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Chemical processing and characterization of barium zirconate nanopowders

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Barium zirconate is the most attractive material to induce artificial pinning centers both in melt textured and $YBa_2Cu_3O_{7-x}$ (YBCO) thin films, in order to increase the critical current density. 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. Ammonium oxalate was used as precipitating agent in order to finally obtain a pure phase. To study the kinetics of the reaction and the optimum synthesis temperature, the as-obtained precipitate was heat treated in air in the temperature range from 500 to 1200 °C. Fourier Transformed Infrared Spectroscopy (FT-IR), thermal analysis (DTA/TG) coupled with mass spectrometry (MS) and X-ray diffraction have shown that between 700-900°C the barium zirconate phase is partially formed, while between 1100-1200 °C a pure barium zirconate phase appears. The preliminary results obtained from the analysis of the X-ray peak profile and scanning electron microscopy (SEM) have indicated a mean powder size of about 80 nm, adequate for artificial pinning centers in YBCO superconducting materials. The YBCO-5 mol. % BZO composite targets have been used for the deposition of high critical current density superconducting thin films by pulsed laser deposition (PLD).

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Keywords: FT-IR spectroscopy, Quadrupole mass spectrometry, Nanopowders, Pinning centers

1. Introduction

Barium-based perovskites, such as $BaZrO_3$ (BZO), $BaTiO_3$ (BTO), $Ba_xSr_{1-x}TiO_3$ (BST) and $BaZr_{0.35}Ti_{0.65}$ (BZT) have attracted much attention for their applications in a variety of microelectronic devices such as: ferroelectric memories, IR pyroelectric sensors, insulation, micro-electro-mechanical systems [1]. Barium zirconate is a ceramic material characterized by a cubic perovskite structure which allows ionic substitutions at various lattice points, producing a large number of compounds with challenging properties. BZO has a congruent melting at a very high temperature (m.p. 2600 °C), a small thermal expansion coefficient (0.87×10^{-5} ºC^{-1} between 25 and 1080 ºC), a poor thermal conductivity and an excellent mechanical and structural integrity and stability under extreme thermal conditions. These properties explain the use of $BaZrO_3$ for passive crucibles for corrosive oxide melts, substrates for thin films and thermal barrier coatings. In addition, barium zirconate is a potential material used as humidity sensor [2-4]. Lately, due to the low reactivity of $BaZrO_3$ with YBCO high temperature superconducting oxide, barium zirconate is the most attractive material used to induce artificial pinning centers for the increase of the critical current density [5]. The main reasons for using BZO as artificial pinning centers 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 a 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 a 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. Varying any 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 [1].

The motivation of this work remains in the synthesis of pure BZO phase, with no trace of any secondary phase, fine powders using a cheap, reproducible, fast and easy to scale-up process, acting as pinning centers in YBCO composite targets for PLD superconducting thin films with high critical current density. In this paper we also report on a BZO formation mechanism using complementary investigation methods.

2. Experimental procedure

Barium acetate $Ba(CH_3COO)_2$ (Alfa Aesar) and zirconium oxychloride $ZrOCl_2.8H_2O$ (Loba-Chemie Wien) 0.5 M solutions, previously prepared by sonication, were thoroughly mixed at ambient temperature. A 1M ammonium oxalate $(NH_4)_2C_2O_4.H_2O$ (Merck) solution was rapidly added under vigorous stirring. The barium acetate, zirconium oxychloride, ammonium oxalate system is more suitable for the stoichiometric precipitation than the oxalic acid systems because the product composition can be more easily controlled. This can be carried out at ambient temperature with a low sensitivity to excess oxalate addition above a 2.4:1 C_2O_4: Ba solution mole ratio. In small scale experiments a slight excess of Ba acetate (2.7%) is required for a quantitative precipitation. Thus it has been taken advantage of performing the precipitation at higher pH than in oxalic acid system [1]. The obtained slurry was stirred for about 30 minutes and the precipitate was filtered using *Whatman # 3* filter paper, washed twice in 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.

The oxalate precursor was characterized by FT-IR spectroscopy and thermal analysis. FT-IR spectra were performed on a Bruker Equinox 55 FT-IR spectrophotometer to identify the IR active functional groups using the KBr pellet technique. Spectra were collected with 2 cm^{-1} spectral resolution and 30 scans.

Thermal analysis (DTA-TG) was performed in air and argon atmosphere, in the temperature range 100-1200°C using an upgraded computer controlled equipment 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 samples were heated at a rate of 10 ºC/min. from ambient temperature to 1200 ºC. The use of argon is necessary in order to eliminate the nitrogen background which has the same molecular mass as CO and, as result, to enhance the sensitivity of the CO detection.

The structural characterization of the powders was performed by X–ray diffraction analysis using a Bruker (θ-θ) diffractometer equipment with a Cu $K\alpha_1$ radiation. The diffractometer is equipped with a Ge monochromator on the diffracted beam to suppress the K_β component and the parasitic scattering. The X–ray diffraction patterns were used to follow the decomposition and formation of the crystalline phases. The scattering intensities were measured in a range of Bragg angle 2θ between 15° and 90°.

The morphology of the powders was investigated by Scanning Electron Microscopy using a LEO 1525 field emission-high resolution scanning electron microscope equipped with an Oxford INCA Crystal electron backscattering diffraction (EBSD) system.

With the as-prepared BZO ground powders, YBCO composite targets have been obtained by weighting the YBCO and BZO powders (5mol. % BZO). The powders were properly mixed together in an agate mortar, pressed into pellets (8 tons force, ϕ=32 mm) and heat treated at 950 °C for 24 hours in flowing oxygen.

3. Results and discussion

Fig. 1 shows the thermal behaviour of the dried hydrated barium zirconyloxalate $BaZrO(C_2O_4)$ $.4.5H_2O$ precursor powder. There is one major exothermic peak present in the DTA traced at 650°C and several endothermic peaks at 140°C, 300 °C, 780 °C. The global weight mass loss of about 50% takes place in several steps.

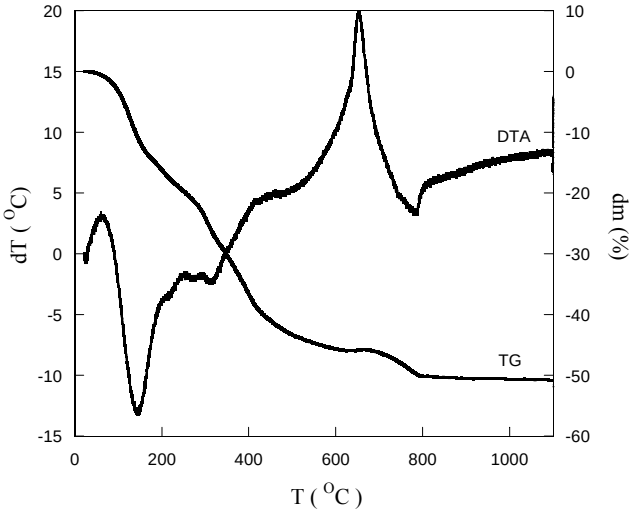

Fig. 1. DTA-TG analysis for the thermal decomposition of $BaZrO(C_2O_4)_2$. $4.5H_2O$.

The mass spectra of the gaseous products evolved during the thermal treatment carried out in argon atmosphere, Fig. 2, correlated with the TG analyses indicate the emission of water, carbon monoxide and carbon dioxide at the different decomposition stages. No significant differences have been registered between the thermal treatments carried out in air and in argon atmosphere. The water peaks from 100 °C and 275 °C are attributed to the physically adsorbed atmospheric water and crystallization water, respectively. After the loss of crystallization water the mass loss between 300 °C and 600 °C is due to the simultaneous evolvement of CO_2 with a maximum peak at 300 °C (indicating the decarboxilation of the dehydrated barium zirconyloxalate) and CO at 400 °C. The last weight loss takes place between 700 °C and 800 °C and is due to the second significant CO_2 emission.

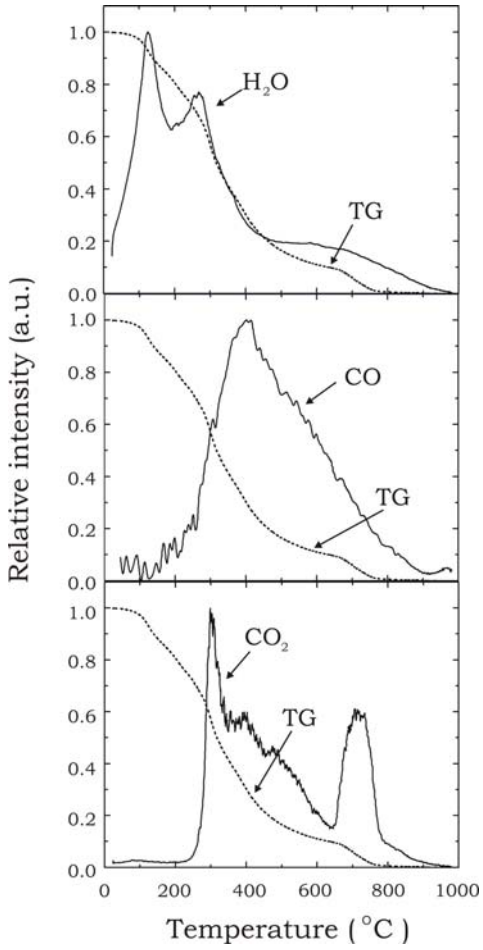

Fig. 2. TG-MS analyses for the thermal decomposition of $BaZrO(C_2O_4)_2 . 4.5H_2O$ in argon atmosphere

Fig. 3 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, 1420, 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 500 °C no evident vibration modes for the oxalate was 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 octaedric coordination in the perovskite structure. The IR spectra are in good agreement with the DTA-TG-MS measurement results.

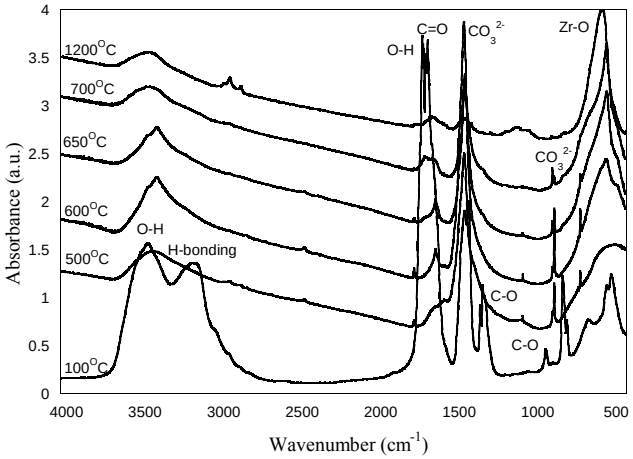

Fig 3. FT-IR spectra of BZO at different temperatures.

The X-ray diffraction patterns of the BZO precusor powder heat treated for two hours at different temperatures is presented in Fig. 4. The powder prepared through coprecipitation was quasi-amorphous to X-ray as long as it was calcined below 500 °C. On heating to 500 °C 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.

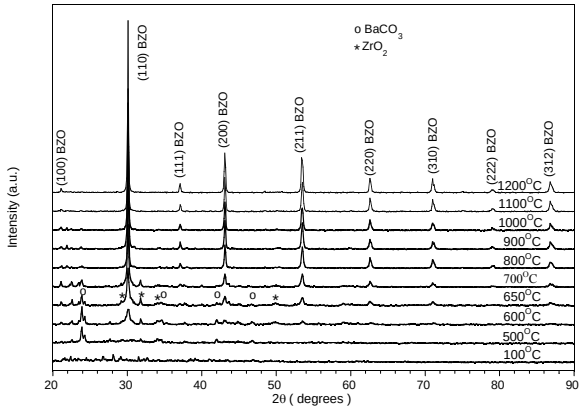

Fig. 4. X-ray diffraction patterns of BZO powders heat treated at different temperatures.

The DTA-TG-MS, FT-IR and X-ray analyses point out that the crystallization process of BZO is complex and can be considered a two step process, as shown in Figure 5. First, it starts at about 600 °C when the decomposition of the dehydrated barium zirconyloxalate to $BaCO_3$, ZrO_2, CO_2, CO takes place and the crystallization of $BaZrO_3$ 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 ^{o}C by the decomposition of the barium carbonate and the formation of BZO, equivalent to a solid state reaction. Since at 1000 ^{o}C a pure BZO phase is evidenced, we conclude that the sintering can be lowered down to this temperature. The results obtained from the analyses of the X-ray peak profile have indicated a mean powder size of about 80 nm, adequate for the composite target preparation [2].

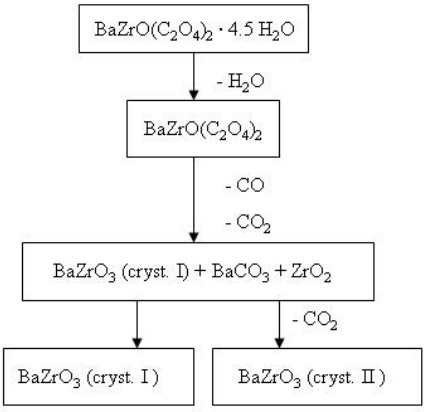

Fig. 5. Two step crystallization mechanism of BZO.

The SEM analyses indicate the presence of well formed BZO crystallites even at 700 ^{o}C. With the increase of temperature up to 1200 ^{o}C the crystallites become larger by the progress of crystallization or by and 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 Fig. 6.

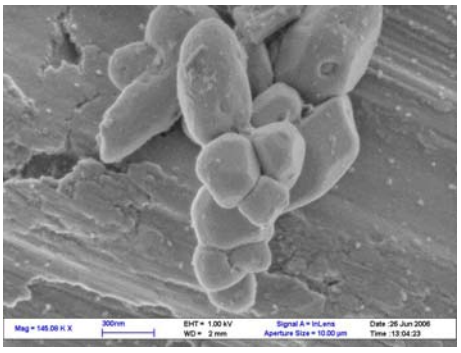

Fig. 6. SEM micrograph of BZO sample heat treated at 1200 ^{o}C.

The exaggerated grown grains have a step-like shape (Fig. 7), suggesting a screw dislocation growth mechanism.

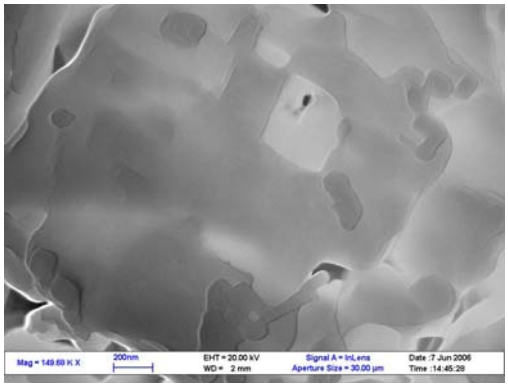

***Fig. 7.** The SEM image of an exaggerated grown BZO grain.*

4. Conclusions

A simple coprecipitation method was used to prepare high purity nanosize barium zirconate powder. The precursor chemistry and the BZO formation study has revealed the folowing:

1). The formation of BZO from oxalate precursors is a complex process by which a part of the barium zirconate is formed at a low temperature directly from the barium zirconyloxalate, while the rest is formed by a "solid state reaction" between the $BaCO_3$ and ZrO_2 resulted from the decomposition of coprecipitation product.

2). The present method permits to obtain a pure BZO phase at temperature as low as 1100 °C.

3). The mean grain size increases from 30 nm to 340 nm for the samples heat treated from 700 °C to 1200 °C, respectively.

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