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Relations between microstructure and superconducting properties of Ce + Sn doped YBCO

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Abstract

Pellets of cerium plus tin doped $YBa_2Cu_3O_{7-\delta}$ (Y123) were textured using the top seeding melt texturing growth method. Amounts of SnO_2 varying from 0.25 to 1.00 wt.% were added to the 0.5 wt.% CeO_2 doped compound. The critical transition temperature, which is 90.5 K for cerium alone doping, recovers gradually the pure Y123 value of 92 K with tin addition. For the lowest tin amount studied, the bean critical current density is enhanced compared to the cerium alone doping, reaching more than 90 kA/cm^2 in self field and 50 kA/cm^2 under 1 T at 77 K. SEM studies have revealed the existence of sub micron size particles containing Y, Ba, Cu, Ce, Sn, and O. Their number increases with tin addition. TEM observations coupled with EDX analyses have shown that their composition largely varies from one particle to another and include impurities such as Sr or Zr. Twin density was also calculated and related to the observed properties of the doped materials. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Large mono-domains of $YBa_2Cu_3O_{7-\delta}$ (Y123) are obtained using the top seeding melt texturing process[1–3] for applications regarding levitation or as superconducting magnets. Small Y_2BaCuO_5 (Y211) inclusions have been proved to increase the critical current density; therefore, in order to refine them, dopants such as platinum or cerium are currently added.[3–7] In previous works,[8,9] the combination cerium + tin oxides has been studied with the aim of associating the benefit of the two dopants alone. Indeed, cerium doping leads to small Y211 inclusions in the textured material. On the other hand, tin doping enhances the crystal growth rates and J_c too, but has no refining effect on the Y211 particles. Previous studies[9] have already shown that the addition of SnO_2 to cerium doped samples can quadruply the crystal growth rates in comparison to cerium alone doping and greatly improve the superconducting properties of the doped material, making this doping very interesting. However, the improvements brought by the tin addition are not yet well understood. In this article, the influence of the tin amount on the critical temperature as well as on the critical current density of cerium plus tin doped samples is reported. SEM studies completed by TEM observations have been performed in order to understand the observed evolution of the properties.

2. Experimental details

Commercial powders of Y123, Y211, CeO_2 with purity of 99.9%, and of SnO_2 with a purity of 99% were used as precursors. Amounts of 0.25, 0.5, 0.75 and 1 wt.% of SnO_2 were added to Y123 + 0.25 mol Y211 + 0.5 wt.% CeO_2, which is the composition previously optimised for cerium alone doping.[3] The powders are mixed by ball milling and uniaxially pressed in 20 mm diameter pellets. A $SmBa_2Cu_3O_{7-\delta}$ melt textured cleaved sample was used as seed and placed at the top of the Y123 pellet. The texturing process was defined for each composition and adapted to texture 20 mm diameter pellets. Details are reported elsewhere.[3,9] The textured pellets were annealed for 100 h at 430°C under flowing oxygen. The superconducting properties were evaluated on

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cleaved samples with a SQUID magnometer. The results given for each composition correspond to the average of several samples and are highly reproducible. The critical temperature was measured under a 10 G field applied parallel to the sample *c* axis and the critical current density was calculated using the modified Bean model[10] from the magnetisation curves registered at 77 K. The carbon content was evaluated in textured samples following the method described in.[11] Briefly, this process consists in dissolving ground doped Y123 samples in sulfuric acid under a nitrogen gas flow. The carbon contained in the sample is released as CO_2 gas in the N_2 flow and measured using a carbon infra-red gas monitor (Guardian plus, Edinburgh Sensors Limited). Microstructural observations were performed on polished samples using a scanning electron microscope (FEG XL 30 Philips). The Ce + 0.25 wt.% SnO_2 doped sample was broken in alcohol. Fragments were deposed on a nickel support and used for transmission electron microscope studies (Jeol 200 CX equipped with EDX).

3. Results

The evolution of the onset critical temperature and of the transition width as a function of the different compositions is illustrated in Fig. 1. For the cerium alone doping, the onset T_c is 90.5 K and the transition width is 2 K. With tin addition, the onset T_c is enhanced and, for Sn contents higher than 0.5 wt.%, stabilises at 91.7 K, which corresponds to the pure Y123 value. The transition width is reduced to 0.5 K for 0.25 wt.% SnO_2, 1 K for 0.5 and 0.75 wt.%, but recovers the value of 2 K for the 1 wt.% SnO_2 doped sample.

Fig. 2 shows the critical current density as a function of the external magnetic field applied parallel to the sample *c* axis and of the composition. The values obtained for the cerium alone doped sample are 65 kA/cm^2 under self field, 20 kA/cm^2 under 1 T and approximately 5 kA/cm^2 under 2 T. The addition of 0.25 wt.% SnO_2 greatly increases J_c over the whole field range in comparison to the cerium alone doped sample. J_c reaches 90 kA/cm^2 under self field, 50 kA/cm^2 under 1 T and 25 kA/cm^2 under 2 T. Nevertheless, with further tin addition, J_c decreases gradually. The 0.5 wt.% SnO_2 doped sample has values under self field similar to the cerium alone doped one, but a higher pinning under field. The lower results correspond to the 1.00 wt.% SnO_2 doped sample, which only attains 32 kA/cm^2 under self field and 5 kA/cm^2 under 1 T.

The carbon presence in Y123 material is known to be detrimental to the superconducting properties and leads in particular in a drop of the critical temperature of Y123.[12] The carbon content was therefore evaluated in all the textured samples. In the cerium doped samples, it is estimated to 270 ppm and is lower than 120 ppm in all the Ce + Sn doped samples. These amounts are sufficiently low not to be detrimental to the superconducting properties.

In order to understand the evolution of the superconducting properties, the micro- and nano-structures of the samples have been studied.

SEM observations of the microstructure for the different compositions show that the Y211 particles are smaller than 3 µm in all the doped samples, although their size slightly increases with tin addition, and homogeneously dispersed in the Y123 matrix. This result can be seen in Fig. 3 corresponding to the 1 wt.% SnO_2 doped sample. However, for the higher tin contents, some Y211 particles reaching 10–15 µm have also been observed (Fig. 4).

These observations also reveal the existence of very small particles only present in tin doped samples and which do not correspond to Y211 phase. These particles appear bright in Fig. 3. Their number grows with tin

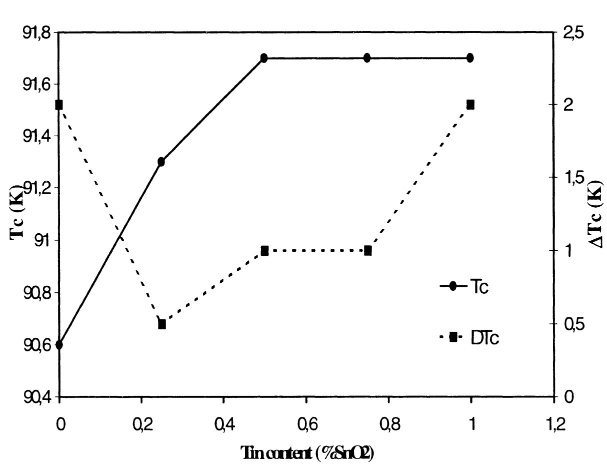

Fig. 1. Evolution of the critical temperature (T_c) and of the width of transition (ΔT_c) as a function of the tin doping amount.

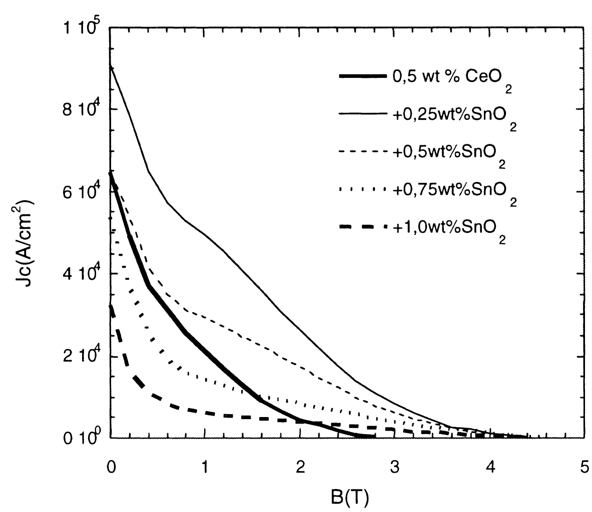

Fig. 2. Evolution of the critical current density (J_c) as a function of the tin doping amount and of the applied magnetic field (H//c).

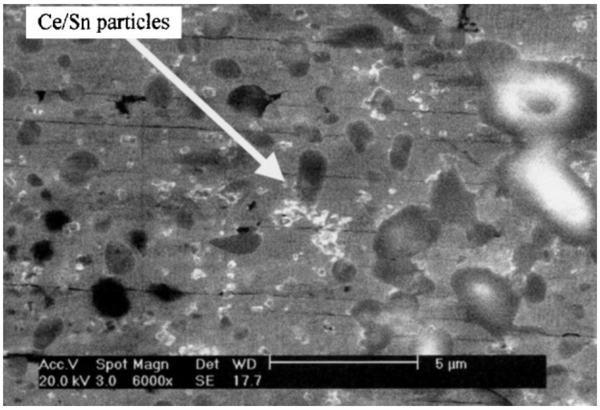

Fig. 3. Typical microstructure of a 0.5 wt.% $CeO_2 + 1.00$ wt.% SnO_2 doped Y123. Sub micron size Ce/Sn particles appear in bright.

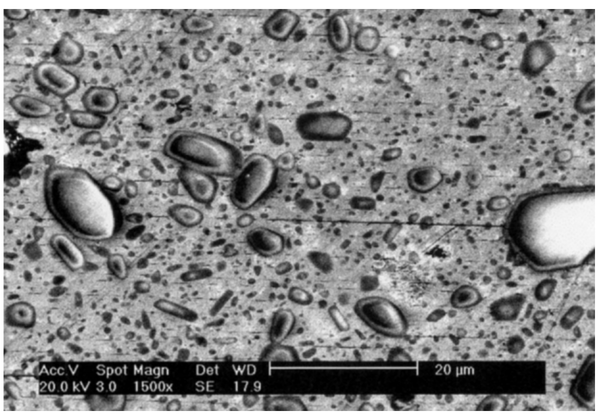

Fig. 4. Large Y211 particles (diameter: 10–15 µm) appear in the higher tin amounts doped samples (0.75 wt.% here).

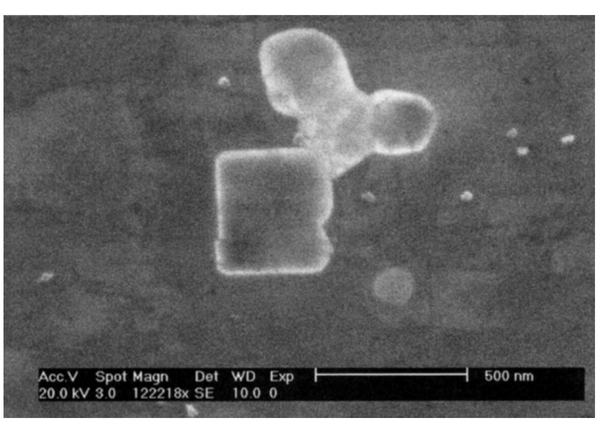

Fig. 5. Photographs of one Ce/Sn particle. Their size never exceeds 1 µm.

addition, but their size never exceeds 1 µm as illustrated in Fig. 5. As their size is too small for EDS with SEM, a precise determination of their composition can not be achieved. Nevertheless, EDS analyses show that they contain the different elements initially introduced, that is to say Y, Ba, Cu, Ce, Sn and O. Analyses performed in the Y123 matrix or on Y211 particles do not detect cerium or tin, suggesting that these elements are only present in these small particles. They will, therefore, be called Ce/Sn particles hereafter.

Ce/Sn particles are homogeneously distributed for the lower tin contents, but tend to agglomerate for the higher ones, resulting in a heterogeneous distribution in the matrix.

Globally, the microstructure appears hence more homogeneous for the lower tin amounts. To further characterise the samples, especially the Y123 purity, the Ce/Sn composition and the twin density, the Ce + 0.25 wt.% SnO_2 doped sample have been studied using TEM.

Works performed by Monot et al.[13] on cerium alone doped sample have revealed the presence of cerium in low proportion in the Y123 matrix and arbitrarily distributed. No cerium was detected in the Y211 particles. The twin density varies from one crystallite to another from 50 to 100 nm.[14]

In the 0.5 wt.% $CeO_2 + 0.25$ wt.% SnO_2 doped sample, cerium was also not detected in the Y211 particles. The Y211 particles size is included in the range 0.1–1 µm, in compliance with the values measured with SEM. The twin size varies from 10–70 nm, with a average width of 50–70 nm.

The Ce/Sn particles seems to crystallise in the perovskite type. Their composition varies largely from one crystal to another, therefore, no exact composition can be given here. The maximum contents in cerium and tin are respectively 0.18 and 0.1 for one unit Y123. These analyses also point out the presence of impurities such as Sr and Zr, which may come from the precursors. This phase seems then to act as a cleaner of the Y123 matrix, concentrating an important number of the impurities initially introduced.

Finally, small particles of $BaCO_3$ were also observed, their size varying from 100 to 200 nm. The presence of this phase is coherent with the existence of carbon in the textured material.

4. Discussion

The content of carbon in all the samples studied here is to low to be detrimental to the superconducting properties. Hence, a carbon pollution could not be in charge for the relatively low T_c of cerium alone doped samples. This phenomenon already observed for this doping is attributed to the cerium entering the Y123 matrix.[13] The cerium ion is believed to introduce in an arbitrarily way the Y^{3+} sites, modifying the oxygen order of the Cu-(1) chains, which results in a tetragonal symmetry and a progressive diminution of T_c.

In the Ce + Sn doped samples, a part of the cerium is incorporated in the Ce/Sn particles. Consequently, less cerium enters the Y123 matrix and the critical temperature recovers gradually the pure Y123 value of 92 K.

The evolution of the critical current density with tin addition is certainly related to several factors. For what concerns the 0.25 wt.% SnO_2 doping, which gives the best results, the high value of J_c under self field should come from the combination of 3 points. First, the fine and homogeneous distribution of Y211 particles similar to the cerium alone doping is beneficial to the pinning under very low fields. Secondly, in the same way, the introduction of sub micron size Ce/Sn particles should also contribute to the pinning under low fields. Finally, the increase of T_c induced by the incorporation of cerium in these particles is favourable to an increase of J_c. On the other hand, we assume that the high pinning under field of this sample is probably due to a higher twin density in comparison to the cerium alone doped one. This hypothesis is consistent with the very high values obtained on the same sample with transport measurements and with the magnetic field applied parallel to the sample c axis.[15] Indeed, transport J_c reaches 60 kA/cm^2 until 2 T and 40 kA/cm^2 under 3 T.

The decrease of the J_c values with tin addition is attributed to a deterioration of the microstructure homogeneity and of the texture quality due to Ce/Sn particles agglomeration.

5. Conclusion

The evolution of the superconducting properties of Ce + Sn doped Y123 has been related to the microstructure of the textured samples as a function of the tin amount. The formation of sub micron size particles containing Y, Ba, Cu, Ce, Sn and O has been shown to be beneficial to the critical temperature of the doped material. These particles act as matrix cleaners, incorporating all the impurities present initially in the powders mixture. In particular, the presence of cerium in the Y123 matrix is believed to decrease with the particles number, allowing T_c to recover from 90.5 K, the pure Y123 value of 92 K. This increase of T_c combined with a fine and homogeneous distribution of the Y211 and of the Ce/Sn particles greatly enhance the critical current density under self field for the lowest tin amount. A higher twin density is assumed to be responsible for the high pinning under field of this sample. However, the deterioration of the microstructure homogeneity and of the texture quality with Ce/Sn particles agglomeration makes the J_c values rapidly drop with further tin addition.

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