.

Table 1. Optimized lattice parameters and total energy of BNT(110) surface with various antisite defects.

System	a (Å)	b (Å)	c (Å)	Total energy (eV)	Formation energy (eV)
Pristine	23.8495	11.6537	7.2537	-43618.18	–
B(Na)NT	17.5716	11.5425	5.9598	-44908.49	-137.083
B(Ti)NT	18.3851	11.0572	5.8477	-45214.09	-144.029
BN(Bi)T	20.1488	11.3207	9.7357	-42598.57	-133.617
BN(Ti)T	18.2436	11.3332	5.6874	-44057.99	-141.156
BNT(Bi)	21.2829	11.6625	10.1726	-42282.43	-116.131
BNT(Na)	19.7455	11.5624	9.6660	-43440.49	-120.964

The total energy in Table 1 refers to final optimized energy which confirms the thermodynamic preference among the defects. The pristine surface has a total energy of -43618.1 eV. The energies of the BNT(110) with antisite defects, while generally lower than the pristine surface due to the definition of the supercell, clearly show variations in stability. The B(Na)NT defect (-44908.49 eV) and the B(Ti)NT defect (-45214.09 eV) are the most stable cases. The highly favorable energy of B(Ti)NT suggests that the substitution of Ti into the Bi-site is energetically preferred at this surface orientation. In contrast, B -site substitutions, particularly BNT(Bi) (-42282.43eV), exhibit the highest total energy and are thus predicted to be the least likely to form spontaneously or be present in high concentrations, correlating with the large structural expansions observed in the c -axis lattice parameter. To deeper evaluate the relative stability of the various antisite defects, we calculated the defect formation energy. Unlike total energy, which depends on the specific stoichiometry of the supercell, the formation energy accounts for the chemical potential of the species exchanged during defect formation. The formation energy is defined by the following expression [23]:

$$E_f = E_{\text{defect}} - E_{\text{pristine}} + \mu_- - \mu_+$$

where E_f is formation energy, E_{defect} is total energy of defect structure, E_{pristine} is total energy of pristine structure, μ_- and μ_+ represent the chemical potentials of the host atom being removed (e.g., Bi, Na, or Ti) and the dopant atom being substituted, respectively.

The formation-energy analysis confirms that antisite defects on the A-site (Bi/Na) are more stable than those on the B-site (Ti), which directly influences the defect populations and their corresponding electronic and optical effects. Among all defect configurations, B(Ti)NT exhibits the lowest formation energy (-144.029 eV), indicating that substituting Ti on the Bi site is the most energetically favorable defect under our calculation conditions. This agrees with the significant

structural relaxation and strong Ti–O hybridization observed in the electronic analysis. The next most favorable defect is B(Na)NT (-137.083 eV), suggesting that Na substituting Bi is also likely to form. In contrast, defects involving substitution at the Ti site, such as BNT(Bi) and BNT(Na), show the highest formation energies (-116.131 eV and -120.964 eV), implying that these configurations are least favorable and should appear with lower concentration. The formation-energy trend is consistent with the total-energy results and reflects the substantial local distortions induced when non-Ti ions occupy the Ti-centered octahedral environment.

The calculated electronic properties of the pristine BNT(110) surface are presented in Fig. 3, which displays the band structure along high-symmetry directions of the Brillouin zone in Fig. 2(a), and the corresponding total and partial density of states (TDOS and PDOS) in Fig. 3(b). The band structure establishes the semiconducting nature for pristine surface. The calculated band gaps are determined to be 3.46V for both direct and indirect behaviors, consistent with the expected wide-band-gap behavior of perovskite titanates. The valence band maximum (VBM) is located at the gamma and Z point, while the conduction band minimum (CBM) is located at Z point. The large number of flat bands observed below the Fermi level (set to at the VBM) indicates the highly localized nature of these valence states [24]. The PDOS clarifies the orbital character that defines the VBM and CBM. The entire valence band is overwhelmingly dominated by the O- $2p$ orbitals, with minor contributions from the Bi- $6p$ and Ti- $3d$ orbitals. Conversely, the CBM is dominated by the unoccupied Ti- $3d$, O- $2p$, and Bi- $6p$ orbitals, which are the primary electron acceptors. This strong separation between O- $2p$ and Ti- $3d$ states confirms the charge transfer mechanism characteristic of TiO_2 -based materials [25].

Figure 4 presents the spin-polarized density of states (SDOS) for the pristine BNT(110) surface, illustrating the electronic contributions of each atom. The total SDOS profile reveals that the Fermi level

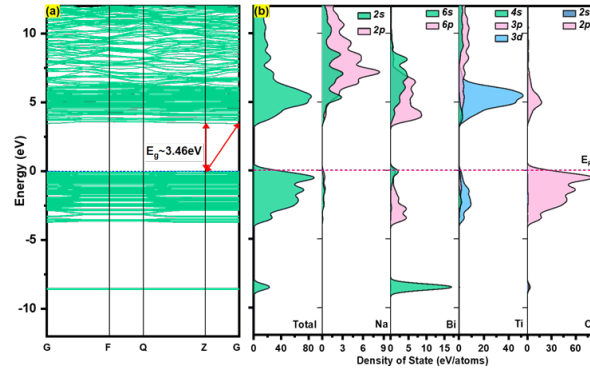


Fig. 3. (Color online) (a) Electronic band structure and (b) density of states of pristine BNT(110).

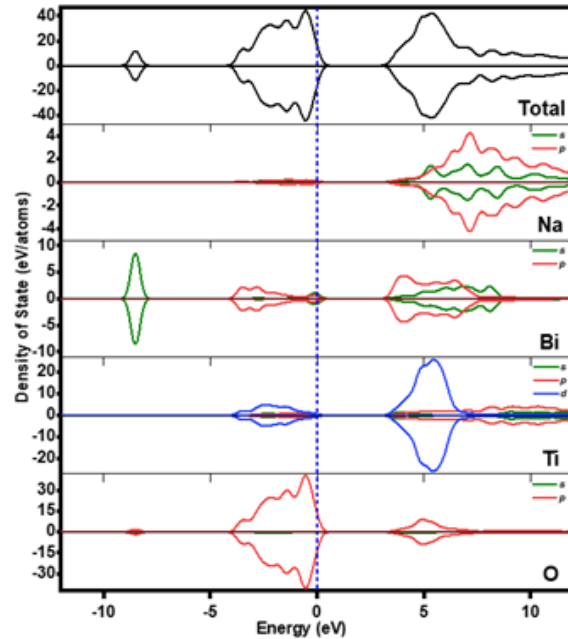


Fig. 4. (Color online) Spin density of states of pristine BNT(110).

lies within a clear energy gap, confirming the semiconducting nature of the pristine surface. The symmetry between the spin-up and spin-down components confirms the non-magnetic ground state of the pristine surface. The absence of spin polarization indicates that all atomic species including Na, Bi, Ti, and O contribute equally to both spin orientations, as expected for a stoichiometric and defect-free surface. Similarly, the partial SDOS profiles for each atom display identical shapes for both spin components, especially evident in the Ti-3*d* and O-2*p* states, which dominate the valence and conduction bands. This balanced behavior further verifies that the pristine BNT(110) retains its non-magnetic and electronically stable after relaxation.

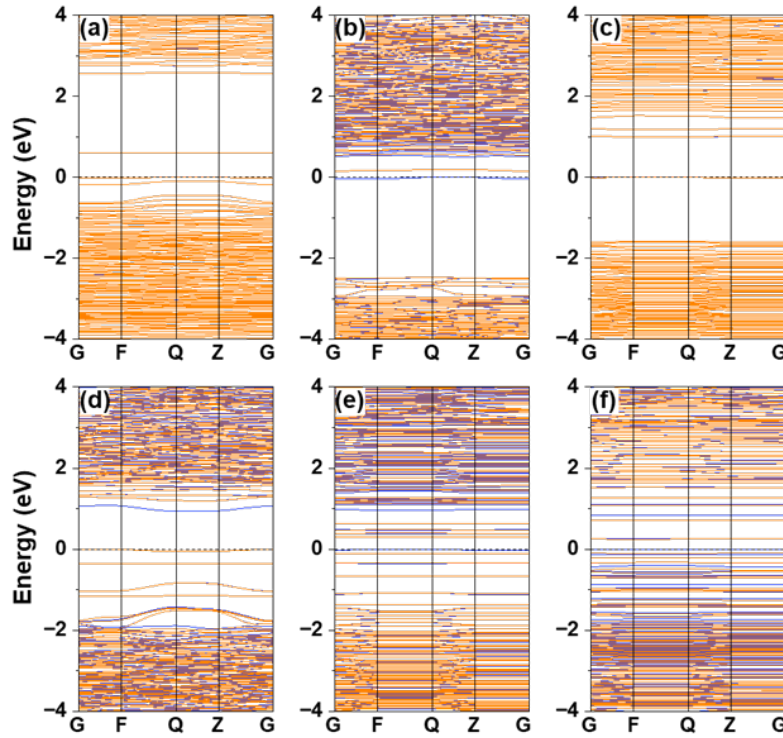


Fig. 5. (Color online) Electronic band structure of BNT(110) with various antisite defects: (a) B(Na)NT; (b) B(Ti)NT; (c) BN(Bi)T; (d) BN(Ti)T; (e) BNT(Bi); (f) BNT(Na).

Figures 5(a)-(f) present the calculated band structures of the BNT(110) surface containing various antisite defects. These band structures illustrate how complex antisite defects profoundly influence the electronic properties of the BNT(110) surface. In the pristine BNT(110), the bands are well ordered and symmetric with a distinct band gap (see Fig. 4(a)). However, the introduction of antisite defects disrupts this periodic potential, leading to notable modifications in the band topology. When substituted Na into Bi site (B(Na)NT in Fig. 5a), the band structure exhibits relatively mild perturbations, retaining semi-symmetric and well-separated valence and conduction bands, retaining the semiconducting nature. In contrast, when we introduced Ti into Bi site, which is called B(Ti)NT (Fig. 5b), the result showed that BNT(110) transferred from *p*-type to *n*-type semiconductor as the Fermi-level shifted up to CBM. Interestingly, in the case of BN(Bi)T

(Fig. 5c) antisite, where a Na atom is replaced by a Bi atom, the mid-state occurred at Fermi-level between VBM and CBM, implying the retaining of intrinsic semiconductor behavior of BNT(110). The band structures for B(Na)NT and BN(Bi)T defects are consistent with our previous study [8]. For BN(Ti)T (Fig. 5d) antisite, the Ti-antisite atom in Na-site leads to the appearance of more additional mid-gap states and broken band symmetry, implying partial metallicity or defect-assisted conductivity. These localized states around the Fermi level are attributed to the unbalanced charge environment created by the substitution of heavier and/or more electropositive atoms (Ti), which modifies the local potential landscape. Lastly, in the case of Bi and Na is substituted into Ti-site (BNT(Bi) in Fig. 5(e) and BNT(Na) in Fig. 5(f)), the band structures exhibited metallic behaviors, with the energy distance between VBM and CBM are quite small, implying that the antisite defects break the electronic symmetry and significantly modulate the band gap and dispersion characteristics of BNT(110), potentially offering tunable electronic and optoelectronic functionalities for lead-free ferroelectric devices.

Figures. 6(a)-(f) present the SDOS for the six distinct complex antisite defects introduced in BNT(110) surface, correlating directly with the band structures presented in Fig. 5. The comparison between the spin-up (positive) and spin-down (negative) components relative to the Fermi level is crucial for determining the magnetic ground state and the nature of the induced electronic properties. Fig. 6(a) is Na substituting Bi (B(Na)NT), which maintains an overall semiconducting-like behavior, similar to the corresponding band structure in Fig. 5(a). A small, localized peak appears near the Fermi level still resulting in a very zero magnetic moment. The system remains largely non-metallic, suggesting minimal charge transfer to the site. The introduction of Ti into the Bi site (Fig. 6(b)) shifts the system to an *n*-type semiconductor, as indicated by the Fermi level moving towards the conduction band edge (correlating with Fig. 5(b)). Crucially, this defect induces clear spin asymmetry. While the spin-down component remains gapped, the spin-up component features occupied states that cross the Fermi level, classifying this system as a half-metal. This half-metallicity is associated with a significant net magnetic moment approximal $0.11 \mu_B/\text{f.u}$ (Table 2), primarily originating from the polarized orbitals. Fig. 6(c) is SDOS for BN(Bi)T (Bi substituting Na) which strongly confirms the symmetric shape of spin-up and spin-down components, the contribution of SDOS located at Fermi level refers to the mid-gap states in the band structure (Fig. 5(c)). The Ti substitution at the Na site is called BN(Ti)T (Fig. 3(d)), resulting net magnetic characteristic. The significant asymmetrical at the Fermi level indicates a robust magnetic moment estimated $0.03 \mu_B/\text{f.u}$ (Table 2). Similarly, Fig. 6(e) is SDOS for BNT(Bi), there are occupies in the band gap, dramatically alters the electronic structure, leading to clear metallic behavior in both spin components. The SDOS confirms this strong metallic character, with substantial density of states crossing the Fermi level for both spin-up and spin-down component, though a slight asymmetry remains, indicating non-zero magnetic moment with the magnetization is $0.13 \mu_B/\text{f.u}$ (Table 2). Fig. 6(f) also claimed that BNT(Na) is a strongly metallic behaviour. The SDOS profile shows significant overlaps and occupation of states across the Fermi level in both spin directions, the magnetic moment is highest $0.17 \mu_B/\text{f.u}$ (Table 2). While the system exhibits the lowest degree of spin polarization among the magnetic defects, the dominant metallic character suggests high conductivity.

These defect-induced electronic states, particularly the Ti-3*d*–O-2*p* hybrid mid-gap states, play a decisive role in shaping the optical response discussed in the following section.

Table 2. Calculated magnetization of BNT(110) surface with various antisite defects.

System	$M_{\text{Na}} (\mu_B/\text{f.u.})$	$M_{\text{Bi}} (\mu_B/\text{f.u.})$	$M_{\text{Ti}} (\mu_B/\text{f.u.})$	$M_{\text{O}} (\mu_B/\text{f.u.})$	$M_{\text{Total}} (\mu_B/\text{f.u.})$
Pristine	0	0	0	0	0
B(Na)NT	0	0	0	0	0
B(Ti)NT	0	0	0.08	0.03	0.11
BN(Bi)T	0	0	0	0	0
BN(Ti)T	0	0	0.02	0.01	0.03
BNT(Bi)	0	0	0.10	0.03	0.13
BNT(Na)	0	0	0.06	0.11	0.17

To confirm the electronic response with complex antisite defects, we examined the real-space visualization of the spin polarization as shown in Figs. 7(a)-(f). The cyan and magenta iso-surfaces represent the positive and negative spin density (net spin-up and spin-down polarization, respectively). Fig. 6(a) shows no spin density localization, resulting consistent with the SDOS (Fig. 6(a)) in B(Na)NT antisite defect. In contrast, a clear localized spin density is observed in the case of B(Ti)NT (Fig. 7(b)). Polarization is primarily centered around the substituted atom Ti and its nearest-neighbor O atoms. Similar to B(Na)NT antisite, BN(Bi)T and BN(Ti)T antisite defects also lack of visual spin density suggests that while the electronic states are highly polarized, the resulting magnetic moment may be diffused across multiple atoms or is visually confined to regions not easily captured in the surface, or the moment is smaller than the visualization threshold used. As predicted by the metallic character observed in the band structure and DOS, the spin density distribution for this Ti-site substitution (Figs. 7(e)-(f)) shows strong localized moments correlate with the delocalized electronic properties of metallic behaviors. In Fig. 7(f), polarization is clearly concentrated on the nearest-neighbor O atoms surrounding the substituted atom (Na into Ti), with significant contributions also visible near the atoms. This strongly localized moment confirms the importance of the $2p$ -orbitals in mediating magnetism, aligning with the partially polarized DOS structure in Fig. 6(f). About the mechanism, the spin density localizes on the substituted cation and its nearest O atoms, and the spin-resolved DOS shows defect-derived Ti- $3d$ -O- $2p$ states near the Fermi level. In case of B(Ti)NT ($M \approx 0.11 \mu_B/\text{f.u.}$): The A-site Ti substitution perturbs the local potential and introduces n -type carriers that populate hybrid Ti- $3d$ -O- $2p$ defect states at the Fermi level. The resulting spin-split, partially occupied Ti- $3d$ states (hybridized with O- $2p$) produce a small net moment; accompanying charge transfer helps stabilize this polarization. Orbital polarization is present but subdominant. In case of BNT(Bi) ($M \approx 0.13 \mu_B/\text{f.u.}$): Distortion of the TiO_6 around the B-site creates Ti- $3d$ -O- $2p$ states near the Fermi level. Defect-induced carriers occupy these spin-split hybrid states, yielding a small moment. Ti-O hybridization is the leading cause, with modest Ti- $3d$ orbital polarization and local charge redistribution setting the degree of spin asymmetry. In case of BNT(Na) ($M \approx 0.17 \mu_B/\text{f.u.}$): The highly electropositive Na at the B-site drives stronger local charge redistribution and forms hybrid defect bands with significant O- $2p$ participation that cross the Fermi level. Spin-selective occupation of these Ti- $3d$ -O- $2p$ states produces the largest moment among the three; orbital polarization again contributes but does not dominate.

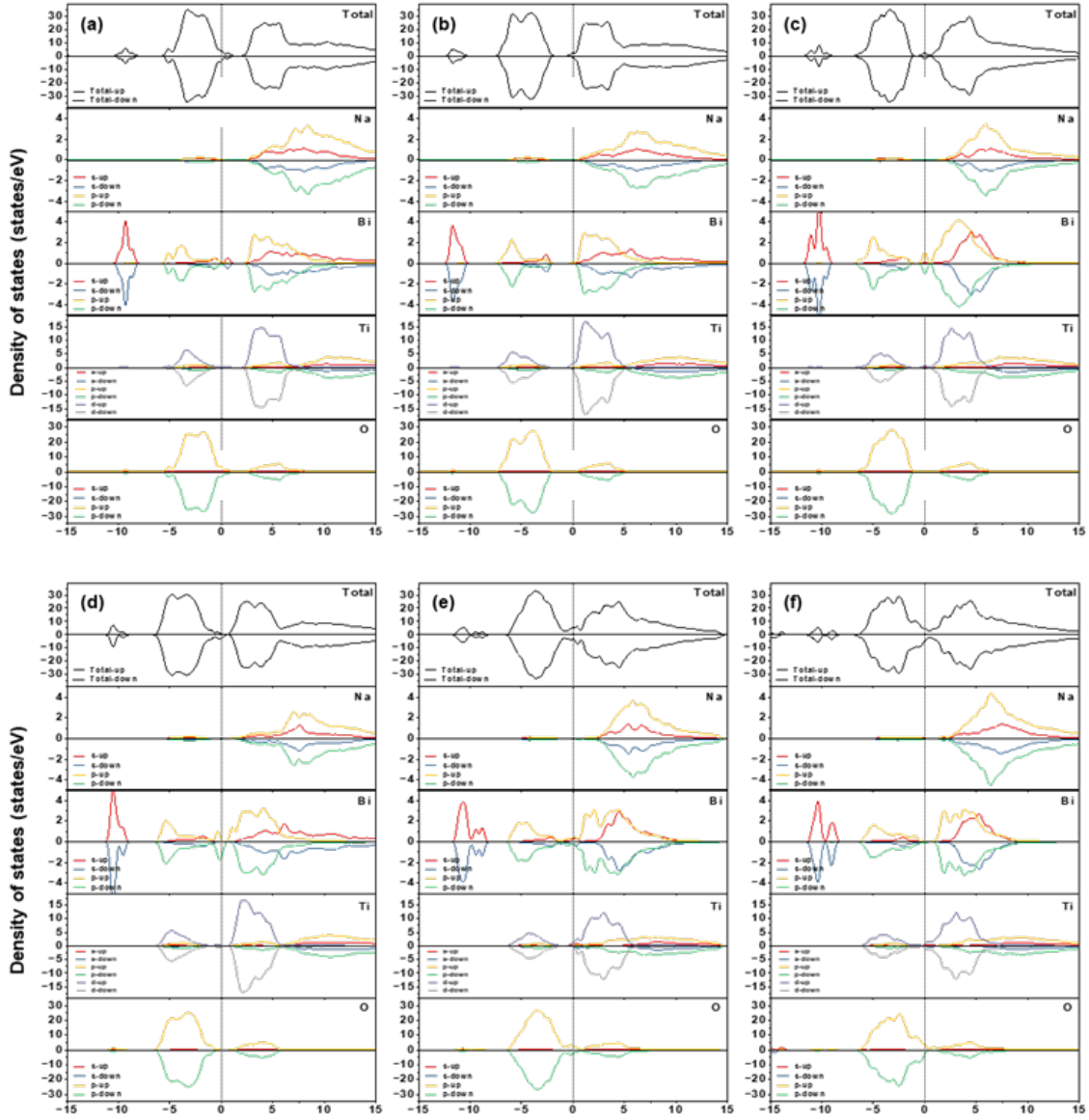


Fig. 6. (Color online) Spin density of states of BNT(110) with various antisite defects: (a) B(Na)NT; (b) B(Ti)NT; (c) BN(Bi)T; (d) BN(Ti)T; (e) BNT(Bi); (f) BNT(Na).

To better understand the origin of the optical response in pristine and defected BNT(110), we analyzed the calculated absorption spectra together with the electronic density of states. The influence of the various complex antisite defects on the optical behavior of BNT(110) surface is discussed and presented in Figs. 8(a)-(c). Fig. 8(a) shows the absorption coefficient as a function of photon energy, covering the ultraviolet to extreme ultraviolet range. The pristine BNT(110) (black line) exhibits a sharp absorption onset around 3.5 eV, and the primary absorption peaks are

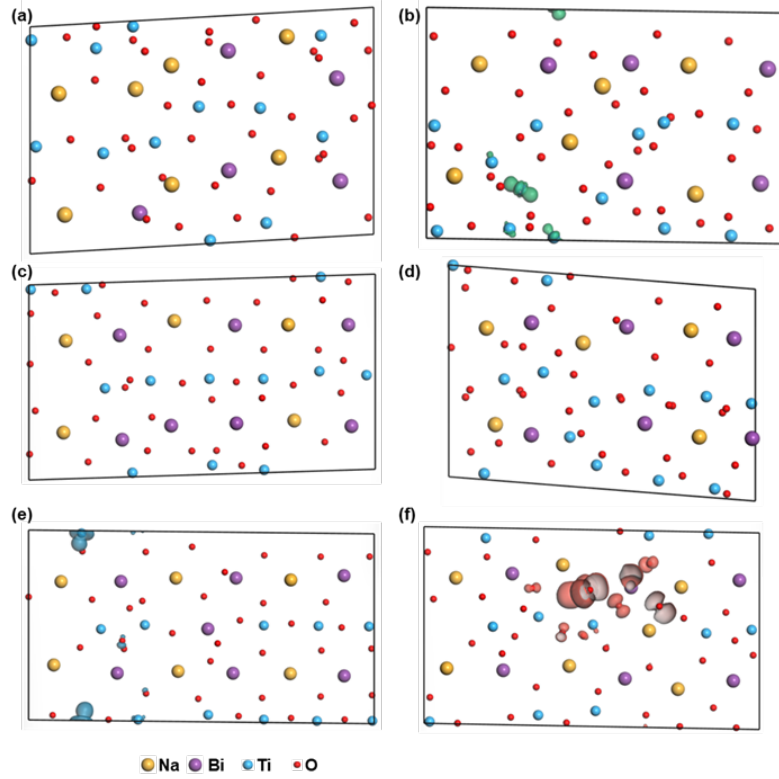


Fig. 7. (Color online) Charge density distribution of BNT(110) with various antisite defects: (a) B(Na)NT; (b) B(Ti)NT; (c) BN(Bi)T; (d) BN(Ti)T; (e) BNT(Bi); (f) BNT(Na).

observed in the high-energy region, specifically around 8.0 eV and 12-15 eV, which correspond to interband transitions from the deep valence states to the conduction band. These peaks arise from deeper valence states, primarily hybridized Bi-6s/6p and O-2p orbitals, transitioning to the Ti-3d-dominated conduction band, corresponding to strong interband transitions typical of perovskite titanates. The introduction of most antisite defects generally enhances the overall absorption intensity across the spectrum, and importantly, introduces new sub-gap absorption features. By using Wood-Tauc equation

$$(\alpha h\nu)^n = A(h\nu - E_g), \quad (1)$$

we determined the direct and indirect optical band gaps. Here, α is absorption coefficient, A is a constant, $h\nu$ refers to the photon energy (with h is Planck constant), E_g is the optical band gap, $n = 2$ for direct optical band gaps, and $n = 1/2$ for indirect optical band gaps [26].

In Fig. 8(b), the Tauc analysis for direct allowed transitions is presented, where the intersection of the fitted linear region with the energy axis yields the direct optical band gap. The direct results were complicated and led to a significant change in the direct optical gap, which is a direct consequence of the defect-induced mid-gap and tail states near the band edges. Also, Fig. 8(c) shows the Tauc plot for indirect optical band gap of BNT(110) with antisite defects. Interestingly, the pristine BNT(110) shows the largest indirect gap whereas those of antisite defects show highly

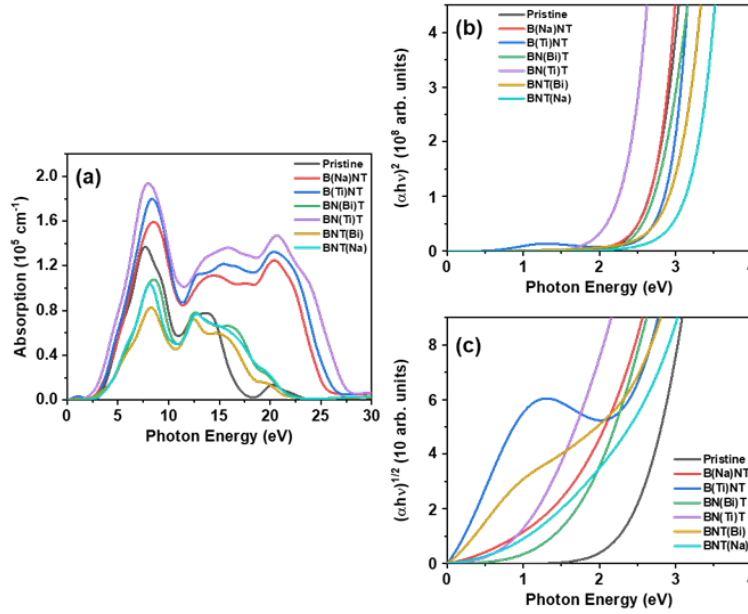


Fig. 8. (Color online) Optical properties of BNT(110) with various antisite defects: (a) optical spectra; (b) direct optical transition; (c) indirect optical transition.

complex behavior at low energy. B(Ti)NT, BNT(Bi), and BNT(Na), the indirect optical band gaps are also substantially reduced. These findings further confirm the high potential for photocatalytic activity under visible light irradiation due to the photo-response into the wide energy spectrum.

To clarify the connection between the optical and electronic properties, we correlate the main features of the absorption spectra with the defect-induced modifications in the band structure and PDOS. The pristine BNT(110) surface shows an optical onset around 3.5 eV, which corresponds directly to the $\text{O-}2p \rightarrow \text{Ti-}3d$ transition across the intrinsic band gap seen in Fig. 2. When antisite defects are introduced, the band structures (Fig. 5) and PDOS (Fig. 6) reveal the appearance of mid-gap states and strong band-edge tailing. These localized $\text{Ti-}3d\text{--O-}2p$ hybrid states enable additional low-energy optical transitions, resulting in the strong sub-gap absorption observed between 1-3 eV. Defects such as B(Ti)NT, BNT(Bi), and BNT(Na), which show the largest density of defect states near the Fermi level, also exhibit the most pronounced reduction in optical band gap and the strongest optical conductivity in the low-energy region. The shifts in the dielectric function and refractive index (Fig. 9) further reflect this defect-induced band-gap narrowing. Thus, the changes in optical spectra arise directly from the reconstructed electronic structure caused by antisite defects.

Figures 9(a)-(g) depict the calculated complex optical properties of the pristine and antisite-defected BNT(110) surfaces, including the real and imaginary parts of the dielectric function, optical conductivity, refractive index, reflectivity, and energy loss function. In case of conductivity and dielectric function, the red line and black line represent for real and imaginary parts, respectively. For the pristine BNT(110) surface (Fig. 9(a)), both the dielectric function and optical conductivity show well-defined peaks in the ultraviolet region, indicating strong interband

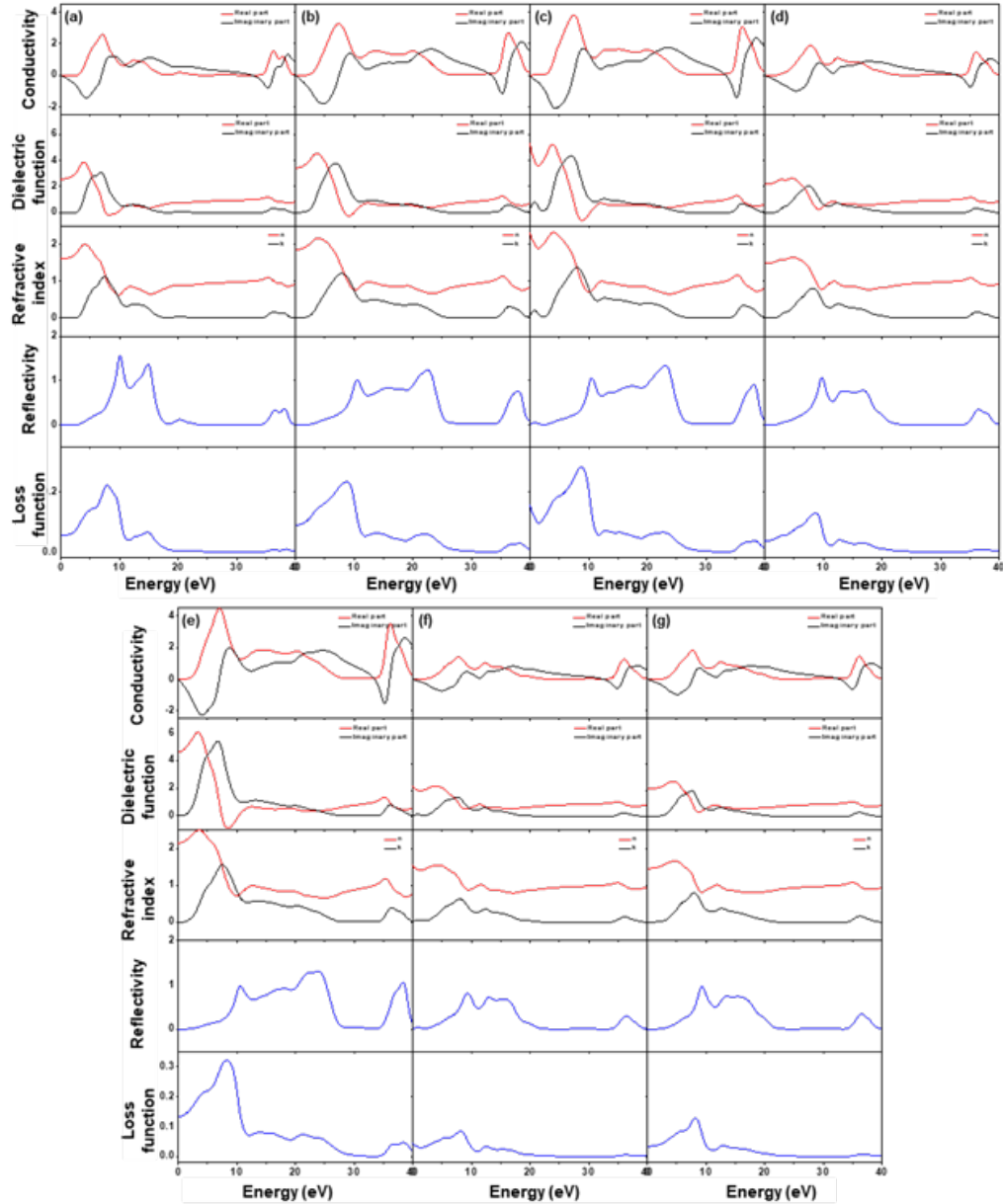


Fig. 9. (Color online) Optical properties of BNT(110) with various antisite defects: (a) Pristine; (b) B(Na)NT; (c) B(Ti)NT; (d) BN(Bi)T; (e) BN(Ti)T; (f) BNT(Bi); (g) BNT(Na).

transitions primarily associated with O-2p to Ti-3d charge transfer. The real and imaginary parts of dielectric function are saturated responses, reflecting the structural and electronic stability of the surface. The refractive index and reflectivity also display regular oscillations, while the loss function exhibits a dominant peak around 8 eV, corresponding to the bulk plasma resonance.

The real and imaginary parts of the conductivity spectra also shift accordingly. Upon introducing antisite defects, substantial changes occur in both peak intensity and position. In B(Na)NT and B(Ti)NT (in Figs. 9(b)-(c)), the main conductivity peaks raised slightly, indicating an enhanced optical conductivity in the low-energy region, the same response appeared in the case of BN(Ti)T defects. However, there are reductions of optical conductivity for BN(Bi)T, BNT(Bi), and BNT(Na) defects. Therefore, by introducing complex antisite defects in BNT(110) surface, we can turn the optical conductivity behavior applications.

The relationship between dielectric function and refractive index is defined by equations [27–29]:

$$n(\omega) = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega)},$$

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

where, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ is real and imaginary part of dielectric function, $n(\omega)$ is refractive index and $k(\omega)$ is extinction coefficient, representing as the red and black line, respectively. As a result, the response of the dielectric function and the refractive index when applying opposite defects corresponds together. Furthermore, the refractive index components for BN(Bi)T, BNT(Bi), and BNT(Na) separated together, implying that more scattering behavior response under energy range [30].

The reflectivity spectrum is defined by:

$$R(\omega) = \left| \frac{\sqrt{\epsilon_1(\omega) + i\epsilon_2(\omega)} - 1}{\sqrt{\epsilon_1(\omega) + i\epsilon_2(\omega)} + 1} \right|^2.$$

In Fig. 9, reflectivity spectrum reveals distinct changes in optical response between the pristine and defected BNT(110) surfaces. When antisite defects are introduced, notable variations appear. In B(Na)NT, B(Ti)NT, and BN(Ti)T the low-energy reflectivity increases slightly, implying enhanced surface charge carrier density and localized electronic states that can promote light reflection. However, the peaks in BN(Bi)T, BNT(Bi) and BNT(Na) shift toward lower photon energies, consistent with shift of optical absorption and partial metallic character induced by defect-states within the band gap.

Lastly, the energy loss function is defined by:

$$L(\omega) = \text{Im} \left(-\frac{1}{\epsilon(\omega)} \right) = \frac{\epsilon_2(\omega)}{(\epsilon_1^2(\omega) + \epsilon_2^2(\omega))}.$$

Energy loss function represents the collective oscillation of valence electrons or plasma resonance, further supports these interpretations. Peaks in the energy-loss function broaden for defect structures, indicating multiple plasmon modes due to non-uniform charge redistribution. Overall, the optical response is therefore strongly governed by the defect-induced reconstruction of the electronic structure, confirming a direct correlation between mid-gap defect states, band-gap narrowing, and enhanced visible-light absorption.

4. Conclusion

In this work, the structural, electronic, and optical properties of the BNT(110) surface with various complex antisite defects has been comprehensively explored using first-principles DFT+U calculations. The pristine surface exhibits pronounced intrinsic *p*-type semiconductor with the band gap of 3.46 eV. When antisite defects are introduced, substantial lattice distortions and changes in local coordination arise, indicating strong coupling between defect chemistry and surface geometry. Electronic structure analysis demonstrates that these defects generate deep-level states within the band gap, effectively narrowing the electronic band gap and modifying charge distribution near the defect sites. The hybridization between Ti-3*d* and O-2*p* orbitals is found to play a dominant role in the formation of these defect-states. Correspondingly, optical analyses reveal enhanced sub-band gap absorption and altered dielectric responses, particularly within the visible-light region. These responses are shown to arise directly from defect-induced mid-gap states and band-edge reconstruction, suggesting the potential of BNT(110) surfaces for photoactive and multifunctional applications.

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Conflict of interest

The authors have no conflict of interest to declare.

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