EFFECT OF THE STRUCTURES ON THE OPTICAL PROPERTIES OF (PbLa)TiO₃ THIN FILMS

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Received 29 March 2003

Abstract. Amorphous thin films of Pb₁₋ₓLaₓTiO₃ (with x = 0, 13 and 27 mol%) were prepared by the polymeric precursor method and deposited on glass substrates by spin coating and characterized by X-ray diffraction (XDR) and scanning electron microscopy (SEM). The band gap energy of the amorphous PLT films was calculated by the UV-VIS spectra. Their values were compared with the values obtained by means of theoretical calculation. The decrease in the band gap was attributed to the high defect density of the amorphous structure. Also photoluminescence (PL) at room temperature was reported in the (PbLa)TiO₃ thin films.

PACS number: 78.66.-w
1 Introduction

Preparation of thin films by deposition of a chemical solution is a particularly promising process for the fabrication of optic-electronic devices [1]. Chemical solution deposition offers a wide variety of applications, including ferroelectric thin films, high-density optical data storage and semiconductors [2,3]. In addition, the chemical solution process allows obtaining amorphous compounds that usually cannot be prepared by melting processes.

Pizani et al. [4] and Leite et al. [5] recently reported intense room temperature PL of amorphous PbTiO$_3$ (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 ($T < 400^\circ$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 formed basically by sixfold oxygen-Ti coordination (TiO$_6$-octahedra) and fivefold oxygen-Ti coordination (TiO$_5$-square-base pyramid) [5].

Firstly, a simple water-based chemical process was used, allowing amorphous titanates to be processed at temperatures as low as 250$^\circ$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.

Our group has recently demonstrated that amorphous titanates (ATiO$_3$, where A = Pb, Ca, Sr and Ba), processed by a soft chemical process called the polymeric precursor method, displayed intense PL at room temperature [4,5].

Other optical properties like PL are not usually observed [5], but amorphous materials of the ATiO$_3$ type, such as Pb(Zr,Ti)O$_3$ (PZT), BaTiO$_3$ (BT) and SrTiO$_3$ (ST) have been the target of recent studies, due to their interesting PL properties [4,6,7].

Investigations of the optical absorption edge give important information on the band structure of a material and its changes, which are especially interesting for crystals having ferroelectric phase transitions [8].

The absorption edge of amorphous semiconductors is structurally sensitive, in other hands, the purity and method of preparation reflect directly on the optical absorption, particularly in the case of thin films [9].

The absorption patterns 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 property [9], which is a typical characteristic of the amorphous semiconductors.

This report presents the preparation of PLT thin films and studies the band gap energy of amorphous PLT films, calculated by UV-VIS spectra and compare them with the theoretical calculations. The PL intensity is also presented as a function of the Pb cation substitution by La in the pure PbTiO$_3$ lattice.
2 Materials, Methods and Computational Calculations

\( \text{Pb}_{1-x}\text{La}_x\text{TiO}_3 \) 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. The polymeric precursor method [10] is based on the chelation of cations (metals) by citric acid in a water solution. After the synthesis of the citrate solution, it is mixed with ethylene glycol to promote polymerization through a polyesterification reaction. The polymeric precursor formed during the polymerization step 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 the spin-coating technique. The rotation speed and spin time were fixed at 6000 rpm and 30 s, respectively. The thin films were dried at 150°C after the spin coating on a hot plate for 15 min to remove residual solvents. After the preannealing, the films were submitted to a heat-treatment. The three alternatives were 200°C/8 h, 300°C/4 h and 500°C/4 h, all of them in an oxygen atmosphere (Fig. 1).

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 by the film thickness.

\[ \text{Lead acetate} \quad \text{Lanthanum oxide} \]

\[ \text{Titanium citrate aqueous solution } (T = 60°C) \]

\[ \text{Ethylene glycol } (T = 90°C) \]

\[ \text{Adjustment of the solution’s pH} \quad \text{Precursor solution} \]

\[ \text{Heat treatment pyrolysis} \]

\[ \text{Adjustment of viscosity} \quad \text{Spin coating deposition} \]

Fig. 1. Flowchart of the thin film preparation by the polymeric precursor method.
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[11] program package. The \textit{ab initio} Restrict Hartree-Fock (RHF) level of the theory was employed with the standard basis sets 6-31 G(d) and 6-31 G(f) [12] for oxygen and titanium atoms, respectively, and LanL2DZ [13] for lead and lanthanum atoms. Two cluster models were selected and optimized to simulate crystalline and the amorphous cluster (PbLa$_2$)$_6$TiO$_6$. The crystalline (c-PLT) cluster was optimized starting from crystallographic data and the amorphous (a-PLT) cluster was obtained from the crystalline structure, by means of applying a deformation of 2.0 Å between the Ti(1) and O(6) centers, (Fig. 2) [14]. This approach was chosen because it is particularly suitable to study local phenomena. We have 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.

3 Results and Discussion

The XRD patterns of the thin films deposited on glass substrates and heat-treated at 200°C for 8 hours are presented in Fig. 3. A diffuse pattern can be observed for the heat-treatment at 200°C for 8 hours, indicating the formation of an inorganic amorphous precursor after the pyrolysis process. The crystallization phase of PLT can
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Fig. 3. XRD pattern of the amorphous and crystalline thin films of (PbLa)TiO$_3$, deposited on glass substrate: (a) 27-PLT, (b) 13-PLT, and (c) 0-PLT.

be observed at a temperature of 500°C (Fig. 3). The O-PLT crystalline film showed the characteristic peaks of the tetragonal phase (macedonite), with the (001) peak at 2$\theta$ = 21.393° and the (002) peak at 2$\theta$ = 43.56°. The 13-PLT and 27-PLT films presented a cubic phase.

Fig. 4 (a, b and c) correspond to the micrographs obtained by SEM 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 (Table 1). It also allows to display the uniform interfaces between the substrates and the thin films.

Fig. 5 shows the UV/Vis transmittance spectra and the wavelength the dependence of absorbance ($\alpha$) for the amorphous (PbLa)TiO$_3$ (a-PLT) heat treated at 200°C for 8 h and for the crystalline (PbLa)TiO$_3$ (c-PLT) heat-treatment at 500°C/4 h. The a-PLT
Fig. 4. SEM images of PLT films deposited on glass substrates, annealed at 200°C for 8 h, obtained using secondary electrons (a) 0-PLT, (b) 13-PLT, and (c) 27-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. In addition, in the high energy region of the absorbance curve (shown in Fig. 5c) the optical energy band gap is related to the absorbance is related to the band gap, allowing its calculation by the so-called Tauc method [9]. The energy band gap of the crystalline and amorphous PbTiO₃ (PT) was calculated to be 3.40 eV and 3.35 eV, respectively. These results (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 disorder, structural and thermal, 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 in the amorphous material there is a significant deformation of the crystalline state, which suggests modifications in the electronic structure, between the crystalline and amorphous films, which may be responsible to the PL observed at room temperature for the amorphous films, Fig. 6. The lanthanum concentration (La = 0, 13 and 27 mol%) influences the PL spectra reflects. It was detected that the addition of La shifts the luminescence band towards higher wavelengths (lower energies), yielding an intense yellow luminescence.

Table 1. Annealing temperature and band gap energy (by UV-Vis) of thin films of PLT on glass substrates

<table>
<thead>
<tr>
<th>Thin films</th>
<th>Annealing temperature (°C)</th>
<th>Number of layers</th>
<th>( E_{\text{gap}} ) (eV)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-LPT</td>
<td>200 (amorphous)</td>
<td>2</td>
<td>3.35</td>
<td>301</td>
</tr>
<tr>
<td></td>
<td>500 (crystalline)</td>
<td>3</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>13-PLT</td>
<td>200 (amorphous)</td>
<td>2</td>
<td>3.18</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>500 (crystalline)</td>
<td>3</td>
<td>3.53</td>
<td></td>
</tr>
<tr>
<td>27-PLT</td>
<td>500 (crystalline)</td>
<td>3</td>
<td>3.53</td>
<td></td>
</tr>
</tbody>
</table>
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Fig. 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.

Fig. 6 shows the PL observed in the amorphous PT and PLT thin films with an exciting wavelength of 488.0 nm at room temperature. PL characteristics showed a broad 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 nonuniform 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 electrons 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$_5$-square base pyramid) and sixfold oxygen Ti coordination (TiO$_6$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 for by negatively charged non-bridging oxygen (NBO).
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 (Figs. 5 and 6). The crystalline cluster presents a higher band gap than the amorphous cluster, what 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 in the amorphous cluster the photoluminescence properties.

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 by Kahn and Leyendecker [15], 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.

Fig. 6 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 atoms of oxygen are what more contribute to the formation of the valence band (Fig. 6). It was verified that the band gap of the crystalline structure is larger than that presented by the amorphous structure. Besides, new electronic levels

![Fig. 6. Total density of states for the atoms Pb, La, O and Ti for the investigated clusters: (a) crystalline, (b) amorphous.](image-url)
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Fig. 7. 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.

appear in ΔLUMO and ΔHOMO (Fig. 6). 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 can be processed as thin films, is an important characteristic for optical-electronic devices.

4 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 applied to 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 the 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.

Acknowledgements

The authors acknowledge the financial support of the following Brazilian research
funding agencies: FAPESP/CEPID, CAPES/PICDT, CNPq, PRONEX.

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tailogr. 19 (1975) 4.