

## STRUCTURE EFFECTS ON THE OPTICAL PROPERTIES OF THIN (PbLa)TiO<sub>3</sub> FILMS

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**Abstract**— Amorphous thin films of Pb<sub>1-x</sub>La<sub>x</sub>TiO<sub>3</sub> (with x=0, 13 and 27 mol %) were prepared by the polymeric precursor method and deposited by spin coating on glass substrates. The films were characterized by X-ray diffraction (XDR) and scanning electron microscopy (SEM) and the band gap energy of the amorphous PLT films was calculated from the UV-VIS spectra. The obtained values were compared to that theoretically calculated. The observed decrease of the band gap was attributed to increased density of defects in the amorphous structure. Furthermore photoluminescence (PL) at room temperature was observed for thin (PbLa)TiO<sub>3</sub> films.

**Keywords**— thin films, optical properties, amorphous, titanate and photoluminescence.

### I. INTRODUCTION

Preparation of thin films by deposition of a chemical solution is a promising process for the fabrication of optic-electronic devices (Ridley *et al.*, 1999). Chemical solution deposition offers a wide variety of applications, including ferroelectric thin films, high-density optical data storage or semiconductors (Pontes *et al.*, 2000a; and Maeda *et al.*, 1993). In addition, the chemical solution process allows to prepare amorphous compounds that cannot be prepared by the usual melting processes.

Pizani *et al.* (2000) and Leite *et al.* (2000a) reported intense room temperature PL for amorphous PbTiO<sub>3</sub> (a-PT) powders and thin films deposited on Si (100). In these studies, a simple chemical method was used to process powders and thin films at low temperatures (T < 400 °C). The PL observed in a-PT showed a strict relationship with disorder in the perovskite structure. Study of the a-PT structure by X-ray absorption near edge structure (XANES) showed that these compounds are basically formed by six-fold oxygen-Ti coordination (TiO<sub>6</sub>-octahedra) and fivefold oxygen-Ti coordination (TiO<sub>5</sub>-square-base pyramid) as it is reported by Pontes *et al.* (2000b).

Firstly, a simple water-based chemical process was used, allowing amorphous titanates to be processed at temperatures as low as 250°C in the form of thin films

or particles. Secondly, theoretical and experimental results suggest that amorphous titanate is composed of a Ti-O network.

Recently our group demonstrated that amorphous titanates (ATiO<sub>3</sub>, with A=Pb, Ca, Sr and Ba), processed by a soft chemical process called the polymeric precursor method, displayed intense PL at room temperature (Pizani *et al.*, 2000; and Leite *et al.*, 2000a).

Optical properties like PL are not usually observed, but due to their interesting PL properties, amorphous materials of the ATiO<sub>3</sub> type, such as Pb(Zr,Ti)O<sub>3</sub> (PZT), BaTiO<sub>3</sub> (BT) and SrTiO<sub>3</sub> (ST) have been the target of several studies (Leite *et al.*, 2000a; Pontes *et al.*, 2000b; and Leite *et al.*, 2000b).

Investigations of the optical absorption edge give information on the band structure of a material and its changes, which are especially important for crystals showing ferroelectric phase transitions (Yakubovs *et al.*, 1974).

The absorption edge of amorphous semiconductors is structure sensitive, on the other hand, the purity and method of preparation directly influence the optical absorption, particularly in the case of thin films (Wood and Tauc, 1972).

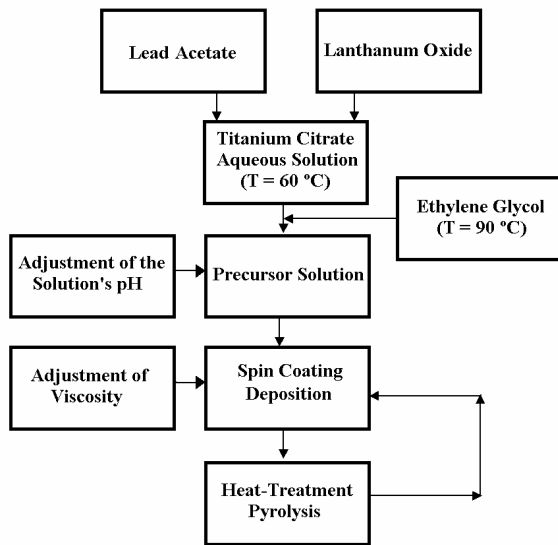
The absorption spectra of amorphous semiconductors at different photon energies suggest three different parts. Two of them are similar in different materials and are easily reproducible. The third part (absorption edge) is a structure-sensitive and a characteristic of amorphous semiconductors (Wood and Tauc, 1972).

This report presents the preparation of thin amorphous PLT films and studies their band gap energy calculated from UV-VIS spectra and compared to that determined by theoretical calculations. The PL intensity is also presented as a function of the Pb cation substitution by La in the pure PbTiO<sub>3</sub> lattice.

### II. METHODS

Pb<sub>1-x</sub>La<sub>x</sub>TiO<sub>3</sub> thin films, in which x is the amount of La that substitutes Pb (x = 0, 13 and 27 in mol%) were prepared by the polymeric precursor method, as it is schematized in Fig. 1. The polymeric precursor method (Le-

ite *et al.*, 2000b.) is based on the chelation of metal cations by citric acid in water. This citrate solution is mixed with ethylene glycol to promote polymerization through a polyesterification reaction. The formed polymeric precursor can be used to prepare thin films or powders. The heat-treatment temperature of the polymeric precursor must be sufficient to promote the polymer pyrolysis, but not the crystallization. The resins with a 20 MPa·s viscosity were deposited on glass substrates by spin-coating at 6000 rpm for 30 s. After the spin coating the films were dried at 150 °C on a hot plate for 15 min to remove residual solvents. After this preannealing, the films were submitted to a further heat-treatment in an oxygen atmosphere at 200 °C for 8 h, 300 °C for 4 h or 500 °C for 4h.



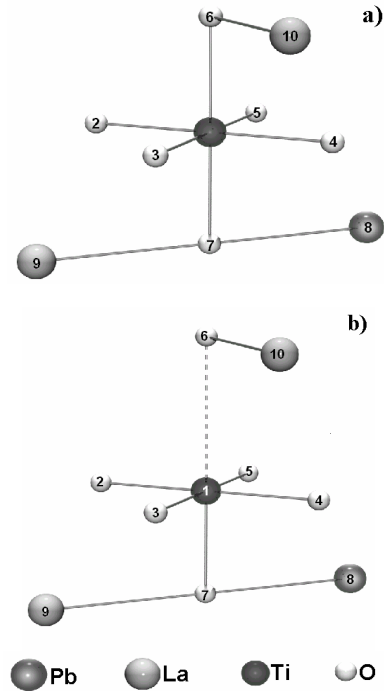
**Figure 1:** Flowchart of the thin film preparation by the polymeric precursor method.

The films were characterized by XRD (Siemens, D5000), SEM (Zeiss, DSM940A). The PL measurements were made in a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system excited with the 457.9 nm argon laser line. All the measurements were taken at room temperature. The values of PL intensity were normalized to the film thickness.

The UV-visible measurements were taken in a spectrophotometer Cary - 5G in the wavelength range of 300 - 800 nm.

The computational calculations were carried out with the GAUSSIAN98 program package (Frish *et al.*, 1998; and Leite *et al.*, 2004c). The *ab initio* Restrict Hartree-Fock (RHF) level of the theory was employed with the standard basis sets 6-31G(d) and 6-31G(f), (Harihara and Pople, 1973) for oxygen and titanium atoms, respectively, and LanL2D (Hay *et al.*, 1985) for lead and lanthanum atoms. Two cluster models were selected and optimized to simulate crystalline and amorphous  $\text{PbLa}_2\text{TiO}_6$  cluster. The crystalline (c-PLT) cluster was optimized starting from crystallographic data and the amorphous (a-PLT) cluster was obtained

from the crystalline structure, by applying a deformation of 2.0 Å between the Ti(1) and O(6) centers, as indicated in Fig. 2 (Farrugia, 1997). This approach was chosen because it is particularly suitable to study local phenomena. We associated the top of the valence band to the HOMO energy (highest occupied molecular orbital) and the bottom of the conduction band to the LUMO energy (lowest unoccupied molecular orbital) of the studied systems. The HOMO-LUMO difference was set to correspond to the optical band gap. The partial density of states (DOS) was obtained for the two clusters.

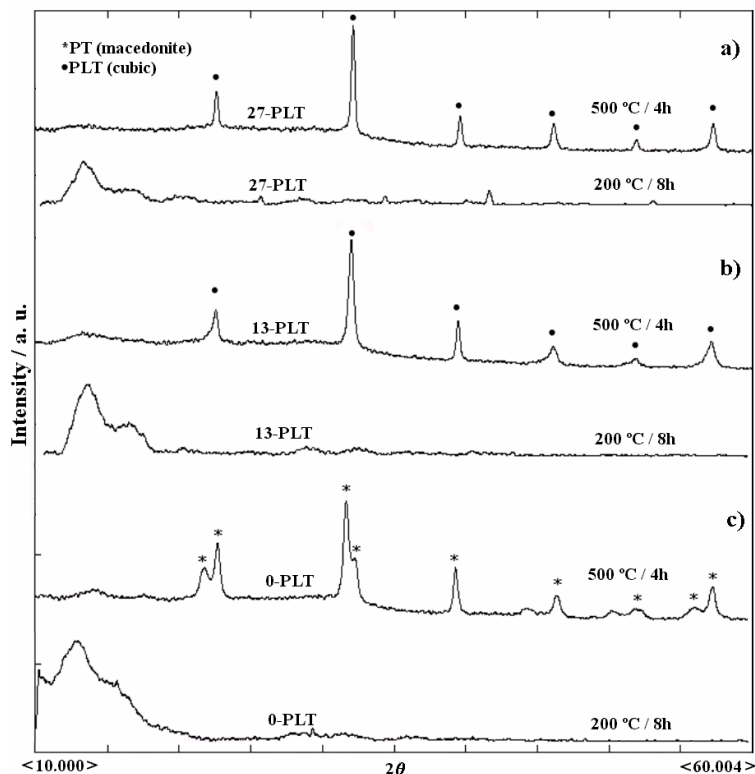


**Figure 2:** Schematic representation of the clusters of  $(\text{PbLa}_2)\text{TiO}_6$ : (a) crystalline and (b) amorphous.

### III. RESULTS AND DISCUSSION

The XRD patterns of the thin films deposited on glass substrates and heat-treated at 200 °C for 8 h and 500 °C for 4 h are presented in Fig. 3. Diffuse patterns are observed for samples obtained after at 200 °C for 8 h, indicating the formation of an inorganic amorphous precursor after the pyrolysis process. The crystallization of PLT can be observed after 4 h at 500 °C (see Fig. 3). The 0-PLT crystalline film (Fig. 3 c) showed the characteristic peaks of the tetragonal phase (macedonite), with the (001) peak at  $2\theta = 21.393^\circ$  and the (002) peak at  $2\theta = 43.56^\circ$  while the crystalline 13-PLT and 27-PLT films presented a cubic phase (Fig 3 b and a).

Figure 4 demonstrates the SEM micrographs of the cross sections of the thin films deposited on glass substrates annealed at 200 °C for 8 h. This technique allows an estimation of the film thickness given in Table 1. They also display the uniform interfaces between the substrates and the thin films. In these films no diffusion process between film layer and glass substrate was observed.



**Figure 3:** XRD pattern of the amorphous and crystalline thin films of  $(\text{PbLa})\text{TiO}_3$ , deposited on glass substrate: a) 27-PLT, b) 13-PLT and c) 0-PLT.

**Table I:** Annealing temperature and energy band gap (by UV-Vis) of thin films of PLT on glass substrates.

Thin films	Annealing Temperature ( $^{\circ}\text{C}$ )	Number of Layers	$E_{\text{gap}}$ (eV)		Thickness (nm)
			Exp.	Theor.	
0-PLT	200 (amorphous)	2	3,336	3,000	301
	500 (Crystalline)	3	3,400	4,320	
13-PLT	200 (amorphous)	2	3,293	3,050	194
	500 (Crystalline)	3	3,530	4,330	
27-PLT	200 (amorphous)	2	3,300	3,050	354
	500 (Crystalline)	3	3,530	4,330	

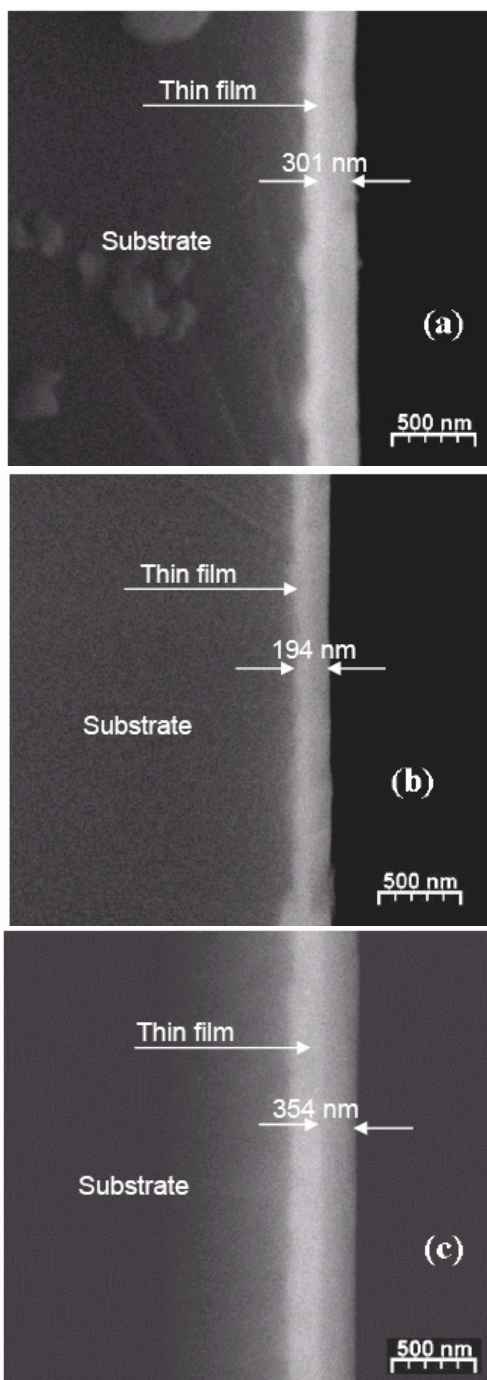
Figure 5 shows the UV/Vis transmittance spectra and the energy dependence of the absorbance ( $\alpha$ ) for the amorphous  $(\text{PbLa})\text{TiO}_3$  ( $a$ -PLT) heat treated at  $200^{\circ}\text{C}$  for 8 h and for the crystalline  $(\text{PbLa})\text{TiO}_3$  ( $c$ -PLT) heat-treatment at  $500^{\circ}\text{C}/4$  h. The  $a$ -PLT showed a spectral dependence of absorbance similar to that found in amorphous semiconductors such as amorphous silicon ( $a$ -Si) and insulators, while the  $c$ -PLT showed a typical interband transition of crystalline materials. The optical difference of similar amorphous semiconductors and crystalline films were discussed elsewhere (Eglitis *et al.*, 2004). In addition, in the high energy region of the absorbance curve (Fig. 5c) the optical energy band gap is related to the absorbance, allowing its calculation by the so-called Tauc method (Wood and Tauc, 1972). The energy band gap of the crystalline and amorphous  $\text{PbTiO}_3$  (PT) was calculated to be  $3.40$  eV and  $3.35$  eV, respectively. These results, demonstrated in Table 1, 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 structural and thermal disorder in the lattice of the PT and PLT samples.

The optical band gap derived from the UV-visible spectroscopy measurement (experimental gap) and the theoretical calculations of the band gap, corroborate that the amorphous material is a significant deformation of the crystalline state, suggesting modifications in the electronic structure, between the crystalline and amorphous films, which may be responsible for the PL observed for the amorphous films at room temperature (Fig. 6), which is influenced by the lanthanum concentration ( $\text{La} = 0, 13$  and  $27$  mol %). It was detected that the addition of La shifts the luminescence band towards higher wavelengths (lower energies), yielding an intense yellow luminescence.

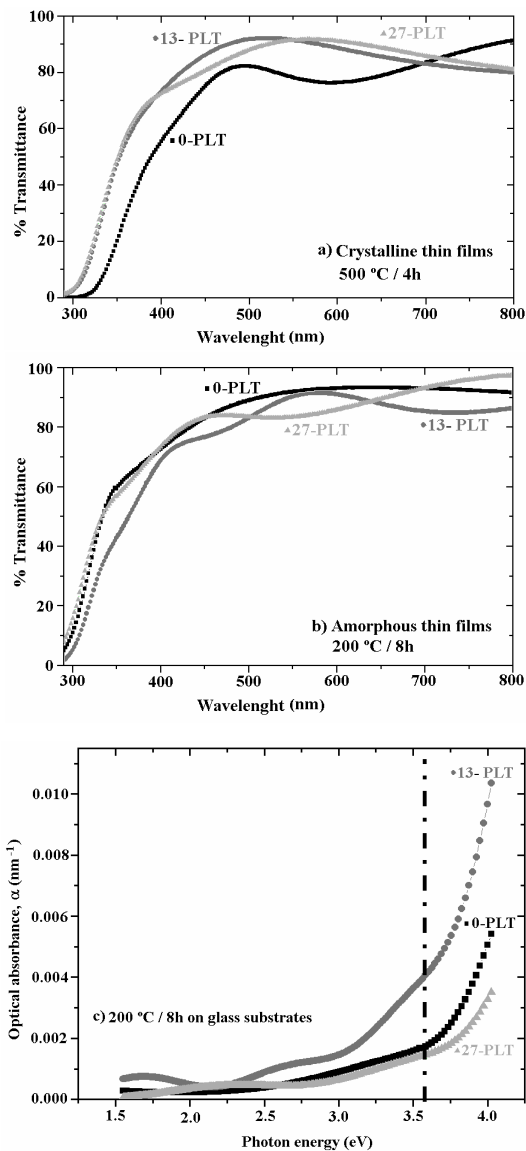
Figure 6 also demonstrates the PL observed for the amorphous PT and PLT thin films with an exciting wavelength of  $488.0$  nm at room temperature, showing a characteristic broad and intense luminescence in the visible region for amorphous materials.

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 may be associated with defect states promoted by the disordered structure of the  $a$ -PLT. The absorbance measurements, associated with the photoluminescence characterization of  $a$ -PLT semiconductor, suggest a non-uniform band gap structure with a tail of localized states and mobile edges. On the other hand, our UV/Vis absorption results are associated with localized energy states in the band gap. We believe that the PL observed in these  $a$ -PLT semiconductors arises from a radiative recombination between trapped elec-

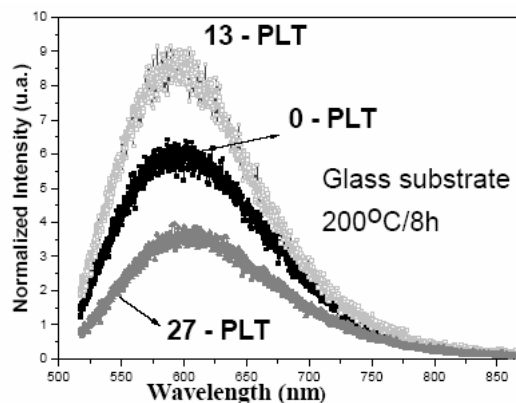
trons and trapped holes in tail and gap states. In addition, experimental results obtained by XANES revealed the coexistence of two kinds of Ti coordination in the *a*-PLT, namely, fivefold oxygen Ti coordination (TiO<sub>5</sub>-square base pyramid) and sixfold oxygen Ti coordination (TiO<sub>6</sub> octahedron). In our opinion, the existence of a fivefold oxygen Ti coordination is indicative of a Ti-O network in the *a*-PLT samples and the charge of the Pb and La cations must be compensated by negative charged non-bridging oxygen (NBO).



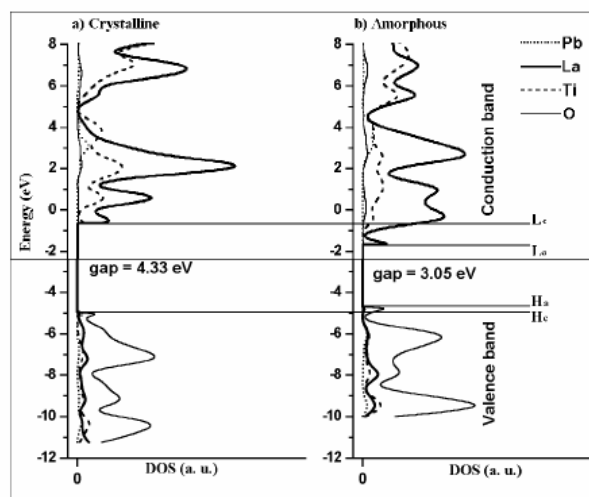
**Figure 4:** SEM images of PLT films deposited on glass substrates, after fracture process to analysis, annealed at 200 °C for 8 h, obtained using secondary electrons (a) 0-PLT, (b) 13-PLT and (c) 27-PLT.



**Figure 5:** The wavelength dependence of the optical transmittance of PLT. a) crystalline thin films annealed at 500 °C during 4 h b) amorphous thin films annealed at 200 °C during 8 h c) Plot of the optical absorbance ( $\alpha$ ) as a function of the photon energy, amorphous films.



**Figure 6:** Normalized PL intensity of the PLT thin films with (a) 0, (b) 13 and (c) 27 La mol% on glass substrates and annealed at 200 °C/8h.



**Figure 7:** Total density of states for the atoms Pb, La, O and Ti for the investigated clusters. (a) crystalline (b) amorphous.

Additional the mechanism that leads to changes in the PL intensity as function of substitution of Pb in structural PLT films by La is not yet clearly known, but it can be associated with defect concentrations, which are related to thermal treatment and material ordering, (Rangel *et al.*, 2002).

The results of theoretical calculations indicate that the formation of an amorphous cluster through the displacement of O(6) may introduce delocalized electronic levels in the forbidden gap of the c-PLT cluster in the regions delimited by  $H_c$  and  $H_a$  (HOMO for the crystalline and amorphous clusters, respectively) - hereinafter called  $\Delta$ HOMO and  $L_a$  and  $L_c$  (LUMO of the amorphous and crystalline clusters, respectively) - hereinafter called  $\Delta$ LUMO. The delocalized electronic levels are ascribed to the formation of a tail in the emission spectrum (Fig. 5 and Fig. 7). The crystalline cluster presents a higher band gap than the amorphous cluster, which is in agreement with the experimental results, observed by the absorbance spectral data. The delocalized electronic levels in the valence and conduction bands may introduce the photoluminescence properties in the amorphous cluster.

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

The calculation using the linear combination of atomic orbitals method (Kahn and Leyendecker, 1964), 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.

Figure 7 also shows the total density of states (DOS) for the atoms Pb, La, Ti and O. The optical band gap and the density of states were calculated using the cluster method. Most of the contribution to the conduction band of PLT comes from the lanthanum atoms whereas the oxygen atoms contribute more to the formation of the valence band (see Fig. 7). It was verified that the band gap of the crystalline structure is larger than

that presented by the amorphous structure. Besides, new electronic levels appear in  $\Delta$ LUMO and  $\Delta$ HOMO (see Fig. 7). These new levels appear to be related to deformations in the structure of the investigated model.

The room temperature PL, identified in the amorphous PLT materials, which are prepared by low-cost chemical methods and which can be processed as thin films, is an important characteristic for optical-electronic devices.

#### IV. CONCLUSIONS

The optical results show that the values of band gap energy for the crystalline films are higher than those for the amorphous films. The theoretical results confirm the experimental observation and suggest the formation of new levels due to deformation of the structure.

It is believed that the La incorporation into the PT amorphous lattice results in significant changes in the optical band gap and the density of states. This interpretation corroborates the PL results for PLT samples, since the PL efficiency decreased with the La addition.

In summary, we have engaged a detailed discussion of experimental results and theoretical calculations about the role of defects in the visible photoluminescence in amorphous PLT thin films. The experimental results showed that the visible PL emission in amorphous material is directly related to the exponential optical edges and tails. The nature of these exponential optical edges and tails may be associated with defects promoted by the disordered structure of the amorphous material. In addition, the results of theoretical calculations indicate that the formation of fivefold coordination through the displacement of O(6) may introduce delocalized electronic levels in  $\Delta$ HOMO and  $\Delta$ LUMO. These delocalized electronics levels are ascribed to the formation of a tail in the absorbance spectrum curve.

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Received: May 24, 2006.

Accepted: December 4, 2006.

Recommended by Subject Editor Walter Ambrosini.