Chemically Processed BaZrO$_3$ Nanopowders as Artificial Pinning Centres

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Abstract. This work reports on the preparation of a BaZrO$_3$ (BZO) nanopowder by the chemical decomposition of an oxalate precursor starting from barium acetate and zirconium oxychloride. The X-ray peak profile analyses and the scanning electron microscopy (SEM) have indicated that the mean powder size ranges from 30nm to 340 nm for the thermal treatment temperature varying from 700°C to 1200°C, respectively. The as prepared powder has been used to manufacture YBCO-5 mol. % BZO composite targets from which epitaxial YBCO thin films on (100)SrTiO$_3$ substrate were ablated. The X-ray analysis have revealed that the BZO nanoislands are epitaxially grown throughout the YBCO film, having the same epitaxial relationship as YBCO. Moreover, as revealed by SEM, the presence of BZO considerably improves the morphology of the YBCO film. The critical temperature ($T_c$) registered a slight decrease with the BZO concentration. Nevertheless, the BZO addition resulted in an improvement of the critical current density, $J_c$. The $J_c$vs$B$ curve exhibits a large plateau extended up to about 2.5 Tesla. The YBCO-BZO composite films showed pinning forces with a $c$-axis correlated character, as revealed by the angular behaviour of $J_c$.

1. Introduction

Barium zirconate (BZO) is the most attractive material to induce artificial pinning centres both in YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) bulk melt textured and thin films, in order to increase the critical current density $[1,2]$. The main reasons for using BZO as artificial pinning centres in YBCO are: (a) BZO has a high melting temperature with respect to YBCO and so the growth kinetics should be slow, leading to small particles, (b) zirconium does not substitute in the YBCO structure and (c) although BZO can grow epitaxially with YBCO, it has a large lattice mismatch (approximatively 9%), so strain between the phases could introduce defects for enhanced pinning. The chemical route synthesis provides an atomic level mixing of elements, reducing the diffusion path up to nanometric scale for obtaining the desired material and, as a consequence, needs lower synthesis temperature than by solid state reactions. The coprecipitation technique is the most common method for the preparation of ceramic oxide powders with an uniform composition on a nanometric level and involves different variables such as: the concentration of the precursors, the pH of precipitation, washing procedure, aging, drying etc. The variation of these parameters will have an important effect on the performance of the final product $[3]$. In case of a multicomponent system, this technique is usually limited to cations of chemically similar properties. However, using BaZrO$_3$ it will be shown that the coprecipitation can be also successfully applied to elements distant in the periodic table. Moreover, the oxalate processing is suited for a large scale manufacturing of BaZrO$_3$ due to the low equipment/reagent costs and high reproducibility.
The paper presents the chemical synthesis of pure BZO nanopowders for YBCO/BZO composite targets manufacturing for the pulsed laser deposition (PLD). The YBCO films ablated from these targets have demonstrated that the BZO nanoislands are epitaxially grown within the YBCO film with the BZO a-axis//YBCO c-axis. The size of the BZO nanoislands, estimated from the full-width at half-maximum (FWHM) of the (100) BZO peak using the Scherrer formula, is of about 20 nm.

2. Experimental

Barium acetate Ba(CH$_3$COO)$_2$ (Alfa Aesar) and zirconium oxychloride ZrOCl$_2$.8H$_2$O (Loba-Chemie Wien) 0.5 M solutions, previously prepared by sonication, were thoroughly mixed at ambient temperature. A 1M ammonium oxalate (NH$_4$)$_2$C$_2$O$_4$.H$_2$O (Merck) solution was rapidly added under vigorous stirring and the resulted precipitate was filtered using Whatman # 3 filter paper, washed with deionised water (0.1 µS), dried at 100°C, then calcined for 2 hours in air between 500 and 1200°C in a tube furnace, at a heating rate of 10°C/min. With the as-prepared BZO ground powders, YBCO composite targets have been prepared by solid sate reaction at 950°C for 24 hours in flowing oxygen. The oxalate precursor was characterized by FT-IR spectroscopy and DTA-TG thermal analysis coupled with a quadrupole mass spectrometer QMS 200 atmospheric sampling system (Stanford Research System) through a 120 cm long stainless steel capillary of an internal diameter of 0.075mm. The capillary was heated at 90°C to prevent water condensation. The thermal analysis (DTA-TG) were performed in air and argon atmosphere, in the temperature range 100-1200°C. The structural characterization of the powders and the YBCO/BZO films was performed by X-ray diffraction analysis using a Bruker (θ-θ) diffractometer with Cu K$_\alpha$ radiation. The morphology was investigated by Scanning Electron Microscopy (SEM) using a LEO 1525 field emission-high resolution scanning electron microscope equipped with an Oxford INCA Crystal electron backscattering diffraction (EBSD) system.

Thin films were grown on (001) SrTiO$_3$ substrates (STO) using a 308 nm XeCl excimer Laser (Lambda Physik 110i cc) by adjusting the laser energy in the range 100÷130 mJoule and with a repetition rate of 10 Hz. All the films were grown in a 300 mTorr oxygen atmosphere at 850 °C. Typical film thickness was about 200-220 nm.

DC transport measurements were carried out by the four point method on 1 mm long and 30 µm or 50 µm wide strips obtained by UV photolitography. The dependence of the critical current density on temperature, applied magnetic field and on the angle between the normal to the film surface and the magnetic field direction was determined from the current-voltage characteristics (I-V) using the standard 1 µV/cm electric field criterion.

3. Results and discussions

3.1. Synthesis and characterization of BZO nanopowders

Figure 1 shows the IR spectra of the barium zirconyloxalate heat treated at different temperatures. At 100°C the precursor powder presents the oxalate characteristic vibration frequencies at 1640, 1280 and 914 cm$^{-1}$. The presence of water is indicated by the broad bands at 3400, 3100 and 1700 cm$^{-1}$ superimposed with the C=O vibration mode at 1640 cm$^{-1}$. The absorbtion band around 500 cm$^{-1}$, is attributed to the Zr-O stretching vibrations in the barium zirconyl oxalate precursor. At 600°C no evident vibration modes for the oxalate were observed, but the carbonate vibration mode is present at 693, 870, 1059, 1431cm$^{-1}$. The 3400 and 3100 cm$^{-1}$ band intensity corresponding to water crystallization decreases, while the Zr-O vibrations become more evident. With the further increase of temperature the characteristic carbonate bands decrease until they almost disappear at 1200°C. At this temperature the peak at 558 cm$^{-1}$ is due to Zr in an octaedric coordination within the perovskite structure. The TG-QMS analyses are presented in Figure 2. After the loss of crystallization water, the mass loss between 300°C and 600°C is due to the evolvement of CO$_2$ with a maximum peak at 300°C, indicating the decarboxilation of the dehydrated barium zirconyloxalate. The last weight loss takes place between 650°C and 750°C and is due to the second significant CO$_2$ emission as a result of the
decomposition of the remaining BaCO$_3$ with the simultaneous formation of BaZrO$_3$. This observation is in agreement with the IR spectra which evidence the decrease of the peaks corresponding to the carbonate vibration mode.

![Figure 1. FT-IR spectra of BZO at different temperatures.](image1)

![Figure 2. TG and QMS analyses for the BZO precursors](image2)

The X-ray diffraction patterns of the BZO precursor powders heat treated for two hours at different temperatures is presented in Figure 3. The powder prepared by coprecipitation was quasi-amorphous to X-ray as long as it was calcined below 500°C. On heating to 500°C, the reflections corresponding to barium carbonate are detected, in agreement with the IR spectrum. Crystalline BZO was detected for the first time at 600°C altogether with the reflections corresponding to BaCO$_3$ and ZrO$_2$. In the temperature range 700-900°C the peaks corresponding to the barium carbonate and zirconia disappear, while those corresponding to a pure BZO crystalline phase increase. In the temperature range 1100-1200°C only pure BZO phase has been detected. The results obtained from the analyses of the X-ray peak profile using the Scherrer formula have indicated that the mean powder size ranges from 30nm to 340 nm for the thermal treatment temperature varying from 700°C to 1200°C, respectively.

![Figure 3. X-ray diffraction patterns of BZO powders heat treated at different temperatures.](image3)
The DTA-TG-MS, FT-IR and X-ray analysis point out that the crystallization process of BZO is complex and can be considered a two-step process. First, it starts at about 600°C when the decomposition of the dehydrated barium zirconyloxalate to BaCO₃, ZrO₂, CO₂, CO takes place and the crystallization of BaZrO₃ initiates, due to the initial atomic scale mixing of the precursor. Carbon has been also traced as a result of the disproportionate reaction of carbon monoxide and is eliminated by combustion. Secondly, simultaneously with the on-going of the decomposition process takes place the second crystallization at about 800°C by the decomposition of the barium carbonate and the formation of BZO, equivalent to a solid state reaction. Since at 1100°C a pure BZO phase is evidenced, we conclude that the sintering can be lowered down to this temperature.

The SEM analyses have indicated the presence of well formed BZO crystallites even at 700°C. With the increase of temperature up to 1200°C the crystallites become larger by the progress of the crystallization or by an exaggerated grain growth. The mean grain size increases from 30 nm to 340 nm for the samples heat treated from 700°C to 1200°C, respectively. It is to be noted that the grain size varies in large limits. For example, for the sample heat treated at 1200°C the grain size is in the 200 nm to 500 nm range, as seen in figure 4.

![Figure 4](image.png)

**Figure 4.** SEM micrograph of BZO samples heat treated at (a) 800°C and (b) 1200°C.

### 3.2. Structural and superconducting properties of the YBCO/BZO composite film.

The θ-2θ x-ray spectra of the YBCO-5mol%BZO composite film is presented in figure 5. The XRD pattern exhibits only YBCO (00l) and BZO (h00) reflections, suggesting that both the YBCO film and the BZO nanoislands are epitaxially grown with the c-axis and a-axis, respectively, perpendicular to the substrate. The size of the BZO nanoislands estimated from the full-width at half-maximum (FWHM) of the (100) BZO peak using the Scherrer formula is of about 20 nm. Apart from the YBCO and BZO peaks the XRD pattern reveals the presence of the Y₂Zr₂O₁₁ phase. The dimension of the Y₂Zr₂O₁₁ inclusions were roughly estimated at about 50-60nm from XRD peak profile at 34°, using the Scherrer formula. Anyway, further TEM investigations are necessary in order to establish more accurate both the dimensions and the shape of the BZO and Y₂Zr₂O₁₁ inclusions.

In the left panel of figure 6 the temperature dependence of the resistivity for the YBCO-5mol%BZO film is shown. The sample exhibits a zero resistance critical temperature, $T_c$, of about 89.7 K. Though a $T_c$ reduction is expected in the BZO-added YBCO films, the observed value is higher than the corresponding values found in other YBCO films with the same BZO content [4]. The observed room temperature resistivity value, $\rho_{RT}=3.06 \, \mu\Omega \, cm$, is typical for good quality PLD YBCO films grown on single crystal substrates.
In the right panel of figure 6 the critical current density as a function of the applied magnetic field is shown both for the pure and the 5at.% BZO-YBCO films at 77K. While the self field $J_c$ value is slightly reduced by the BZO addition (1.6 MA/cm$^2$ against 2.5 MA/cm$^2$ exhibited by the pure YBCO film), the in field performances of the YBCO/BZO films are remarkably increased if compared with the pure film. The improving of the transport properties can be estimated through the $J_c(B)/J_{c0}$ ratio at 77 K (where $J_{c0}$ is the self field critical current density value) for $B=1$ and 3T. While in pure YBCO a ratio of 0.10 and 0.008 is achieved, in the YBCO/BZO samples the corresponding values are 0.34 and 0.09, respectively. The irreversibility field $B^*$, computed as the field where the pinning force density ($F_p=J_cB$) is lower than 1% of its maximum, is increased from 4.6 T for pure YBCO to 8.8 T for the YBCO/BZO film. This analysis suggests that the BZO inclusions introduce strong pinning sources.

**Figure 5.** XRD $\theta$–$2\theta$ pattern of YBCO-5mol% BZO composite film grown on (100) SrTiO$_3$ in a logarithmic scale.

**Figure 6.** Left panel: resistivity versus temperature measurement collected for the BZO-added YBCO film. In the inset the transition region is magnified. Right panel: critical current density dependence on the applied magnetic field at 77K for pure (squares) and BZO-added (circles) YBCO films. In the inset the YBCO/BZO film angular dependences of $J_c$ at 77K and three different field values are shown.
inside the YBCO films. As showed in the inset of the right panel, where the angular properties at 77K and three different field values are reported for the YBCO/BZO film, the BZO introduction induces the formation of correlated defects. Apart from the intrinsic peak observed at 90° (magnetic field parallel to the \(ab\)-planes), which is due to the layered structure of YBCO, a broad peak centered at 0° (magnetic field parallel to the \(c\)-axis) is exhibited by the BZO-added YBCO film. This feature has to be ascribed to the BZO crystallites since it is not observed in the pure YBCO films and it is a direct evidence of the extended defects along the YBCO \(c\)-axis, such as dislocations or \(a\)-axis epitaxial BZO nanorods [2,5].

4. Conclusions
A simple coprecipitation method was used to prepare high purity nanosize barium zirconate powder for the manufacturing of YBCO/BZO composites targets for PLD. The present method permits to control the mean grain size of the BZO powders in the range from 30 nm to 340 nm by means of the thermal treatment temperature. The YBCO films ablated from these targets have demonstrated that the BZO nanoislands are epitaxially grown within the YBCO film with the BZO \(a\)-axis//YBCO \(c\)-axis. The size of the BZO nanodislands estimated from the full-width at half-maximum (FWHM) of the \((100)\) BZO peak using the Scherrer formula is of about 20 nm. The magnetic field dependence of the \(J_\text{c}\) at 77 K has demonstrated that the BZO nanoislands represent strong pinning centres. Moreover, the angular dependence of \(J_\text{c}\) evidences extended defects along the YBCO \(c\)-axis, in agreement with the X-ray analysis, which have demonstrated that the BZO nanoislands are epitaxially grown with the \(a\)-axis parallel to the YBCO \(c\)-axis.

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