The role of network modifiers in the creation of photoluminescence in CaTiO₃

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Abstract

We discuss the nature of visible photoluminescence (PL) at room temperature in amorphous calcium titanate in the light of the results of recent experimental and quantum mechanical theoretical studies. Our investigation of the electronic structure involved the use of first-principle molecular calculations to simulate the variation of the electronic structure in the calcium titanate crystalline phase, which is known to have a direct band gap, and we also made an in-depth examination of amorphous calcium titanate. The results of our theoretical calculations of amorphous calcium titanate indicate that the formation of fivefold coordination in the amorphous system may introduce delocalized electronic levels in the highest occupied and the lowest unoccupied molecular orbitals. These delocalized electronic levels are related to the formation of a tail in the absorbance spectrum curve. The results indicate that amorphous calcium titanate has the conduction band near the band gap dominated by Ca states contribution. Experimental optical absorption measurements showed the presence of a tail. These results are interpreted by the nature of these exponential optical edges and tails, associated with defects promoted by the disordered structure of the amorphous material. We associate them with delocalized states in the band gap.

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1. Introduction

The development of semiconductor materials with active optical properties such as photoluminescence (PL), electroluminescence, or non-linear optic properties may lead to new optoelectronic devices with superior performance. Much interest has been evinced in the study of PL in amorphous or nanostructured materials since the first time visible PL at room temperature was observed in porous silicon [1]. During the past decades, the luminescence of several types of compounds has been extensively studied in crystalline or single crystals doped with rare-earth ions such as Eu³⁺, Nd³⁺, Er³⁺ and Mn⁴⁺, due to potential optoelectronic applications [2–4]. Bryknar et al. [5] reported the PL of a Mn-doped SrTiO₃ single-crystal at low temperature (T = 15 K) under laser excitation at 532 nm. The behavior of Mn⁴⁺ luminescence is discussed taking into account the specificity of impurity-lattice interaction in ABO₃ perovskites. Murakami et al. [6] reported the PL of the PLZT (lead lanthanum zirconate titanate) ceramics doped with Eu³⁺, Nd³⁺ and Cr³⁺ at 10 K. The authors reported that the luminescence centers are discussed with regard to trapping-limited energy transfer processes from Eu³⁺ in the framework of a band model involving perturbed ions and traps.

On the other hand, semiconducting titanate-type compounds have presented various luminescence phenomena known for a long time [7–9]. Since the PL emission is observed in these materials with crystalline structure at low temperature and several authors have associated it with the presence of excitons self-trapped within the TiO₆ octahedra, amorphous titanate-type compounds with PL at room temperature have not yet been extensively by studied. The optical properties of amorphous semiconductor compounds are characterized by the presence in the plot of photon energy versus optical absorption of a tail. In this so-called tail the optical absorption falls almost asymptotically to zero, in
a region which is normally transparent in crystalline solids [10,11]. The so-called Urbach edge is attributed to the presence of localized electronic states near the band edges of amorphous semiconductors [11]. Materials with this optical characteristic may present properties such as PL. Several interesting properties of these amorphous titanates have been reported, including the fact that the PL emission wavelength is related to the exciting wavelength and that PL phenomena are related to the amorphous state [12,13].

In this paper, we have synthesized amorphous (a) CaTiO$_3$ samples and investigated, for the first time, the causes of their PL properties in order to gain a better understanding of the PL processes by means of a using quantum mechanical theoretical study.

2. Experimental

Amorphous and crystalline CaTiO$_3$ powders were synthesized by the polymeric precursor method. This method has been used to synthesize nanoparticles and thin films of several polycations complex oxides [14–16] and it is based on the chelation of cations (metals) by a hydroxycarboxylic 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 at temperatures ranging from 90 to 120 °C and it is favored by the reduction of water concentration. 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 matter.

The PL measurements were taken using a U1000 Jobin-Yvon double monochromator 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 CaTiO$_3$ powders were structurally characterized by X-ray diffraction (XRD) (Cu Kα radiation) in the mode of 2θ–θ scan ($θ$ is the diffraction angle), recorded on a Siemens D5000 diffractometer. The spectral dependence of the optical absorbance of the crystalline and a-CaTiO$_3$ were taken at room temperature in the total reflection mode, using a Cary 5G equipment. Raman data were taken on a RFS/100/S Bruker FT-Raman with Nd:YAG laser providing an excitation light at 1064 nm. The spectral resolution was 4 cm$^{-1}$. The 100–1000 cm$^{-1}$ spectral range was analyzed. All the measurements were taken at room temperature.

The first-principle molecular calculation was used to simulate the variation of the electronic structure when the sixfold oxygen Ti coordination was changed to fivefold oxygen Ti coordination. For this simulation clusters were build whose geometry was optimized using lanL2DZ on Ca, 6-31G (d) and 6-31G (f) on O and Ti, respectively. The Gaussian 98 [17] 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 natural bond orbital. In our approach, the sixfold and fivefold
oxygen Ti coordination structure both were represented by a Ca$_8$Ti$_3$O$_{12}$ (see Fig. 1a) derived from crystallographic data. The sixfold structure was were optimized by $D_4h$ symmetry. The model of the amorphous cluster was build with $C_4v$ symmetry by successively increasing the Ti (1)–O (7) distance, leading to a displacement of O (7) atoms of 1.5 Å (see Fig. 1b), allowing the rest of the structure to relax for each Ti (1)–O (7) frozen distance. We have associated the top of the valence band to the HOMO (highest occupied molecular orbital) and the bottom of the conduction band to the LUMO (lowest unoccupied molecular orbital) of the studied systems.

3. Results and discussions

Fig. 2 shows XRD analysis of the CaTiO$_3$ powders calcined at different temperatures. The samples calcined at a low temperature showed a pattern of amorphous materials, while that treated at 600°C showed a pattern of crystalline material. All the peaks are ascribed to an orthorhombic perovskite structure. In addition, thermogravimetric analysis of the powder showed no weight loss for calcination times longer than 20 h at 300°C, in an oxygen flow. These results suggest that an inorganic amorphous material was formed.

Fig. 3 shows the PL behavior observed in the amorphous and crystalline CaTiO$_3$ powders 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, with maximum at about 600 nm. As illustrated in the PL spectra of Fig. 3, when the annealing time was increased (under isothermal conditions), the intensity of PL increases. The effect of carbon content on the PL of CaTiO$_3$ material is evident. The carbon content was measured by thermogravimetric analysis. After the heat treatment a low temperature, the material processed by the polymeric precursor method presents basically two phases, an inorganic and a carbon bearing amorphous phases. Increasing the heat treatment times causes a decrease in the total carbon material content. If the PL behavior observed comes from the disordered inorganic phases, more intense PL must occur for the material submitted to heat treatment in oxygen for a longer time. This behavior was observed in the PL spectra shown in Fig. 3. On the other hand, when the material is calcinated at 600°C in crystalline form, the PL intensity is virtually zero at room temperature and at liquid nitrogen temperature. This behavior matched the one observed in the spectral dependence of absorbance as a function of the annealing temperature. This is a strong indication that the disordered phase (amorphous phase) is responsible for the PL phenomena. In addition, Fig. 4 shows the room temperature Raman spectra of crystalline and a-CaTiO$_3$. The main presence of the phonon modes in the Raman spectra indicates the orthorhombic phase of crystalline CaTiO$_3$, while a-CaTiO$_3$ shows a diffuse patterns, characteristics of the 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-CaTiO$_3$. The absorbance measurements, associated with the PL characterization of a-CaTiO$_3$ semiconductors, suggests a non-uniform band gap structure with a tail of localized states and mobile edges. On the other hand, our results are shown in terms of absorption associated with localized energy states in the band gap. We believe that the PL observed in this a-CaTiO$_3$ semiconductors arises from a radiative recombination between trapped electrons and trapped holes in tail and gap states.

Fig. 5 illustrates the spectral dependence of absorbance for the a-CaTiO$_3$ treated at 300°C for 32 h in an oxygen flow, and for the crystalline CaTiO$_3$. a-CaTiO$_3$ showed a spectral dependence on absorbance similar to that found in amorphous semiconductors such as amorphous silicon (Si) and insulators, while crystalline CaTiO$_3$ showed a typical interband transition of crystalline materials. In addition, in the high energy region of the absorbance curve (Fig. 5) the optical energy band gap is related to the absorbance and to the photon energy by the following equation:

$$h\nu \propto (h\nu - E_{\text{opt}}^g)^{2}$$

where $h$ is the Plank constant, $\nu$ the frequency and $E_{\text{opt}}^g$ the optical band gap (Tauc gap). The energy band gaps of the crystalline and a-CaTiO$_3$ were calculated to be 3.48 and 2.22 eV, respectively. These results (Fig. 5) 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 CaTiO$_3$ sample.

Experimental results by Balachandran and Eror [18] and Chan et al. [19] can be correlated by means of an oxygen vacancy defect model. The basis for the model is the loss of oxygen from the lattice to the gas phase with the formation of a doubly ionized vacancy, $V_o^{2+}$, with the two extra electrons being donated to the conduction band. The representation of this model for the hole states is the O$^-$ ion, while for the electron states it is the Ti$^{3+}$ species. However, we can assume, by our results, that electron transfer occurs between calcium and titanium ions. Our model for the hole states is O$^-$ ion, while for the electron states are the Ca$^{\alpha+}$ and Ti$^{\beta+}$ species, where $\alpha$ and $\beta$ are effective charges. The results of theoretical calculations indicate that the formation of an amorphous cluster through the displacement of O (7) may introduce delocalized electronic levels in the forbidden gap of the octahedron cluster in the regions delimited by Hc and.
Ha (hereinafter called $\Delta$HOMO). The delocalized electronic levels are ascribed to the formation of a tail in the emission spectrum (Fig. 5). Partial densities for the crystalline and amorphous clusters investigated are presented in Fig. 6. The partial densities of Ti, Ca and O states are presented for the valence and conduction bands in Fig. 6. In crystalline and a-CaTiO$_3$ clusters there is a weak contribution of Ca states to the density of states in the bottom of the valence bands while there is a strong contribution of O states for the density of states of the main part of the valence bands.

The shape of the density of states distribution curve for the these valence bands (Ti, Ca and O) has two main features. The upper portion of the bands presents roughly equal contributions from Ti and Ca states, while the lower portion contains states of primarily O character. From this point of view, it is clear that O states dominate the character of these valence bands in the crystalline and amorphous clusters investigated. On the other hand, there is a significant contribution of the Ca and Ti states for the conduction band states. Fig. 6 shows significant contributions of Ca and Ti states throughout the conduction bands of these amorphous materials. The crystalline cluster presents a higher band gap than the amorphous cluster, what is in agreement with experimental results, observed by absorbance spectral data. The delocalized electronic levels in the valence band may introduce in the amorphous cluster the PL properties (dashed line). From this figure, it is apparent that the p orbitals of the oxygen are weighted toward the top of the valence band.

Fig. 7. Schematic diagram of the energy levels and charge distribution in the molecular orbitals of the Ti (16), Ca (8) and O (22). (a) Crystalline (c-CT) and (b) amorphous (a-CT) energy levels and charge distributions of the stable orbitals in the Ti (1)-O (7) bond.
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 conduction band of CaTiO$_3$ is mostly of calcium s and titanium s and d character and the valence band is formed by oxygen 2p states (Fig. 7). The results of theoretical calculations indicate a charge transfer between (TiO$_6$) and (TiO$_5$) centers.

Fig. 7 shows the energy levels and charge distribution in the molecular orbitals for the titanium and calcium ions, stressed by the neighboring oxygen vacancies. In this case, one titanium ion forms an octahedral TiO$_6$ complex, but the other titanium ion, in a different octahedron, forms an TiO$_5$ complex plus an oxygen vacancy. If these two different structures V$_{O}^{++}$ coexist, the charge of the two holes is compensated by one oxygen vacancy. This suggests that the formation of an amorphous cluster may introduce electronic levels in the forbidden gap.
in the amorphous materials of CaTiO$_3$, can form various animated energy levels localized within the forbidden gap and they act as optical absorption centers, which make large modifications in the optical properties of the materials, and are responsible for the visible PL at room temperature.

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