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Critical parameters for the preparation of Tl-1223 superconducting films by spray pyrolysis

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Abstract. Thick films of the high temperature $TlBa_2Ca_2Cu_3O_z$ superconductor have been prepared from a precursor $Ba_2Ca_2Cu_3O_z$ obtained by spray pyrolysis. In this paper, we report on the parameters which mainly control the formation of the superconducting phase: the composition of the nitrates solution, the substrate temperature and the subsequent ex-situ thallination annealing. The sample were analyzed by X-ray diffraction and by secondary electron microscopy. Epitaxial film (1 to 2 μm thick) with a critical temperature T_c=107 K and a critical density of current J_c(77 K, 0T)=2.10^3 A/cm^2 have been obtained.

1. INTRODUCTION

The recent improvements in the field of high critical temperature superconductors involve the preparation of tapes for applications. Among thallium based cuprates which critical temperatures vary form 92 K to 130 K, the $TlBa_2Ca_2Cu_3O_z$ (Tl-1223) phase which T_c reaches 115 K is one of the most interesting for high current applications. Indeed, this latter presents a higher irreversibility line than the one given by bismuth system. Moreover, the line is as high as the one given by YBCO superconductors.

Among the used methods for preparation of Tl-1223 long tapes, the spray pyrolysis method [1] is one of the most promising if the deposition parameters are controlled. We have used this method to prepare precursors layer with the composition Ba: Ca: Cu = 2: 2: 3. Basing on the knowledge in the Tl-Ba-Ca-Cu-O system, the ex-situ thallination leads to the formation of Tl-1223 thick films. The properties of these ones have been characterized.

2. EXPERIMENTAL AND ANALYSIS

Precursor layers with composition Ba: Ca: Cu = 2: 2: 3 have been prepared by spray pyrolysis. The starting solution is a mixture of Ba^{2+}, $Ca^{2+}$and Cu^{2+} nitrates prepared by dissolution of $BaCO_3$, $CaCO_3$ and CuO in concentrate nitric acid (65%).The ratios of the different cations have been changed in order to optimize the deposit composition. The spray has been produced from the solution by ultrasonic waves generated at 775 kHz by a piezoelectric ceramic. It was blown up with an argon flow (2 l/mn) to a MgO substrate, heated at 800°C. The deposition time was 5 minutes.

Following the procedure established in previous works [4,5], the precursor layers have been thallinated at 900°C, during 3 hours, in a sealed quartz tube under an oxygen pressure of 0.5 bar. In order to produce Tl-1223, the thallium source, here, is a bulk sample (300 mg) with a nominal composition Tl-1223, prepared by annealing of a mixture of oxides at 800°C under oxygen flow, during 6 hours.

At each step of the preparation, the morphology and the composition of the films samples have been analyzed using an EDS attached to an electronic microscope. The $K\alpha_1$ radiation of Ca and Cu and the $L\alpha_1$ radiation of Ba were used for quantitative analysis. The different phases have been identified by X-ray diffraction using an Inel curved detector. The preferential orientation of the grains has been

revealed by a classic Bragg-Brentano geometry $\theta/2\theta$. The critical temperature T_c have been obtained from *a.c.* susceptibility χ. The critical current J_c have been deduced form screening experiments.

3. RESULTS AND DISCUSSION

3.1 DEPOSITION OF PRECURSORS

In the case of deposition at high temperatures, the composition of the deposit layer differs considerably from the composition of the nitrate solutions. This is due to the difference between the decomposition temperatures of the solution components. Based on recent studies in the $(Hg,Re)Ba_2Ca_2Cu_3O_x$ system [2,3], for which a $Re_xBa_2Ca_2Cu_3O_y$ precursor is used, the copper concentration in the solution was fixed at x_{Cu} =0.10. The optimum conditions were then determined by varying the barium and calcium concentrations. Figure 1 shows, in a ternary diagram, the compositions of the various tested solutions and of the resulting deposits.

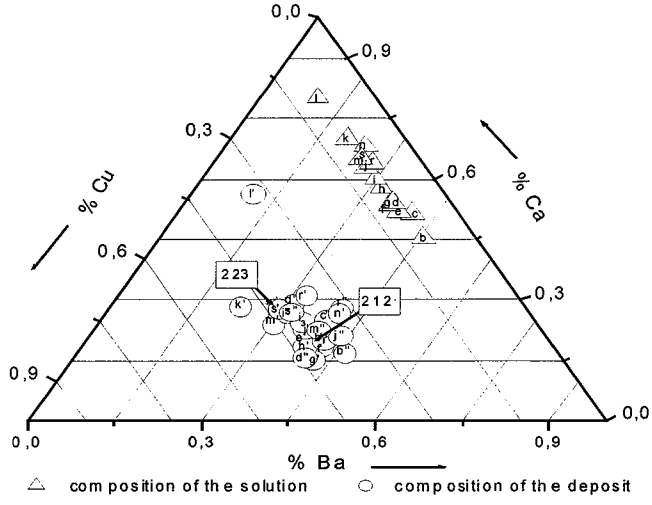

Figure 1. Ternary diagram which shows the compositions of the tested nitrate solutions and the compositions of the corresponding deposits.

We note that the small grains (<1 μm) and thickness (1 to 2 μm) of deposit do not allow absolute EDS analysis. Nevertheless, the relative change in the composition measured in a window of several mm^2 are significant. They reveal that the ratios in the sprayed layers range between Ba: Ca: Cu = 2: 1: 2 and Ba: Ca: Cu = 2: 2: 3.

According to this preliminary study, the precursor films with the expected optimum composition have been prepared using a solution with molar fractions x_{Ba} =0.25, x_{Ca} = 0.65 and x_{Cu} = 0.10.

As deposited, the precursor films are highly homogeneous as revealed by secondary electronic image (Fig.2). The layers are formed by submicronic grains which do not allows XRD characterization. Grain growth is observed after an annealing of the film at 850°C in oxygen atmosphere. In agreement with the phases equilibria studies [4,5], $BaCuO_2$ and Ca_2CuO_3 phases have been found to coexist.

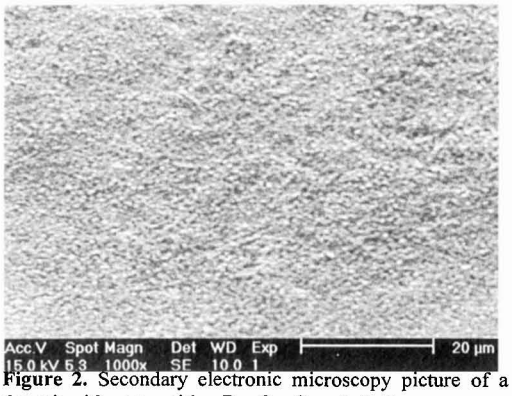

Figure 2. Secondary electronic microscopy picture of a deposit with composition Ba: Ca: Cu = 2: 2: 3.

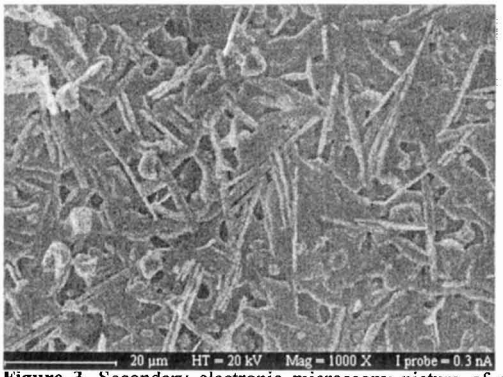

Figure 3. Secondary electronic microscopy picture of a thallined film with composition Tl-1223. Ca_2CuO_3 and $BaCuO_2$ impurity phases appear like needles of about 10 µm large and like knots respectively.

3.2 FORMATION OF THE SUPERCONDUCTING Tl-1223 PHASE

After thallination, the obtained layer thickness ranges between 1 and 2 µm. The superconducting Tl-1223 phase is found to grow as platelet-like grains with maximum size as larger as 20 µm (Fig.3). Traces of Ca_2CuO_3 and $BaCuO_2$ impurity phases are also observed. The well-defined grain boundaries revealed in Fig.3 are clear evidence that the formation of the superconducting Tl-1223 phase does not imply a liquid phase, and is mainly controlled by solid-gas reactions. The X-ray diffraction (Fig.4) confirms the good purity of the Tl-1223 phase and suggests an orientation of the grains according to the *00l* direction.

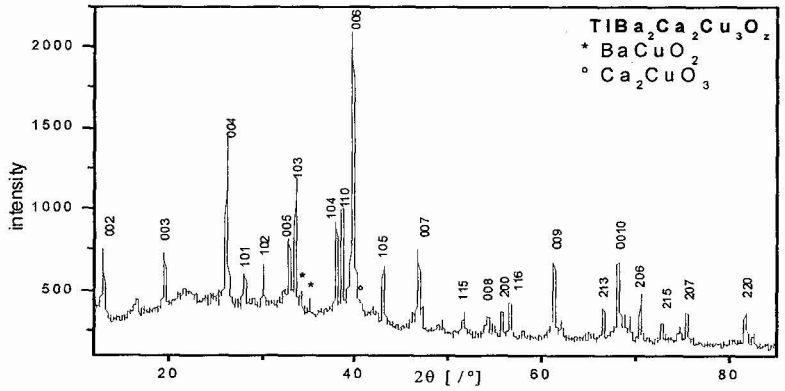

Figure 4. X-ray diffraction spectrum of a film with composition Tl-1223.

This preferential orientation is, however, better revealed by a Bragg-Brentano geometry experiment (Fig.5). The angular dispersion measured on the *006* line , shown in the insert of the figure 5, is $\Delta\omega$=3.4° which point out actually a rather disorientation of the plates.

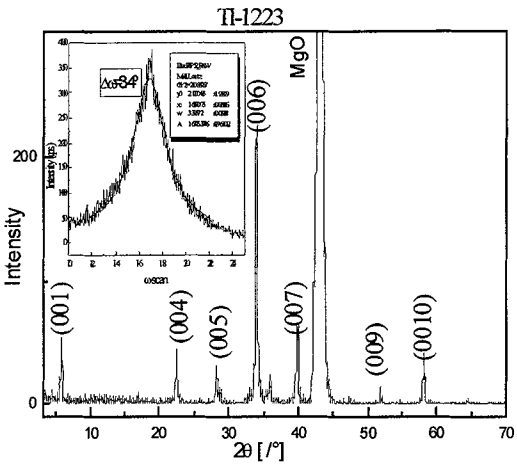

Figure 5. θ/ 2θ X-ray diffraction spectrum of a film with composition Tl-1223.

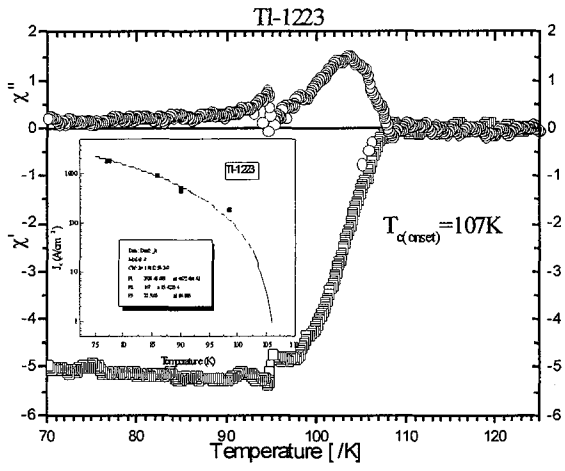

Figure 6. Measurement of *a.c.* susceptibility χ and critical current J_c (insert) of a Tl-1223 film.

The samples are superconducting with critical temperatures T_c of about 110 K (Fig.6). The large transition, about 7 K, is attributed to the existence of homogeneity range of the Tl-1223 phase-field. At 77 K (0 T), the critical current is about 2.10^3 A/cm^2 (insert of Fig.6).

4. CONCLUSION

The results which have been reported here, show the possibility to prepare a non-substituted Tl-1223 superconducting phase by a spray pyrolysis process. the critical temperature of the thick films are comparable to that of bulk samples and a texturation has been observed. However, the critical currents remain low due to a rather disorientation of the superconducting grains. Improvements of these properties are under work.

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