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Single-domain HTc superconducting materials synthesis: BaZrO₃ substrates as a tool for optimized systems

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ABSTRACT

Large Dy-123 single-domains have been grown by the top-seeding melt-textured growth technique on yttrium oxide substrates. The main obstacles in fabricating such "single grain" 123 superconducting samples are discussed, i.e.

(i) the dissolution of the seed during the melting and the peritectic cooling stages

(ii) the nucleation of subsidiary 123 grains at the compact/substrate interface.

Such secondary nucleation process prevents the single grain from growing further. Solutions are suggested as for example by considering the use of a modified coating. BaZrO₃ displays a strong inertia in barium cuprate fluxes which suggests to use it as a very promising candidate for buffer layer in between the 123 compact and the furnace "environment". In order to provide such "high quality" sufficiently dense BaZrO₃ coatings, soft solution routes have been investigated. Advantages of these are a lower calcination temperature and the production of very homogeneous and fine monodisperse powders. The influence of the synthesis conditions on the properties of BaZrO₃ and on the sintering process is thus reported.

Keywords : superconductors, single domain, barium zirconate, syntheses, sintering

1.INTRODUCTION

Superconducting ceramics are promising materials for a wide variety of applications going from conductors to magnetic energy storage systems¹. YBa₂Cu₃O₇ is one member of this large family of compounds exhibiting a high magnetic irreversibility field at liquid nitrogen temperature. In fact, single domain melt textured YBa₂Cu₃O₇ has been shown to be able to trap significant magnetic induction (>2T) at liquid nitrogen temperature². As a consequence, these materials have clear potential for applications such as superconducting magnetic bearings³. The maximum induction which can be achieved in bulk superconductors is determined by the product of the critical current density and the radius over which the current flows. It is therefore limited by any weak links. The ability to fabricate HTS in large-grain form by a variety of melt processed techniques has overcome many of the problems associated with the weak intergrain links observed in polycrystalline specimens. The top seeding melt textured growth technique has been developed in order to grow large and well oriented single domain 123 monoliths⁴. The microstructure of the melt-processed 123 monoliths generally consists of pseudo-crystalline Y-123 matrix containing secondary phases, mostly 211, and other defects such as cracks, twins, stacking faults⁵. Another problem related to the microstructure of 123 monoliths is the following : the quality of the seed used in the top seeded melt textured growth process, i.e. a single crystal of Nd-123, can influence strongly the crystallinity of the grown 123 single domain. Three different modes for the 123 single-domain have been reported which are dependent on the degree of the dissolution of the single crystal seed⁶. In fact, although the processing temperature is lower than the peritectic decomposition of the Nd-123 single crystal seed, the single crystal dissolves completely or partially in the liquid formed by the incongruent melting of the Y-123 compact:

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1. When the seed dissolves completely, it no longer acts as a seed : a random growth process is observed leading to a polycrystalline material.
2. When the seed dissolves partially, the dissolved parts tend to resolidify which leads to more or less controlled growth of the Y-123 single domain at the seed, depending on the degree of dissolution.
3. A perfectly oriented single domain is obtained when the seed doesn't dissolve during the course of the reaction.

So, taking into account the main features of the microstructure of melt-textured grown YBCO materials, and keeping in mind the dissolution of the seed during the process, the main obstacles in fabricating a single grain 123 superconducting sample are the following:

1.a subsidiary misoriented 123 grain grown at the seed: generally due to a partial dissolution and resolidification of the seed during melting and peritectic cooling.

2.the nucleation of 123 grains at sample surface and at the compact/substrate interface.

Indeed, the substrate plays an important role in controlling the growth parameters of the 123 single-domain. As for example a high porosity of the substrate can induce porosity and microcracks formation in the 123 single-domain related to liquid losses during melting. In order to put into evidence the role of the substrate, different substrates have been used in this top seeding melt-textured growth process. Yttrium oxide has been used as a buffer layer. This oxide reacts with the solid phase above the solidification point of the 123 phase leading to the precipitation of very fine 211 particles at the compact/substrate interface⁷. The resulting locally high concentration of 211 particles reduces the supersaturating level necessary for the growth of 123 phase itself from the liquid. Secondary nucleation appears at the compact/substrate interface that prevents the single grain from growing further and does not grow to consume the entire sample volume. Solutions for the "substrate issue" have been proposed. Ytterbium oxide has been used as a buffer layer : in this case, the liquid containing ytterbium solidifies last during the peritectic cooling process due to the fact that the peritectic recombination temperature decreases with the size of the rare earth ion, and thus suppressing the 123 grain nucleation at the compact/substrate interface⁸. Another possibility is to use a barium zirconate coating. In fact lets remind that BaZrO₃ displays a strong inertia towards Ba-Cu-O fluxes making it the best material for single crystal growth⁹. Hence it should be considered as a promising candidate to be used as a buffer layer for the top-seeding melt textured growth process.

2. BARIUM ZIRCONATE AS A BUFFER LAYER FOR THE GROWTH OF HIGH QUALITY Y-123 SINGLE DOMAIN

The quality of the substrate used in the process is an important parameter for the controlled growth of a single domain. The morphology and properties of the ceramic powders have been shown to be dependent on the preparation mode. We have synthesized barium zirconate by three different techniques : solid state syntheses, precipitation and combustion techniques. The powders obtained have been compared from scanning electron microscope images. The different powders are then uniaxially pressed into pellets and sintered for 12 hours at 1400°C. The pellets are cut, a vertical section is inserted in resin and coated for SEM observation.

2.1. Solid state route

Barium zirconate is classically prepared by the classical solid state route starting from barium carbonate and zirconium oxide¹ in stoichiometric quantities (powder 1). The precursor powders are mixed in an agate mortar and calcined at 1200°C for 5 hours. A mixture of barium carbonate and basic zirconium carbonate hydrate has also been calcined (powder 2).

The solid state syntheses are known to present several drawbacks : high calcination temperatures, chemical inhomogeneity of the product; broad particle size distribution. This has been confirmed in both cases.

SEM images of both calcined powders showed a high degree of agglomeration. Powder 2 prepared starting from barium carbonate and basic zirconium carbonate presents a particular mode of agglomeration as can be seen on fig.1a. Agglomerates are made of smaller spherical-like agglomerates having a mean diameter of 2.5µ.

After sintering at 1400°C, the samples have undergone abnormal grain growth. Large polyhedral grains are observed. The pellets also show a high porosity.

The drawbacks related to the classical solid state synthesis have led to the development of soft solution methods for the preparation of ceramic powders. The methods tested for the preparation of barium zirconate are : calcination of an oxalato complex of barium-zirconium¹⁰, calcination of a mixed citrato complex¹¹, the controlled double jet precipitation¹², the precipitation in the presence of urea¹³, and a combustion method using oxalic dihydrazide as a fuel¹⁴. Preparation modes of the previous techniques can be found elsewhere.

2.2. Precipitation methods.

This group of methods includes precipitation and calcination of a mixed oxalato or citrato complex of barium-zirconium, the controlled double jet precipitation and the precipitation in the presence of urea. Powders obtained by these preparation

modes are characterized by a similar morphology after calcination. An electron micrograph of a powder prepared by calcination of an oxalato complex is presented for example in Fig.1b. The powders are constituted by spherical grains. The size distribution of the particles is homogeneous with a mean diameter of 0.2μ in this case. They show a small degree of agglomeration.

The microstructures observed after sintering are different for the four powders. The powders prepared by the oxalate and urea methods seem to be denser. For the oxalate method the small grains are still distinguishable. For the urea method some parts are almost pore free, a good coalescence has occurred and the particles are not distinguishable anymore. In other parts the formation of necks has only begun and polyhedral particles can be seen (Fig.2b). The powders prepared by the citrate method show an abnormal grain growth with large polyhedral grains. For powders prepared by the controlled double jet precipitation, no diffusion occurred. The temperature of 1400°C is not sufficient to induce sintering of the powders prepared by the controlled double jet precipitation. This temperature has to be increased or a sintering aid has to be added to the powder before sintering.

2.3. Combustion method

An organic fuel, namely oxalic dihydrazide $\text{NH}_2\text{NHCOCNHNH}_2$, is added to a mixture of the nitrates salts of barium and zirconium¹⁴. The solution is placed in a furnace and heated at a temperature sufficient to induce ignition of the mixture. In our case the ignition temperature is 400°C . The powder is calcined at 600°C for 12 hours.

The morphology of the calcined powder is totally different from what has been observed until now (Fig.1c). The grains have grown as cube with a size of the order of $1\mu^3$. Barium zirconate being a perfect cubic perovskite compound, the formation of cubic microcrystals is not astonishing. The conditions of obtention of barium zirconate by this combustion method are probably suitable to the growth of single microcrystals. The better crystallinity of the product has been confirmed using X-ray diffraction. The intensity is twice or thrice what is generally observed for barium zirconium oxide prepared by precipitation techniques.

After sintering, a denser pellet is obtained as in the case of the oxalate and urea methods. Some cubic particles are still present (Fig.2c).

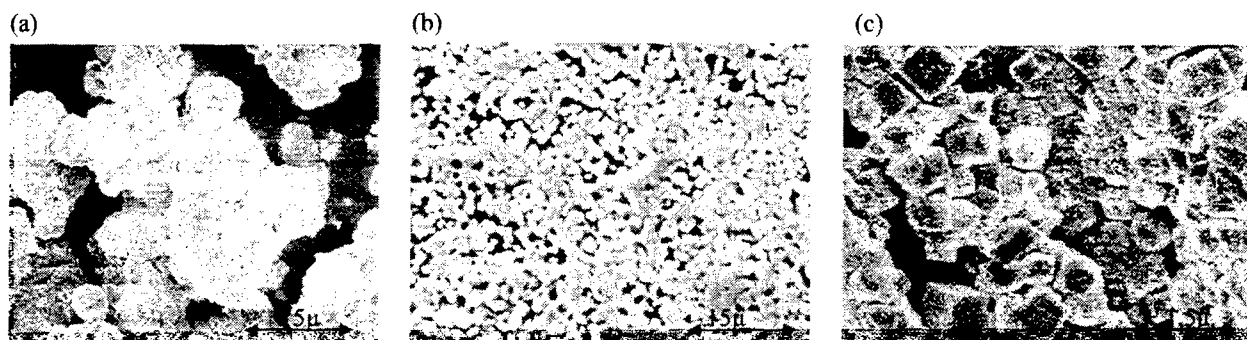


Fig.1 : Electron micrographs of the calcined powders. (a) BaCO_3 and ZrO_2 solid state synthesis, (b) calcination of an oxalato complex, (c) combustion using oxalic dihydrazide.

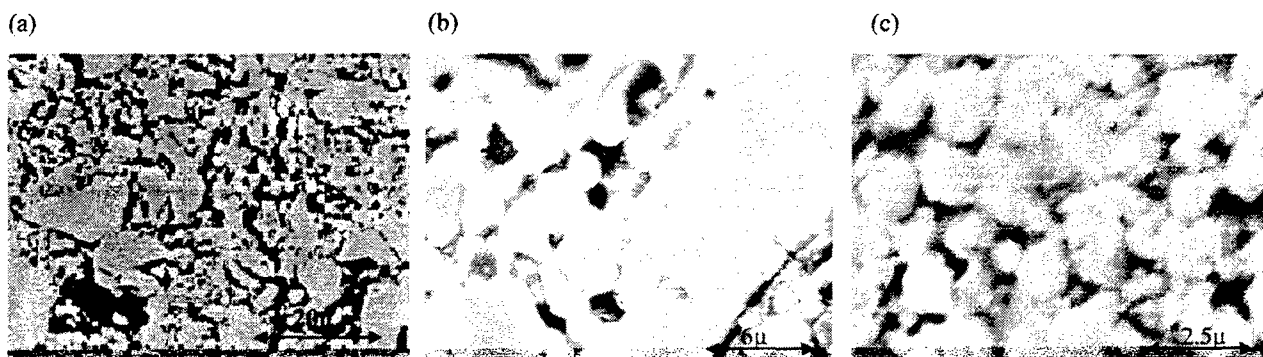


Fig.2 : Electron micrographs of pellets sintered at 1400°C for 12 hours. (a) BaCO_3 and ZrO_2 solid state synthesis, (b) precipitation using urea, (c) combustion using oxalic dihydrazide

The differences observed from the electron micrographs clearly demonstrate that the preparation mode strongly influences the sintering behavior. In order to determine which preparation mode leads to the densest substrate, porosity measurements have to be made.

4. INTERACTION BETWEEN THE SUBSTRATE AND THE COMPACT DY-123

The inertia of barium zirconate towards the fluxes of Ba-Cu-O has been demonstrated in our laboratory. Pellets of $\text{DyBa}_2\text{Cu}_3\text{O}_7$ powders were laid on two different substrates : Al_2O_3 and BaZrO_3 . The heat treatment was conducted simultaneously for the two samples. Al_2O_3 was used for comparison as it is well known to react with the fluxes.

The interaction layer between alumina and the 123-material is visible to the naked eye. A micrograph of a polished section analysed by optical microscopy is shown here. The interaction layer noted 1 represents 1/6 of the total sample height. The compound found at the interface is a mixed oxide of barium, dysprosium and aluminium. Its composition is close to $\text{Ba}_2\text{AlDyO}_5$.

The same experiment conducted on a BaZrO_3 substrate leads to a clear interface between compact and substrate. Yet the pellet of Dy-123 is attached to the substrate. This is due to the high porosity of the substrate used in this experiment inducing diffusion of the liquid phase formed during the peritectic reaction into the porous substrate. But no barium oxide nor zirconium oxide has been observed into the 123 material.



Fig.3. Optical micrograph of a Dy-123 pallet grown on alumina substrate.

5. CONCLUSIONS

The synthesis of large single domain 123-compounds requires a thorough control of the growth parameters. The quality of the substrate used in the top seeding melt textured method is one important parameter to avoid segregation of 211 particles at the compact/substrate interface which is deleterious to the growth of large single domains. Barium zirconate has gained much interest because of its inertia towards the Ba-Cu-O melts. The preparation mode of the BaZrO_3 directly influences the sintering behavior of the powders and subsequently the properties of the sintered substrate. Solid state synthesis should be abandoned to the profit of soft solution methods. None of the sintered material can be used as such for the growth of large single domains. Sintering aids have to be added in order to improve the final density and to control the morphology of the final product.

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