Intense visible photoluminescence in Ba (Zr 0.25 Ti 0.75) O 3 thin films

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Photoluminescence at room temperature in Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$ thin films was explained by the degree of structural order-disorder. Ultraviolet-visible absorption spectroscopy, photoluminescence, and first principles quantum mechanical measurements were performed. The film annealed at 400 °C for 4 h presents intense visible photoluminescence behavior at room temperature. The increase of temperature and annealing time creates [ZrO$_6$]–[TiO$_6$] clusters in the lattice leading to the trapping of electrons and holes. Thus, [ZrO$_5$]–[TiO$_6$]/[ZrO$_6$]–[TiO$_6$] clusters were the main reason for the photoluminescence behavior. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2425013]

Photoluminescence (PL) is a powerful tool to discover the energy levels of materials when used in combination with absorption and PL excitation measurements. PL provides fundamental information of the structural degree within the band gap of materials. Much interest has been focused on the photoluminescence of disordered or nanostructured material, since this phenomenon was first observed in porous silicon at room temperature.[1] In this context, the development of new environmentally friendly materials is of fundamental importance. ABO_3 perovskites (A=Ba,Ca,Sr and B=Ti) have been the focus of research aiming at their potential for photoluminescence properties.[2–5] Kan *et al.*[6] reported that the main cause for PL emission at room temperature in polycrystalline SrTiO$_3$ is oxygen deficiency. However, there are several papers explaining the favorable conditions for PL emission in materials presenting an order-disorder degree.[7–9] Recently, Ba(Zr$_x$Ti$_{1-x}$)O$_3$ (BZT) has been chosen as an alternative material to (Ba,Sr)TiO$_3$ in the fabrication of ceramic or thin films because the Zr^{4+} ion is chemically more stable than the Ti^{4+} ion.[10,11] However, its PL properties have not yet been reported.

In this letter, we present the role of order-disorder to explain the intense visible photoluminescence of Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$ (BZT) thin films at room temperature. The films annealed at 400 °C for different times and at 700 °C for 2 h were characterized by ultraviolet-visible (UV-vis) absorption spectroscopy, PL, and quantum mechanical calculation measurements. This dual approach renders a plausible quantitative description of BZT thin film behavior under laser excitation and an interesting correlation with experimental results. Quantum mechanical calculations have been carried out with the CRYSTAL98 package,[12] which is based on both density functional and Hartree-Fock methods. The gradient-corrected correlation functional by Lee *et al.*[13] and Becke[14] was used, combined with the Becke3 exchange functional, B3LYP. The atomic centers have been described

by all electron basis sets 9763-311(d631)G for Ba,[15] 976 -31(d62)G* for Zr,[15] 86-411(d31)G for Ti,[16] and 6-31G* for O.[16]

BZT thin films were prepared by the soft chemical method, as described in the following article.[17] The viscosity of the resulting solution was adjusted to 13 mPa s, controlling the water content using a Brookfield viscosimeter. The polymeric solution was spin coated on the substrates by a commercial spinner operating at 7500 rpm for 20 s (spin coater KW-4B, Chemat Technology). Such solution was deposited onto the Pt/Ti/SiO$_2$/Si substrates via a syringe filter to avoid particulate contamination. After deposition, the films were kept on a hot plate at 150 °C in air ambient for 10 min to remove residual solvents. The films were annealed at 400 °C for 1, 2, 4, 8, and 16 h and at 700 °C for 2 h with a heating rate of 3 °C/min in oxygen atmosphere.

The UV-vis absorption spectra of the optical absorbance for disordered BZT thin films and crystalline BZT film were taken at room temperature using Cary 5G equipment. The PL spectra of the thin films were taken with a U-1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 514.5 nm exciting wavelength of an argon ion laser was used, with the laser's maximum output power kept at 30 mW. A cylindrical lens was used to prevent the sample from overheating. The slit width used was 100 μm. All measurements were taken at room temperature.

Figure 1 illustrates the UV-vis spectral dependence of absorbance for BZT thin films annealed at 400 °C for different times and annealed at 700 °C for 2 h in oxygen atmosphere. The optical band values obtained from the UV-vis spectroscopy is shown in Fig. 1.

The exponential optical absorption edge and the optical band gap are controlled by the structural order-disorder degree in the BZT film lattice. The increase of band gap can be ascribed to the reduction of defects or impurities that give rise to intermediary energy levels in the band gap region of disordered BZT films. The films annealed at 400 °C for 1, 2,

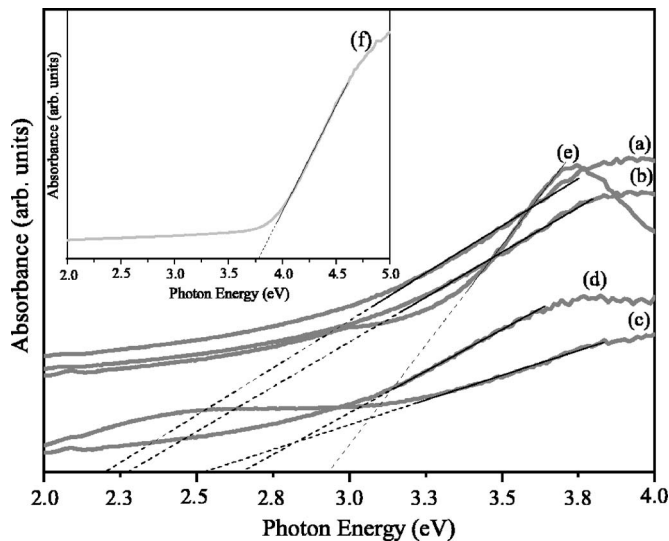a)Electronic mail: laeciosc@bol.com.br

FIG. 1. UV-vis absorbance spectra for the BZT thin films annealed at 400 °C for (a) 1 h, (b) 2 h, (c) 4 h, (d) 8 h, and (e) 16 h. Inset shows the BZT film annealed at 700 °C for (f) 2 h in oxygen atmosphere.
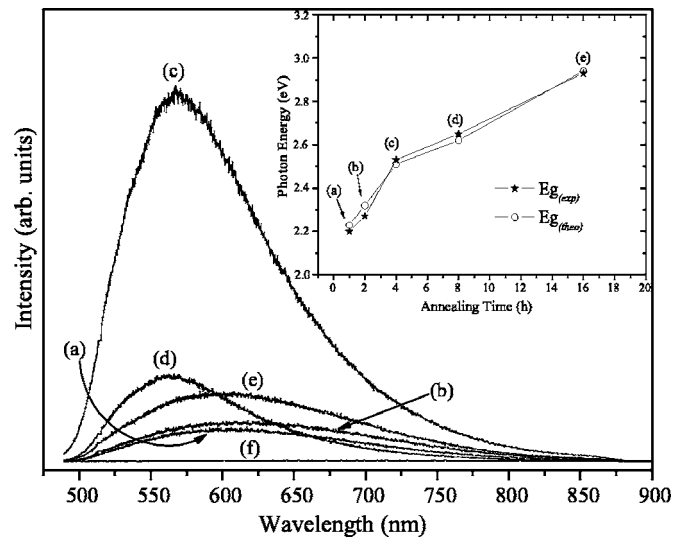

FIG. 2. PL spectra of BZT thin films annealed at 400 °C for (a) 1 h, (b) 2 h, (c) 4 h, (d) 8 h, and (e) 16 h and (f) annealed at 700 °C for 2 h in oxygen atmosphere. Inset shows experimental $E_{g(exp)}$ and theoretical $E_{g(theo)}$ gap energies for the films annealed at 400 °C for different times.

4, 8, and 16 h showed a similar spectral dependence to that found in amorphous semiconductors such as silicon and insulators [see Figs. 1(a)–1(e)], while the BZT film annealed at 700 °C showed a typical band for crystalline materials. In addition, in the high energy region of the absorbance curve [see Fig. 1(f)], the optical band gap energy is related to the absorbance and to the photon energy by Wood and Tauc.[18] In the disordered films, the absorbance measurements suggest a nonuniform band gap structure with a tail of localized states. The optical energy band gap is related to the absorbance and to the photon energy by Eq. (1):

$$h\nu\alpha \propto (h\nu - E_g^{opt})^2, \qquad (1)$$

where α is the absorbance, h is the Planck constant, ν is the frequency, and E_g^{opt} is the optical band gap.

Table I illustrates the charge variations for each $[TiO_6]$ and $[ZrO_5]$, after displacement of Zr to deformation of $Ba(Zr_{0.25}Ti_{0.75})O_3$, and the charge difference between the individual clusters of periodic models for theoretical gap energies. Theoretical calculations indicate that the atom generated intermediary energy levels in the band gap, increasing the trapping of electrons and holes. The trapping of charges is the condition for a good PL emission. This accordance between experimental and theoretical gap energy results illustrates the reliability of our distorted model.

Figure 2 illustrates the PL spectra recorded at room temperature for the BZT thin films annealed at 400 °C for different times and annealed at 700 °C for 2 h in oxygen atmo-

sphere. The excitation line of argon ion laser was 514.5 nm ($\cong$2.41 eV). The PL emission is associated with the structural order-disorder degree. A broad intense luminescence in the visible region (yellow) with a maximum at about 568 nm was observed. The emission band profile is a typical multiphonon process, i.e., a system in which the relaxation occurs by several paths, involving the participation of numerous levels within the perovskite band gap.

The presence of several delocalized energy levels in the band gap and the structural disorder are responsible for the weak PL behavior observed in Figs. 2(a) and 2(b). The increase of annealing time reduces the oxygen vacancies and decrease the structural disorder, due to the presence of $[ZrO_5]$–$[TiO_6]$ clusters leading to an increase of PL intensity [Fig. 2(c)]. Fig. 2(d) and (e) illustrates that the PL intensity reduces with the increase of annealing time due the formation of the $[[ZrO_6]$–$[TiO_6]]$ clusters as can be observed by the increase of optical gap (see inset in Fig. 2). When the annealing temperature is increased, ordered $[ZrO_6]$–$[TiO_6]$ clusters are obtained and the charge transference between them [Figs. 1(f) and 2(f)] is inhibited. Experimental and theoretical band gap results strongly indicate that PL is directly linked to the optical tail existing in the disordered films (see inset in Fig. 2). Absorbance measurements associated with the PL properties of noncrystalline BZT thin films lead to a nonuniform band gap structure with a tail of delocalized levels and mobile edges. The nature of these exponential optical

TABLE I. Charge variations for the $[TiO_6]$, $[ZrO_5]$, and $[TiO_6]$–$[ZrO_5]$ clusters and experimental gap energy $E_{g(exp)}$ in axis x (Fig. 1) and theoretical gap energy $E_{g(theo)}$ for $Ba(Zr_{0.25}Ti_{0.75})O_3$ thin films.

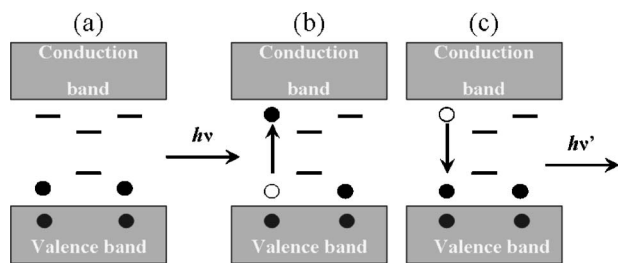| Displacement in axis z (Å)	Charge of the $[TiO_6]$ (e^-)	Charge of the $[ZrO_5]$ (e^-)	Charge difference $[TiO_6]$–$[ZrO_5]$ (e^-)	$E_{g(exp)}$ (eV)	$E_{g(theo)}$ (eV)
0.75	−2.37	−1.98	−0.39	2.20	2.23
0.70	−2.35	−1.97	−0.38	2.27	2.32
0.50	−2.26	−1.90	−0.36	2.53	2.50
0.40	−2.20	−1.85	−0.35	2.65	2.62
0.20	−2.06	−1.74	−0.32	2.93	2.94
0.00	−1.93	−1.60	−0.33	3.78	3.70

FIG. 3. Wide band model: (a) before excitation, (b) excitation→formation of STE, and (c) after excitation→recombination of e^- and h^0.

edges and tails is probably associated with defects promoted by the disordered structure.

A wide band model of photoluminescence process in Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$ thin films is shown in Fig. 3. The localized levels are energetically distributed being able to excite the trapped electrons [see Fig. 3(a)]. According to the hypothesis of Korzhik *et al.*[19] there are vacant localized states linked to local defects such as oxygen vacancies in the band gap above the valence band and below the conduction band.[6] In the model of Leonelli and Brebner[20] some electrons are promoted to the conduction band by absorption of photon, creating small polarons. The polarons interact with holes trapped in the crystal (defects or impurities) and form self-trapped excitons (STEs) that contribute to the visible PL emission [see Fig. 3(b)]. The short and intermediate range structural defects generate localized states in the band gap and inhomogeneous charge distribution in the cell, thus allowing the trapping of electrons. Furthermore, it will also leave an electron hole that can flow as current exactly like a physical charged particle. Figure 3(c) describes the recombination process in which an electron of conduction band loses its energy and reoccupies the energy levels of an electron hole (h^0) in the valence band.

This model suggests that the increase of annealing time reduces the surface, creating electron-captured oxygen's vacancies, according to Eq. (2):

$$(ZrO_5 \cdot V_o^z) + \frac{1}{2}O_2 \rightarrow ZrO_2, \qquad (2)$$
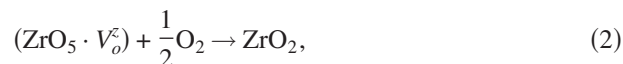
where $V_O^z = V_O^*$, V_O, or $V_O^{..}$.

In the complex, $(ZrO_5 \cdot V_O^z)$ cluster acts as hole traps, while the V_O^z vacancy tends to trap electrons ($z = \cdot$ or $\cdot\cdot$) or holes ($z = ^*$). Previous studies of our group assume the existence of TiO$_6$ and distorted ZrO$_6$ clusters in lattice before complete film crystallization. A random mixture of TiO$_6$ and $(ZrO_5 \cdot V_O^z)$ complex octahedral linked by barium ions is found in this case. The displacements performed in axis z for Zr atom, such as breaking of the bonds (Zr–O) and formation of vacancy V_O^z, give the band gap energy approaching experimental data. In BZT, the transport properties such as electrical conductivity and photoluminescence are governed by electrons, as well as some phenomena are related to holes.

In conclusion, intense visible photoluminescence (around 568 nm) was observed for the Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$ thin films and is caused by structural defects such as [ZrO$_5$]–[TiO$_6$] clusters. The oxygen vacancies play an important role on the PL emission via a recombination of electrons in oxygen vacancies (V_O^z) with photoexcited holes in the valence band. Our theoretical models are consistent with the experimental data and confirm that the localized levels in the band gap are controlled by the order-disorder degree in the lattice.

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