



Dyna

ISSN: 0012-7353

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Colombia

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Dyna, vol. 81, núm. 183, febrero, 2014, pp. 126-131

Universidad Nacional de Colombia  
Medellín, Colombia

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# ELECTRONIC, STRUCTURAL AND FERROELECTRIC PROPERTIES OF THE $\text{Ba}_2\text{ZrTiO}_6$ DOUBLE PEROVSKITE

## PROPIEDADES ELECTRÓNICAS, ESTRUCTURALES Y FERROELÉCTRICAS DE LA DOBLE PEROVSKITA $\text{Ba}_2\text{ZrTiO}_6$

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Received for review November 08<sup>th</sup>, 2012, accepted October 18<sup>th</sup>, 2013, final version December, 08<sup>th</sup>, 2013

**ABSTRACT:** We report the synthesis, the structural characterization, the ferroelectric behavior and the electronic properties of complex perovskite  $\text{Ba}_2\text{ZrTiO}_6$ . Samples of  $\text{Ba}_2\text{ZrTiO}_6$  were synthesized through the standard solid state reaction method. The crystalline structure was studied by means of X-ray diffraction experiments and Rietveld-like analysis. Results reveal that the material crystallizes in a rhomboidal structure, space group  $R-3$  (#148), with cell parameter  $a=5.8038(7)$  Å. The ferroelectric response of material was established from curves of polarization as a function of applied electric field. Our results reveal that the double perovskite  $\text{Ba}_2\text{ZrTiO}_6$  has a ferroelectric hysteretic behavior at room temperature. The studies of the electronic structure show that  $\text{Ba}_2\text{ZrTiO}_6$  behaves as a nonmetallic material with gap energy 2.32 eV. The structural parameters obtained from energy minimization, through the Murnaghan equation state are 99.5% in agreement with the experimental data.

**Key words:** Double perovskite, ferroelectric properties, electronic structure

**RESUMEN:** En este trabajo reportamos la síntesis, la caracterización estructural, el comportamiento ferroeléctrico y las propiedades electrónicas de la perovskita compleja  $\text{Ba}_2\text{ZrTiO}_6$ . Las muestras fueron sintetizadas mediante el método estándar de reacción de estado sólido. La estructura cristalina se estudió a través de experimentos de difracción de rayos X y análisis de tipo Rietveld. Los resultados revelan que el material cristaliza en una estructura romboédrica, perteneciente al grupo espacial  $R-3$  (#148), con un parámetro de red  $a=5.8038(7)$  Å. La respuesta ferroeléctrica del material se estableció a partir de curvas de polarización en función del campo eléctrico aplicado. Nuestros resultados muestran que la perovskita  $\text{Ba}_2\text{ZrTiO}_6$  evidencia un comportamiento histerético ferroeléctrico a temperatura ambiente. Los estudios de la estructura electrónica muestran que esta cerámica se comporta como un material no metálico con brecha de energía 2,32 eV. Los parámetros estructurales obtenidos a partir de la minimización de energía, a través de la ecuación de estado Murnaghan, son 99.5% acordes con los datos experimentales.

**Palabras clave:** Perovskita compleja, propiedades ferroeléctricas, estructura electrónica

### 1. INTRODUCTION

Complex perovskites with formula  $\text{A}_2\text{BB}'\text{X}_6$ , where A represents an alkaline earth, B and B' are metal transition and X is the oxygen, have been studied because of their physical properties [1], which depend on structural distortions and the characteristic properties of B and B' cations. This chemical configuration results in multiple opportunities to combine different elements of the periodic table, generating the possibility of synthesizing new materials that involve a larger gamma of physical properties. One

well-known simple perovskite, which is well known because it exhibits a ferroelectric character, is  $\text{BaTiO}_3$  [2]. Partial substitutions of Ti by the Zr cation have been done by other authors, showing the evolution of the electric behavior from a ferroelectric response, for low concentration of Zr, to a ferroelectric relaxor [3] and a dielectric behavior for high concentrations of Zr [4]. However, the position of the substitutive cations in the crystallographic cell of the material is not usually reported. Location of all ions in the lattice is important for inferring the possibility of obtaining spontaneous polarization, in order to give rise to ferroelectric

behavior. In the case of polycrystalline samples, the ferroelectric behavior depends greatly on the grain size, because the effects of imperfection frequently dominate the ferroelectric response of small grains, where a significant fraction of the material volume may be influenced by grain boundaries. It is known that cationic disorder produces substantial changes of the ferroelectricity of complex perovskites [5]. The aim of this paper is to show the synthesis process for producing the double perovskite  $\text{Ba}_2\text{ZrTiO}_6$ ; to analyze the crystallographic single phase; to study the electronic structure; and, the most important objective of the study being to investigate the ferroelectric response of the material at room temperature. Our results reveal that  $\text{Ba}_2\text{ZrTiO}_6$  crystallizes in a rhomboidal double perovskite structure, which is a convenient lattice for determining the occurrence the ferroelectric character, observed by the occurrence of hysteretic curves of electric polarization as a function of variable applied fields.

## 2. EXPERIMENTAL PROCESS

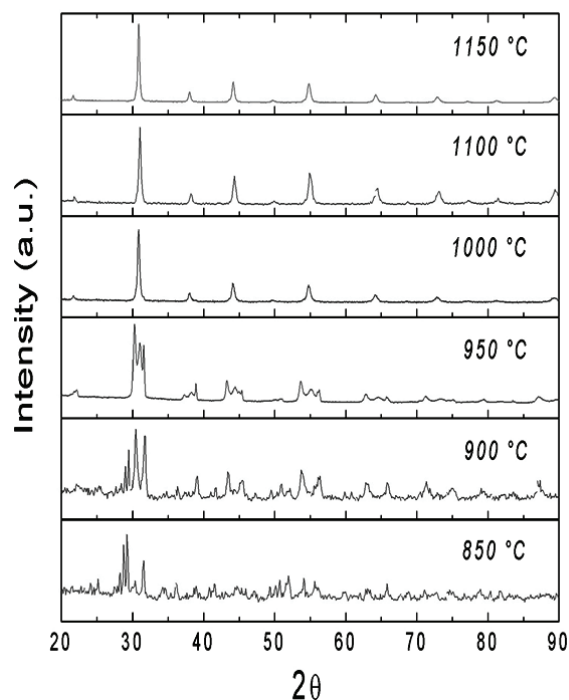
Samples were synthesized by means of the solid state reaction recipe. The precursor powders  $\text{BaCO}_3$  (Aldrich 99.9%),  $\text{TiO}_2$  (Aldrich 99.99%) and  $\text{ZrO}_2$  (Aldrich 99.99%) were stoichiometrically mixed according to the chemical formula  $\text{Ba}_2\text{ZrTiO}_6$ . The mixture was ground to form pellets of 9.55 mm diameter and 1.85 mm thickness. Then the material was annealed in a sequential thermal procedure at 850, 900, 950, 1000, 1100 and 1150 °C for 144 hours, including five regrinding and pelletizing procedures to make six thermal steps of 24 hours each. An X-Ray diffraction (XRD) experiment was performed by means of a PW1710 diffractometer with  $\lambda_{\text{CuK}\alpha} = 1.54064 \text{ \AA}$ . Rietveld refinement of the diffraction pattern was made by the GSAS code [6]. Electric polarization curves were obtained by means of a Radiant Ferroelectric Tester, which included a  $\pm 10 \text{ kV}$  source for measurements in bulk-samples.

## 3. CALCULATION METHOD

We applied the Full-Potential Linear Augmented Plane Wave method (FP-LAPW) within the framework of the Kohn-Sham Density Functional Theory (DFT) [1], and adopted the Generalized Gradient (GGA) approximation for the exchange-correlation energy

due to Perdew, Burke and Ernzerhof [7]. The self-consistent process was developed using the numeric package Wien2k [8]. Taking the experimental unit cell data as input, the structures studied in this work were fully relaxed with respect to their lattice parameters and the internal degrees of freedom compatible with the space group symmetry of the crystal structure. The resulting energies versus volume functions have been fitted to the equation of state due to Murnaghan [9] in order to obtain the minimum energy value, the bulk modulus, its pressure derivative and the equilibrium lattice parameters and associated volume. The muffin-tin radii used were 2.40, 1.74, 2.14 and 1.53 for Ba, Ti, Zr and O respectively, angular momentum up to  $l = 10$  inside the muffin-tin sphere, a maximum vector in the reciprocal space of  $G_{\text{max}} = 12.0$ ,  $\text{RMT} \cdot K_{\text{max}} = 7.0$ , and a mesh of 800 points in the first Brillouin zone (equivalent to a maximum of 85 k points in the irreducible Brillouin zone). Finally, the convergence criteria for the self-consistent calculation was 0.0001 Ry for the total energies, 0.0005 u.a. in the charge and 1.0 mRy/u.a. in the internal forces.

## 4. RESULTS AND DISCUSSION

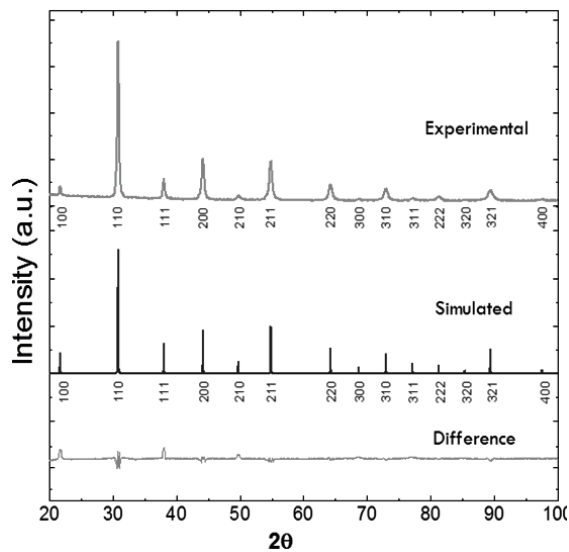


**Figure 1.** Diffraction patterns showing results of thermal treatment for obtaining rhomboidal structure for the double perovskite  $\text{Ba}_2\text{TiZrO}_6$ .

The sequence of crystallization obtained by the thermal process, described in the experimental setup, for  $\text{Ba}_2\text{TiZrO}_6$  samples is shown in the diffraction patterns of Figure 1. As shown in Figure 1, the fourth thermal step, at 1000 °C, evidences the perovskite phase of  $\text{Ba}_2\text{TiZrO}_6$ . However, some incipient peaks corresponding to impurities are observed close to 24°. These impurities vanish after the last thermal treatment at 1150°C. A rigorous Rietveld refinement from experimental data of the diffraction pattern reveals that crystallization of material occurs in a rhombohedral double perovskite, which belongs to the space group  $R-3$  (#148).

The difference between simulated and experimental patterns is shown in Figure 2. The lattice parameters obtained from the refinement process were  $a=5.803(8)$  Å; primitive vectors angle  $\alpha=59.9675^\circ$ . This result is  $\sim 98.5\%$  in agreement with the value supplied by the Structure Prediction Diagnostic Software [10], which gives  $a=5.7177$  Å.

In Figure 2, the top plot represents experimental data, the middle plot is the simulated refined diffractogram, and the line at the bottom corresponds to the difference between experimental and simulated patterns. Indexes of crystallographic planes are indicated in figure 2. The parameters of refinement are:  $R_p^2=4.69\%$  and  $\chi^2=2.26$ .



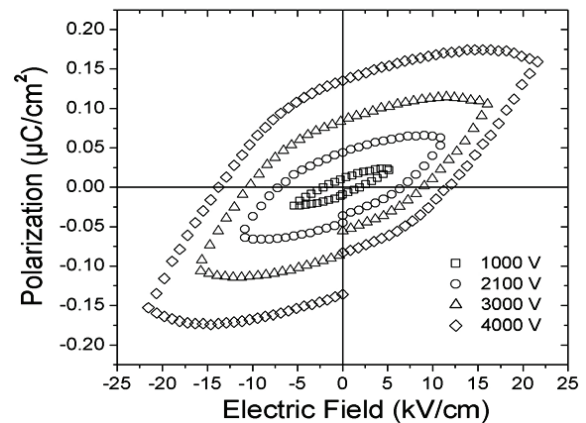
**Figure 2.** Experimental and simulated diffraction patterns of  $\text{Ba}_2\text{TiZrO}_6$  material after Rietveld refinement. The bottom line corresponds to the difference between experimental and theoretical diffractograms.

Atomic positions and occupancies of ions in the structure are shown in table 1.

**Table 1:** Atomic position for the rhombohedral structure of  $\text{Ba}_2\text{TiZrO}_6$ , obtained by Rietveld refinement of diffraction patterns through the GSAS code.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ba	0.7558	0.7558	0.7558
Ti	0.0000	0.0000	0.0000
Zr	0.5000	0.5000	0.5000
O	0.7745	0.7745	0.2255
Ba	0.2442	0.2442	0.2442
O	0.2255	0.7745	0.7745
O	0.7745	0.2255	0.7745
O	0.2255	0.2255	0.7745
O	0.7745	0.2255	0.2255
O	0.2255	0.7745	0.2255

One important parameter in perovskite materials is the tolerance factor, which is related to the probability of the formation of octahedral coordination of B and B' cations with the oxygen anion. The tolerance factor calculated for  $\text{Ba}_2\text{TiZrO}_6$  material was 1.0312. This value, above 1.0, suggests the possibility of obtaining spontaneous polarizations from structural distortions that give rise to the ferroelectric character in the simple perovskite  $\text{BaTiO}_3$  [11], for example.

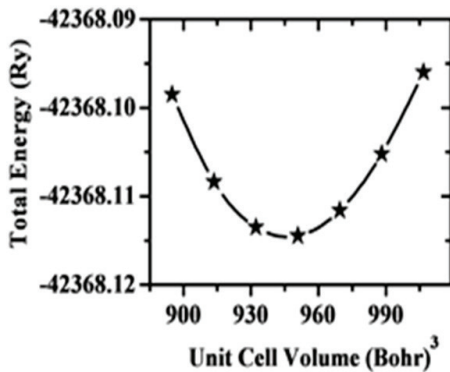


**Figure 3.** Ferroelectric hysteresis measured at ambient temperature for the perovskite  $\text{Ba}_2\text{TiZrO}_6$ , for several applied fields up to  $2.16 \times 10^4$  V/cm.

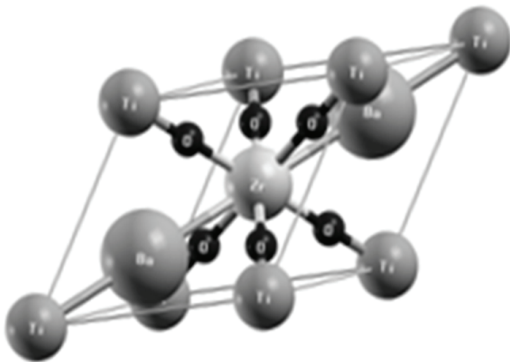
Another important characteristic for the possible application of the material in ferroelectric devices is the

response to high applied fields. In Figure 3 sequence of polarization for applied electric fields up to 22.5 kV/cm is shown. As observed in Figure 3, for the higher applied field we determine a saturation polarization of  $0.175 \mu\text{C}/\text{cm}^2$ , in a curve with a remnant polarization of  $0.3125 \mu\text{C}/\text{cm}^2$  and a coercive field of 12.0 kV/cm. These values are in agreement with strong ferroelectric materials of the  $\text{BaTiO}_3$  family [12,13] that evidence polarization saturation, remnant polarization and coercive fields, which are appropriate for technological applications in ferroelectric memories.

Figure 4 shows the optimization of energy as a function of volume. The minimum energy value is obtained for  $-42368.114575 \text{ Ry}$ . The equilibrium volume is  $945.7608 \text{ Bohr}^3$ , which corresponds with a lattice constant  $a=11.0206 \text{ Bohr}$  [ $a=5.831(8)$ ] with a volume modulus  $B_0=155.9553 \text{ GPa}$ . The lattice parameter obtained from the GGA approximation is 99.5% in agreement with our experimental results.



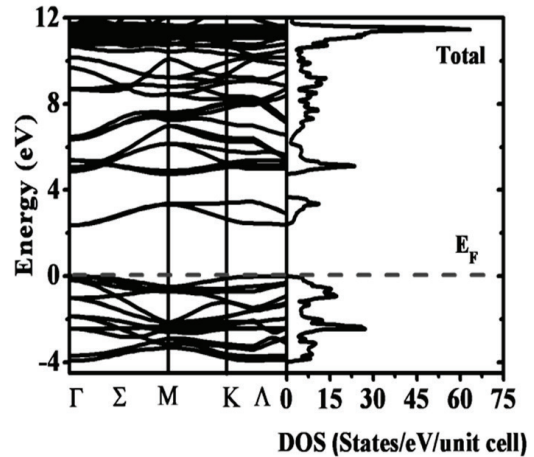
**Figure 4.** Calculated total energy as a function of volume and  $c/a$  factor for the  $\text{Ba}_2\text{TiZrO}_6$  material



**Figure 5.** Rhombohedral structure of the  $\text{Ba}_2\text{TiZrO}_6$  perovskite for the R-3 space group.

The difference between the two minimums is less than the convergence parameter. The minimums for the energy as a function of volume were obtained by adjusting Murnaghan's state equation to the square points [9]. The rhombohedral structure obtained by both procedures, Rietveld refinement of diffraction patterns and theoretical minimization of energy by the DFT method, is shown in figure 5.

Figure 6 corresponds to electronic properties of the perovskite  $\text{Ba}_2\text{TiZrO}_6$ . The Density of States (DOS) along the high symmetry directions in the first Brillouin zone and the band structure are shown. The energy of the electrons as a function of the wave vector  $k$  is also observed, which was taken along the  $\Gamma$ - $\Sigma$ -M-K- $\Lambda$ - $\Gamma$  directions.



**Figure 6.** Band structure and total DOS for the  $\text{Ba}_2\text{TiZrO}_6$  material. The Fermi level is the energy reference.

The DOS and band structure are calculated for the equilibrium configuration by using the lattice constant corresponding to the volume which minimizes the energy of the system.

The energy reference is selected to be the Fermi level in  $E=0$ . It is observed that the  $\text{Ba}_2\text{TiZrO}_6$  material presents a nonmetallic behavior with a direct energy gap of 2,32 eV at the Fermi level. Furthermore, a valence sub-band sited in the regime between -4 eV and the Fermi level is observed in Figure 6, due to principal contributions of the  $2s$ -O,  $3d$ -Ti and  $4d$ -Zr orbital, as corroborated in Figure 7. A minority contribution of the  $4s$ -Ti and  $5s$ -Zr electrons is also observed. In the intermediate region



of the conduction band, between 2,32 eV and 3,7 eV, the majority contribution is due to the 3*d*-Ti orbital.

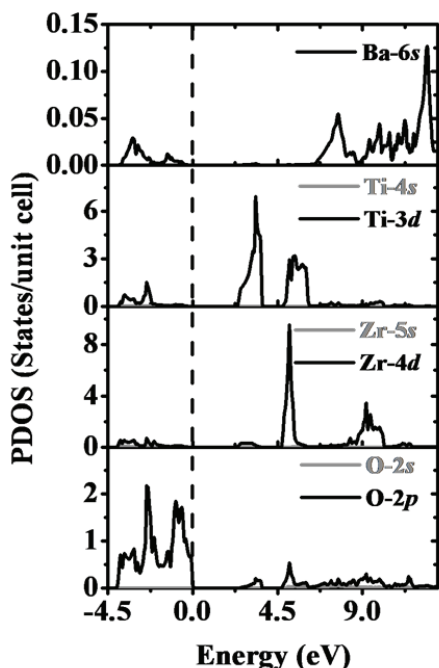


Figure 7. Partial DOS calculated for the Ba<sub>2</sub>TiZrO<sub>6</sub> material.

On the other hand, from 3,7 eV up to 4,71 eV a gap of forbidden energies, internal to the conduction band, is determined. Likewise, the 6*s*-Ba, 4*d*-Zr, 3*d*-Ti and 2*p*-O electron contributions give rise to the regime between 4,74 eV and 12,0 eV, with a small share of 4*s*-Ti, 5*s*-Zr and 2*s*-O orbitals.

## 5. CONCLUSIONS

In summary, we report the synthesis of polycrystalline Ba<sub>2</sub>TiZrO<sub>6</sub> double perovskite. The complete thermal process is seen through a sequence of diffraction patterns. Rietveld refinement reveals that a single crystallographic phase of rhombohedral perovskite was obtained, space group *R*-3 (#148), with lattice parameters  $a=5.803(8)$  Å. The tolerance factor was calculated to be 1.03. Measurements of polarization as a function of applied electric fields show a hysteretic behavior, which is characteristic of ferroelectric materials. Values of saturation and remnant polarization suggest that this material may be used for technological applications in devices for information storage. Lastly, calculations of band and electronic structure reveal the nonmetallic behavior of Ba<sub>2</sub>TiZrO<sub>6</sub>, with an energy gap of 2.32 eV and  $B_0=155.9553$  GPa volume modulus.

## 6. ACKNOWLEDGMENTS

This work was partially supported by the *División de Investigaciones Sede Bogotá* (DIB) of the *Universidad Nacional de Colombia*.

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