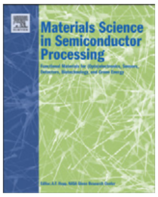
Materials Science in Semiconductor Processing 16 (2013) 1035–1045

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Local electronic structure, optical bandgap and photoluminescence (PL) properties of $Ba(Zr_{0.75}Ti_{0.25})O_3$ powders

L.S. Cavalcante [a,b,]*, N.C. Batista [a], T. Badapanda [c], M.G.S. Costa [d], M.S. Li [e], W. Avansi [e], V.R. Mastelaro [e], E. Longo [b], J.W.M. Espinosa [f], M.F.C. Gurgel [f]

[a] *Departamento de Química, UESPI-CCN, Rua João Cabral, P.O. Box 2231, 64002-150 Teresina-PI, Brazil*
[b] *Universidade Estadual Paulista, P.O. Box 355, CEP, 14801-907 Araraquara, São Paulo, Brazil*
[c] *Department of Physics, National Institute of Technology, Rourkela 769008, India*
[d] *Instituto Federal do Maranhão, Química, CEP 65025-001, Sao Luís, MA, Brazil*
[e] *IFSC-Universidade de São Paulo, P.O. Box 369, 13560-970 São Carlos, São Paulo, Brazil*
[f] *Universidade Federal de Goiás, Câmpus de Catalão, Engenharia de Produção, Avenida Dr. Lamartine Pinto de Avelar, 1120 CEP 75700-000, Brazil*

ARTICLE INFO

Available online 18 April 2013

Keywords:
Defects
Density functional theory calculations
X-ray absorption near-edge structure
Crystal structure
Optical properties

ABSTRACT

$Ba(Zr_{0.75}Ti_{0.25})O_3$ (BZT-75/25) powders were synthesized by the polymeric precursor method. Samples were structurally characterized by X-ray diffraction (XRD), Rietveld refinement, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) techniques. Their electronic structures were evaluated by first-principle quantum mechanical calculations based on density functional theory at the B3LYP level. Their optical properties were investigated by ultraviolet-visible (UV-Vis) spectroscopy and photoluminescence (PL) measurements at room temperature. XRD patterns and Rietveld refinement data indicate that the samples have a cubic structure. XANES spectra confirm the presence of pyramidal $[TiO_5]$ clusters and octahedral $[TiO_6]$ clusters in the disordered BZT-75/25 powders. EXAFS spectra indicate distortion of Ti–O and Ti–O–Ti bonds the first and second coordination shells, respectively. UV-Vis absorption spectra confirm the presence of different optical bandgap values and the band structure indicates an indirect bandgap for this material. The density of states demonstrates that intermediate energy levels occur between the valence band (VB) and the conduction band (CB). These electronic levels are due to the predominance of 4d orbitals of Zr atoms in relation to 3d orbitals of Ti atoms in the CB, while the VB is dominated by 2p orbitals related to O atoms. There was good correlation between the experimental and theoretical optical bandgap values. When excited at 482 nm at room temperature, BZT-75/25 powder treated at 500 °C for 2 h exhibited broad and intense PL emission with a maximum at 578 nm in the yellow region.

1. Introduction

Solid solutions known as barium zirconate titanate $[Ba(Zr_xTi_{1-x})O_3$ ceramics, BZT] are prepared by merging barium zirconate ($BaZrO_3$) and barium titanate ($BaTiO_3$) ceramics. BZT ceramics have been used as alternative dielectric materials to replace barium strontium titanate $[(Ba_xSr_{1-x})TiO_3$, BST] ceramics [1–7]. BZT compounds have two main advantages over BST ceramics, low dielectric loss and a high dielectric constant [8]. Moreover, BZT ceramics exhibit excellent microwave dielectric properties at gigahertz frequencies [9,10]. The Zr/Ti ratio is a very important parameter that tailors the type of ferroelectric–paraelectric phase transition and its characteristic Curie temperature

---

* Corresponding author at: Departamento de Química, UESPI-CCN, Rua João Cabral, P.O. Box 2231, 64002-150 Teresina-PI, Brazil.
Tel.: +55 016 3351 82 14.
E-mail addresses: laeciosc@gmail.com, laeciosc@bol.com.br (L.S. Cavalcante).

1369-8001/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2012.12.010

[11]. Several studies on ferroelectric–relaxor properties and diffuse transition of BZT ceramics with different compositions and dopants have been published [12–17].

In general, this material can easily be synthesized because Zr^{4+} ions are chemically more stable than Ti^{4+} ions [18]. BZT ceramics can be prepared by substitution of Ti atoms (atomic weight 47.9 g/mol, ionic radius 74.5 pm) by Zr atoms (atomic weight 91.2 g/mol, atomic radius 86 pm) in the B-sites of this perovskite [19]. Replacement of Ti by Zr depresses the conduction by small polarons hopping between Ti^{4+} and Ti^{3+} ions and decreases the leakage current [20]. A few studies on the optical properties of crystalline and non-crystalline BZT powders or thin films have been reported, including their infrared [21,22], refractive index [23–25], and photoluminescence (PL) properties [26–28].

The electronic structure of BZT ceramic powders has only been addressed in some of the relevant studies. Lauhé et al. [29] used density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package and projection augmented plane waves with the Perdew–Wang exchange correlation potential to determine deformations induced by substitution of octahedral $[ZrO_6]/[TiO_6]$ clusters in the B-sites of perovskite BZT ceramics. Chibisov [30] used quantum mechanical calculations based on electronic DFT and pseudopotential theory to verify the effect of Zr on the atomic and local distortions of $BaTiO_3$. Yin et al. [31] used first-principle calculations based on the pseudopotential plane wave method with the generalized gradient approximation to calculate the optical bandgap and static dielectric constants for cubic and tetragonal structures of $Ba(Zr_xTi_{1-x})O_3$ ($x=0$, 0.25, 0.5, and 0.75). However, there are few reports on *ab initio* theoretical and experimental investigations of the electronic structure of BZT perovskite [32–34]. In these studies, the electronic structure was evaluated by first-principle quantum mechanical calculations based on DFT at the B3LYP level [35,36]. In recent years, huge computational advances have been possible because of technological progress in storage capacity and computer processing. The new generation of computers with multiple processors can drastically reduce the processing time required to investigate the electronic structure of complex solids. This study provides information on the local structure at long and short range by means of X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) techniques. Moreover, first-principle quantum mechanical calculations of the electronic structure [band structure and density of state (DOS)] were performed to determine the optical bandgap values and electronic transitions responsible for the room-temperature PL properties of $Ba(Zr_{0.75}Ti_{0.25})O_3$ (BZT-75/25) powders synthesized by the polymeric precursor method (PPM).

2. Experimental details

2.1. Chemical synthesis of BZT-75/25 powders

BZT-75/25 powders were prepared by PPM with barium nitrate $[Ba(NO_3)_2$, 99% pure, Sigma-Aldrich], titanium (IV) isopropoxide $[Ti(OC_3H_7)_4$, 99%, Aldrich], zirconium *n*-propoxide $[Zr(OC_3H_7)_4$, 99%, NOAH Technologies], ethylene glycol ($C_2H_6O_2$, 99.8%, Sigma-Aldrich) and citric acid ($C_6H_8O_7$, 99.5%, Mallinckrodt) were used as raw materials. First $Ti(OC_3H_7)_4$ was quickly added to an aqueous solution of citric acid to avoid hydrolysis of the alkoxide in air. A clear and homogeneous titanium citrate solution was formed under constant stirring at 90 °C for 8 h. The TiO_2 mass contained in the titanium citrate was determined gravimetrically and corrected to yield the stoichiometric mass. In the second stage, $Zr(OC_3H_7)_4$ was quickly added to an aqueous solution of citric acid and constantly stirred at 90 °C for 8 h to yield a clear and homogeneous zirconium citrate solution. The ZrO_2 mass contained in the zirconium citrate was determined gravimetrically. In the third stage, the Zr and Ti citrate solutions were mixed in a stoichiometric molar ration of 0.75 Zr:0.25 Ti. Then $Ba(NO_3)_2$ was dissolved in the mixed citrate solution at a stoichiometric molar ratio of 1 Ba:0.75 Zr:0.25 Ti. The solution was adjusted to pH 7 by addition of ammonium hydroxide (NH_4OH, 30% in NH_3, Synth) to prevent barium citrate precipitation, which is favored in acid solutions. Then $C_2H_6O_2$ was added to the solution and heated at 120 °C to promote the citrate polymerization by polyesterification [37]. In this system, the citric acid/ethylene glycol ratio was fixed at 60/40 wt%. After polyesterification, a BZT-75/25 polymeric resin formed. The resin was placed in a conventional furnace and heat-treated at 350 °C for 8 h to decompose organic matter derived from $C_6H_8O_7$ and $C_2H_6O_2$. The precursor powders obtained were finally heat-treated at different temperatures (400, 500, 600 and 700 °C) for 2 h.

2.2. Sample characterization

The samples were structurally characterized using various techniques. XRD patterns were recorded on a diffractometer (Rigaku DMax/2500PC, Japan) using Cu K_α radiation in the 2θ range 10°–70° (normal routine) or 10°–110° (Rietveld routine) at a scan rate of 0.02°/min. XANES spectra were collected using the D04B-XAS1 beamline of the Brazilian Synchrotron Light Laboratory (LNLS). The storage ring was operated at 1.36 GeV and ~160 mA. XANES spectra were collected at the Ti K-edge (4966 eV) in transmission mode using a Si(111) channel-cut monochromator. For comparison, after removing the background, all spectra were normalized to obtain the first extended X-ray absorption fine structure oscillation. EXAFS measurements at the Ti K-edge were carried out for each sample between 4850 and 5900 eV (in steps of 2 eV). To provide good energy reproducibility during the measurements, three EXAFS spectra were collected and the energy calibration of the monochromator was checked after each spectrum using a Ti metal foil. The EXAFS spectra were analyzed using ATHENA software with the IFEFFIT code [38]. EXAFS analyses were carried out using the software suite written by Michalowicz [39] according to procedures recommended by the International Workshop on Standards and Criteria in X-Ray Absorption Spectroscopy [40]. After atomic absorption removal and normalization, the $k^3\chi(k)$-weighted EXAFS signal was Fourier-transformed to R distance space in the range 2–8 Å^{-1} k, where k is the wavenumber array. Each spectrum was Fourier-transformed using a Kaiser apodization window, which is a mathematical process used to obtain