Theoretical and experimental study of disordered $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ photoluminescence at room temperature

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Abstract

Disordered and crystalline $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ (BST) powder processed at low temperature was synthesized by the polymeric precursor method. The single-phase perovskite structure of the ceramics was identified by the Raman and X-ray diffraction techniques. Photoluminescence at room temperature was observed only in a disordered BST sample. Increasing the calcination time intensified the photoluminescence (PL), which reached its maximum value in the sample heat treated at 300 °C for 30 h. This emission may be correlated with the structural disorder. Periodic ab initio quantum-mechanical calculations using the CRYSTAL98 program can yield important information regarding the electronic and structural properties of crystalline and disordered solids. The experimental and theoretical results indicate the presence of intermediary energy levels in the band gap. This is ascribed to the break in symmetry, which is responsible for visible photoluminescence in the material's disordered state at room temperature.

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1. Introduction

Much interest has focused on the photoluminescence (PL) of disordered or nanostructured material since this phenomenon was first observed in porous silicon at room temperature [1]. The luminescence of different kinds of compounds has been extensively studied in doped crystalline samples or single crystals, due to their potential optoelectronic applications [2–6]. Semiconductors of titanate-type compounds have presented many luminescence phenomena [7–9]. The optical properties of disordered semiconductor compounds are characterized by the presence of a tail in the plot of photon energy versus optical absorption. The optical absorption in this so-called tail falls almost asymptotically to zero in a region that is normally transparent in crystalline solids [10]. The Urbach edge is attributed to the presence of localized electronic states near the band edges of disordered semiconductors [11]. Several interesting properties of these disordered materials have been reported and it has been emphasized that the PL emission wavelength is related to the exciting wavelength and to the disordered state [12–14]. There are many hypotheses to explain the photoluminescence phenomenon in crystalline or disordered titanate compounds [15–17]. Leite et al. discuss the nature of visible photoluminescence at room temperature in disordered lead titanate in the light of the results of recent experimental and theoret-

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rical calculations. According to them, there is a possible formation of a fivefold coordination of the disordered system to introduce the localized electronic levels between valence and the conduction band. They also suggest the possibility of a radioactive recombination (electron–hole pairs), which may be responsible for the emission of photoluminescence [18]. Another study recently reported by our group involved the photoluminescent properties and structural disorder of BaSrTiO3 films and SrTiO3 powder, in which it was assumed that the presence of localized electronic levels in the band gap resulting from the break in symmetry is responsible for the visible photoluminescence of the disordered state at room temperature [19].

In this article we present, for the first time, measurements of broad PL as a function of heat treatment in BST samples prepared by the polymeric precursor method and it was also investigated the electronic structure and optical properties of perovskites using the first-principles with the density functional theory (DFT). The theoretical results are confronted with experimental data and both are coherent.

2. Experimental procedure

Ba_{0.45}Sr_{0.55}TiO3 (BST) powders were prepared by the polymeric precursor method (PPM), which is based on the chelation of the metal cations by citric acid in a solution of water and ethylene glycol. The precursor solution for BST coating was prepared from a titanium citrate formed by dissolving titanium isopropoxide in an aqueous solution of citric acid heated to about 70 °C. A stoichiometric amount of BaCO3 was added to the titanium citrate solution, which was stirred slowly until the reactional mixture became clear. SrCO3 was then also added slowly. To completely dissolve the BaCO3 and SrCO3, ammonium hydroxide was added a drop at a time until the pH reached 7–8. The complete dissolution of the salts resulted in a transparent solution. After the solution containing Ba and Sr cations was homogenized, ethylene glycol was added to promote the polyesterification reaction. The solution became more viscous as the heat rose to 90 °C, albeit without any visible phase separation. The molar ratio of strontium–barium and titanium cations was 1:1, the citric acid/metal molar ratio was fixed at 3:1, and the mass ratio of the citric acid/ethylene glycol was set at 60:40. This resin was then placed in a furnace and heated to 350 °C for 4 h, causing it to pulverize into powder. This powder was heated at 300 °C for 20, 30 and 40 h to obtain the disordered phase of the BST. The crystalline phase was obtained by heating the powder at 700 °C for 4 h.

2.1. Rietveld refinements and characterization

The disordered and crystalline BST powders were characterized by X-ray diffraction (XRD). The diffraction patterns of the crystalline powders were recorded in a Rigaku RINT2000 diffractometer in the step scan mode (Δ2θ = 0.02°, 20° ≤ 2θ ≤ 130°) using copper radiation (λKα1 = 1.5406 Å, λKα2 = 1.5444 Å, Kα1/Kα2 = 0.5) monochromatized by a graphite crystal. The tube power was 42 kV×120 mA, with a divergence slit of 0.5 mm and receiving slit of 0.30 mm.

The Rietveld refinements [20] were done with the GSAS program [21]. The peak profile function was modeled using the Thompson-Cox-Hastings pseudo-Voigt (pV-TCH) convolution with the asymmetry function described by Fingerprint et al. [22]. The strain anisotropy broadening was corrected by the phenomenological model described by Stephens [23]. Raman spectra were recorded on a RFS/100/S Bruker FT-Raman spectrometer with Nd:YAG laser providing an excitation light at 1064 nm, at a spectral resolution of 4 cm−1. The UV–vis absorption spectra of the BST powders were measured with a Cary 5G device.

The photoluminescence spectra were measured with a U 1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system, using the 488 nm exciting wavelength of an argon ion laser. The laser’s maximum output was 500 mW and a cylindrical lens was utilized to prevent the sample from overheating. The slit used was 250 μm. All the measurements were taken at room temperature.

2.2. Methods and models

The CRYSTAL98 package [24,25] is a periodic ab initio quantum-mechanical calculation which was used to study the BSTs structural and electronic properties. This method was applied with the B3LYP hybrid functional combined with the density functional theory (DFT). This functional has already been successfully employed in studies to calculate the structural parameters and band structures of a wide variety of solids [26]. The basic set described 9763-311(d631)G for Ba, 976-41(d51)G for Sr, 86-41(d31)G for Ti, and 6-31G* for O [27,28].

We built two models based on the Rietveld refinement results (see Table 1) for the crystalline structure of BST using a 1×1×2 supercell to represent the periodic models. The first model represents the crystalline BST structure (Fig. 1(a)) while the second model represents the disordered BST structure (Fig. 1(b)). In this model, we simulated the 0.5 Å displacement of Ti1–O3 along the

<table>
<thead>
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<th>Table 1</th>
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<tr>
<td>Unity cell dimensions, atomic coordinates and site occupation obtained from the Rietveld refinements</td>
</tr>
<tr>
<td>Ba_{0.45}Sr_{0.55}TiO3 700 °C/2 h-sp. gr. Pm3m</td>
</tr>
<tr>
<td>a = 3.9577 (1) Å; Y = 61.994 (5) Å³; d = 5.497 g/cm³</td>
</tr>
<tr>
<td>Atoms</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Sr</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>O1</td>
</tr>
<tr>
<td>R_{wp} = 18.15%; R_{E} = 5.46%; R_{G} = 2.99%; S = 1.234</td>
</tr>
</tbody>
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The R indexes are defined by Larson and Von Dreele [21].
c-axis. This new BST structure was simulated using the ATOMDISP feature of the CRYSTAL software. This model was used to study the optical, structural and electronic properties of the disordered state of BST and to understand the photoluminescence phenomenon of this material at room temperature.

3. Results and discussion

Fig. 2 shows the Raman spectra of the barium titanate (BT) (a) and barium strontium titanate (BST) (b) powders.

The modes further split into longitudinal (LO) and transverse (TO) components the long electrostatic forces associated with lattice ionicity. The spectrum in Fig. 2(a) shows the stretching mode of $A_1(TO_1)$, $A_1(TO_2)$ and $A_1(TO_3)$ at around 155, 260 and 518 cm$^{-1}$, respectively [29–31]. The stretching mode of $E(TO_2)$ associated with the tetragonal–pseudocubic phase transition appeared at 305 cm$^{-1}$ [32,33], while $A_1(LO_1)$ and $A_1(LO_2)$ revealed stretching modes at 189 and 470 cm$^{-1}$, respectively. The Raman spectrum of the BST sample (Fig. 2(b)) showed the same BT bands, but its intensity showed a decrease accompanied by a slight shift to a higher range of energy frequencies. The intensity of the peak at $\sim$518 cm$^{-1}$ in the BT Raman spectrum decreased in the BST spectrum. The band at 718 cm$^{-1}$ observed in BT was considered to be associated with a crystallographic transformation from the tetragonal to the pseudocubic phase. Note that this band does not appear in the BST spectrum, since it is closely related with the material’s tetragonality.

Table 1 lists the unity cell dimensions, atomic coordinates and site occupation and agreement indexes of the BST obtained from Rietveld refinements.

The Rietveld refinements were obtained from the XRD patterns of the crystalline sample (Fig. 3(b)), which were consistent with a cubic structure. The XRD patterns shown in Fig. 3(a), however, reveal the characteristic pattern of a disordered phase in the material treated at 300 °C for 30 h in an oxygen flow.

Fig. 3(a) shows the XRD pattern of disordered BST powder annealed at 300 °C for 30 h in an oxygen flow, while Fig. 3(b) is the XRD pattern for the crystalline BST powder heat treated at 700 °C for 4 h.

Fig. 4 presents the PL spectra of the BST powders annealed at 300 °C in an oxygen flow during (a) 20, (b) 30 and (c) 40 h, and (d) at 700 °C for 4 h. The broad PL peak of the BST in its disordered state is shown in the visible range with a maximum at around 595 nm. The PL is
strongly dependent on the heat treatment conditions, revealing the influence of temperature or thermal exposure time on the organization of the disordered material. This disordered material is initially composed of the polymeric precursor, which already presents a slight photoluminescence. The PL intensity increases as the organic matter is eliminated, as indicated in Fig. 4 (a) and (b). Fig. 4 (b) depicts the maximum PL intensity observed in this experiment. This intensity is likely associated with the structural order/disorder. Fig. 4 (c) shows the PL spectra of the disordered material in a more organized phase, which is why their intensities decrease progressively to zero, characterizing the crystalline phase shown in Fig. 4(d).

Fig. 5(a) shows the spectral dependence of the energy-related absorbance (eV) of the BaSrTiO$_3$ disordered powder heat treated at 300 °C for 30 h under an oxygen atmosphere, and Fig. 5(b) displays the material’s crystalline phase curve when heat treated at 700 °C for 4 h. The values of the optical band derived from the UV–vis spectroscopy measurement (Fig. 5(a) and (b)) for the disordered and crystalline BST were, respectively, 2.10 and 3.08 eV. These results indicate that the data confirm our 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 BST sample. This decrease in the band gap can be ascribed to defects or impurities that give rise to intermediary levels of energy in the range of the band gap promoted by the BSTs disordered structure [19]. In this work, we present the calculation of the electronic structure of the BST with cubic symmetric (BST-o) in order to compare it with the BST-d periodic model.

Our aim with the use of these BST-o and BST-d models is to offer a simple scheme to help understand the effects of structural deformation on the electronic structure without completely suppressing the geometry that is useful for the periodic calculations. Although it does not represent reality, it is consistent with the electronic structure of a compound containing local defects.

Fig. 6(a)–(c) shows the projection of the density of states (DOS) of the oxygen and titanium atoms of the ordered and disordered structures. An analysis of the DOS projected over the BST atomic orbitals reveals a clear predominance of the oxygen’s 2p atomic orbitals in the valence band and a predominance of the titanium’s 3d atomic orbitals in the conduction band and the gap is 3.78 eV. In relation to the photoluminescence properties of this material, the DOS analysis indicates that in the disordered material, the oxygen atomic orbitals cause a decrease in the band gap value (3.06 eV), which is responsible for the photoluminescence phenomenon at room temperature in the visible range.
The theoretical results thus prove the existence of localized states that are related to the measured optical edges and tails. These results confirm that our theoretical models are consistent with the reality and with our interpretation that the exponential optical absorption edge and the optical gap are controlled by the degree of structural and thermal disorder in the lattice of the BST system.

The diagram of the electronic density of the Ti and O atoms is shown in Fig. 7(a) and (b) for the ordered and disordered BST, respectively. Fig. 7 shows homogeneous contour lines representing the interactions of the Ti and O atoms, indicating the presence of bonds of a covalent nature. In this model there is a homogeneous charge density between the Ti and O atoms. An analysis of Fig. 7(a) and (b) shows the bonding between Ba and [TiO₆] is ionic, while a covalent bonding nature is visible between Ti and O, as a result of the hybridization between the O(2p) and Ti(3d) states. The contour lines of the model, which represents the disordered structure, Fig. 7(b), indicate that displacement of the Ti₁ and O₃ atoms causes the interaction between the Ti₁ and O₂ atoms to decrease. The breaking of the Ti₁–O₂ bond is visible in Fig. 7(b). The displacement of a metallic center on going from BST-o to BST-d results in the deformation of a symmetric [TiO₆–TiO₆] structure into two fragments: [TiO₆] and [TiO₃]. When the distortion occurs through the displacement of Ti₁ atom, there is a degeneracy lift, exactly like in the case of a Jahn–Teller interaction. Therefore, our distorted model BST-d can also be seen as a crystalline model where Jahn–Teller distortion would have occurred every two [TiO₆] clusters. The charge transfer occurring from [TiO₅] to [TiO₆] clusters creates electron and hole polarons that can be designed as Jahn–Teller bipolarons. They have already been evidenced by means of electron paramagnetic resonance measurements in pure BaTiO₃ monocrystal [34] or by theoretical calculations where they were considered as point defects [35,36]. Stashans et al. [37] announced that they had to be expected for perovskite-type titanates. Our disordered BST powders thus intrinsically possess the necessary condition for creating PL, which is not the case for the crystalline powder where the quasiperfect structure does not allow the creation of point defects.

4. Conclusions

Low cost soft-chemical processing was used to prepare the Ba₀.₄₅Sr₀.₅₅TiO₃ powders, which displayed an intense broad photoluminescence at room temperature in the visible range in the structurally disordered material. The experimental results revealed by Raman, XRD, Rietveld refinements, UV–vis and photoluminescence measurements, combined with the periodic ab initio quantum-
mechanical method, indicated the presence of intermediary energy levels in the band gap. These intermediary levels led to a decrease in the gap band of the disordered material. The decline in the experimental value of the optical gap from the crystalline to the disordered phases indicated the appearance of intermediary levels in the band gap, suggesting that the theoretical models employed in this work were consistent.

The DOS analysis revealed that both ordered and disordered models presented the contributions oxygen’s 2p atom orbitals in the valence band and the contributions of the Ti’s 3d atom orbitals in the conduction band. According to the periodic models, the contour lines illustrate the electronic density. The model representing the ordered material showed homogeneous contour lines characterizing the symmetrical structure. However, this homogeneity was absent from the disordered model, indicating an asymmetric structure.

The crystalline model presents indeed a higher band gap than the disordered model, which is in agreement with experimental gap determined from absorbance spectral data. Moreover, a charge transfer occurs from [TiO\textsubscript{5}] clusters to the [TiO\textsubscript{6}] one, revealing the intrinsic presence of trapped holes and electrons, Jahn–Teller bipolarons, in the disordered phase of BST powders. The presence of those trapped holes and electrons, existing before the excitation process, is the main factor allowing that the radiative emission process prevails on the non-radiative recombination one in disordered perovskite compounds.

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