Materials Research. 2013; 16(5): 1002-1005
DOI: 10.1590/S1516-14392013005000093

Structural and Magnetic Properties of $YBa_2Cu_3O_7/BaZrO_3$ Composites

David A. Landínez-Téllez[a], Jairo Roa-Rojas[a], Gabriel Peña-Rodríguez[b]*

[a]*Physics of New Materials Group, Department of Physics, Universidad Nacional de Colombia* – UNAL, Bogotá-Colombia
[b]Ceramic Technology Research Group, Universidad Francisco de Paula Santander – UFPS, Av. Gran Colombia, 12E-96 Cúcuta-Colombia

Received: December 20, 2012; Revised: February 5, 2013

We reported a study of the structural and magnetic properties of $BaZrO_3$ (BZO) as possible substrate material for the production of $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting films. Rietveld analyses of the X-ray diffraction pattern show that BZO crystalizes as a cubic perovskite, space group Pm3m (#221). Chemical stability and crystallographic coupling between BZO and YBCO were examined by characterizing YBCO/BZO (10, 30 and 50 YBCO vol%) polycrystalline composites. Morphological and compositional analyses of composites were performed through scanning electron microscopy and energy dispersive X-ray experiments, respectively. Response of magnetization measurements revealed that the proximity of BZO does not affect the superconducting transition temperature (T_c=90,2 K) of YBCO material. Our results evidenced that the BZO is an excellent candidate to be substrate for the fabrication of YBCO superconducting thin films.

Keywords: *complex perovskite, magnetic properties, superconducting film substrates*

1. Introduction

The complex cubic perovskite oxides have been investigated for their use as potential new substrates for the production of cuprate superconducting films[1,2]. For good quality substrates, the material candidate must satisfy the following requirements: chemical stability, e. g., absence of chemical reaction at the interface substrate-film; good lattice parameter coupling at the crystallographic plane substrate-film to guarantee the epitaxial growth; and the presence of the substrate material must not affect the superconducting properties of the film[3]. The high chemical reactivity of $YBa_2Cu_3O_{7-\delta}$ (YBCO) with most conventional substrate materials at the processing temperature imposes severe restrictions on the availability of substrates for the YBCO superconducting films[4]. Moreover, the divergence of the crystallographic properties at the interface between YBCO and the commonly available substrates, as well as the difficulty in obtaining chemical and structural properties compatible with the YBCO superconductor, constitute a great motivation to produce new optimal materials for this application. For example, MgO, the widely utilized substrate for YBCO thin films, produces an interlayer of barium salt at the YBCO/MgO interface when the processing temperature is above 700 °C[5]. Another extensively used substrate for YBCO, $LaAlO_3$, exhibits an excellent lattice coupling but it has the disadvantage of being available only as twinned single-crystal[6]. Studies on the effect of $BaZrO_3$ on $YBa_2Cu_3O_7$ superconducting thin films as pinning centers in order to improve the critical current density have been reported[7]. A microstructural analysis of the $BaZrO_3$ as potential substrate for $YBa_2Cu_3O_7$ films was performed without consider it effect on the superconducting properties[8]. In this paper, we reported the systematical steps followed for the production and characterization of $BaZrO_3$ (BZO) as eventual substrate for the fabrication of YBCO high temperature thin films. Pure BZO and YBCO/BZO (0 to 100 vol%) were produced and characterized to study the viability of utilizing BZO as substrate to produce YBCO superconducting thin films.

*e-mail: gpenaro@ufps.edu.co; ggabrielp@yahoo.com

2. Experimental

BZO polycrystalline samples were prepared by a solid-state reaction process. Stoichiometric ratios of the precursor powders $BaCO_3$ (purity 99,98%) and ZrO (99.99%) were finely ground and thoroughly mixed. The precursor powder was pressed into a disc and the material was calcined at 850 °C for 148 h in an ambient atmosphere. By using a Nickel-filtered CuKα radiation (λ=1.5406 Å) of a SIEMENS D5000 diffractometer, X-ray diffraction (XRD) spectra were taken of the calcined powder of samples. The material was again crushed, finely ground and pressed at 6 ton/cm^2 to form a disc (10 mm diameter, 2 mm thickness). This disc was sintered at 900 °C for 17 h in a vacuum atmosphere and furnace-cooled to room temperature. The XRD pattern of the sintered material was analyzed by a Rietveld refinement through the GSAS code[9]. For chemical stability studies, a single-phase YBCO superconductor was prepared by solid-state synthesis[10]. 50%, 70% and 90% vol% of BZO were mixed in YBCO superconductor powder (50/50, 30/70 and 10/90) and the mixture was pressed into circular discs (10 mm diameter, 1 mm thickness) at a pressure of 5 ton/cm^2 and heat treated at 960 °C in oxygen atmosphere for 12 h. After the heat treatment, YBCO-BZO samples were slowly cooled down to room temperature for proper oxygenation. XRD spectra of these samples were recordered from 20° to 90° for crystallographic phase characterization, the chemical stability and the crystallographic parameter coupling of the YBCO/BZO composites. The morphological characterization of samples was systematically effectuated from scanning electron microscopy (SEM), by using Quanta 200 SEI Electron-Optics equipment. Compositional analysis of films was performed by energy dispersive X-ray (EDX) experiments by means of a microprobe coupled to the SEM microscopy. The influence of BZO on the superconducting properties of YBCO was studied in the composite samples through DC magnetization measurements by using a Quantum Design model 2000 MPMS SQUID system.

3. Results and Discussion

The XRD pattern of Figure 1 consists of strong peaks which are characteristics of a primitive cubic perovskite ABO_3, where A=Ba is the large ion (149 Å) suitable to the 12-coordinated cube-octahedral sites and B=Zr is the smaller ion (86 Å) suitable to the 6-coordinated octahedral site. No evidence for a distortion from the cubic symmetry is observed in the XRD pattern.

The lattice parameters of BZO, calculated from the Rietveld refinement of the XRD data is *a=4,196(9) Å*. This result is 99% in agreement with the theoretical value given by the Structure Prediction Diagnostic Software,[11] which predicts a cell parameter *a=4,156(0) Å*. The Rietveld parameters were χ^2=1,497 and R_F=6%, which are between the considered acceptable values χ^2<2 and R_F<10%. For the YBCO, the obtained XRD pattern is close to the standard reported in the JCPDS crystallographic database[12].

In the perovskite like materials the distortion of the octahedral from the ideal ABO_3 cubic structure is determined by the tolerance factor

$$\tau = \frac{r_A + r_0}{\sqrt{2}\left(r_B + r_O\right)} \quad (1)$$

where r_A, r_B and r_O are the ionic radii of the A, B and O ions[13]. The calculated value of the tolerance factor for the BZO compound is τ=*1.004*, which is close to the ideal τ=*1.000* of the perfect cubic perovskite.

The atomic positions of Ba, Zr and O ions into the unit cell are shown in Table 1.

In order to verify the possibility of using BZO as a substrate material for thin films of YBCO superconductor, we have studied the chemical reactivity of YBCO with BZO (50/50, 30/70 and 10/90). XRD patterns of these composites are shown in Figure 2. As seen in this figure, all the peaks in the XRD could be indexed either for YBCO or for BZO and there is no extra XRD peak is found. Within the accuracy of XRD technique, these results show that YBCO and BZO remain as two distinct separate phases in the YBCO/BZO composites and BZO is chemically stable with YBCO superconductor for all vol% addition of BZO. Regarding the crystallographic coupling, we notice that there is a matching of 1.3% between the BZO lattice parameter and the crystallographic constant of the most used substrate MgO (*a=4,212 Å*). Figure 2 shows the XRD pattern analyzed for the YBCO/BZO 50/50 composite.

It is observed that for all vol% of YBCO/BZO concentrations, only the crystalline phases of YBCO (orthorhombic) and BZO (cubic) were obtained.

Energy dispersive X-ray (EDX) analysis was performed on the single phase BZO for the quantitative elemental chemistry analysis. The result revealed the expected percentages for the calculated stoichiometric composition (up to 98%), without evidences of impurity traces in the samples (Table 2).

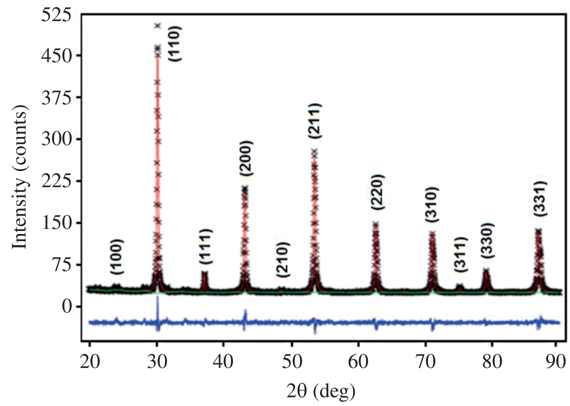

Figure 1. Characteristic XRD pattern for the BZO cubic perovskite. Symbols represent experimental diffraction data, and the base line is the difference between experimental and simulated patterns (continuous line).

Table 1. Atomic positions of the BZO ions.

Atom	X	y	Z
Ba	0	0	0
Zr	0.5	0.5	0.5
O	0	0.5	0.5
O	0.5	0	0.5
O	0.5	0.5	0

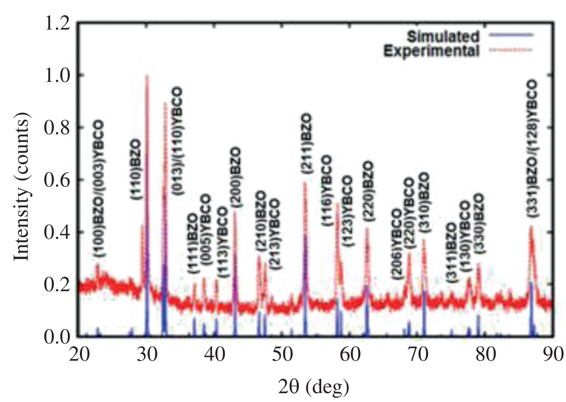

Figure 2. Refined XRD pattern for the 50/50 YBCO/BZO composite.

The surface morphology of sintered YBCO/BZO composites was investigated by scanning electron microscopy (SEM). The result for the 50/50 YBCO/BZO composite is shown in the micrograph of Figure 3. This indicates that the surface of the samples presents a crystalline character, which is typical of a polycrystalline ceramic material.

Additionally, Figure 3 shows a homogeneous surface morphology and particle size distribution with the grain average size estimated to be *2 μm* for the YBCO material and sub-micrometric for the BZO compound. We notice that there is no detectable interface interaction between the BZO and the YBCO grains. It is observed that the BZO particles are clearly distributed in the YBCO matrix. This result was corroborated from the EDX experiments. From these results, it can be confirmed, that there is chemical stability between the YBCO and BZO compounds in the material.

Table 2. Comparison between expected and obtained percentages.

Theoretical %	Experimental %
10/90	11.35/88.65
30/70	36.95/63.05
50/50	51.03/48.97

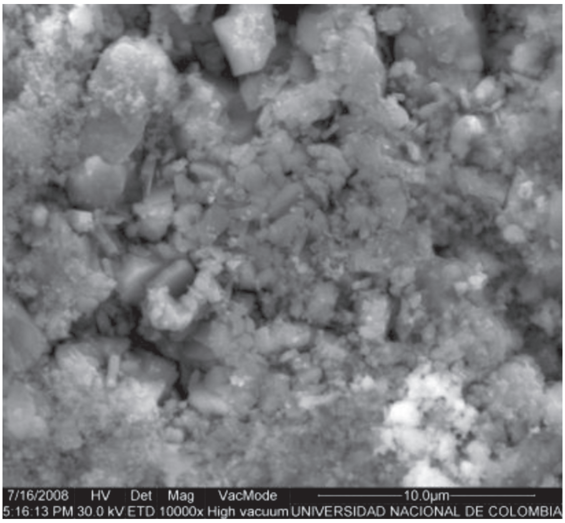

Figure 3. SEM micrograph for the 50/50 YBCO/BZO composite. YBCO are the particles with size varying from 1 to 4 μm, and the BZO particles are of the order sub-micrometer[14].

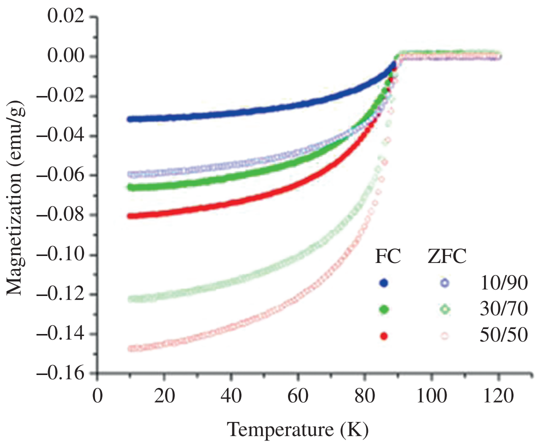

Figure 4. Critical temperature and Meissner effect for (50/50, 30/70 and 10/90) YBCO/BZO composites in curves of DC magnetization as a function of temperature.

The superconductivity of YBCO/BZO composite samples was studied by measuring the DC magnetization with an applied field $H=100\ Oe$ and in the temperature range *10* to *120 K*. Figure 4 shows curves of the DC magnetization as a function of temperature for the YBCO/BZO composites with 50, 70 and 90 vol% of BZO addition in YBCO superconductor.

As shown on this picture, all the YBCO/BZO composites have the same superconducting transition temperature $T_c=90{,}2\ K$ as expected in a pure YBCO superconductor[15]. This shows that for all vol% of an insulating ceramic oxide (BZO) addition in YBCO there was not any deteriorating effect on the transition critical temperature of YBCO superconductor.

The Meissner effect, characterized by the negative magnetization response, is also observed in all composites. Thus as discussed earlier BZO is chemically stable with YBCO superconductor and at the same time it did not have any deteriorating effect on the superconducting property characterized by the transition temperature.

4. Conclusions

It is found by the structural characterization that the cell parameter of BZO is close to the commercial MgO lattice parameter and is chemically non-reacting with the YBCO superconducting even under extreme processing conditions. It is observed that there is no chemical reaction between these compounds into the YBCO/BZO composites. Were carried out morphological characterization to evaluate the chemical reaction between the insulating BZO and the metallic YBCO materials. In the YBCO/BZO composites experimental analysis, the formation of separate single-phase grains of YBCO and BZO was observed by SEM images and XRD characterization. Energy dispersive X-ray (EDX) analysis shows that there is no evidence of impurity traces in the samples. DC magnetization measurements reveal that the presence of BZO does not affect the superconducting properties of YBCO. This systematic work corroborated our hypothesis that the BZO cubic perovskite can be utilized as substrate material for the fabrication of YBCO thin films.

Acknowledgments

This work was partially financed by Division of Investigations of the National University of Colombia (DIB – Hermes Code 13893) and “El Patrimonio Autónomo Fondo Nacional de Financiamiento para la Ciencia, la Tecnología y la Innovación Francisco José de Caldas” Contract RC - No. 0850-2012”. Authors wish to thank Karen Hallt and Vanessa Rangel, for careful review of the paper.

References

1. Madueño Q, Landínez Téllez DA and Roa-Rojas J. Production and characterization of Ba_2NdSbO_6 complex perovskite as a substrate for $YBa_2Cu_3O_{7-}\delta$ superconducting films. *Modern Physics Letters B*. 2006; 20(8):427. http://dx.doi.org/10.1142/S021798490601069X
2. Tovar H, Ortiz Díaz O, Landínez Téllez DA and Roa-Rojas J. $Ba_2NdZrO_{5.5}$ as a potential substrate material for $YBa_2Cu_3O_{7-}\delta$ superconducting films. *Physica Status Solidi (C)*. 2007; 4(11):4294. http://dx.doi.org/10.1002/pssc.200675921
3. Ortiz Díaz O, Roa-Rojas J, Landínez Téllez DA and Albino Aguiar J. Evaluation of Sr_2YSbO_6 as a new substrate for $YBa_2Cu_3O_{7-}\delta$ superconductor thin films. *Modern Physics Letters B*. 2004; 18(19-20):1035. http://dx.doi.org/10.1142/S0217984904007578
4. Ortiz-Díaz O, Landínez Tellez DA and Roa-Rojas J. Properties of $Yba_2Cu_3O_{7-}\delta$ Superconducting Films on Sr_2YSbO_6 Buffer Layers. In: Grigorashvili Y. *Superconductors, Properties, Technology and Applications*. Rijeka: Ed. Intech; 2012. p. 261-284.
5. Perng LH, Chin TS, Chen K and Lin CH. Y-Ba-Cu-O superconducting films grown on (100) magnesia and sapphire substrates by a melt growth method without crucible. *Superconductor Science and Technology*. 1990; 3(5):233. http://dx.doi.org/10.1088/0953-2048/3/5/004
6. Phillips JM. Substrate selection for high-temperature superconducting thin films. *Journal of Applied Physics*. 1996; 79(4):1829. http://dx.doi.org/10.1063/1.362675
7. Ichinose A, Naoe K, Horide T, Matsumoto K, Kita R, Mukaida M et al. Microstructures and critical current densities of YBCO films containing structure-controlled $BaZrO_3$ nanorods. *Superconductor Science and Technology*. 2007; 20(12):1144. http://dx.doi.org/10.1088/0953-2048/20/12/010
8. Baca FJ, Emergo RL, Wu JZ, Haugan TJ, Reichart JN and Barnes PN. Microstructural Characterization of $YBa_2Cu_3O_{7-x}$ Films With $BaZrO_3$ Nanorods Grown on Vicinal $SrTiO_3$ Substrates. *IEEE Transactions on Applied Superconductivity*. 2009; 19:3371-4. http://dx.doi.org/10.1109/TASC.2009.2017908
9. Jiang XP, Zhang JS, Huang JG, Jiang M, Qiao GW, Hu ZQ et al. Study on solid state reaction process of the $YBa_2Cu_3O_{7-x}$ compound. *Materials Letters.* 1988; 7(7-8):250-5. http://dx.doi.org/10.1016/0167-577X(88)90151-6
10. Toby BH. EXPGUI, a graphical user interface for GSAS. *Journal of Applied Crystallography*. 2001; 34:210-3. http://dx.doi.org/10.1107/S0021889801002242
11. Lufaso MW and Woodward PM. Prediction of the crystal structures of perovskites using the software program *SpuDS*. *Acta Crystallographica Section B*. 2001; 57:725-38. http://dx.doi.org/10.1107/S0108768101015282
12. Joint Committee on Powder Diffraction Standards – JCPDS. *Crystallographic database*. PDF # 84-1760.
13. Triana CA, Landínez Téllez DA and Roa-Rojas J. Synthesis process and structural characterization of the Sr_2EuRuO_6 complex perovskite. *Journal of Alloys and Compounds*. 2012; 516:179-85. http://dx.doi.org/10.1016/j.jallcom.2011.12.033
14. Mohanta A and Behera D. Fluctuation induced magneto-conductivity studies in $YBa_2Cu_3O_{7-}\delta + xBaZrO_3$ composite high-T_c superconductors. *Physica C*: Superconductivity. 2010; 470(4):295-303. http://dx.doi.org/10.1016/j.physc.2010.01.038
15. Wu MK, Ashburn JR, Torng CJ, Hor PH, Meng RL, Gao L et al. Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure. *Physical Review Letters*. 1987; 58:908-10. http://dx.doi.org/10.1103/PhysRevLett.58.908