Photoluminescence of crystalline and disordered BTO:Mn powder: Experimental and theoretical modeling

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Abstract

Disordered and crystalline Mn-doped BaTiO\textsubscript{3} (BTO:Mn) powders were synthesized by the polymeric precursor method. After heat treatment, the nature of visible photoluminescence (PL) at room temperature in amorphous BTO:Mn was discussed, considering results of experimental and theoretical studies. X-ray diffraction (XRD), PL, and UV–vis were used to characterize this material. Rietveld refinement of the BTO:Mn from XRD data was used to built two models, which represent the crystalline BTO:Mn (BTO:Mn\textsubscript{c}) and disordered BTO:Mn (BTO:Mn\textsubscript{d}) structures. Theses models were analyzed by the periodic ab initio quantum mechanical calculations using the CRYSTAL98 package within the framework of density functional theory at the B3LYP level. The experimental and theoretical results indicated that PL is related with the degree of disorder in the BTO:Mn powders and also suggests the presence of localized states in the disordered structure.

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1. Introduction

The ABO\textsubscript{3}-type perovskite compounds (A = Ba, Sr, Ca, or Pb and B = Ti) are intensively investigated materials due to their electronics, ferroelectrics and optical properties. These materials have wide range of applications as capacitors, sensors and photocatalysis [1–5]. The interest in this kind of material is already great nowadays because in many optoelectronic devices, structurally disordered semiconductors can replace single crystal semiconductors, particularly in photoluminescent properties [6–11].

Titanates with photoluminescent properties have been extensively used in modern applied technology areas of the electronic industry [1,2]. Many papers report on the luminescence properties of perovskite-type compounds, especially SrTiO\textsubscript{3} (STO) and BaTiO\textsubscript{3} (BTO) [12–15]. Bouma and Blasse [9] concluded that the BTO photoluminescence (PL) property is related with the short Ti–O atomic distances into the regular octahedral of the BT unit cell and by the charge transferences between titanium and oxygen atoms. Eglitis et al. [12] demonstrated very recently through semiempirical quantum chemical calculations that the origin of the intrinsic excitonic (‘‘green’’) luminescence of ABO\textsubscript{3} perovskite at low temperature is linked to the recombination of electrons and hole polarons forming a charge transfer vibronic exciton. Zhang et al. [16,17] reported the PL properties of nanocrystalline BTO synthesized by hydrothermal method at room temperature and concluded that the origin for the PL is due to the intrinsic defect distribution (oxygen vacancy). These
vacancies promote localized states in the gap region, decreasing the gap value. The PL is also attributed to the charge transference from the central Ti$^{3+}$ ion to a neighboring O$^{2-}$ ion inside the [TiO$_6$] octahedron [18] via intrinsic defects, mainly oxygen vacancies.

Meng et al. [19] studied the nature of visible emission in nanocrystalline BTO and STO. Based on their results, these authors considered that this visible transition emission may be induced to a direct recombination of a conduction electron in the Ti-3d bands localized at the titanium site be induced to a direct recombination of a conduction electron in the Ti-3d bands localized at the titanium site and a hole in the O-2p valence band. This electron–hole interaction makes possible the trapped near-crystal defects or impurities, and form an intermediate state attributed to self-trapped excitons.

During the last years the electronic properties and atomic structure of a great variety of ABO$_3$-type perovskite thin films have been extensively studied both experimentally and theoretically [20–29]. Our group [30–34] has discussed the nature of visible PL at room temperature in amorphous perovskite-type titanates prepared by the polymeric precursor method. In the light of the results of recent experimental and theoretical calculations, it was concluded that experimental results obtained by X-ray absorption near-edge structure (XANES) for the structurally disordered phase of these materials revealed the coexistence of two types of Ti coordination in the PT cluster, namely, fivefold oxygen Ti coordination [TiO$_5$] and sixfold oxygen Ti coordination [TiO$_6$] and also suggested that [TiO$_5$] is absent in well-crystallized titanates. These experimental results have given support for the building of the theoretical model, which indicated the appearance of new states into the band gap region. This is ascribed to the breakage in the symmetry, which is responsible for visible PL in the disordered material at room temperature.

Since the use of dopants forms a very effective approach for microstructural control, various authors have studied doped-barium titanates using different dopants. Yamamoto et al. [35] reported the luminescence of rare-earth ions in perovskite-type oxides and concluded that these ions can improve the photoluminescent property in this material. Rahaman and Manalert [36] investigated the grain boundary mobility of BTO with the aliovalent cations concentration in terms of the defects in chemistry and space-charge concept. Buscaglia et al. [37] studied the influence of transition metals and rare-earth ions on the BTO crystal structure and observed that dopants substitution depends on the site element. The BTO lattice changes from tetragonal to pseudocubic, and the dielectric constant is very low, because of the influence of the dopants [38,39]. Stojanović et al. [40] reported the dielectric properties of barium titanate and the structure–property relationship was established.

In the present work, BTO:Mn powders were obtained by the polymeric precursor method to understand the visible photoluminescent properties in the disordered structure of this material. The electronic structure and structural properties in this crystalline (BTO:Mn$_d$) and disordered (BTO:Mn$_q$) structures were analyzed by periodic ab initio quantum-mechanical calculations with the density functional theory (DFT). Thus, the influence of the doping element itself on the electronic configuration is just local; hence, it is not included in the simulation. The aim of the theoretical study is to investigate the electronic structure of BTO:Mn using periodic models representing their crystalline and disordered structures giving an interpretation in terms of the density states (DOS), band structure, band gap, electron density map and correlating them with the experimental results.

2. Experimental

BTO:Mn powders were prepared by the polymeric precursor method [41]. Barium-(II) acetate, manganese carbonate, and titanium tetraisopropoxide were used as starting materials. Ethylene glycol and citric acid were used as polymerization/complexation agents for the process. Ammonium hydroxide was added drop by drop to adjust the pH and to prevent barium citrate precipitation. The polymeric precursor method is based on the chelation of the metal cations by citric acid in a solution of water and ethylene glycol.

Titanium citrate was formed by the dissolution of titanium tetraisopropoxide in an aqueous solution of citric acid (70–90 °C). To this solution was added 0.01 mol% of manganese carbonate and after homogenization, a stoichiometric amount of 0.99 mol% of barium acetate previously dissolved in water was added forming the BTO:Mn precursor solution.

Ammonium hydroxide was added drop by drop until the solution reached 7–8. Ethylene glycol was added after the homogenization of the solution containing the Ba$^{2+}$, Ti$^{4+}$, and Mn$^{2+}$ cations. Upon continued heating at 150 °C, the solution became more viscous, forming a polymeric resin with no visible phase separation. The citric acid/metal molar ratio was fixed at 3:1, and the citric acid/ethylene glycol mass ratio was fixed at 60:40. The polymeric resin was initially heat treated at 200 °C for 2 h and after that at 300 °C for 4 h in a muffle furnace-type to promote the polymer pyrolysis process. After that these polymeric precursors were de-agglomerated and heat treated at 450 °C for 12, 20 and 36 h to obtaining the amorphous material, and the crystalline samples were formed after heat treatment at 700 °C for 4 h under ambient atmosphere.

The BTO:Mn powders were structurally characterized by X-ray diffraction (XRD), using a Siemens, D5000 diffractometer in a 0–20 configuration ranging from 5° to 75°, $\lambda = 1.5406$ Å, with a graphite monochromator. The obtained results were compared with the Joint Committee on Powder Diffraction Standard (JCPDS). The Rietveld refinements [42] were carried out with the program GSAS [43]. The peak profile function was modeled using the convolution of the Thompson–Cox–Hastings pseudo-Voigt (pV-TCH) with the asymmetry function described...
by Finger et al. [44]. The strain anisotropy broadening was corrected by the phenomenological model described by Stephens [45].

The PL spectra were measured using 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 maximum output power kept within 20 mW. The spectral dependence of the optical reflectance, UV–vis, of the BTO:Mn was taken in the total reflection mode, using a Cary 5G equipment. All the measurements were taken at room temperature.

3. Computing method and periodic models

Periodic ab initio quantum-mechanical calculations have been carried out by means of the CRYSTAL98 computer code [46], which is based on both density functional (DFT) and Hartree–Fock theories. The gradient-corrected correlation functional by Lee et al. was used, combined with the Becke3 exchange functional, B3LYP [47,48]. This method was used by Sambrano et al. [49] to study the BTO:Mn structural and electronic properties. The basic sets are described by 9763-311(d631)G for Ba [50], 86-411(d31)G for Ti [50], and 6-31G* for O [51]. We built two models based on the Rietveld refinement results for the crystalline structure of BTO:Mn using a super cell (1, 1, 2) to represent the periodic models. The first model represents the crystalline BTO:Mn structure (Fig. 1(a)) while the second model represents the disordered BTO:Mn_d structure (Fig. 1(b)). In this disordered model, we simulated the 0.5 Å displacement of Ti1 along the z-axis. This new BTO:Mn_d structure was simulated using the ATOMDISP feature of the CRYSTAL98 software. This model was used to study the optical, structural, and electronic properties of the disordered state of BTO:Mn_d and to understand the PL phenomenon of this material at room temperature [33].

4. Results and discussion

Fig. 2 shows the XRD patterns of the BTO:Mn_c and BTO:Mn_d powders calcined at 700 °C for 4 h and 450 °C for 12, 20 and 36 h, respectively. The XRD patterns at 700 °C for 4 h illustrated in Fig. 2(a) showed a pattern of crystalline material (ordered structure) corresponding to the BTO tetragonal perovskite phase. For the BTO:Mn samples heat treated at 450 °C for 12, 20 and 36 h showed in Fig. 2(b)–(d), respectively, it is observed a pattern of a typical disordered material, presenting only the barium carbonate peaks.

Photoluminescence spectra of the BTO:Mn_d heat treated at 450 °C for 12, 20, and 36 h are illustrated in Fig. 3(a)–(c), respectively, while the crystalline BTO:Mn_c heat treated at 700 °C for 4 h are showed in Fig. 3(d). All measurements were carried out at room temperature and the samples were excited by the 488 nm line of an argon laser. The PL spectra of the amorphous materials show a broad and intense band in the visible region with a maximum at about 600 nm. As observed in Fig. 3(d), the heat treatment at 700 °C for 4 h results in a material that did not present any PL at room temperature. This behavior is related with the material having a complete structural order.

The material processed by the polymeric precursor method presents an inorganic and an organic phase. As the increase of heat treatment occurs, a decreasing in the carbon content and an ordering in the organic phase is observed. This behavior can be followed by Fig. 3. At the beginning of the heat treatment, the material is composed by a large amount of carbon and presents a high disorder degree in its structure. This is represented in Fig. 3(a). When the structure of the material presents an intermediate degree of order/disordered intermediary, it is observed an intense PL at room temperature (Fig. 3(b)). As the material became more ordered with the increase of the heat treatment at 450 °C for 36 h, it was observed a decrease in

Fig. 1. Super-cell representation 1 × 1 × 2 of the tetragonal BTO:Mn structure: (a) ordered BTO:Mn_c and (b) disordered BTO:Mn_d.
Finally, at 700 °C, all the organic materials are absent from the sample and there is a complete structural order in the crystalline material resulting in a nonluminescent compound (Fig. 3(d)). As observed in Fig. 3d, the heat treatment at 700 °C for 4 h results in a material that did not present PL at room temperature.

Fig. 4 depicts the spectral dependence of absorbance for the BTO:Mn heat treated at 450 °C for 20 h under oxygen flow (a), and for the crystalline BTO:Mn at 700 °C for 4 h (b). Fig. 4(a) shows a spectral dependence on absorbance similar to that found in amorphous semiconductors, while Fig. 4(b) showed a typical interband transition of the crystalline materials.

According to Wood and Tauc [52], the nature of these exponential optical edges and tails may be associated with defect states promoted by the disordered structure. This fact is observed for the BTO:Mn<sub>d</sub> samples. The absorbance measurements of BTO:Mn<sub>d</sub>, associated with the PL characterization, suggest a nonuniform band gap structure with a tail of localized states. However, our results are interpreted in terms of the absorption associated with the localized energy states in the band gap. Therefore, the PL observed in this BTO:Mn<sub>d</sub> arises from a radiative recombination of the electrons–holes into the gap region. The experimental values of the optical band gap of BTO:Mn<sub>c</sub> and BTO:Mn<sub>d</sub> are 3.06 and 2.15 eV, respectively. These gap values are related to the nonuniform band gap structure with a tail of localized states and mobile edges into the band gap region. Fig. 4 illustrates that these data are consistent with the interpretation that the exponential optical absorption edge and the optical band gap are controlled by the structural disorder degree and thermal effect in the lattice of BTO:Mn sample. The nature of these exponential optical edges and tails may be associated with defect states promoted by the structural disorder of the BTO:Mn<sub>d</sub>.

Fig. 5(a) and (b) shows calculated total DOS and band structure for the BT:OMn<sub>c</sub> and BTO:Mn<sub>d</sub> periodic models, respectively. Fig. 5(a) shows that the valence band (VB) is observed between 0 and −2 eV. The conduction band (CB) was evaluated between 3.54 and 6.25 eV, while the gap value was 3.54 eV. Fig. 5(b) shows that for the BTO:Mn<sub>d</sub>,
the VB is between 1.2 and 3.6 eV while CB is between 3.6 and 6.25 eV, gap value was 2.04 eV. This decrease can be associated to the Jahn–Teller effect. Fig. 5(a) and (b) representing the band structures shows that the BTO:Mnc and BTO:Mnd gaps are indirect from the M to $\Gamma$ points. The total DOS of the periodic models show that the contribution of oxygen atoms derived from the 2p atomic orbital is predominant in the VB region. The contributions of the titanium atoms derived from 3d atomic orbital are predominant in the CB region. The BTO:Mnd periodic model shows a decreasing in the gap values originated from the breaking of structural symmetry. This decreasing in the gap value is due to the appearing of the localized states into the gap region. The localized states are responsible for the PL phenomenon at room temperature in the visible range for the BTO:Mnd sample.

The energy level diagram for BTO:Mnc and BTO:Mnd samples can be observed in Fig. 6(a) and (b), respectively. These figures show that in the VB region there is a contribution of the 2p atomic orbitals from the oxygen, while in the BC region is observed the contribution of the 3d atomic orbitals from titanium atoms. Fig. 6(b) illustrates the degeneracy of the atomic orbitals of the oxygen atoms in their respective regions (Jahn–Teller effect). The degeneracy in the VB promotes the decrease in the gap values with the appearing of the localized states into the gap region.

Fig. 7(a) and (b) depicts the electron density maps for the BTO:Mnc and BTO:Mnd, respectively, showing the contour and surface lines correspondent to the square base planes involving the Ti and O atoms. Fig. 7(a) illustrates the strongly covalent character of the interaction of the Ti1 atom with the O3 and O5 atoms on the $xy$ plane that results from the hybridization between the 2p atomic orbital of the O and the 3d atomic orbital of the Ti. This behavior is represented by the homogenous distributions of the contour lines. However, Fig. 7(b) shows a inhomogeneous distribution of the contour lines, which represents...
the decreasing in the interaction between the Ti1 and O2 atoms due to the break of this bond.

Fig. 8(a) and (b) illustrates the electron density maps of the electronic density in the (1 1 0) diagonal plane of the BTO:Mnc and BTO:Mn\textsubscript{d}, respectively. The diagonal cutting plane is passing through the oxygen, titanium, and barium atoms that are perpendicular to the square base plane. Fig. 8(a) shows an homogeneous distribution of the electronic density representing the covalent bonding character of the Ti–O and the strong ionic character between Ba and O atoms bonding. The formal charge of the symmetric [TiO\textsubscript{6}][TiO\textsubscript{6}] clusters for the ordered structure possesses the same values and, consequently, the difference of the charge densities is zero. In the disordered structure a structural asymmetry occurs and consequently the difference between the formal charge of the clusters is 0.5\(e\), suggesting the presence of polarization in this system [19]. This charge gradient and the presence of the localized states provide a good condition for the trapping of electrons and holes. The recombination electron–hole generates the polaron favoring the photo-luminescent emission at room temperature in the visible region for the disordered BTO:Mn\textsubscript{d} powders.

The theoretical results obtained by the BTO:Mnc periodic model represented by [TiO\textsubscript{6}][TiO\textsubscript{6}] clusters are designed by the regular octahedral where there are six oxygens surrounding the titanium atom. The BTO:Mn\textsubscript{d} periodic model is designed by the [TiO\textsubscript{5}][TiO\textsubscript{6}] clusters. The formation of fivefold oxygen–titanium coordination [TiO\textsubscript{5}] cluster is caused by the displacement of the titanium atom (Ti1). The displacement of Ti1–O2 bond promotes the appearing of localized states originating the atomic orbital (2px, 2py, 2pz) of the oxygen atom (O2) in the band gap region. The gap value for the BTO:Mnc was calculated as 3.54\(eV\) and for the BTO:Mn\textsubscript{d} was 2.04\(eV\) generated by Jahn–Teller effect.

The experimental results obtained here, according to Wood and Tauc [52], can be related to the UV–vis and the PL measurements. According to Zhang et al. [17], Cai et al.
[18] and Meng et al. [19], the localized states are linked to local defects like oxygen vacancies in the band gap above the valence band and below the conduction band. In the model presented by Meng et al. [19] and Leonelli and Brebner [53], some of the electrons promoted to the conduction band by absorption of photon give rise to small polarons. The polaron interacts with trapped holes in the crystal (defects or impurities) and form self-trapped excitons. The BT: Mn\textsubscript{d} model proposed in this work consider that occur charge transference between [TiO\textsubscript{5}] and [TiO\textsubscript{6}] clusters. The presence of this charge transference promotes the hole–electron recombination, which give rise to the polaron in this cluster system. These results are justified because the PL property at room temperature are observed in the visible region only for the BT: Mn\textsubscript{d} sample. Our paper presents a different approach and brings new calculations for the BTO: Mn band structure, DOS, and electron density maps to understand the origin of PL of the disordered BTO: Mn, which was correlated with the experimental results.

5. Conclusion

The polymeric precursor method is efficient for synthesis of BTO: Mn powders. The experimental results showed that the visible PL emission in amorphous materials is directly related to the exponential optical edges and tails and can be associated with structural defects in the BTO: Mn\textsubscript{d}. For the crystalline BTO: Mn\textsubscript{c}, a band characteristic of crystalline material was observed.

These results are in agreement with the theoretical analysis which allowed us to describe some of the main factors responsible for the PL of the BTO: Mn\textsubscript{d}: (a) defects distribution represented by the coexistence of both [TiO\textsubscript{5}] and [TiO\textsubscript{6}] clusters, (b) the induction of the presence of localized states into the gap region, and (c) the existence of the charge differences between the [TiO\textsubscript{5}] and [TiO\textsubscript{6}] clusters that induces spontaneous polarization into this system. The simultaneous utilization of theoretical and experimental results is important tool for understanding the PL properties in the visible region at room temperature in disordered perovskite materials.

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