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Journal of the European Ceramic Society 25 (2005) 2337–2340

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Theoretical and experimental study of the relation between photoluminescence and structural disorder in barium and strontium titanate thin films

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Abstract

Thin films of barium and strontium titanate (BST), synthesized by the polymeric precursor solution and spin coated on [Pt (140 nm)/Ti (10 nm)/SiO_2(1000 nm)/Si] substrates were found to be photoluminescent at room temperature when heat treated below 973 K, i.e. before their crystallization. First principles quantum mechanical techniques, based on density functional theory (DFT) were employed to study the electronic structure of two periodic models: one is standing for the crystalline BST thin film and the other one for the structurally disordered thin film. The aim is to compare the photoluminescence (PL) spectra of the crystalline and disordered thin films with their UV–vis spectra and with their computed electronic structures. The calculations show that new localized states are created inside the band gap of the crystalline model, as predicted by the UV–vis spectra. The study of the charge repartition in the structure before and after deformation of the periodic model shows that a charge gradient appears among the titanate clusters. This charge gradient, together with the new localized levels, gives favorable conditions for the trapping of holes and electrons in the structure, and thus to a radiative recombination process. Our models are not only consistent with the experimental data, they also allow to explain the relations between structural disorder and photoluminescence at room temperature.

Keywords: Films; Precursors-organic; Microstructure-prefiring; Optical properties; $BaTiO_3$ and titanates

1. Introduction

Several phenomena of photoluminescence (PL) have been reported for the $BaTiO_3$ crystal, and the observed effects have been correlated to impurity centers, e.g. rare earth ions in doped $BaTiO_3$ compound,[1] while it was discovered that, when pure $SrTiO_3$ crystal samples are excited by radiation above their energy band gap, a broad luminescent band appears at low temperatures.[2–4]

Among the perovskite-type compounds, $Ba_xSr_{1-x}TiO_3$, $x = 0–1$, in the powder and thin film forms, has been exhaustively investigated owing to its high dielectric constant coupled with its good thermal stability. However, its PL properties have not yet been reported. In this study, we present the results of PL measurements on $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films heat treated at various temperatures. Only the non-crystalline thin films present a PL emission at room temperature.

We are combining laboratory experiments and high level quantum-mechanics calculations into a synergetic strategy for identifying the origin of PL in structurally disordered BST. With this study, we do not pretend to explain *how* the photoluminescence appears because many authors have al-

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doi:10.1016/j.jeurceramsoc.2005.03.053

ready proposed satisfactory mechanisms (radiative recombination, self-trapped excitons, etc.) but we attempt to explain *why* photoluminescence exists in those non-crystalline thin films.

2. Experimental and computational details

The BST thin films studied in the present work were obtained from a soft chemical processing. Details of the preparation method can be found in the literature.[5] The polymeric precursor solution was spin coated on substrates [Pt (140 nm)/Ti (10 nm)/SiO_2 (1000 nm)/Si] by a commercial spinner operating at 6000 rpm for 20 s, via a Syringe filter to avoid particulate contamination. After spinning, the films were kept in ambient air at 423 K on a hot plate for 20 min to remove residual solvents. The room temperature PL spectra of the BST thin films were taken with a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelength of an argon ion laser was used, with the output power kept at 20 mW. A cylindrical lens was used to prevent the sample from overheating. The slit width was 100 μm.

The calculations were made within the framework of the density functional theory (DFT) using the gradient-corrected correlation functional by Lee et al.,[6] combined with the Becke3 exchange functional,[7] B3LYP. The atomic centers have been described by all electrons basis sets 9763-311(d631)G for Ba, 976-41(d51)G for Sr, 86-411(d31)G for Ti and 6-31G* for O.[8,9] All the calculations were carried out with the crystalline orbital program CRYSTAL98.[10]

3. Crystal structure

BST crystallizes in the cubic perovskite-type structure (space group *Pm*3*m*, O_h symmetry). The experimental and calculated values of the *a* parameter are, respectively, 3.951 and 3.901 Å. We built a 1 × 1 × 2 supercell resulting in 10 atoms in the unit cell. Each Ti is surrounded by six O in a O_h configuration. This crystal structure will be called BST-c and can also be designed as [TiO_6]–[TiO_6] (D_{4h}). XANES experimental results on the amorphous phase of $SrTiO_3$[11] and $PbTiO_3$[12] pointed out the coexistence of two types of environments for the titanium, namely, five-fold ([TiO_5] square-base pyramid) and six-fold coordination ([TiO_6] octahedron). Based on these results, we constructed another BST structure to represent the amorphous by shifting the upper Ti by a (0 0 0.5 Å) vector. This displacement turns asymmetric the unit cell, in which upper Ti is now surrounded by five oxygen atoms in a square-base pyramid conformation, while lower Ti stays in an octahedral environment. This asymmetric BST unit, BST-a, is the most simple model for representing the two titanium coordinations of the amorphous phase and can be designed as [TiO_6]–[TiO_5] (C_{4v}).

4. Results and discussion

Fig. 1 shows the PL spectra performed at room temperature of BST thin films annealed at 573 K for 2, 4, and 8 h, and at 973 K for 2 h in an oxygen flow. A comparison of the different samples reveals that the PL behavior of the amorphous BST thin films is sensitive both to the thermal treatment temperatures and to the duration of thermal treatment. The intensity of PL increased with the time of heat treatment and as the crystallization temperature (973 K) is reached, the PL emission vanishes. All spectra are large band spectra. They have been deconvoluted into two Gaussian-type curves, one peaking at 2.1 eV (orange band) and the other one at 2.3 eV (green band). With the heat treatment time augmentation, both components grow but the proportion of the green component clearly increases. The green band must be linked with some kind of order in the structure.

Absorbance measurements performed on the different thin films showed that the disordered films present exponential optical edges and tails as regard to the crystalline film.

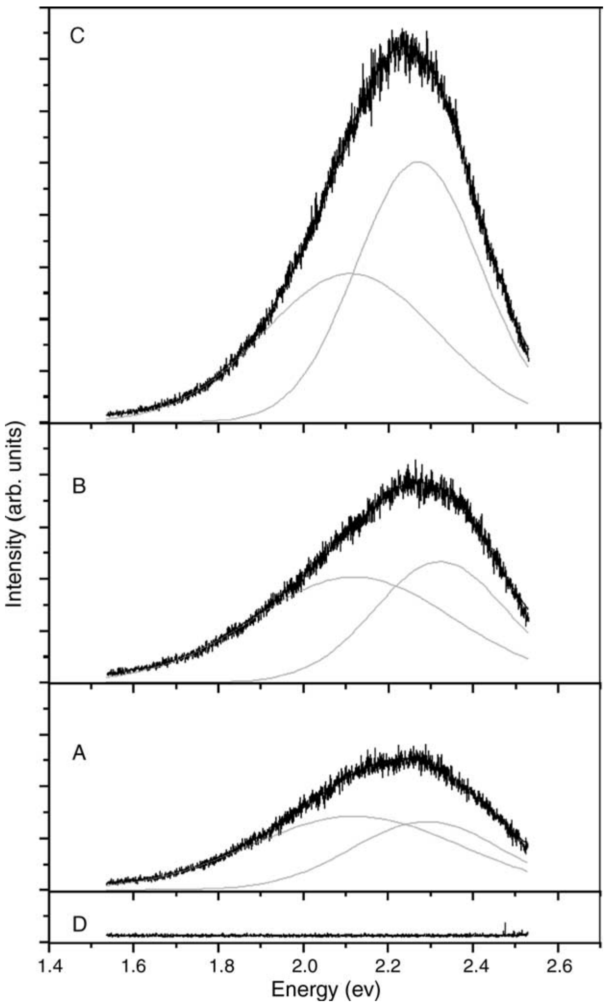

Fig. 1. Room temperature photoluminescence spectra for (Ba, Sr)TiO_3 thin films heat treated at 300 °C for (A) 2 h, (B) 4 h, (C) 8 h and 700 °C for (D) 2 h.

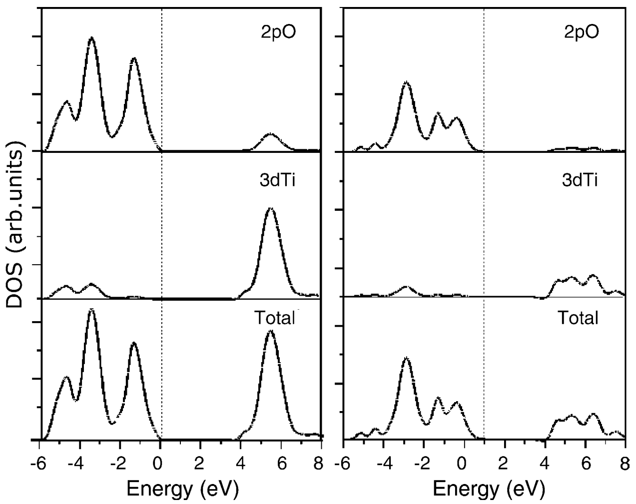

Fig. 2. The total and projected density of states for crystalline model (BST-c) (left) and asymmetric model (BST-a) (right). The zero of the energy scale was set at the Fermi energy of BST-c.

Associated with the PL characterization of BST system, they suggest a non-uniform band gap structure with a tail of localized states and mobile edges. The measured optical gaps are 3.78 and 3.25 eV, respectively, for the crystalline sample and for the disordered one annealed at 300 K for 8 h.

In order to understand the relationship between the structural disorder and the electronic defects that it generates, we performed a detailed theoretical study of the electronic structure in a crystalline (BST-c) and disordered (asymmetric) model (BST-a).

The DOS of BST-c and BST-a structures are shown in Fig. 2, left and right, respectively. For the BST-c model, the upper valence band (VB) is predominately made of the O (2p) states, equivalently distributed on the six oxygens of the structure. The conduction band (CB) is clearly made of the Ti (3d) states. The Ti–O covalent bond creates a limited Ti (3d) contribution in the O (2p) region, as well as a weak O (2p) contribution to the Ti (3d) area. The calculated indirect gap, 3.78 eV is equal to the optical gap of the crystalline film.

For the BST-a (Fig. 2, right), although the VB is globally constituted of O (2p) character states, the top mainly depends on the oxygen located at the center of the structure, the one that looses the connection with the dislocated titanium. The CB is composed of the 3d states of both titanium, in an apparently random splitting of the bands. The calculated indirect gap energy is 3.06 eV, to be compared with the 3.25 eV value of the optical measurements.

By elongating a Ti–O bond, we created new states located within the band gap of BST-c. This is in accordance with the absorbance tail observed for disordered BST. The bottom of the CB is also destabilized by the distortion, but in a minor way.

These results show that our data are consistent with the interpretation that the band gap is controlled by the degree of disorder, structural and thermal, in the lattice of BT system. This is this disorder that is at the origin of the apparition of PL.

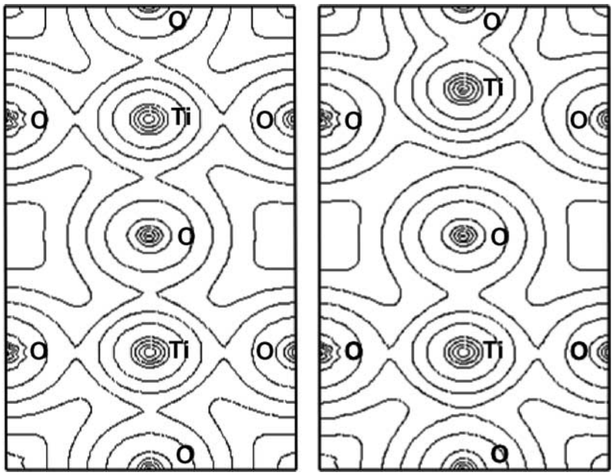

Fig. 3. The compared charge density contour plots for BST-c and BST-a in a vertical plane.

In order to further understand the electronic states in greater detail, we constructed contour of the electronic charge density calculated in a plane parallel to *z*-axis. From Fig. 3, it is obvious that substantial covalent bonding exists between Ti and O, due to the hybridization between the O (2p) states and the Ti (3d) states. The bond rupture in the BST-a model is also visible. We computed the formal charges of each titanium cluster before and after the dislocation of the titanium. In the BST-c, the [TiO_6] charge is 1.9 e, in the BST-a, 2.6 e. The [TiO_5] cluster of BST-c has a 1.2 e charge. On the other hand, the individual charges of the atoms are poorly modified. This seems to indicate that the charge transfer allowing the PL emission occurs from the [TiO_5] to the [TiO_6] cluster, and not from O to Ti atom like widely seen in the literature.

The theoretical results indicate that the formation of a five-fold oxygen titanium coordination [TiO_5] through the displacement of a Ti and the rupture of a Ti–O bond introduces localized electronic levels with O (2p) character above the VB of the structure before deformation. The BST-c presents indeed a greater band gap than the BST-a, what is in agreement with the experimental PL measurements and UV–vis spectra that indicate that the band structure of amorphous BST must contain localized levels that broaden the energy bands. This was confirmed by the calculations on a simple deformed crystal structure, BST-a, showing clearly the creation of those defect states. Moreover, the coexistence of two types of cluster differently charged in the disordered films creates a charge gradient facilitating the trapping of electron and holes and thus the radiative emission.

5. Conclusions

The photoluminescence at room temperature of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) was interpreted by means of first principle calculations based on the density functional theory at B3LYP level, using a periodic supercell model.

The electronic structures derived from the models proposed in this study for both crystalline (symmetric) and amorphous (asymmetric) structures allow to calculate electronic energy band gap, as well as energy band structures that are consistent with experimentally determined optical band gap. Moreover, the foresight of localized electronic levels in asymmetric structure within the energy band gap of crystalline BST is in accordance with the experimental extra states observed in the absorbance spectra of amorphous BST and with the dependence of the PL emission band on the disorder degree. A charge gradient also exists in the structure, allowing the easy trapping of electrons and holes in the created states and auxiliating the radiative decay.

Therefore, the localized electronic levels and the charge gradient induced in the valence band by the symmetry break may be the reason for the apparition of the visible photoluminescence emission in disordered BST.

Acknowledgements

This work was partially supported by the Brazilian research-financing institutions: Fundação de Amparo à Pesquisa do Estado de São Paulo-FAPESP/CEPID and Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq/PRONEX.

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