

Influence of the addition of SnO₂ nano-particles on Bi-2223 phase formation

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The effect of the addition of SnO₂ nano-particles on Bi-2223 phase formation has been studied. Tin oxide was added at different intervals of the synthesis process. It is shown that the addition of SnO₂ inhibits the Bi-2223 phase formation regardless of when it is introduced to the system. SnO₂ partially reacts with calcium to form the Ca₂SnO₄ phase. This phase is stable throughout the synthesis process. As a consequence, the formation of the Bi-2223 phase is compromised for the benefit of secondary phases such as Bi-2212, Ca₂SnO₄, Sr_{0.15}Ca_{0.85}CuO₂ and Cu₂SrO₂. The *c* parameter of the Bi-2223 phase increases when tin is added. A possible explanation is a partial substitution of Cu²⁺ by Sn⁴⁺.

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1. Introduction

Since the discovery of the (Bi,Pb)₂Sr₂Ca₂Cu₃O_x phase (Bi-2223) [1], a considerable amount of research dealing with the development of synthetic processes in order to obtain single-phase Bi-2223 has been done. In order to improve the superconducting properties of this material, such as its critical temperature (*T_c*) and its critical current density (*J_c*), different dopants have been tested with more or less success [2–4]. Bismuth substitutes easily for lead since the Bi³⁺ and Pb²⁺ share the same outer shell electronic configuration 6s²6p⁰. In a similar manner, Sn²⁺ has an outer shell electronic configuration of 5s²5p⁰; that means that the substitution of bismuth with tin may occur. We have thus studied the effects of this doping on the Bi-2223 phase formation by studying, in particular, the possibility or not, for the tin to enter to the Bi-2223 matrix. We opted for a cationic initial stoichiometry of Bi_{1.85}Pb_{0.35}Sr₂Ca₂Cu_{3.1}Sn_{0.1}. This composition is widely used in the literature [5–8], and has been shown to be optimal in terms of both the phase formation and the superconducting properties [9]. However, contradictory results have been found on the effect of tin doping. These results include both the facilitation [9] and the hinderance of this doping on the Bi-2223 phase formation, as well as tin substitution for bismuth [8], for copper [10] or not at all [6]. The aim of this work is to clarify the effect of SnO₂ addition on the Bi-2223 phase formation. We chose to add SnO₂ nano-particles in order to reduce the secondary phase's size to introduce as small as possible pinning centers [11], the final objective is to improve the *J_c* of this material.

2. Experimental

Starting from the stoichiometric composition Bi_{1.85}Pb_{0.35}Sr₂Ca₂Cu_{3.1}, powder precursor was prepared using the polymer matrix method [12]. This powder was calcined 24 hours at 820°C in air [13], milled and pelletized (3 g., 1.5 T/cm², Ø16 mm). The resulting pellets were sintered three times at 838°C for 100 hours, each time under air. The sintering temperature was in the same range as that used by other groups [6, 9]. Although it may not be the optimal temperature for Bi-2223 phase formation, that is not a concern for this present study.

Stoichiometric amounts of tin were added in the form of SnO₂ nanosize powder, prepared by a sol-gel method [14]. The average particle size of the nano-particles was about 20 nm and the dopant was introduced at varying intervals of the synthesis procedure: (i) in the powder precursor preparation, noted Sn(0); (ii) before the first sintering step, noted Sn(1); (iii) before the second sintering step, noted Sn(2) and (iv) before the third sintering step, noted Sn(3). XRD measurements were performed (Philips PW3710, λ_{Cu} [K_{α1}]) to follow the Bi-2223 phase evolution in order to estimate its volume fraction. This estimation was possible thanks to the W. W. Schmahl program [15] which enables the comparison of the areas of several peaks ((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 lattice parameter *c* was estimated using the (*hkl*) peak positions. The microstructure and X ray mapping of different atomic elements of the sintered pellets were observed on a

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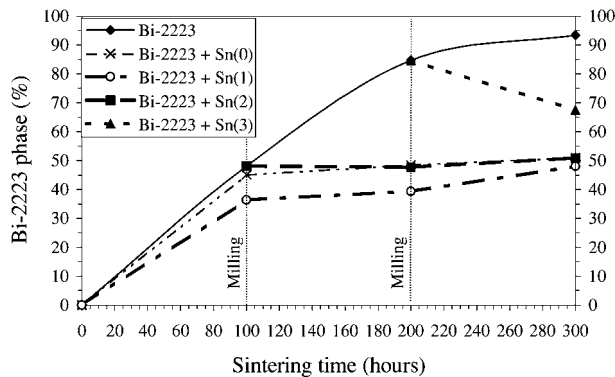


Figure 1 Bi-2223 phase percentage evolution versus sintering time at 838°C as a function of tin doping.

fractured part of the sample using a scanning electron microscope (SEM Philips XL30) equipped with an EDS analysis (System Oxford, Link ISIS).

3. Results and discussion

3.1. Bi-2223 phase evolution during the sintering process

Fig. 1 shows the Bi-2223 phase evolution versus time, as a function of the tin doping. During all the sintering processes, the temperature is fixed at 838°C. It is shown that during the first sintering step (up to 100 hours of sintering), the Bi-2223 phase content is 50%, 48% and 36% when respectively, the sample is tin free, the tin is added before the synthesis step Sn(0) and before the first sintering step Sn(1). The first milling stage causes a significant improvement in the precursor reactivity for the tin free sample, as previously published [16]. Indeed, in the undoped sample, the percentage of Bi-2223 phase reaches 87% after the second thermal treatment of 100 hours. When the sample contains SnO₂ nanoparticles, the behavior changes drastically. For samples Sn(0) and Sn(1), the Bi-2223 phase content increases only 3 and 2% respectively, during the second sintering step. Moreover, the addition of SnO₂ just before the second sintering step, Sn(2), totally inhibits the Bi-2223 phase formation since the percentage of this phase is stabilized (about 50%). The addition of SnO₂ before the latest sintering step Sn(3) leads to a decrease of the Bi-2223 phase content, which drops from 85% to 67%. These results demonstrate without any ambiguity that SnO₂ particles added during the Bi-2223 phase formation is detrimental to obtain high Bi-2223 phase purity. It is well known that the Bi-2223 phase is formed from different secondary phases such as Bi-2212, CuO and Ca₂CuO₃ [17]. According to the above results, it is demonstrated that the SnO₂ addition moves the phase equilibrium from the Bi-2223 phase to the secondary phases.

3.2. Phases evolution

Fig. 2 shows the powder XRD patterns resulting from milled pellets quenched in air at different steps of the synthesis. Sint 1, Sint 2 and Sint 3 correspond respectively to pellets quenched after the first, the second

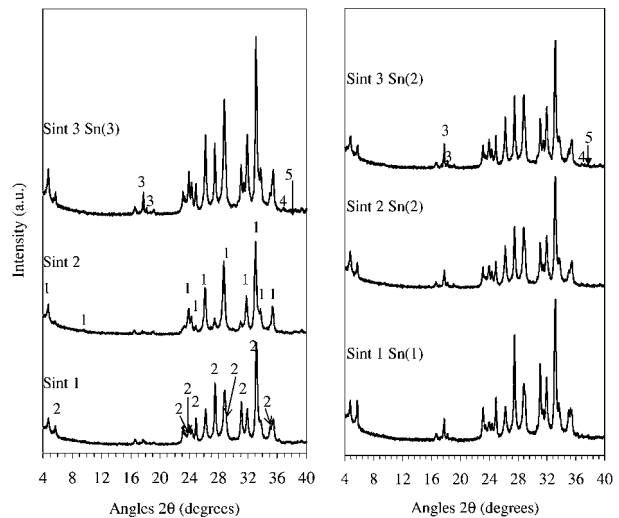


Figure 2 XRD patterns of samples during the synthesis, with or without tin. 1: Bi-2223; 2: Bi-2212; 3: Ca₂SnO₄; 4: Sr_{0.15}Ca_{0.85}CuO₂; 5: Cu₂SrO₂.

and the third sintering step. When samples are tin free (Sint 1 and Sint 2), XRD patterns mainly reveal the presence of the Bi-2212 phase after the first sintering step and the presence of the Bi-2223 phase after the second sintering step. On the contrary, when tin is added, two characteristic peaks appear ($2\theta = 17.9^\circ$ and $2\theta = 18.27^\circ$) which may correspond to the Ca₂SnO₄ phase, which is isotype of Ca₂PbO₄. The presence of different secondary phases such as Sr_{0.15}Ca_{0.85}CuO₂ and Cu₂SrO₂ are also observed. To confirm the presence of the Ca₂SnO₄ phase, SEM microscopy and X ray mapping were performed (Fig. 3). Acicular grains are observed as shown in Fig. 3A. This morphology is characteristic of Ca₂SnO₄ and Ca₂PbO₄ [17], which are isostructural, orthorhombic (space group Pbam). Moreover, the X-ray mapping reveals that these precipitates contain mainly calcium and tin (Fig. 3C and D). However, since the lead distribution is relatively uniform (Fig. 3B), it is difficult to say whether or not the acicular grains contain this element. But, as the Ca₂PbO₄ phase melting point is about 822°C [18], and the sintering temperature used in this study is 838°C, this phase must be decomposed. Nevertheless, tin and calcium elements are concentrated around the acicular grains and suggest that the Ca₂SnO₄ phase is formed in this zone. EDS quantitative analysis of a platelet grain, indicated by the letter "M", shows that this grain is composed of Bi: 23.17%, Pb: 4.38%, Sr: 21.74%, Ca: 13.18% and Cu: 37.53%, which corresponds to the Bi-2212 phase. This observation is in agreement with the XRD patterns previously described. To summarize, the introduction of SnO₂ nano-particles at the beginning of the synthesis or during the sintering of the Bi-2223 phase is detrimental to its formation, since SnO₂ reacts with calcium to form the Ca₂SnO₄ phase, which is stable up to 1400°C [19]. Thus, the Bi-2223 phase formation is inhibited for the benefit of secondary phases such as Bi-2212, Ca₂SnO₄, Sr_{0.15}Ca_{0.85}CuO₂ and Cu₂SrO₂. The subsequent question is to determine whether tin substitutes into the Bi-2223 structure.

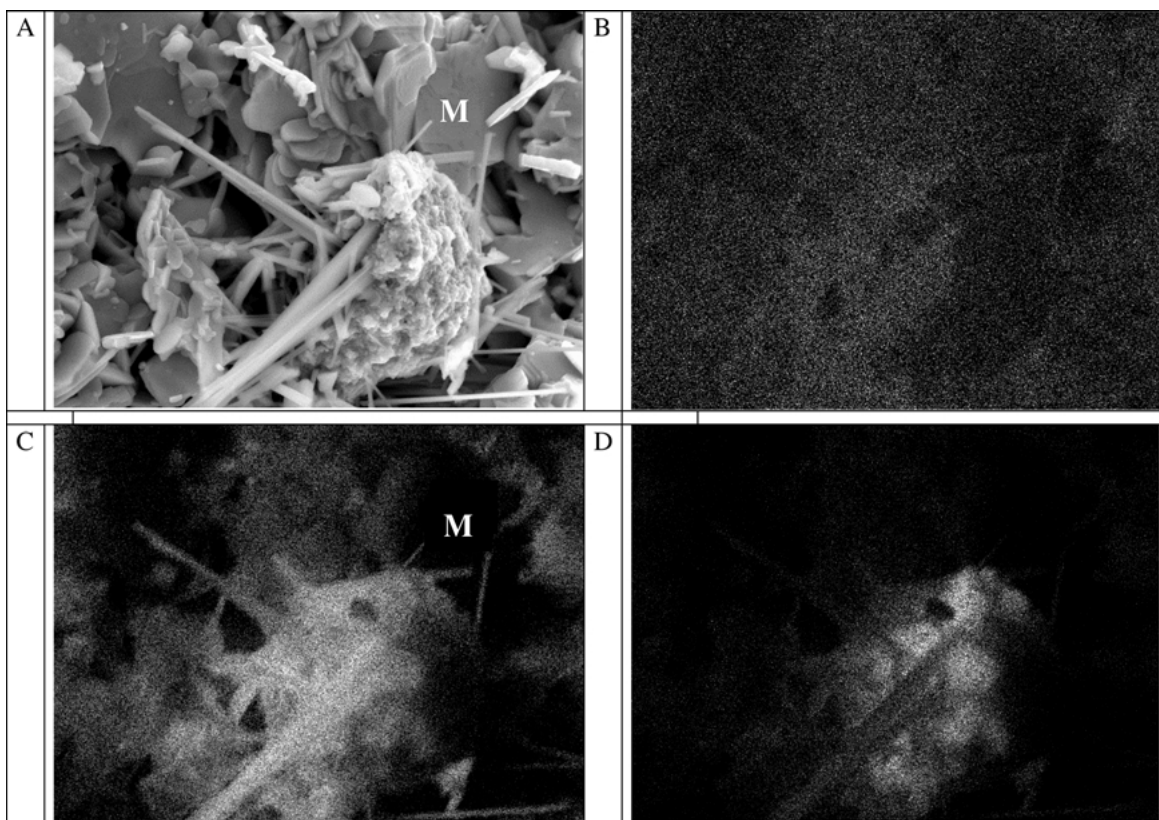


Figure 3 SEM micrograph (A) and element mapping: Lead (B), Calcium (C), and tin (D).

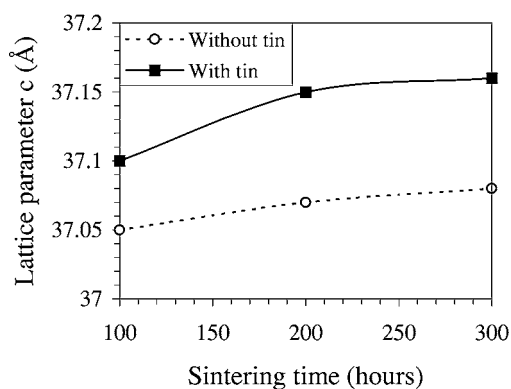


Figure 4 Lattice parameter c versus sintering time depending on the presence of tin in the samples.

3.3. Affinity between tin and the Bi-2223 phase

The c parameter of the Bi-2223 phase varies with both the sintering time and the composition, as shown in Fig. 4. For the tin-free sample, the c parameter increases monotonously with the sintering time. This behavior has been often reported, but the interpretation of this evolution has not been clearly established. However, a reasonable explanation can be found with the oxygen level, which increases with the sintering time, as does the c parameter. This phenomenon is also observed for the tin doped sample and the same explanation can be given, although the c parameter for the tin doped sample is higher than that of the tin-free sample. In the Bi-2223 material, Pb^{2+} which has an ionic radius of 1.2 Å [20] can substitute for Bi^{3+} (ionic radius = 0.96 Å [20]). We may suppose that the Sn^{2+} ion, owing to

its small ionic radius (0.93 Å [20]), can also substitute for Bi^{3+} ion. However, this substitution should lead to a reduction of the c parameter, which is not confirmed by our experimental results. Another possibility may be that during the sintering process, the Sn^{2+} ion is oxidized to Sn^{4+} , which has a smaller ionic radius (0.71 Å) [20] close that of Cu^{2+} (0.72 Å) [20]. Therefore, it is possible that Sn^{4+} may replace Cu^{2+} in the structure. This behavior has been observed using Mössbauer spectroscopy by Nishida *et al.* [10] who found that Sn^{4+} could replace the copper ion in a triangular CuO_3 geometry and in a pyramidal BiO_5 geometry [21]. Taking into account the charge balance, if the Cu^{2+} ion is partially substituted by Sn^{4+} , the oxygen content should increase, explaining the increase of the c parameter when the tin is added. This hypothesis is justified since the Cu^{2+} ionic radius is similar to that of Sn^{4+} . The presence of secondary phases such as $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ and Cu_2SrO_2 , which contain large amounts of copper, in the tin doped samples could also support this hypothesis, since this copper may have been displaced by the tin in the Bi-2223 structure. However, additional investigations are needed to clearly establish this assumption.

4. Conclusion

The effect of SnO_2 nano-particle addition on the Bi-2223 phase formation has been studied. Tin oxide was added at different steps of the synthesis process: in the powder precursor preparation and at each sintering step. It has been shown that the addition of SnO_2 inhibits the Bi-2223 phase formation, independently of the moment we introduce the dopant, by reacting

with calcium to form the Ca_2SnO_4 phase. This phase is stable throughout the sintering process and consumes part of the Ca^{2+} ions. As a consequence, the formation of the Bi-2223 phase is compromised for the benefit of the secondary phases such as Bi-2212, Ca_2SnO_4 , $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ and Cu_2SrO_2 . Moreover, the c parameter of the Bi-2223 phase increases when tin is added. A possible explanation can be related with a partial substitution of Cu^{2+} by Sn^{4+} . The ionic radii of these elements are similar and according to the charge balance principle, the partial substitution of Cu^{2+} by Sn^{4+} should be accompanied by the introduction of supplementary oxygen, explaining the increase of the c parameter with tin addition.

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