BaZrO₃ Photoluminescence Property: An Ab Initio Analysis of Structural Deformation and Symmetry Changes

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ABSTRACT: This article reports a theoretical study based on experimental results for barium zirconate, BaZrO₃ (BZ) thin films, using periodic mechanic quantum calculations to analyze the symmetry change in a structural order-disorder simulation. Four periodic models were simulated using CRYSTAL98 code to represent the ordered and disordered BZ structures. The results were analyzed in terms of the energy level diagrams and atomic orbital distributions to explain and understand the BZ photoluminescence properties (PL) at room temperature for the disordered structure based on structural deformation and symmetry changes. ©2009 Wiley Periodicals, Inc. Int J Quantum Chem 111: 694–701, 2011

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Introduction

ABO₃ perovskites thin films (A = Ba, Sr, Ca, or Pb; and B = Ti, Zr, or Mo) are important for numerous technological applications. Structurally disordered perovskite compounds are technologically interesting ferroelectric materials with dielectric, pyroelectric, piezoelectric, and electro-optic properties that favor a variety of applications in electronic devices [1–3].

Numerous papers report mechanisms attributed to the nature of the luminescent perovskite properties in the visible range. These are inherent properties in the ABO₃ perovskite crystal, given that intrinsic defects occur within this structure [4, 5].

Our group has conducted theoretical and experimental studies in ABO₃ perovskites to understand the luminescent properties [5–9], and to analyze the Jahn–Teller effect on structural deformations [9, 10]. These defects, as well as structural deformations in the disordered structure, generate asymmetry in the crystal. This asymmetry can promote degeneracy in the atomic orbitals, which in turn induces intermediary states inside the gap region and a reduction in the gap value. Such decrease in the gap value is explained by the modification in the splitting of the atomic orbitals, which can be associated to the structural deformation and symmetry change.

In this article, we report an alternative theoretical methodology using a quantum mechanic model to correlate the structural deformation with the symmetry type present in the disordered barium zirconate. The program employed to perform the periodic quantum-mechanic calculations was CRYSTAL98 [11].

The structural deformation and symmetry change were investigated from energy level diagrams and atomic orbital distribution with the purpose of understanding the PL property in the disordered BZ structure.

Computational Methods and Periodic Models

Quantum mechanical calculations were carried out with the CRYSTAL98 package [11], which is based on density functional theory (DFT) and Hartree–Fock methods. The gradient-corrected correlation functional by Lee et al. [12] and Becke [13] was used combined with the Becke3 exchange functional, B3LYP. The atomic centers were described by all the electron basis sets, 9763-311_d631_G for Ba [14], 976-31_d62_G* for Zr [14], 86-411_d31_G for Ti [15], and 6-31G* for O [15]. The BZ system is described for 40 k points, with the valence and conduction bands exhibiting (3 0 0) and (0 0 3) directions, respectively for cubic structures.

Four different periodic models were built. The first model represents the ordered structure (crystalline) (BZord) [see Fig. 1(a)]. The three other periodic models were simulated by displacement of the zirconium, BZ_Zr [see Fig. 1(b)], barium, BZ_Ba [see Fig. 1(c)], and zirconium-barium simultaneously, BZ_Zr–Ba [see Fig. 1(d)] to typify the disordered structures. The Zr and Ba atoms were displaced 0.5 Å in the z and diagonal (0.5, 0.5, 0.5) directions, respectively. To achieve the atomic displacements in the structure, the ATOMDISP option provided with the CRYSTAL98 program were used. The CRYSTAL03 [16] code was used to optimize the cell parameters and the XCrysden [17] program was employed as a graphical tool to design the BZ energy level diagrams.

Experimental

BaZrO₃ thin films were prepared by the polymeric precursor method that has proved to be efficient in the synthesis of many polycation oxides [18–20]. Thus, metallic alkoxides were added to an aqueous solution of citric acid in order to obtain a metallic citrate complex. Zirconium butoxide (99% purity, Aldrich) was utilized as source of Zr⁴⁺. Afterward, a stoichiometric amount of barium carbonate (99% purity, Mallinckrodt) was added to the solution, followed by adding ethylene glycol (99.5% purity, Merck) to promote the polymerization reaction. The obtained polymeric
Resins were deposited by spin coating onto Si(111) substrates using a Chemat Technology KW-4B spin coater at 7,000 rpm. The films were annealed at 350°C and 550°C for 2 h in air atmosphere. The samples were structurally characterized by X-ray diffraction (XRD) in a Rigaku DMax 2500PC, with Cu Kα radiation and graphite monochromator. The photoluminescence spectra of the films were recorded at room temperature with a U-1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system, with 488 nm excitation and laser maximum output power of 27 mW.

**Results and Discussion**

The crystallization process of the BZ thin films, annealed at 350°C and 550°C for 2 h in air atmosphere, was verified by XRD (see Fig. 2). Figure 2 shows that the sample annealed at 350°C displays a broad pattern with a unique peak of the silicon (111) substrate, indicating a disordered arrangement of the BZ structure. The XRD result for the sample annealed at 550°C (see Fig. 2) shows a crystalline material with a cubic BZ pattern and space group Pm3m (JCPDS card 06-0399).

Figure 3 demonstrates the PL spectra recorded at room temperature for BZ thin films annealed at 350°C and 550°C for 2 h. In this figure, an intense broad band in the visible region for the disordered sample treated at 350°C (see Fig. 3) can be observed. With the crystallization process, the end of the PL property is discerned, as observed for the sample annealed at 550°C (see Fig. 3). This behavior is correlated to the material’s complete structural order.

Our group [19–24] considered the nature of visible photoluminescence at room temperature in disordered perovskite-type titanates prepared by the polymeric precursor method (used in this work). Recently, XANES (X-ray Absorption Near Edge Structure) results evidenced that in structurally disordered phases of perovskite materials the coexistence of two types of Ti coordination in the PbTiO₃ cluster occur, namely, five-fold oxygen Ti coordination [TiO₅] and six-fold oxygen Ti coordination [TiO₆], such results also suggested that [TiO₅] is absent in well-crystallized titanates. These experimental results have provided support for the building of theoretical models, which have indicated the appearance of new states inside the band gap region. Such aspect is ascribed to a breaking of the symmetry, which is accountable for visible photoluminescence in the disordered materials at room temperature. The localized states promote the trapping of electrons and holes [25]. This electron-hole recombination generates the polarons, favoring the photoluminescent emission at room temperature in the visible region. Thus, theoretical calculations were conducted to verify the influence of the displacement type mechanism in disordered BZ compounds with the purpose of understanding the PL property at room temperature in the visible region. The results were interpreted in terms of the energy level diagrams to study the behavior of the atomic orbitals and to determine the symmetry.
change associated to the atomic displacements employed. The structural modeling was built from elaborated periodic models for Ba and Zr displacements in a range of 0.5 Å. In these structure-types, the Ba atom is coordinated by 12 oxygen atoms and the Zr by 6 oxygen atoms in an elongated octahedral configuration.

The primitive cell Brillouin zone and band structures obtained for the BZ models are presented in Figures 4(a)–(e). The $k$ points considered for building the primitive cell Brillouin zone for BZ$_{Zr}$, BZ$_{Ba}$, and BZ$_{Zr-Ba}$ models were $\Gamma$, $X$, $M$, $A$ and $R$ [Fig. 4(a)], where $\Gamma = 0,0,0$; $X = 0,1/2,0$; $M = 1/2,1/2,0$; $A = 1/2,1/2,1/2$; $R = 0,1/2,1/2$; and $\Gamma = 0,0,0$, the reciprocal co-ordinates employed. An indirect gap was verified for all BZ models, according to band structure representation [Figures 4(b)–(e)] [9]. The calculated indirect band gap energies were obtained by the top of the valence band (VB) and bottom of the conduction band (CB). In this case, the VB is in the $M$ point and the CB is in the $\Gamma$ point, respectively. The value of the band gap energy for BZ$_{ord}$ model is 4.73 eV, with this value being lower than the BZ models with disordered structure [Figures 4(c)–(e)].

In [Figures 5(a)–(d)], the energy level diagrams show the behavior of the BZ atomic orbitals for each mechanism generated by simulated displacements. Figure 5(a) shows the energy levels diagrams for BZ crystalline model in an ordered cubic structure (BZ$_{ord}$). The simulated disordered structures were built to represent the defect types...
TABLE I
Simulated displacements for the BZ system with the respective symmetries and gap values.

<table>
<thead>
<tr>
<th>Simulated displacement</th>
<th>Symmetry</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZ_{oxid}</td>
<td>O_h</td>
<td>4.73</td>
</tr>
<tr>
<td>BZ_{Zr}</td>
<td>D_{4h}</td>
<td>3.69</td>
</tr>
<tr>
<td>BZ_{Ba}</td>
<td>C_{2v}</td>
<td>3.61</td>
</tr>
<tr>
<td>BZ_{Ba-Zr}</td>
<td>C_{4v}</td>
<td>2.93</td>
</tr>
</tbody>
</table>

that may be responsible for the PL property. The results are depicted in Figures 5(b)–(d) for BZ_{Zr}, BZ_{Ba}, and BZ_{Zr—Ba}, respectively, where the subscript term indicates the displaced element. The analysis of these three tetragonal models indicates that the displacement of the Zr, Ba, and Ba—Zr induces an increase of the structural defects, resulting in a decrease of the symmetry and a gap value reduction that corroborates with the PL behavior. Figure 5(a) indicates that the BZ_{oxid} system presents a cubic structure with Zr atomic orbitals described as d_{x^2} and d_{x^2—y^2} (E_g) and d_{xy}, d_{xz}, d_{yz} (T_{2g}), being that both are degenerated. This crystal presents a high (O_{h}) symmetry described for [ZrO_{5—ZrO_{6}}] clusters with gap value of 4.73 eV, as depicted in Table I.

The displacements of the network former (Zr) and modifier (Ba) can be associated to three types of mechanisms involving oxygen vacancies that generate synergy in the system: V_{O}^{0}, V_{O}^{*}, and V_{O}^{**}. The local defects into the structure caused by the [ZrO_{5—V_{O}^{0}}] complex clusters are associated to the oxygen vacancies, which can present up to three different charge states: (I) neutral V_{O}^{0}—capture up to two electrons, (II) singly ionized V_{O}^{*}—capture only one electron and (III) double ionized V_{O}^{**}—it is not able to trap electrons. These species play an important role in the formation of hole-electron (h^*—e^*) pairs, resulting in a charge gradient in the lattice. The disordered models indicated that defects in the lattice are linked to structural defects composed of oxygen-deficient complex clusters of Zr_{O_{5—V_{O}^{0}}} and BaO_{11—V_{O}^{0}}.

These mechanisms defect in the BZ system were simulated by displacements of the Zr and Ba atoms together and isolating one to reproduce a disordered system.

Figure 5(b) enables to visualize that the breaking of Zr—O bonding results in a decrease of the D_{4h} symmetry. Such symmetry diminishing occurs on account of Zr displacement to the z direction (BZ_{Zr}) to O_{5} and O_{7} atoms, inducing [ZrO_{5—ZrO_{6}}] system formation. In this system, it can be observed that for the conduction band the zirconium’s atomic orbital’s present the following energy value sequence: d_{xy} < d_{xz} < d_{z^2} < d_{x^2—y^2}. In this case, the gap value obtained was 3.69 eV. A reduction is observed when comparing this value with that obtained for the O_{h} symmetry (Table I). This fact can be attributed to the appearance of defects and vacancies induced by displacement of the Zr atom in the z direction and, consequently, a disturbance is observed in the stabilization of the zirconium’s 4d and oxygen’s 2p atomic orbitals. The resulting effect of the Zr atom displacement can be represented by the following equations:

\[ [\text{ZrO}_{6}]^{+} + [\text{ZrO}_{5—V_{O}^{0}}] \rightarrow [\text{ZrO}_{6}^{+}] + [\text{ZrO}_{5—V_{O}^{0}}] \]  
\[ [\text{ZrO}_{6}]^{+} + [\text{ZrO}_{5—V_{O}^{0*}}] \rightarrow [\text{ZrO}_{6}^{+}] + [\text{ZrO}_{5—V_{O}^{0**}}] \]  

In the case of the zirconium’s 4d atomic orbitals for the BZ_{Ba} model [Fig. 5(c)], the following distribution is obtained: d_{xy} < d_{xz} < d_{z^2—y^2} < d_{x^2—y^2} (C_{2v} symmetry). The obtained gap value was 3.61 eV, indicating increase of the disorder degree in the crystal when compared to O_{h} and D_{4h} symmetries (Table I). Such decreasing in the gap value for BZ_{Ba} model is associated to the appearance of the oxygen’s 2p atomic orbitals inside the gap region. This fact is associated to diagonal displacement of the Ba—O bonding at 

\[ [\text{BaO}_{12}]^{+} + [\text{BaO}_{11—V_{O}^{0}}] \rightarrow [\text{BaO}_{12}]^{+} + [\text{BaO}_{11—V_{O}^{0}}] \]  
\[ [\text{BaO}_{12}]^{+} + [\text{BaO}_{11—V_{O}^{0*}}] \rightarrow [\text{BaO}_{12}]^{+} + [\text{BaO}_{11—V_{O}^{0**}}] \]  

Figure 5(d) represents the energy level diagrams for BZ_{Ba—Zr} models, illustrating the distribution for zirconium’s 4d. In this case, the obtained gap value was 2.93 eV for d_{xz} — d_{yz} < d_{xy} < d_{z^2—y^2} distribution (C_{4v} symmetry). Table I indicates that a gap diminishing occurred, when compared to the other obtained values (O_{h}, D_{4h} and C_{2v}), attributing this to the disorder generated by two different types of displacements (Zr—Ba), as demonstrated by Eqs. (1)–(4). In these equations, the systems [BaO_{12}]^{+}, [\text{ZrO}_{6}]^{+}, and [\text{BaO}_{11—V_{O}^{0}}], [\text{ZrO}_{5—V_{O}^{0}}] are acceptor and donor candidates, respectively. A charge compensation occurs with the presence of the complex clusters [ZrO_{6}], [ZrO_{5—V_{O}^{0}}], [BaO_{12}], and [BaO_{11—V_{O}^{0}}], which are donor-acceptor species, favoring the PL
Increasing the heat treatment of the BZ thin films from 350°C to 550°C for 2 h causes a reduction of the oxygen’s vacancies and consequently an ordering in the structure is observed. Thus, there is no recombination of the electron-hole pairs and the PL is concluded.

According to Eqs. (1)–(4), the molecular orbitals for the zirconium and barium atoms demonstrate the stress generated by the oxygen vacancies of the lattice. This fact, related to the gap value reduction, suggests that the formation of disordered clusters may introduce electronic levels in the forbidden gap that are responsible for the PL property. In the complex, the ZrO₆ or BaO₁₂ clusters act as electron donors, while the vacancy complex ZrO₅/V⁰ or BaO₁₁/V⁰ tends to trap electrons and/or holes and ZrO₅/V⁵⁺ or BaO₁₁/V⁰⁺ acts as an electron trap.

Figure 6 illustrates that a decrease occurs in the total energy of the system with alteration of the symmetry group from O₈ (symmetric) to C₄ᵥ (asymmetric), in agreement with the decreasing of the gap values (Table I), since the structural disorder degree is increased by induced symmetry change. As confirmed by Figure 6, the Zr displacement (D₄h) promotes a major variation in the system’s total energy when compared to Ba displacement (C₂ᵥ). This fact supports the idea of a disturbance induced to the crystal with the employed displacements, which promotes the PL in the BZ system.

Figures 7(a)–(b) show the electron density maps (contour and surface lines) proportional to the square base planes involving the Zr and O atoms of the BZord and BZZr, respectively. Figure 7(a) illustrates the strongly covalent character in the interaction of the zirconium with the oxygen...
atoms on the analyzed plane, which is represented by homogenous distributions of the contour lines. The observed behavior takes place because of the hybridization between the oxygen’s 2p atomic orbitals and the zirconium’s 4d atomic orbitals. Because of the Ba displacement that was performed outside the analyzed plane, no response was observed for BZ_{Ba} model. The density distribution remained the same for Figure 7(a). Figure 7(b) illustrates the inhomogeneous distribution of the contour lines that represent the interaction decreasing between the Zr—O_{4} atoms. This fact is attributed to a breaking of these bonds and consequent approximation of Zr—O_{3} atoms. No alteration was observed in the electronic distribution for the BZ_{Ba—Zr} model. This fact suggests a non-dependence of the Ba atom displacement in the system due to the low influence of the Ba—O ionic bonding in the crystal.

Figures 7(c)–(d) illustrate the electronic density maps in the diagonal plane of the BZ_{ord} and BZ_{Bar} respectively. A similar behavior was obtained by BZ_{ord} and BZ_{Bar} and for BZ_{Zr} and BZ_{Zr—Ba}. Thus, the results related to Ba atom were omitted. The diagonal analyses were conducted as a complementary study due to the cutting plane passing through the oxygen, zirconium and barium atoms, which are perpendicular to the squared base plane. Figure 7(c) shows a homogeneous distribution of the electronic density, which represents the covalent bonding character of the Zr—O and the strong ionic character between Ba—O atoms. This behavior remains in Figure 7(d), but a different distribution is observed in the homogeneity of the electronic density generated on account of the displacement of the Zr atom. Thus, the theoretical calculations indicate that the Zr atom is responsible for lattice orientation, and the Ba atom only complements the material structure, indicating a minor influence in the BZ electronic density.

The observed charge difference results from the electronic density maps [see Figures 7(a) and (b)] among the [ZrO_{4}] — [ZrO_{3}], [ZrO_{5}V_{2}^{0}] — [ZrO_{3}], [BaO_{11;11;V_{2}^{0}}] — [ZrO_{3}], [BaO_{11;11;V_{2}^{0}}] [ZrO_{5}V_{2}^{0}] — [ZrO_{3}] clusters that are 0.0, −0.74, −0.07, 0.08 e for BZ_{ord}, BZ_{Bar}, BZ_{Zr} and BZ_{Zr—Ba}, respectively. The charge gradients presented by the disordered structure, result in a formation of the intermediary states inside the band gap, hence providing conditions for hole-electron (h^{*}•e\textsuperscript{−}) pairs recombination, favoring the PL emission at room temperature.

Conclusion

The theoretical-experimental analyses indicate that the nature of the PL at room-temperature is related to the structural disorder of the BaZrO_{3} thin films. The disorder generated in the BZ system by structural deformation, indicates a major dependence of the Zr than Ba arrangement, due to a covalent character presented by Zr—O bonding. The observed visible PL is strongly related to the appearance of such defects, as oxygen vacancies in the system. The presence of these defects is confirmed by the diminishing of the gap value and appearance of the intermediary states inside the band gap with decreasing of the symmetry in the BZ system, which are responsible for PL response at room temperature, in agreement with the experimental results.

References