Theoretical and experimental study on the photoluminescence in BaTiO₃ amorphous thin films prepared by the chemical route

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Abstract

A polymeric precursor method was used to synthesize BaTiO₃ amorphous thin film processed at low temperature. The luminescence spectra of BaTiO₃ amorphous thin films at room temperature revealed an intense single-emission band in the visible region. The visible emission band was found to be dependent of the thermal treatment history. Photoluminescence (PL) properties for different annealing temperatures were investigated. It was concluded that the intensity of PL is strongly dependent on both the heat treatment of the films and the presence of an inorganic disordered phase. Experimental optical absorption measurements showed the presence of a tail. These results are interpreted by the nature of these exponential optical edges and tails, associated with defects promoted by the disordered structure of the amorphous material. We discuss the nature of visible PL at room temperature in amorphous barium titanate in the light of the results of recent experimental and quantum mechanical theoretical studies. Our investigation of the electronic structure involved the use of first-principle molecular calculations to simulate the variation of the electronic structure in the barium titanate crystalline phase, which is known to have a direct band gap, and we also made an in-depth examination of amorphous barium titanate.

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1. Introduction

Interest has long been shown in perovskite-type materials owing to their dielectric, ferroelectric and optical properties. The optical properties, particularly the luminescence, of nanostructured material have attracted considerable attention [1,2]. Indeed, the luminescence of perovskite-type materials such as titanates is well known, and luminescence is observed in these materials in crystal form at room temperature or when pure titanate samples are excited by radiation above the

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band gap energy \([3,4]\). In perovskite-type crystals, a broad luminescence band is usually observed at low temperatures and is associated to the presence of imperfections or defects \([5]\). These properties have led to renewed interest in the luminescence properties of semiconducting titanate compounds. For this reason, amorphous semiconductor compounds such as BaTiO\(_3\) and SrTiO\(_3\) appear particularly promising, since amorphous solids can present greater numbers of imperfections and can be produced at low temperature by chemical processes such as sol–gel. Many reports have been published about investigations of the luminescence of perovskite-type compounds of both bulk and nanometer sizes in the form of crystalline structures \([6–11]\), but little or no information is available about the effects of amorphous thin films of the perovskite-type structure compounds. Meng et al. \([6]\) observed a visible emission band by the 514.5 nm line in nanocrystalline BaTiO\(_3\), its nature and origin are attributed to the recombination of self-trapped excitons. Zhang et al. \([12]\) investigated the photoluminescence (PL) in nanostructured Er\(^{3+}\)-doped BaTiO\(_3\) crystalline films prepared by sol–gel method; a luminescence at 1.54 \(\mu\)m was achieved under excitation of both 514 and 980 nm lasers. Nanocrystalline barium titanate was synthesized by hydrothermal technique by Zhang et al. \([13]\) and strong PL was observed centered at 696 nm, which was attributed to charge transfer via intrinsic defects inside oxygen octahedron. Pizani et al. \([14]\) recently reported efficient room-temperature PL in amorphous BaTiO\(_3\) (a-BaTiO\(_3\)) powders. In that work, a simple chemical process was used to process the powders at a low temperature \((T < 400^\circ\text{C})\). In addition, the PL peak position of this material was observed to depend on the exciting wavelength.

In this paper, we describe efficient room-temperature PL in BaTiO\(_3\) amorphous thin films prepared by a chemical process known as the polymeric precursor method (PPM) \([15,16]\) and investigated for the first time the causes of their PL emission to gain a better understanding of the processes using quantum mechanical theoretical study.

2. Experimental

BaTiO\(_3\) amorphous thin films were processed by the PPM. The flow chart of BaTiO\(_3\) synthesis used in this study is outlined in Fig. 1. Titanium citrates were formed by the dissolution of titanium isopropoxide in an aqueous solution of citric acid \((60–70^\circ\text{C})\). After homogenization of the Ti solution, BaCO\(_3\) was slowly added. In order to achieve total BaCO\(_3\) dissolution, ammonium hydroxide was added drop by drop until the pH reached 7–8. The complete dissolution of the salts produced a clear solution. After complete dissolution of the BaCO\(_3\) salt, ethylene glycol was added to promote polymerization of the mixed citrates by polyesterification reaction. The molar ratio between the barium and titanium cations was 1:1 and the citric acid/ethylene glycol ratio was fixed at 60/40 (mass ratio).

Platinum-coated (111)-oriented silicon and quartz were used as substrates. The substrate was spin-coated by dropping a small amount of the polymeric precursor solution onto it. Rotation speed and spin time were fixed at 4000 rpm and 30 s, respectively. After deposition, each layer was dried at 150°C on a hot plate for 20 min to remove residual solvents.

The heat treatment was carried out at different temperatures for 8 h, at a heating rate of 5°C/min, in a tube furnace in an oxygen flow to pyrolyze the organic materials.

The BaTiO\(_3\) films were characterized structurally using X-ray diffraction (XRD) \((\text{Cu K}_\alpha\) radiation). The diffraction patterns were recorded on a Siemens D5000 machine in a \(\theta – 2\theta\) configuration, using a graphite monochromator. Microstructural characterization was performed by atomic force microscopy (AFM) to obtain a 3D image reconstruction of the sample surface. A Digital Instruments Multi-Mode Nanoscope IIIa was used. Film thickness was measured by a thin film cross-section analysis made by SEM \((\text{Zeiss, DSM940A})\).

The PL spectra of the BaTiO\(_3\) amorphous thin films were taken with a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelength of an
argon ion laser was used, with the laser’s maximum output power kept at 20 mW. A cylindrical lens was used to prevent the sample from overheating. The slit width used was 100 μm. All the measurements were taken at room temperature. The spectral dependence of the optical absorbance of the crystalline and amorphous BaTiO₃ thin films were taken at room temperature, using a Cary 5G equipment.

For the simulations, three clusters were built with the following symmetries: \(D_{4h}\), \(C_{4v}\), and \(C_s\), see Figs. 2(a), (b) and (c) [17], respectively. The Hartree–Fock formalism has been considered to optimize the geometries of the systems considered. We have performed all the calculations by using the Gaussian98 [18], with effective core potential and double-\(\zeta\) basis set, LanL2DZ on Ba and 6–31G(d) and 6–31G(f) on O and Ti, respectively.

The optical band gap and the state densities were calculated using the cluster method. Atomic charges were computed using Natural Bond Orbital. In our approach, all structures were represented by a \(\text{Ba}_8\text{Ti}_3\text{O}_{14}\) (see Fig. 2). The six-fold structure was optimized by \(D_{4h}\) symmetry. The models of the amorphous clusters were built with \(C_{4v}\) symmetry by increasing the Ti(1)–O(7) distance, leading to a displacement of O(7) atoms of 1.5 Å, allowing the rest of the structure to relax for each Ti(1)–O(7) frozen distance (see Fig. 2b) and a cluster with symmetry \(C_s\) was build with rotation of 90° of the O(18) atom (see Fig. 2c). We have associated the top of the valence band to the highest occupied molecular orbital (HOMO) and the bottom of the conduction band to the lowest unoccupied molecular orbital (LUMO) of the studied systems.
3. Results and discussion

Fig. 3 shows the evolution of the XRD patterns of BaTiO$_3$ thin films prepared by the PPM, deposited on platinum-coated silicon substrate and annealed at different temperatures for 8 h in an oxygen flow. A diffuse XRD pattern can be observed at the temperature range from 200°C to 500°C, indicating the formation of an inorganic amorphous precursor after the pyrolysis process.
The observed peaks are related to the platinum substrate. The crystallization phase of BaTiO$_3$ can be observed at temperatures above 500°C. No intermediate phase was observed, suggesting that a direct crystallization occurred from the amorphous phase [19]. After heat treatment at 600°C for 8 h in an oxygen flow, the diffraction patterns of the films showed a well-crystallized structure. All the peaks are attributed to a tetragonal perovskite structure except those ascribed to the substrate (Pt peak). In addition, the BaTiO$_3$ powder obtained by the PPM showed the formation of an amorphous inorganic phase, revealed by both XRD analysis and infrared spectroscopy.

Fig. 4 shows PL spectra, at room temperature, of thin films treated for 8 h at different annealing temperatures in an oxygen flow. A comparison of the different samples reveals that the PL behavior of amorphous BaTiO$_3$ thin films is sensitive to its thermal treatment history. Accordingly, in the room-temperature PL spectra of Fig. 4, when the annealing temperature was increased, the intensity of the PL changed. This increase is ascribed to a decrease in the total carbon content. Similar behavior was observed in a-PbTiO$_3$ (amorphous) and a-BaTiO$_3$ (amorphous) in the powdered form [14]. This finding is strongly indicative that the room-temperature PL stems from an inorganic disordered phase. In addition, in the case of pure bulk materials [20,21], e.g., BaTiO$_3$ and SrTiO$_3$, a visible structureless emission band appears at ~500 nm only at low temperatures. However, BaTiO$_3$ thin films annealed at higher temperatures, i.e., $\geq$400°C, showed no detectable photoluminescent response. As postulated by Leite et al. [22], crystallization can lead to the elimination of defects or imperfections, particularly of non-bridging oxygen (NBO, with the formation of TiO$_2$), of a TiO$_5$ group, in which Ti is penta-coordinated by oxygen and displays the geometry of a square-based pyramid, which is probably the defect responsible for the PL. Since our XRD analysis showed no sign of crystallization, it remains unclear why a decrease in PL intensity was observed between 400°C and 700°C. Therefore, a comparative analysis between the photoluminescent response of BaTiO$_3$ thin films and their surface morphology was made using AFM. The AFM analysis showed a considerable variation in the surface morphology between the annealing temperatures of 200°C and 700°C. Table 1 shows the evolution of sample roughness measured by AFM.

The AFM analysis revealed that the samples annealed from 200°C to 350°C had a homogeneous surface morphology, with only slight roughness and no evidence of a granular structure (See Fig. 5). The increased roughness of the sample annealed at 400°C suggests that the material’s structure became increasingly ordered (in a medium-order range). This increased structural order is believed to be responsible for the decrease in the intensity of the photoluminescent response. In addition, the AFM analysis showed that the sample heat-treated at temperatures $\geq$600°C showed a granular morphology (see Fig. 5), which is typical of crystalline or semicrystalline materials. This result is in agreement with the XRD analysis; no sign of PL was observed in those samples which

![Fig. 4](image-url)

Fig. 4. Room-temperature PL spectra of BaTiO$_3$ thin films annealed at different temperatures; (a) 200°C, (b) 300°C, (c) 350°C, (d) 400°C, (e) 450°C, (f) 600°C, and (g) 700°C, excited with the 488 nm line of an argon ion laser.

<table>
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<tr>
<th>Temperature (°C)</th>
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<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>700</th>
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<td>Roughness (nm)</td>
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<td>1.4</td>
<td>2.7</td>
<td>4.0</td>
<td>5.1</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Table 1

Roughness evolution of BaTiO$_3$ thin films as a function of temperature.
Fig. 5. AFM of BaTiO$_3$ thin films on the Si/SiO$_2$/Ti/Pt substrate at; (a) 200°C, (b) 300°C, (c) 350°C, (d) 400°C (e) 450°C, and (f) 700°C.
are in evidence of a long-range order (crystalline structure).

Fig. 6 shows the optical transmission spectra of a crystalline and amorphous BaTiO$_3$ thin film, recorded in the 200–800 nm wavelength range. Quartz was chosen as substrate, because the energy of optical absorption of the substrate is larger than that of the BaTiO$_3$ thin film. The aforementioned experimental results strongly indicate that PL is directly related to the exponential optical edges and tails. The nature of these exponential optical edges and tails maybe associated with defect states promoted by the disordered structure of the amorphous BaTiO$_3$ thin film. The absorbance measurements associated with the PL characterization of amorphous BaTiO$_3$ thin film, suggests a non-uniform band gap structure with a tail of localized states and mobile edges. On the other hand, our results are shown in terms of absorption associated with localized energy states in the band gap. We believe that the PL observed in this amorphous BaTiO$_3$ thin film arises from a radiative recombination between trapped electrons and trapped holes in tail and gap states. Fig. 6 illustrates the spectral dependence of absorbance for the amorphous BaTiO$_3$ treated at 350°C for 8 h in an oxygen flow, and for the crystalline BaTiO$_3$. Amorphous BaTiO$_3$ showed a spectral dependence on absorbance similar to that found in amorphous semiconductors such as amorphous silicon (Si) [23], while crystalline BaTiO$_3$ showed a typical inter-band transition of crystalline materials. In addition, in the high-energy region of the absorbance curve (Fig. 6), the optical energy band gap is related to the absorbance and to the photon energy by the following equation:

$$hve \propto (hv - E_{opt}^{\text{gap}})^2,$$

where $h$ is the Plank constant, $v$ is the frequency, and $E_{opt}^{\text{gap}}$ is the optical band gap (Tauc gap). The energy band gaps of the crystalline and amorphous BaTiO$_3$ were calculated to be approximately 3.74 and 2.22 eV, respectively. In addition, the energy band gap associated with the tail states (see Fig. 6) was calculated to be approximately 0.97 eV. These results (Fig. 6) show that our data are consistent with the interpretation that the exponential optical absorption edge and the optical band gap are controlled by the degree of disorder, structural and thermal, in the lattice of BaTiO$_3$ thin films.

Experimental results by Balachandran and Eror [24] and Chan et al. [25] were explained by means of an oxygen vacancy defect model. The basis for this model is the loss of oxygen from the lattice to the gas phase with the formation of a doubly ionized vacancy, $V_{\text{o}}^{2-}$, with the two extra electrons being donated to the conduction band. However, we can assume, by our results, that electron transfer occurs between barium and titanium ions. Our model for the hole states is O$^{-\gamma}$ ion, while for the electron states are the Ti$_{\alpha}^{+\gamma}$ and Ba$^{+\beta}$ species, where $\alpha$, $\beta$ and $\gamma$ are effective charges. The results of theoretical calculations indicate that the formation of an amorphous cluster through the displacement of O(7) and an other amorphous with rotation may introduce delocalized electronic levels in the forbidden gap of the octahedron cluster in the regions delimited by Hc and Ha (hereinafter called $\Delta$HOMO). Partial densities for the crystalline and amorphous clusters investigated are presented in Fig. 7. The partial densities of Ti,

![Fig. 6](image-url)
Ba and O states are presented for the valence and conduction bands in Fig. 7. In crystalline and amorphous BaTiO₃ clusters, there is a weak contribution of Ba states to the density of states at the bottom of the valence bands while there is a strong contribution of O states for the density of states of the main part of the valence bands.

The shape of the density of states distribution curve for these valence bands (Ti, Ba and O) has two main features. The upper portion of the bands presents different contributions from Ti and Ba states, while the lower portion contains states of primarily O character. From this point of view, it is clear that O states dominate the character of these valence bands in the crystalline and amorphous clusters investigated. On the other hand, there is a significant contribution of the Ba and Ti states for the conduction band states. Fig. 6 shows significant contributions of Ba and Ti states throughout the conduction bands of these amorphous materials. The crystalline cluster presents a higher band gap than the amorphous cluster, which is in agreement with experimental results, observed by absorbance spectral data (see Fig. 6). The delocalized electronic levels in the valence band may introduce in the amorphous clusters the PL properties. From this figure, it is apparent that the p orbitals of the oxygen are weighted toward the top of the valence band.

However, it is very important to note that there are electronic levels of the amorphous clusters included in the wide band gap of the crystalline cluster.

The conduction band of BaTiO₃ is mostly of barium s and titanium s and d character and the valence band is formed by oxygen 2p states (Fig. 7). The results of theoretical calculations indicate a charge transfer between TiO₆ and TiO₅ centers with mainly barium participation.

Fig. 8 shows the energy levels in the molecular orbitals for the titanium and barium ions, stressed by the neighboring oxygen vacancies, whereas their charge distribution is presented in Table 2. In this case, one titanium ion forms an octahedral TiO₆ complex, but the other titanium ion, in a different octahedron, forms a TiO₅ complex plus an oxygen vacancy. If these two different $V_{o}^{*}$ structures coexist, the charge of the two holes is compensated by one oxygen vacancy. This suggests that the formation of amorphous clusters...
may introduce electronic levels in the forbidden gap.

The calculation by Kahn and Leyendecker [26], using the linear combination of atomic orbitals method showed that the fundamental band gap is indirect, and the filled valence bands are derived from oxygen 2p orbitals and the empty conduction bands derived from titanium 3d orbitals. In this

\[ \text{Fig. 8. Schematic diagram of the energy levels and charge distribution (see Table 2) in the stable molecular orbitals of the Ti(16), Ba(8) and O(23).} \]

\[ \text{D}_{4h}—\text{crystalline cluster of symmetry; } C_{4v}—\text{amorphous cluster of symmetry; and } C_{s}—\text{amorphous cluster of symmetry.} \]

\[ \text{Table 2} \]

<table>
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<th>Atom</th>
<th>Orbital</th>
<th>C\text{\textsubscript{4v}}</th>
<th>D\text{\textsubscript{4h}}</th>
<th>C\text{\textsubscript{s}}</th>
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</thead>
<tbody>
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<td>0.41</td>
<td>0.40</td>
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<td>d\text{\textsubscript{xy}}</td>
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<td>B\text{\textsubscript{2g}}</td>
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<td></td>
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<tr>
<td></td>
<td>d\text{\textsubscript{z}2}</td>
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<td></td>
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<td>Ba(8)</td>
<td>s</td>
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<td>1.90</td>
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<td></td>
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</tr>
<tr>
<td>O(23)</td>
<td>p\text{\textsubscript{y}}</td>
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<td>A\text{\textsubscript{2u}}</td>
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D\text{\textsubscript{4h}}—crystalline cluster of symmetry; C\text{\textsubscript{4v}}—amorphous cluster of symmetry; C\text{\textsubscript{s}}—amorphous cluster of symmetry. A or B—1D representations; E—2D representations; The totally symmetric representation (all characters +1) is denoted always by A (or by A\text{\textsubscript{1}}, A\text{\textsubscript{1g}} or A').
present case, there is a strong participation of the barium atoms.

The band states correspond to the bonding states in the valence band and the antibonding states in the conduction band in an “ideal” glass. We shall call a glass ideal if it has all chemical bonds satisfied. The tail states may correspond to the defects in this ideal structure such as dangling bonds, but, alternatively, similar states may be present even in an ideal glass [27].

The octahedral geometry of the crystalline cluster is favored for TiO₆ because it minimizes the electrostatic interactions among the six oxygen ligands arranged around the positively charged titanium (Ti(1)) center (see Fig. 2a). The s orbital of the Ba and of the Ti s as well as the Ti d orbitals, dₓᵧ, dₓz, dᵧz, dₓz, and dₓ²−ᵧ² form bonds with the oxygen; as a consequence, they must have corresponding ligand-antibonding combinations. These appear in the conduction band (LUMO) and the orbitals p of the oxygens in the valence band (HOMO) (Fig. 8). Conceptually, the two amorphous clusters may be obtained from a crystalline cluster. One cluster, (TiO₅), by lengthening one O(7)–Ti(1) bond, as the metal–ligand distance increases to 3.54 Å, the configuration becomes Ti(16)–O(22). The other cluster, (TiO₅)⁰, derives from a rotation of 90° of the O(18) atom. As one bond removed or rotated around the y-axis, the 3dₓz and 3dₓ²−ᵧ² antibonding orbitals will be stabilized in Ti(16)–O(23) (TiO₅) and (TiO₅)⁰ clusters and they will be more stable, because they now have only one antibonding interaction with a ligand lone pair, rather than the two which are present in TiO₆. The theoretical results indicate that the formation of a five-fold oxygen titanium coordination TiO₅ through the displacement of O(23) or rotation of O(18) may introduce delocalized electronic levels at a higher energy than the HOMO of the crystalline cluster derived from the 2pₓ, 2pᵧ and 2p₂ oxygen orbitals (Fig. 8).

The interactions between Ba, Ti and O in the (TiO₃) complex are important, while in the (TiO₅) complexes they are weak. This means that the dₓz and dₓ²−ᵧ² bonding combinations in the crystalline cluster are unstable and in the amorphous cluster they are stable (Fig. 8). As a consequence, the gap between the orbitals s and d (Ti) and s (Ba) (LUMO) and p (O) (HOMO) is larger for the crystalline cluster and thus the gap of the amorphous clusters is shorter. In this case, the titanium s and d and barium s electrons strongly favor the more stable configuration for all d orbitals and s orbitals of the Ti(16) and of the Ba(8) and the promotion of electron density in 3dₓz and 3dₓ²−ᵧ² is not prohibitive (Fig. 8). In addition, the crystalline cluster has energy levels in the stable orbitals s and d (Ti), s (Ba) and p (O) and has a charge distribution slightly higher in the Ti(16)–O(23) bond. Otherwise, the amorphous cluster has energy levels in the orbitals s of the Ba(8) markedly higher than d orbitals of the Ti(16) and has a charge distribution slightly lower. From these results, it is apparent that the top of the valence band receives contributions from orbitals p of the oxygen.

The results show that the transfer charge is not only for the network former (TiO₆), but also for the network modifier (BaO₂). Thus, the symmetry of the BaTiO₃ system is modified intrinsically by the random movement of the barium, due to its ionic character, associated differently to the titanium, to the ligand defects.

4. Conclusions

In summary, the results of XRD, AFM, and PL indicate that the nature of room-temperature PL must be related to the disordered structure of amorphous BaTiO₃ thin films. Our AFM measurements suggest that even a small change in the material’s structure may lead to a significant change in the concentration of defects, particularly in NBO, and a resulting loss in the intensity of PL. In addition, we have correlated the evolution of visible PL with a change in the surface morphology of BaTiO₃ thin films. The visible PL observed is strongly related to changes in surface morphology and temperature. This work involves important aspects that are applicable to the production of ATiO₃ (A = Pb, Ca, Ba, Sr) perovskite-type structure amorphous thin films prepared by PPMs, with active optical properties such as PL at room temperature. The energy band gaps of the crystalline and amorphous BaTiO₃ films were calculated
to be approximately 3.74 and 2.22 eV, respectively. However, by first-principles calculations, we believe that the visible emission cannot be attributed to a band-to-band transition of BaTiO$_3$, because the energy of the excitation line (488.0 nm/2.52 eV) used in our experiments is much lower than the band gap of our crystalline BaTiO$_3$ (3.7 eV) prepared by PPM, and consequently it is impossible to excite an electron directly from the oxygen 2p orbitals (valence bands) to the barium 4s and titanium 4s and 3d orbitals (conduction bands). The conduction band in the amorphous BaTiO$_3$ is largely formed from Ba states contribution, while that valence band is primarily composed of O states contribution. In addition, the results of theoretical calculations indicate that the formation of five-fold coordination through the displacement of O(7) or rotation of the O(18) may introduce delocalized electronic levels in D$_{HOMO}$. However, a large amount of “broken” surface or dangling bonds and defect centers intrinsically existing in the amorphous materials of BaTiO$_3$ can form various energy levels localized within the forbidden gap and they act as optical absorption centers, which make large modifications in the optical properties of the materials, and are responsible for the visible PL at room temperature.

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