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The origin of photoluminescence in amorphous lead titanate

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We discuss the nature of visible photoluminescence at room temperature in amorphous lead titanate in the light of the results of recent experimental and theoretical calculations. Experimental results obtained by XANES and EXAFS revealed that amorphous lead titanate is composed of a Ti-O network having fivefold Ti coordination and NBO-type (non-bridging oxygen) defects. These defects can modify the electronic structure of amorphous compounds. Our calculation of the electronic structure involved the use of first-principle molecular calculations to simulate the variation of the electronic structure in the lead titanate crystalline phase, which is known to have a direct band gap, and we also made an in-depth examination of amorphous lead titanate. The results of our theoretical calculations of amorphous lead titanate indicate that the formation of fivefold coordination in the amorphous system may introduce delocalized electronic levels in the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital). A comparison of the experimental and theoretical results of amorphous compounds suggests the possibility of a radiative recombination (electron-hole pairs), which may be responsible for the emission of photoluminescence. © *2003 Kluwer Academic Publishers*

1. Introduction

The development of new semiconductor materials with wide band gaps (2.0–4.0 eV) may give rise to new optoelectronic devices, particularly to materials for application in the development of green or blue light emission diodes (LED) or laser diodes. In many optoelectronic devices, amorphous semiconductors can replace single crystal semiconductors, particularly when cost is an important factor.

Amorphous materials of the ABO_3 family (A and B are cations and O is the oxygen anion), such as $BaTiO_3$, $Pb(Zr,Ti)O_3$, and $SrTiO_3$, have recently attracted a good deal of attention due to their ferroelectric [1, 2] and electro-optical properties [3]. In crystalline form, ABO_3 compounds are typically wide band gap semiconductors. Photoluminescence in crystalline titanates [4] is well known, but this property has only recently been identified in amorphous titanate synthesized at low temperatures for thin film and powder [5, 6].

The optical properties of amorphous semiconductors are dominated by the presence of a tail in the optical absorption, which falls exponentially into a spectral region in which it is normally transparent in crystalline solids [7, 8]. The so-called Urbach edge is attributed to the presence of localized electronic states near the band edges of amorphous semiconductors [8]. This optical behavior is often observed in chalcogenide glasses and in tetrahedral (group IV) amorphous solids. Materials with this optical characteristic may present properties such as photoluminescence, electroluminescence, photodarkening and photoconductivity. This letter describes the optical characterization and theoretical study of amorphous $PbTiO_3$ (PT) particles processed by the Sol-Gel method [9, 10].

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2. Experimental

In this work, amorphous PT was synthesized by the polymeric precursor method. This method has been used to synthesize nanoparticles and thin films of several ferroelectric materials [9] and is based on the chelation of cations (metals) by a hydroxycarboxide acid, such as citric acid, in an aqueous solution. The citrate solution is then mixed with a glycol, such as ethylene glycol, to promote polymerization through a polyesterification reaction. This reaction occurs after the water has been eliminated, at temperatures ranging from 90°C–120°C. The polymeric precursors were calcined at 300°C for different lengths of time in an oxygen flow to promote pre-pyrolysis and total oxidation of the organic precursor.

The photoluminescence measurements were taken using a U1000 Jobin-Yvon double monochomator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelengths of an argon ion laser was used, with maximum output power of the laser kept within 20 mw. All the measurements were taken at room temperature. The spectral dependence of the optical absorbance of the crystalline and amorphous PT were taken at room temperature in the total reflection mode, using Cary 5G equipment. First-principle molecular calculation was used to simulate the variation of the electronic structure. GAUSSIAN98 package was used for these calculations.

3. Results and discussions

An X-ray diffraction (XRD) analysis of the PT particles calcined at a low temperature showed a pattern of amorphous material. A thermogravimetric analysis (TGA) of the powder showed no weight loss for calcination times longer than 10 h at 300°C, in an oxygen flow. These results suggest that an inorganic amorphous material was formed.

Fig. 1 illustrates the spectral dependence of absorbance (a) for the amorphous $PbTiO_3$ (a-PT) heat treated at 300°C for 24 h and 26 h, and for the crystalline $PbTiO_3$ (c-PT). The a-PT showed a spectral dependence on absorbance similar to that found in amorphous semiconductors such as amorphous silicon (a-Si), while the c-PT showed a typical interband transition of crystalline materials. A small Urbach edge can be observed in the c-PT, which may be indicative of residual amorphous material or the result of poor crystallinity of the nanometric c-PT powder.

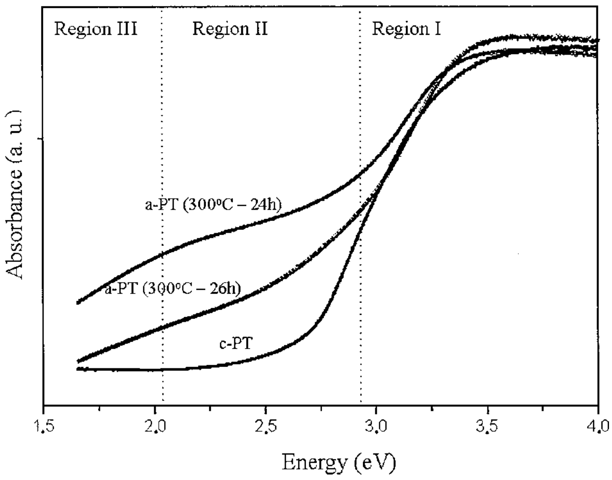

Figure 1 Spectral dependence of the absorbance for the a-PT heat treated at different lengths time and for the crystalline PT (c-PT).

Considering that the absorbance curve (Fig. 1) can be divided into three regions, these regions can be described by the following equation:

$$\text{Region I:} \quad h\nu\alpha \propto \left(h\nu - E_g^{opt}\right)^2 \tag{1}$$

$$\text{Region II:} \quad \alpha \propto e^{\frac{h\nu}{E_1}} \tag{2}$$

$$\text{Region III:} \quad \alpha \propto e^{\frac{h\nu}{E_t}} \tag{3}$$

where h is the Plank constant, ν is the frequency, E_g^{opt} is the optical band gap (Tauc gap), E_1 is a constant associated with the Urbach edge, and E_t is a constant associated with the tail. In general, $E_t > E_1$.

For the a-PT, Regions I, II and III were very well fitted by Equations 1, 2 and 3, while regions I and II of the c-PT were well fitted by Equations 1 and 2. Region III was not observed in the c-PT. The E_g^{opt} , E_1 and E_t values for the different samples are given in Table I. The different E_g^{opt} , E_1 and E_t values for the samples heat-treated for different lengths of time suggest that there is a direct relation between the amorphous structure and the electronic band gap structure. However, contrary to the case of a-Si, this relation is not simple. A linear relationship between E_g^{opt} and E_t was found in the a-Si [8]. The E_g^{opt} plot as a function of E_1, illustrated in Fig. 2, shows a nonlinear relation. It was also observed that increasing the E_1 value increases the E_g^{opt}.

Fig. 3 shows the PL behavior observed in the amorphous $PbTiO_3$ obtained with an exciting wavelength

TABLE I The E_g^{opt}, E_1 and E_t values for the a-PT heat treated for different lengths time and for the c-PT

Sample	E_g^{opt} (eV)	E_1 (eV)	E_t (eV)
c-PT	2.55	0.53	—
a-PT (treated during 26 h)	2.40	0.51	6.6
a-PT (treated during 24 h)	2.18	0.32	7.4

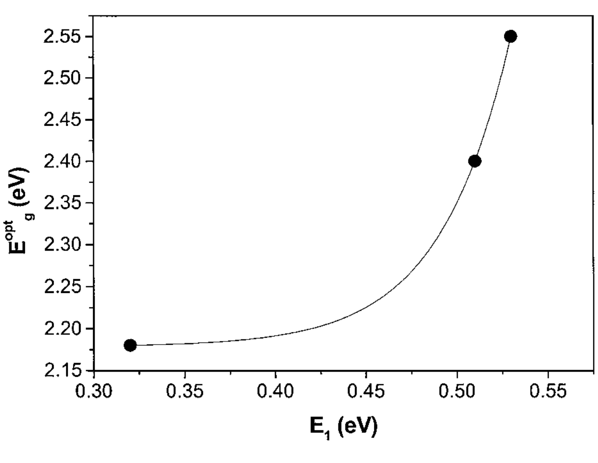

Figure 2 Optical gap E_g^{opt} as a function of E_1 for samples of a-PT heat treated for different lengths of time and for the c-PT.

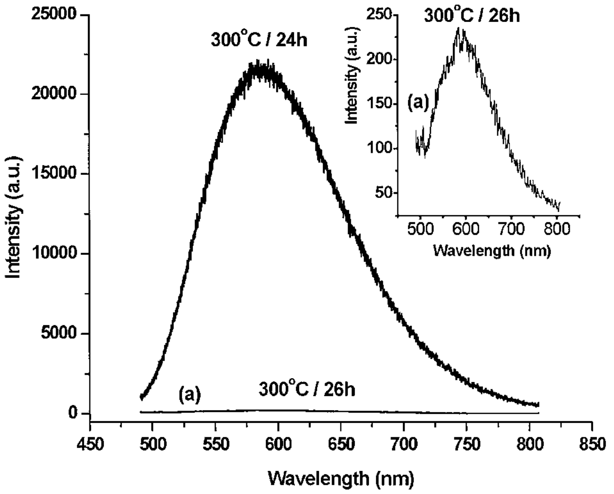

Figure 3 PL spectrum of the a-PT heat treated at different lengths time. The sample annealed during 26 h showed week PL intensity, as showed in the inset (a).

of 488.0 nm at room temperature. PL characterization showed a broad, intense emission spectrum in the visible region. As illustrated in the PL spectra of Fig. 3, when the annealing time was increased (under isothermal conditions), the intensity of PL decreased. When the material is ordered (in crystalline form), PL intensity is virtually zero at room temperature. This behavior matched the one observed in the spectral dependence of absorbance as a function of the annealing time.

The experimental above-described results strongly indicate that PL is directly related to the exponential optical edges and tail. The nature of these exponential optical edges and tail may be associated with defects promoted by the disordered structure of the amorphous $PbTiO_3$. The absorbance measurement, associated with the PL characterization of amorphous $PbTiO_3$ semiconductors, suggests a non-uniform band gap structure with a tail of localized states and mobile edges. We believe that the photoluminescence observed in this class of semiconductors arises from a radiative recombination between trapped electrons and trapped holes in tail and gap states. The peak PL position is chiefly determined by the separation energy between those states.

Experimental results obtained by XANES revealed the coexistence of two kinds of Ti coordination in the a-PT, namely, fivefold oxygen Ti coordination (TiO_5-square base pyramid) and sixfold oxygen Ti coordination (TiO_6 octahedron) [9]. In addition, an EXAFS analysis [10] showed that the overall sum of Ti-O distance around the Ti center was 11.35 Å for the latter, while a value of 9.75 Å was found for the former. Considering the XANES and EXAFS results, we can postulate that amorphous titanate is formed of a Ti-O network and the charge of the Pb cation must be compensated for by negatively charged non-bridging oxygen (NBO). Other defects, such as oxygen vacancies, may be present in the amorphous structure in addition to NBO. These positively charged defects stem from possibly different states of valence of the Ti ion (Ti^{+4} and Ti^{+3}). We believe that NBO (as the main defect) can modify the electronic structure of the PbTiO3 compound. NBO may be responsible for the tail and, consequently, for the electronic state inside the band gap of the a-PT.

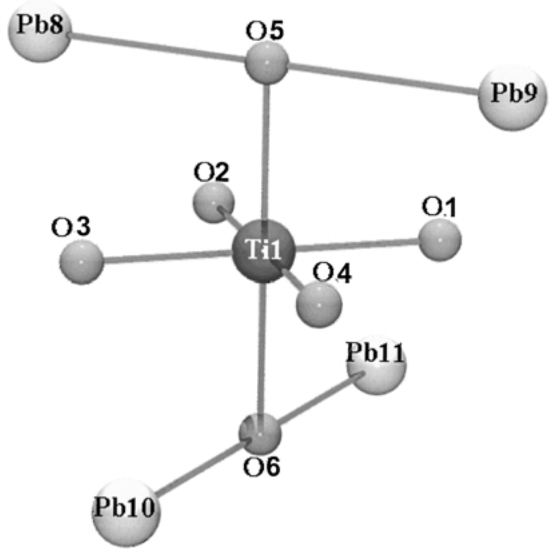

Figure 4 Sixfold oxygen Ti coordination structure represented by a cluster Pb_4TiO_6.

In our opinion, the existence of a fivefold oxygen Ti coordination is indicative of the presence of NBO in the a-PT. Thus, a first-principle molecular calculation was used to simulate the variation of the electronic structure when sixfold coordination changed to fivefold coordination. A small cluster was built for this simulation and the geometry of the clusters were optimized using the hybrid Hartee-Fock/density functional method at the B3LYP level of theory, with effective core potential and double-ζ basis set, LanL2DZ on Pb and 6-31G(d) and 6-31G(f) on O and Ti, respectively. The GAUSSIAN98 [11] package was used for these calculations. The optical band gap and the state densities were calculated using the cluster method. Atomic charges were computed using Mulliken's population analysis.

In our approach, the sixfold oxygen Ti coordination structure was represented by a Pb_4TiO_6 cluster (see Fig. 4) derived from crystallographic data, which was optimized by C_{2v} symmetry. The model for the fivefold oxygen Ti coordination structure was built by successively increasing the distance Ti(1)-O(6), allowing the rest of the structure to relax for each Ti(1)-O(6) frozen distance until the experimental value of the sum of Ti-O distances around the Ti center for fivefold oxygen Ti coordination was reproduced, leading to a displacement of O(6) atoms of 1.0 Å. The calculated geometry for both clusters is shown in Table II.

TABLE II Calculated geometry for both compounds 5- and 6-coordinate

Distance	Fivefold coordination (Å)	Sixfold coordination (Å)
Ti-O(n), $n = 1, 2, 3$ or 4	1.9203	1.9533
Ti-O(5)	1.7720	1.8338
Ti-O(6)	2.8338	1.8338
O(5)-Pb(n), $n = 8$ or 9	2.1096	2.0839
O(6)-Pb(n), $n = 10$ or 11	1.9681	2.0839

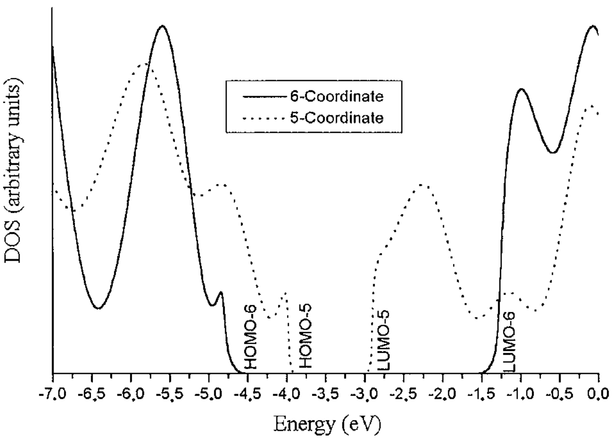

Figure 5 Electronic levels density (DOS) around the band gap for clusters of the c-PT and a-PT.

The calculated sum of the entire distance of Ti-O around the Ti center is 9.4532 Å and 11.4808 Å for fivefold oxygen Ti coordination and sixfold oxygen Ti coordination compounds, respectively, which is in very good agreement with the experimental results (9.75 and 11.35). Thus, it is expected that these clusters can reproduce the main features of the compounds identified by EXAFS measurements.

Fig. 5 illustrates the electronic levels around the band gap for both the clusters investigated. The dotted line refers to fivefold oxygen Ti coordination, while the full line refers to sixfold oxygen Ti coordination. In our approach, we have associated the top of the valence band to the HOMO and the bottom of the conduction band to the LUMO of the systems studied. The sixfold coordination presents a larger band gap than the fivefold one, namely, 3.5 (LUMO-6–HOMO-6), and 1.1 eV (LUMO-5–HOMO-5), respectively, which are in good agreement with experimental results, i.e., 3.0 and 1.8 eV, respectively. However, it is very important to note that there are electronic levels of the fivefold coordination included in the wide band gap of the sixfold coordination cluster. This result suggests that the formation of a fivefold structure may introduce electronic levels in the forbidden gap of the octahedron cluster in the regions delimited by HOMO-5 and HOMO-6 (hereinafter called ΔHOMO), and LUMO-6 and LUMO-5 (hereinafter called ΔLUMO).

The results of theoretical calculations indicate that the formation of fivefold coordination through the displacement of O(6) may introduce delocalized electronic levels in ΔHOMO and ΔLUMO. These delocalized electronic levels are ascribed to the formation of a tail in the absorbance spectrum (Fig. 1). It is also important to note that a decrease of 21.5% occurs in the charge of the Ti atom in the transition from sixfold to fivefold coordination. This charge redistribution might lead to electron-hole recombination of localized exciton Ti^{+3}-O^{-} in a regular octahedron (TiO_6), which may be responsible for PL emission.

4. Conclusion

In summary, we have engaged in a detailed discussion of the theoretical calculations of the origin of visible photoluminescence in amorphous lead titanate. One of the main conclusions of this work is that the comparison between theoretical and experimental results indicates the possibility of radiative recombination, since isolated titanate with a short Ti-O distance presented evidence of the electron-hole pairs in amorphous lead titanate, which is responsible for visible photoluminescence at room temperature.

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