Rapid synthesis of the Bi(Pb)-2223 110 K superconductor by the EDTA sol-gel method

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EDTA sol–gel methods have previously been employed successfully to synthesize Bi(Pb)-2223 phase. But heat-treatment optimization to transform the precursor solution into the final 2223 powder seems to have been neglected, leading to long heat-treatment times as in the classical powder method. In this paper, a route is proposed to accelerate 2223 phase kinetics formation, by improving calcination, sintering and intermediate grindings. Thus a nearly pure 2223 powder is obtained consecutive to a relatively short total duration of heat treatment.

1. Introduction

The high-T_c (Bi, Pb)-2223 cuprate merits great attention owing to its several inherent advantages over $YBa_2Cu_3O_{7-\delta}$ such as its higher critical temperature around 110 K, its atmospheric stability, its ability to be rolled into long wires or tapes, and its weak superconductivity dependence upon oxygen stoichiometry. Major efforts have been focused on the mass production of pure (Bi, Pb)-2223 materials, because the superconducting properties of the as-produced wires or tapes depend principally on the phase purity. However, it has been found that the formation kinetic is very sluggish, because it needs long-range diffusion of cations.

Currently, the most common method for the preparation of Bi(Pb)-2223 with regard to the conventional one, is based on the solid-state reaction involving oxide and carbonate powders (Bi_2O_3, PbO, CuO, $SrCO_3$ and $CaCO_3$). Such a method has several drawbacks, mainly poor homogeneity, which causes very long heat-treatment times and repeated intermediate grindings to obtain a nearly pure phase. Chemical synthesis method have been shown to be more advantageous because the initial mixture of cations has been made on an atomic scale in a solution. It was reported that several methods, such as spray-drying [1, 2], aerosol [3], spray pyrolysis [4], are very attractive for the rapid conversion of 2212 into 2223 single phase. However, such methods use low pH solutions, which could be harmful to the apparatus. A sol–gel technique based on the EDTA solution [5–8] has also been reported, but the procedure needs to be optimized by studying the chronology of the formation of the different phases versus the experimental conditions.

In this study, we used the EDTA method and focused on temperatures of calcination and duration of heat treatments to accelerate 2223 phase formation. We tried to relate the kinetic of 2223 formation to the amounts of 2212 phase and especially of Ca_2PbO_4, which is the main non-superconductive impurity. The results obtained by this process route are compared to the results available in the literature from the conventional method [9–12].

2. Chemical synthesis

The starting materials were oxides and carbonates, as generally used in the classical powder synthesis method. Adequate proportions of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO (purity above 99%) were weighed to yield the nominal composition $Bi_{1.85}Pb_{0.35}Sr_2Ca_2Cu_{3.1}O_y$ and dissolved together in 65% nitric acid. During dissolution, CO_2 from carbonates was evolved. In order to dissolve Bi_2O_3, excess acid was required. The final solution had a limpid pale blue colour, due to copper ions.

A second solution was prepared by dissolving solid ethylenediaminetetracetic acid in ammonium hydroxide in a molar ratio 1:4. The as-prepared EDTA basic solution was then poured into the dissolved precursors solution in the ratio of one EDTA formula for each metallic cation present. The solution became dark blue, the colour of chelated cupric ions. If the initial excess of nitric acid (added to dissolve Bi_2O_3) is too large, the mixed solution can precipitate, due to a too low pH-value needed for EDTA dissociation; this white EDTA precipitate can be redissolved by adding ammonium hydroxide to reach a pH value between 5 and 10. The solution returns to the dark blue colour and becomes limpid again. The advantages of such a solution are multiple. In particular, the pH can be set around a neutral value and the stability of metallic cation–EDTA complexes is high.

The water was then evaporated from this limpid solution by heating strongly. During evaporation, pH was maintained above 6 to prevent EDTA precipation, by adding NH_3. When the concentration, i.e. the viscosity, became important (about 50 g initial precursors for 100 ml solution left), the blue mixture turned to a dark green gel. Care should be taken at this step to avoid EDTA precipitation. Further heating turned the

gel into a dark-brown foam and finally, after self-combustion with exhausting vapours (water, CO_2, NO_x), a dark-brown powder precursor was obtained. This powder consisted mainly of Bi_2CuO_4 and a small amount of CuO (Fig. 1). The other oxides were not yet crystallized, relating to X-ray diffraction. The mass of this powder was higher than the mass of the initial oxides, indicating that the calcination was incomplete. Therefore the powder precursor was heated up to 730 °C for 12 h or 840 °C for 10 h to remove remaining volatile materials. The obtained calcined powder was ground by attrition, pressed into pellets (300 MPa) and sintered at 845 °C for 24 h on zirconia supports, reground by attrition and finally re-sintered at 850 °C for 24 h (Fig. 2). The first sintering temperature was slightly lower than that of the second sintering to prevent any partial melting which lead to strong proportions of 2201 and 2212 phases without any amount of 2223, for temperatures above 845 °C. During the second sintering, neither partial melting nor decomposition was observed.

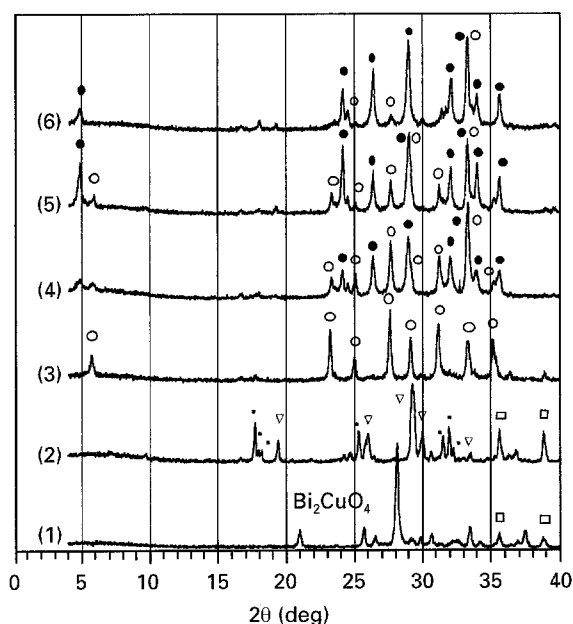After the two sinterings, a nearly pure 2223 phase was obtained according to X-ray diffraction as shown

Figure 1 X-ray diffraction spectra of powder during synthesis. 1, Precursor powder after self-combustion; 2, after 730 °C/12 h as-powder calcination; 3, after 840 °C/10 h as powder calcination; 4, as 2 + sintering (845 °C/24 h) 5, as 2 + sintering (845 °C/24 h + 850 °C/24 h). 6, as 4 + sintering (850 °C/24 h).
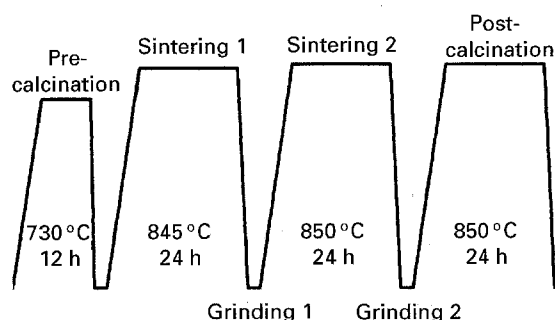

Figure 2 Schematic illustration of the heat-treatment cycle.

in Fig. 1 with traces of 2212, but the crystallinity was low. For a better crystallized powder, without changing, the purity of 2223, the thermal cycle was completed by a 850 °C/24 h powder post-calcination. In that case, XRD peaks were thinner (Fig. 1).

3. Results and discussion

In order to quantify the 2223 amount formed during the different steps of the process, X-ray diffraction was performed, using an addition method based on the intensity measurement of the (1 1 5) peaks of the 2212 and 2223 phases, respectively. According to this method, the amount of 2223 phase was estimated to be close to 95% after the two sinterings.

3.1. Effect of pre-calcination temperature
The amount of 2223 phase present after the first sintering at 845 °C/24 h for pellets can be compared for powders previously calcined at two different temperatures. The 730 °C/12 h calcination leads to a powder principally composed of the 2201 phase, CuO and a significant quantity of Ca_2PbO_4. On the other hand, an 840 °C/10 h calcination forms mainly the 2212 phase, a small amount of 2201 and a very small amount of Ca_2PbO_4, which means that most of the lead cations have already been incorporated into the superconductive oxide lattice. In comparison with the classical powder method, the first calcination temperature does not seem to be an important factor to accelerate the 2223 phase formation. This different behaviour can be explained by the fact that, in our case, the precursor is not composed of simple oxides but of already reactive combined compounds (Bi_2CuO_4, CuO and uncrystallized matrix).

It was reported by several authors [15, 16] that when using a conventional method, the role of the second phase Ca_2PbO_4 is very important due to the fact that, as a liquid phase at the 2223 formation temperature, it enhances greatly the transport of matter and consequently favours the long-range cation diffusion. In the sol–gel method, we find that the amount of 2223 after the first sintering was no more significant in pellets made from a low-temperature calcined powder than in those made from a high-temperature calcined powder (i.e. without Ca_2PbO_4 phase) as shown in Fig. 1. This can be explained by the fact that the present sol–gel method yields a much better homogeneity in the precursor powder than the classical method and long-range diffusion of cations is no longer required.

3.2. Effect of grinding and compaction
Intermediate grindings are necessary to accelerate the 2223 phase formation. Without them, the amount of 2223 is not significantly more important after an 845 °C/48 h sintering than after an 845 °C/24 h one (Fig. 1). No noticeable difference between the phase composition in the core of the pellets and in the periphery is observed by XRD. We can conclude that the effect of grinding on the 2223 formation kinetics is

due to the increased reactivity of small-sized grains after attrition. On the other hand, a direct sintering of pellets made of precursor powder (without powder pre-calcination) leads to 2212 in a major quantity (Fig. 1). Thus the calcination and first grinding are also necessary.

The amount of 2223 is much smaller after a pre-calcination followed by an 845 °C/24 h powder-like calcination (about 30%) than in pellets from the same pre-calcination schedule but pressed at 300 MPa and sintered at 845 °C/24 h (60%). Thus, we can state that the effect of compaction is determinant, although the formation kinetics of 2223 does not seem to vary noticeably for compacting stress levels between 100 and 300 MPa.

3.3. Effect of lead content

Another comparison can be made, between two different initial stoichiometries, especially by changing the Pb/Bi ratio, keeping the (Bi + Pb) amount constant. No significant difference is observed with regard to the 2223 amount (60%) in pellets between the two compositions $Bi_{1.85}Pb_{0.35}Sr_2Ca_2Cu_{3.1}O_x$ and $Bi_2Pb_{0.2}Sr_2Ca_2Cu_{3.1}O_x$ after the first sintering (Fig. 3). On the other hand, after the second sintering (850 °C/24 h), even if the 2212 phase amount is very small in the two compositions, the proportion of

Figure 3 Comparison of the remaining amount of 2212 of two nominal compositions.

Ca_2PbO_4 in $Bi_{1.85}Pb_{0.35}Sr_2Ca_2Cu_{3.1}O_x$ is more significant and the 2223 amount is slightly enhanced (90%–95%) starting with the latter composition (Fig. 3). This amount of lead necessary to stabilize the 2223 phase is consistent with the results reported for the classical method [17].

3.4. Lead loss
With the same amount of the 2223 phase, the amount of lead element, measured in atomic absorption, is significantly higher in the EDTA sol–gel method than in the classical mixed and ground powder method (Fig. 4). The very long heat-treatment time of the classical method, to eliminate the remaining 2212, may be attributed to an important loss of lead, which can reach 20%, leading to a lead content lower than that necessary to stabilize the 2223 phase. In the EDTA sol–gel method, a (Bi, Pb)-2223 lead-rich phase can be obtained.

In any case, the amount of 2223 in pellets after the same pre-calcination and sintering steps but using classical mixed and ground oxides and carbonates, is much lower than that given by the EDTA sol–gel method. Moreover, the time required to obtain a nearly pure 2223 phase with this method is much shorter. A total of only 3 day is necessary to obtain an almost pure 2223 phase, which is about three times shorter than that of the conventional powder method.

For information, 5000 p.p.m. carbon has been measured after the two sinterings and the post-annealing but this amount does not seem to be detrimental to the physical properties.

3.5. Superconductivity
Fig. 5 represents susceptibilities as a function of the temperature of as-sintered samples measured in zero field cold ZFC on a Quantum Design SQUID. The curves exhibit $T_{CO} = 108$ K. An intermediate temperature transition is also observed which cannot in any case be attributed to another superconducting cuprate. The shift of the intermediate transition towards a higher temperature when decreasing the magnetic field from 10 G to 0.01 G, shows indeed that this
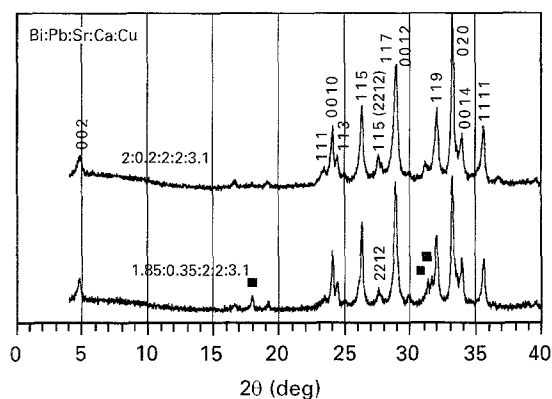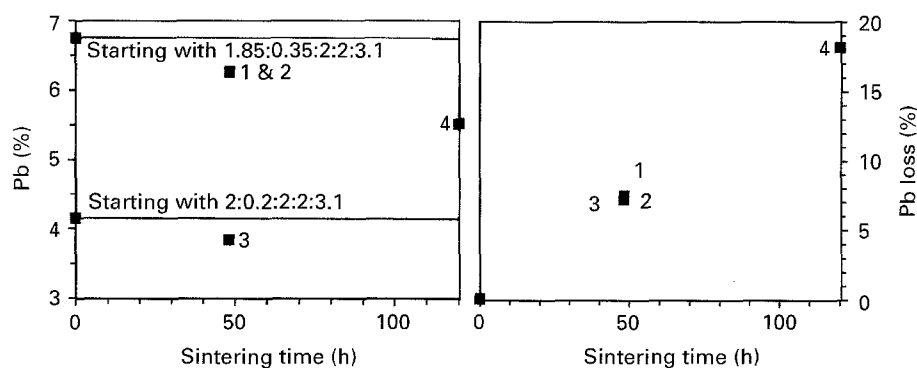

Figure 4 Lead losses as a function of sintering time. 1, 1.85:0.35:2:2:3.1 calcined 730 °C/12 h, sintered 845 °C/24 h and 850 °C/24 h; 2, 1.85:0.35:2:2:3.1 calcined 840 °C/10 h, sintered 845 °C/24 h and 850 °C/24 h; 3, 2.0:0.2:2:2:3.1 calcined 730 °C/12 h, sintered 845 °C/24 h and 850 °C/24 h; 4, 1.85:0.35:2:2:3.1 calcined 730 °C/12 h, sintered 845 °C/24 h and 850 °C/24 h four times (classical synthesis method).
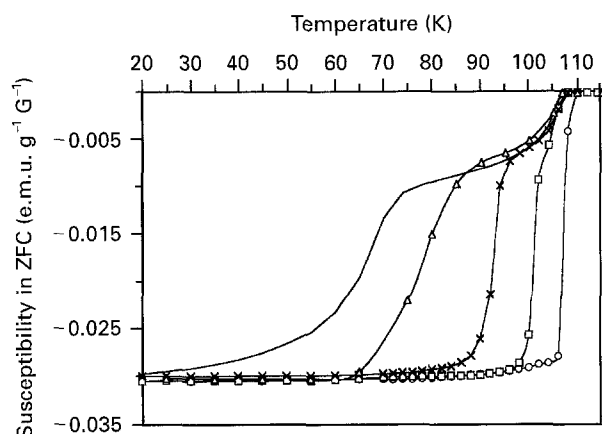
Figure 5 Magnetic susceptibility versus temperature and magnetic field. (◯) Dense textured and annealed 840 °C/50 h, 0.01 G, (▢) porous bulk and annealed 840 °C/50 h, 0.01 G; (×) porous bulk, 0.01 G; (△) porous bulk, 1.5 G; (—) porous bulk, 10 G.

transition is due to the grain boundaries and to the multiple orientations of the grains. The best sample is the fully dense one (textured by hot-pressing) where the T_{C0} is best, 110 K, and the transition is sharper, below 4 K, because of the more important and better grain boundaries.

4. Conclusion

We have succeeded in obtaining quite pure 2223 phase in a relatively short time by adjusting different parameters: the initial EDTA-method precursor, pre-calcination steps, sintering temperatures, duration and number of heat treatments. From X-ray diffraction patterns, the purity is estimated to be 95% 2223 phase. We conclude that the EDTA method is very efficient, relative to the conventional mixed oxides and carbonates method. It also appears that the presence of Ca_2PbO_4 is unnecessary to accelerate 2223 phase formation, contrary to what was observed when using the classical route. However, the water evaporation stage is a critical step: EDTA precipitation must be avoided to obtain a gel with the same homogeneity as the complexed cations solution.

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