(Bi–Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ ceramic synthesized using a polymer matrix method

V. Garnier [a,*], R. Caillard [b], G. Desgardin [a]

[a]*Laboratoire CRISMAT, UMR CNRS-ISMRa 6508, 6 Bd Maréchal Juin, 14050 Caen cedex, France*
[b]*Laboratoire ESCTM, UMR CNRS-ISMEa 6508, 6 Bd Maréchal Juin, 14050 Caen cedex, France*

Abstract

Bi-2223 ceramic has been prepared by a polymer matrix method using polyethylenimine (PEI, 50 wt.% H$_2$O). This route leads to an intimate and a homogeneous mix of the starting metal acetates, and allows a rapid Bi-2223 phase formation compare to the solid state method. Nevertheless, the grain size and the kinetics of formation of the Bi-2223 phase depends on the calcination conditions and thus on the phase assemblage formed at the end of the calcination, which determined the reactivity during sintering. The sintering time, temperature and intermediate milling have also been optimized to reach the Bi-2223 powder purity up to 95%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: (Bi–Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$; Calcination; Powders-chemical preparation; Sintering; Superconductors

1. Introduction

A lot of research concerning the development of synthetic processes in order to obtain the purest Bi-2223 phase, which possesses the best possible values of the critical temperature (T_c) and critical current density (J_c), has been undertaken after the work of Michel et al.[1] and Maeda et al.[2] on superconductivity in the Bi–Sr–Ca–Cu–O (BSCCO) system. However, many parameters such as temperature, thermal processing time, milling, texturing, synthesis atmosphere and powder precursor strongly influence the J_c of Bi-2223. Although it seems that most of these parameters have been optimized, a better control of the powder precursor is still needed in order to improve reproducibility and transport properties.

The presence of a large number of elements in the Bi–Pb–Sr–Ca–Cu–O system induces very complex relations between the different phases according to the selected powder precursor. The formation of Bi-2223, which takes place during sintering, is thus very sensitive to the assemblage of the initial phases and to the prereactive conditions. To contribute to the comprehension and the optimization of the synthesis of Bi-2223, many methods of development of the powder precursor have been implemented: solid state method,[3–5] sol-gel method,[6,7] aerosol pyrolysis technique,[8] coprecipitation of oxalate,[9,10] spray dried nitrate precursors,[11] freeze-dried precursors,[12] and polymer matrix method.[13] The study of all these methods of preparation of the precursor powder has led to improvement in the kinetics of formation and in the purity of the Bi-2223 phase.

We chose the polymer matrix method for the synthesis of the powder precursor. This method appears promising due to its high kinetics of formation of the phase Bi-2223, and also due to the large grain size, which are routinely obtained using this route.[13] A larger grain size allows, in principal, better grain orientation during the texturation by rolling or sinter forging. Moreover, a large grain size has an influence on the superconductive properties of bulk bismuth ceramics. Particularly, it has been shown that the critical current density increases when grain size increases.[14]

By this study we seek to understand and optimize the influence of the following three parameters which are the temperature, time and intermediate milling on the Bi-2223 superconductor synthesis using a polymer matrix method.

* Corresponding author. Tel.: +33-231-45-2915; fax: +33-231-45-1600.

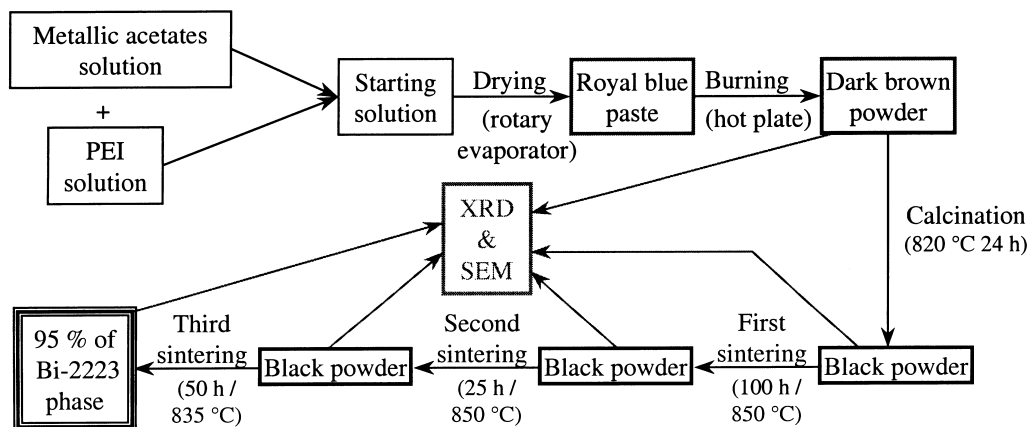*E-mail address:* vincent.garnier@ismra.fr (V. Garnier).

Fig. 1. Schema of the polymer matrix method synthetic procedure.

2. Results and discussion

The powder precursor was prepared by the polymer matrix method (Fig. 1) with a composition $Bi_{1.85}Pb_{0.35}Sr_2Ca_2Cu_{3.1}O_{10+\delta}$ suggested by Maeda.[15]

The starting materials acetates $Bi(CH_3COO)_3$, $Pb(CH_3COO)_2$, $Sr(CH_3COO)_2\cdot$, $Ca(CH_3COO)_2\cdot$ and $Cu(CH_3COO)_2\cdot H_2O$ were dissolved in a mixture of acetic acid and distilled water to obtain a pale blue solution. To this solution, another solution of poly ethyleneimine in distilled water was added and the resulting solution turned royal blue immediately. This dark blue solution was then introduced into a rotary evaporator to reduce the volume to approximately 10% of the initial volume. The concentrated solution was then introduced into a crucible and placed on a hot plate, increasing slowly the temperature until total evaporation of the solvent occurs. The thermoplastic paste that forms was subsequently fired on a hot plate at approximately 400°C. Due to the exothermic reaction which takes place, the temperature of the crucible is around 750°C.

Fig. 2 shows the SEM micrograph of this precursor; the resulting powder is formed of small and compact agglomerates.

The fired powder is then crushed by hand in an agate mortar and powder XRD measurement is performed (see Fig. 3a). Few crystalline phases are formed, the spectra exhibit principally Bi_2CuO_4 and CuO phases, and a small quantity of $SrCO_3$ and PbO in an amorphous matrix.

Then, the powder is calcined under air at 820°C for 24 h. Fig. 3b shows the XRD spectra after this calcination. Bi-2212 is the major phase, accompanied principally by intermediate phases like Ca_2PbO_4 and CuO, these three phases are necessary to the Bi-2223 phase formation. Ca_2PbO_4 decomposes around 822°C,[16] and forms CaO and a liquid phase rich in Pb, which reacts with CuO to form Ca_2CuO_3,[17] which in turn accelerate the formation of the Bi-2223 phase.
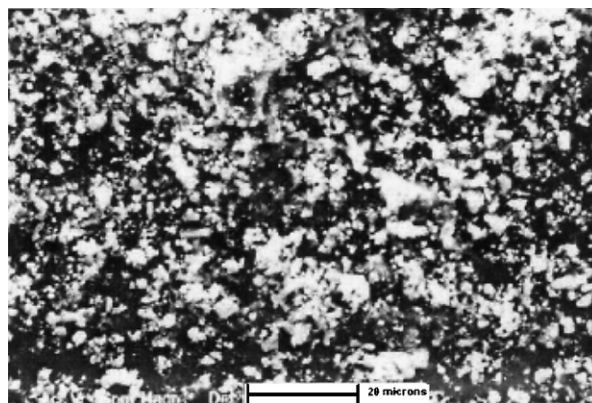

Fig. 2. SEM micrograph of precursor powder before the calcination process.

The calcined powder is milled, pelletized (200 MPa, 16 mm diameter, 3 g), and sintered under air at different temperatures (from 830 to 865°C) measured with a Pt-PtRh thermocouple placed close to the sample. The Bi-2223 phase volume fraction evolution of these pellets versus the sintering time is shown Fig. 4. This volume fraction estimation has been possible thanks to the W.W. Schmahl program[18] which enabled us to take into account several peak area $((0010)_{2223}$; $(115)_{2223}$; $(006)_{2212}$; $(115)_{2212}$; $(006)_{2201}$; $(115)_{2201})$ with their relative intensity and the preferential orientation phenomena of these different phases. The Bi-2223 calculated ratio, shows that sintering at 850°C leads to the largest Bi-2223 amount, 75% in 100 h without intermediate milling (using XRD spectra Fig. 3c). A lower sintering temperature is less efficient to rapidly obtain the 2223 formation, and, on the other hand, a higher sintering temperature induces the 2223 decomposition[19] and elements losses[19–21] especially Pb, resulting in the nominal composition changes.

SEM observation (Fig. 5) on the fractured part of the pellet sintered 100 h at 850°C (1st sintering) shows large spaced out grains (10 μm on average).

The Bi-2223 phase content improvement is then carried out with an intermediate milling and a new pelletizing. The resulting pellets are sintered again at 850°C
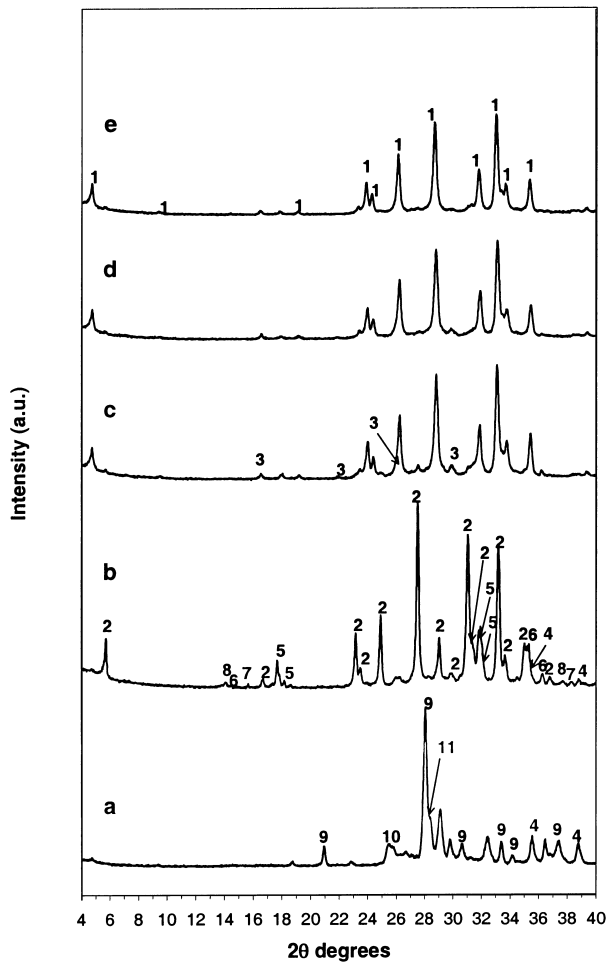

Fig. 3. XRD pattern of: (a) precursor powder, (b) calcined powder (820°C/24 h), (c) after first sintering (850°C/100 h), (d) after second sintering (850°C/100 + 25 h), (e) after third sintering ([850°C/100 + 25 h] + [835°C/25 h]), marked as follows: 1: 2223; 2: 2212; 3: 2201; 4: CuO; 5: Ca_2PbO_4 6: Ca_2CuO_3; 7: $Sr_{14}Cu_{24}O_{41}$; 8: Cu_2SrO_2; 9: Bi_2CuO_4; 10: $SrCO_3$; 11: PbO; 12: Sr_2CuO_3.
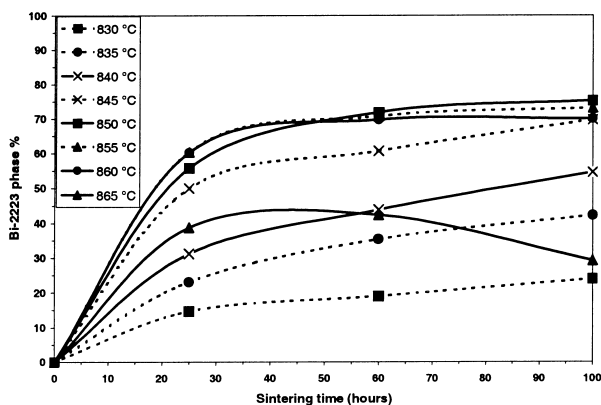

Fig. 4. Volume fraction of the Bi-2223 phase (%) as a function of sintering time and temperature (between 830 and 865°C).

to take advantage of the high Bi-2223 phase kinetics formation at this temperature, as previously shown, for various times ranging from 25 to 100 h. The second sintering step, 25 h additional dwell at 850°C (Fig. 3d) allows an increase in the Bi-2223 phase content from 75 to 86% and at the same time the Bi-2201 phase amount does not change. If the sintering time is prolonged (50, 75 and 100 h), the Bi-2223 phase content increases slightly (only 1%). Then, 25 h sintering at 850°C after the first intermediate milling is sufficient to obtain a new phase equilibrium, which does not evolve significantly with further sintering time.

To complete the optimization of the sintering conditions on the Bi-2223 formation a third sintering is performed. After milling and pelletizing, the samples are then sintered at 835°C for 25–100 h; the sintering temperature is decreased in order to reduce the Bi-2201 phase content.[22] A last sintering step at 835°C during 25 h allows achieving high Bi-2223 phase purity. Indeed, the Bi-2223 phase content varies from 86 to 95% owing this last thermal treatment. Further sintering time at 835°C do not increased the 2223 phase content. The Bi-2201 phase content is reduced, and nearly pure Bi-2223
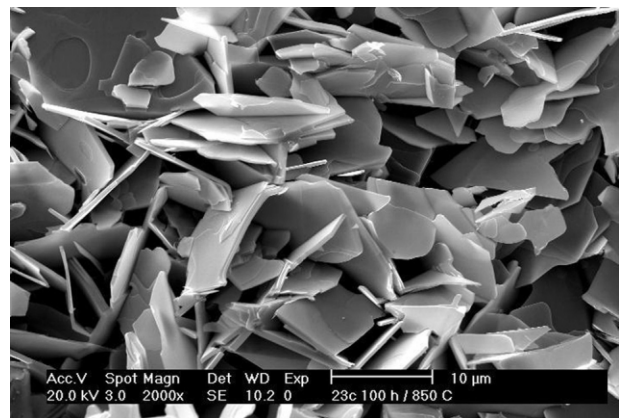

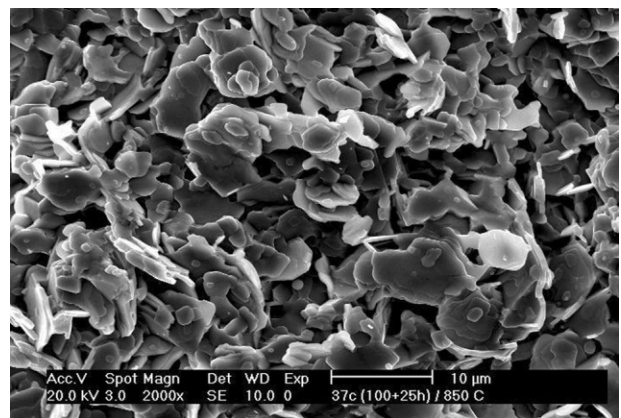Fig. 5. SEM micrograph of the fractured part of a pellet after first sintering.

Fig. 6. SEM micrograph of the fractured part of a pellet after third sintering.

phase is obtained (see Fig. 3e). SEM micrograph (Fig. 6) after the third sintering exhibits small Bi-2223 grain size (between 2 and 3 μm), resulting from the second intermediate milling and also from the lower sintering temperature for a relative short time.

3. Conclusion

Bi-2223 ceramic has been prepared by a polymer matrix method. Three sintering steps are necessary to obtain high 2223 phase content. First, 100 h sintering at 850°C allow formation of 75% of the Bi-2223 phase. A first intermediate milling performed before doing the second sintering step at 850°C for 25 h, leads to 86% of the 2223 phase. Then, a second intermediate milling, followed by the third sintering step at 835°C for 25 h leads to a final Bi-2223 phase content reaching 95% with a resulting grain size between 2 and 3 μm.

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