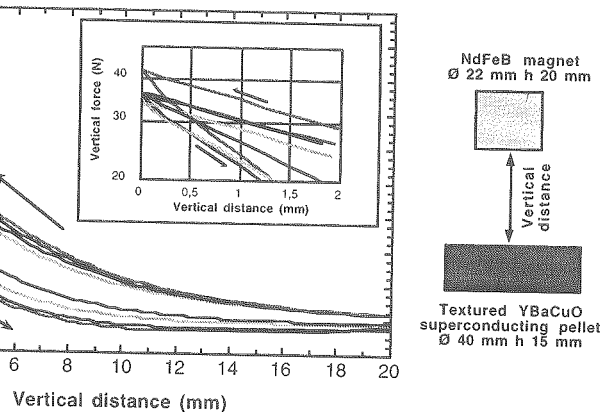


showing a very large grain and two smaller ones on a Ø40 mm pellet. The confirms that the currents are flowing on the grains scale.



Large reproducible levitation forces of large pellets.

s are obtained on samples which are not single grain and with a optimized. The levitation forces reach 70%-80% of the ones seeded samples (35-40 N compared to 50 N with the same ult of a good grain orientation and controlled solidification.

# Unidirectional solidification of $Y_1Ba_2Cu_3O_{7-\delta}$ , effect of a magnetic field applied during solidification

L. Durand\*, D. Dierickx<sup>†</sup>, D. Chateigner<sup>°</sup> and P. Régnier\*

\* CEA/C.E. Saclay/CEREM/SRMP, 91 191 Gif sur Yvette, France.

<sup>†</sup> KUL-MTM de Croylaan 2 B-3001 Heverlee Belgium

<sup>°</sup> Laboratoire de Cristallographie associé à l' Université Joseph Fourier, CNRS, 38 042 Grenoble cedex 09, France.

**Abstract.** The growth of large 123 grains containing homogeneously distributed ultra fine 211 precipitates can be achieved by acting on the grain size of the 123 powder, adding properitectic 211 particles and Pt powder to the precursor.

Application of a vertical magnetic field during horizontal solidification tends to align the a-b planes parallel to the main axis of the sample. It was found that 211 precipitates can be oriented by a magnetic field ( $b_{211} // H$ ).

## 1. Introduction

Looking for 123 grain of size as large as possible and containing homogeneously distributed ultra fine 211 precipitates, has led us to study 123 peritectic melting and 211 coarsening in the peritectic liquid. We have investigated the effects of grain size of 123 starting powder, properitectic 211 and platinum additions on the final distribution of 211 particles trapped in the crystal. The consequences of the 211 distribution size variation along the growth direction [1] on the super cooling at the solidification front level are discussed.

Unfortunately, application of a thermal gradient alone is not sufficient to align the 123 a-b planes of the grains parallel to the main axis of the sample. P. de Rango et al. [2] have discovered that a magnetic field induces an alignment of the c axis of 123 grains parallel to it and hence controls their a-b planes orientation. A set-up has been built allowing to apply a 4T vertical magnetic field during horizontal solidification. The effect of magnetic field application on c123 orientation during the growth is reported. Moreover, looking for a possible effect of the magnetic field on the 211 particles in the melt, EPR and X-ray pole figures of 211 particles trapped in 123 crystals have been performed.

## 2. Experimental

In order to investigate the effect of grain boundaries on the peritectic 211 nucleation, a 123 HOECHST powder of mean grain size  $d=3\mu m$  has been used. Two different routes have been used to prepare precursor samples containing 123 of two different grain size. Precursor powder A: has been uniaxially cold pressed (100MPa) and then sintered at 930°C during 12 hours in air. Precursor powder B: has been isostatically cold pressed at 13000 bar (the grain are broken during pressing) without sintering. Precursor sample A contains large 123 sintered grains and precursor sample B contains small 123 grains unsintered. The influence of additions on the 123 precursor powder on the size distribution of the 211 precipitates has been studied on the following samples: a) pure 123, b) 123 + 20% wt 211 sol-gel powder [3] and c) 123 + 20% wt 211 + 0,5% wt Pt wich has been prepared by mixing 123 + 20% wt 211 and Pt powder in an agate mortar. Those powders have been isostatically cold pressed (not sintered to prevent any coarsening of the grain before melting).

Details of experimental procedure used for unidirectional solidification have been published elsewhere [4]. Microstructural characterization has been performed on longitudinal polished sections of the samples by optical microscopy. Observation of the 211 morphology in quenched samples were made with EMPA Cameca SX50.

The super cooling temperatures have been estimated from measurements of the length of the solidified part of the bar knowing the thermal gradient in the furnace.

### 3. Results

#### 3.1. Unidirectional solidification

Using exactly the same experimental procedure, precursor A and B have been melted and slowly solidified (3°/h) under a thermal gradient [4]. It is very difficult to quantitatively compare the size distribution of the 211 particles trapped in the 123 solidified crystal for each precursor because samples A exhibit large areas without any precipitate. Table 1 qualitatively gives the main trends.

Table 1 : Main 211 distribution tendency for precursor A and B

Precursor	A	B
211 volume fraction	low	high
211 morphology	acicular	more spherical
211 distribution	non homogeneous	homogeneous

Figure 1 is an X-ray image of Yttrium on 123 and 123+20% wt 211 precursor quickly melted (10<sup>4</sup> °/h) at 1150°C during 5 mn and then air quenched. We can see the morphology of the 211 precipitates and the volume fraction changes.

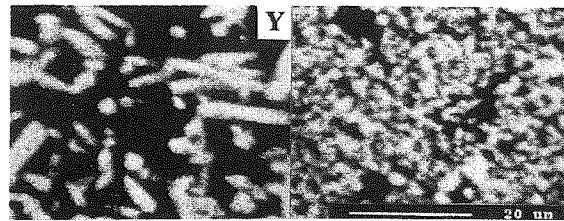


Fig. 1 : EMPA image of Yttrium on 123 and 123 + 20% wt 211 precursor melted 5 mn at 1150°C and then air quenched.

Figure 2 shows 211 mean diameter and volume fraction along the growth direction, from the cold end (firstly solidified) to the hot end for precursor b) and c). Note that the Pt doped sample has a 211 mean diameter smaller and a higher volume fraction than those of the undoped sample.

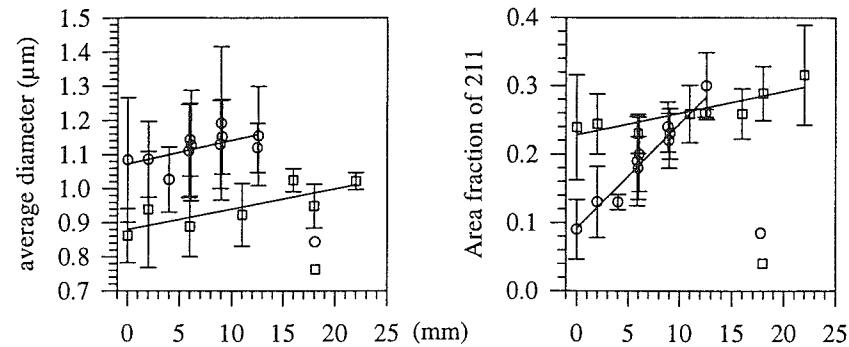


Fig. 2a and 2b : 211 size distribution along the bar from cold end to hot end. Respectively mean diameter and area % 211

Pt addition to 123 + 20% wt 211 powder has allowed us to grow a single 123 grain 20mm x 2mm x 2mm and to homogenise the 211 distribution along the bar.

Table 2 shows the temperature  $T_s$  of the solidification front for different lengths of solidified crystal. The super cooling  $\Delta T$  is calculated using the melting temperature which is  $T_p = 1030^\circ\text{C}$  under  $\text{PO}_2=1$  atm of flowing oxygen. Super cooling increases with the length of the solidified part of the sample.

Table 2: Super cooling versus the length of the solidified part of the sample

sample	$T_s$ (°C)	$\Delta T$	length of the solidified part (mm)
D4	1022	8	6
D2	1016	14	15

#### 3.2. Unidirectional solidification under 4T magnetic field

The c axis orientation of the grains has been determined on the face perpendicular to the direction of the magnetic field and plotted on a stereographic projection (Fig. 3). Applying a vertical magnetic field during the growth tends to align the  $c_{123}$  axis of the grain parallel to the direction of the magnetic field.

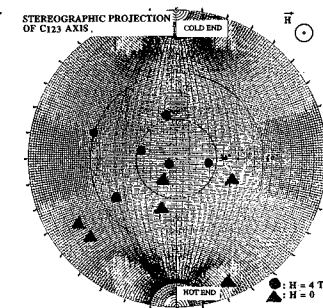


Fig.3 : Stereographic projection of the  $c_{123}$  axis on the face perpendicular to the magnetic field direction of samples processed with and without applied magnetic field.

A careful study has been made on one sample particularly well textured; the  $c_{123}$  axis of the grain is at less than 8° from the direction of the magnetic field [4]. Fig.4 presents the central zone of the {040}211 pole performed on a face perpendicular to the applied magnetic field. While it subsists a proportion of 211 phase randomly oriented (constant diffracted signal over the entire pole figure), there is a preferential orientation of 211 crystallites.

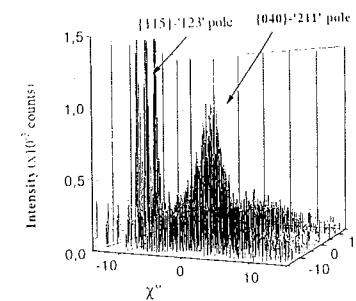


Fig. 4 : {040}211 pole figure on the face perpendicular to the magnetic field and the  $c_{123}$  direction on a particularly well textured sample processed under magnetic field.

## 4. Discussion

### 4.1. Unidirectional solidification

The difference in size distribution between samples A and B confirms that 211 precipitates nucleate at grain boundaries. Besides, as Griffith et al [5] have shown, when equiaxed properitectic 211 are added to 123, the resulting 211 precipitates are still equiaxed.

The fact that the mean radius and volume fraction of the 211 particles increase along the growth direction (fig. 2a and 2b) is believed to be due to several phenomena: 211 coarsening and agglomeration in the melt, precipitates pushed by the solidification front motion and 211 dissolution in the super cooled liquid in front of the solidification front [1].

The increase in super cooling with the solidified length seems correlated with that of the mean diameter and volume fraction of the 211 particles (figure 2a and 2b). Indeed 211 dissolution ahead of the solidification front is more and more difficult as the 211 precipitates coarsen and consequently a stronger driving force is needed. This is in disagreement with P. de Rango et al [6] who explain the increase in super cooling with increasing cooling rate by a decreasing in the oxygen exchange rate.

Pt addition modifies the particle distribution along the bar. Indeed Pt particles should provide nucleation sites for peritectic 211 precipitates but also, as shown in figures 2a and 2b, they should inhibit their coarsening in the melt [7].

### 4.2. Unidirectional solidification under a 4T magnetic field

The essential result shown in figure 4 is a strong orientation effect of the  $b_{211}$  axis parallel to the magnetic field direction. Anisotropy of the susceptibility of the 211 precipitates has been confirmed [8]. The fact that we have here  $c_{123} // H // b_{211}$  lead us to wonder about the mechanisms involved during solidification under magnetic field. Does this 211 orientation induced by the magnetic field impose the 123 growth direction?

## 5. Conclusion

Peritectic 211 precipitates nucleate on the 123 grain boundaries and on introduced nucleation sites like 211 or Pt particles. Moreover, Pt inhibits 211 particles coarsening in the melt. A single grain: 20mm x 2mm x 2mm was grown in a sample prepared with isostatically cold pressed (13000 bar) 123 + 20% wt 211 + 0,5% wt Pt powder.

Application of a 4T magnetic field during solidification tends to align the  $c_{123}$  axis of the grains parallel to the magnetic field direction. On a particularly well textured sample, we have found that a substantial proportion of 211 particles had their  $b_{211}$  axis parallel to the magnetic field direction. It has been confirmed that 211 phase is magnetically anisotropic [8].

## References

- [1] Durand L and Pastol J L 1994 *Materials Letters* **19** 291
- [2] de Rango P, Lees M, Lejay P, Suplice A, Tournier R, Ingold M, Germi P and Pernet M 1991 *Nature* **349** 770
- [3] Van der Biest O and Kwarciak J 1992 *J. Austr. Ceram. Soc.* **27** 51.
- [4] Durand L, Kircher F, Régnier P, Chateigner D, Pellerin N, Gotor F J, Simon P and Odier P 1995 *Supercond. Sci. Technol.* **8** 214
- [5] Griffith M L, Hauffman R T and Holloran J W 1994 *J. Mat. Res.* **9** 1633.
- [6] de Rango P, Chaud X, Gautier-Picard P, Beaunon E and Tournier R 1993 *Eucas-93* 305
- [7] Varanasi C, Black M A and McGinn P J 1994 *Supercond. Sci. Technol.* **7** 10
- [8] Pellerin N, Gotor F J, Simon P, Durand L and Odier P 1995 *Solid. State Commun.* submitted