Bulk YBCO Growth Monitored By In Situ High-Temperature Magnetic Susceptibility

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Abstract. In Situ high-temperature Susceptibility Measurement (ISSM) is a method to monitor the phase transformations in a material in real time depending on its susceptibility change. Examples are given where the effects of composition, heating rate and geometry on the growth of YBCO bulk sample have been investigated by ISSM. Differences in the behaviour during melting and solidification are shown for MTG and PMP samples because of their composition. The effect of processing condition is illustrated by higher heating rate increasing the temperature solidification onset, and the effect of geometry by a comparison of the thin-wall geometry of a drilled sample with a plain one, showing a faster growth rate.

1. Introduction

We do hope that, in near future, YBCO single domains will have significant applications at 77K. They can be used for Maglev train, magnetic bearings (flywheels for energy storage, frictionless linear translation systems), for producing high magnetic field (motors, superconducting pseudo permanent magnets) [1-3]. From the discovery of high-Tc superconductor in 1986, the fabrication of YBCO bulk sample has been developed from solid-synthesis method in 1986 [4] to top-seeding melted textured growth [5]. Recently, a large bulk GdBCO superconductor of 140 mm in diameter has been grown [6].

Melted Textured Growth (MTG) with seed is an effective process to grow single-domain bulk YBCO samples. But there are still many problems in growing large samples because parameters vary from one composition to another and an accurate determination of the solidification range is needed. ISSM can be used to better understand the growth mechanisms and to optimize the heat treatment for a given composition and set of precursors [7]. ISSM was used to observe for instance that oxygen uptake before the solidification can influence the solidification itself during MTG process [8]. Accurate determination of the phase transitions of MTG-YBCO bulk in situ for real processing conditions enabled the growth of large single-domain YBCO bulk sample up to 93 mm [9].

Powder Melting Process (PMP) [10] is efficient to reduce the size of Y211 particles so as to introduce more pinning centers. Indeed, the PMP method is reported to improve the Jc of YBCO bulk samples and so is beneficial to their applications. But the mechanisms of nucleation and growth of PMP are not clear. It is more difficult to grow large single-domain samples with PMP than with MTG at present.
Thin-wall geometry fabrication by drilling a hole network in YBCO samples [11] is an effective mechanical method to reduce the distance of oxygen diffusion. It enables a new strategy to increase the oxygen diffusion speed and to limit the cracks expand.

In this paper, we report our investigation by ISSM on phase transitions of PMP-YBCO sample during process and on the influence the geometry (drilled or plain) of samples prepared by PMP method on the growing process.

2. Experimental
The ISSM are performed in a specially designed furnace combining high temperatures and the high magnetic field (maximum 8T) given by a superconducting coil. The magnetic susceptibility is derived by measuring the force that a strong magnetic field gradient exerts on it. The magnetic force can be described by the following formula: 

\[ F = \chi \cdot B \cdot dB/dz \]

where the \( B \cdot dB/dz \) is a constant (263.618 T^2/m) depending of our coil. The magnetic force is measured by an electronic balance with a 1200 g capacity and a 1 mg resolution.

The MTG- or PMP- YBCO sample is put on a substrate with a double layer, first a mixture of 80wt%Yb123 +20wt%Y123, then an Y2O3 powder. This is a buffer layer to prevent reactions between the YBCO sample and the Al2O3 crucible. The total measured balance signal \( S_{\text{total}} \) is as follows:

\[ S_{\text{total}} = W \text{ (sample weight)} + F \text{ (sample magnetic force)} + [W' \text{ (substrate and crucible weight)} + F' \text{ (substrate and crucible magnetic force)}] \]

Because the signal of substrate and crucible is less than 6% of the total signal, the \( S_{\text{total}} \) can be used for studying the susceptibility transition of YBCO sample. In this paper, we used \( S_{\text{total}} \) as Y-axis and normalized the Y-scale with the sample mass; the unit of Y-scale is g/g which represents the weight and force signal per gram referred as “\( S_{\text{total}} \text{ (g/g)} \)”. The Y-scale of thermogravimetry is also normalized by mass; the unit is as g/g.

In this experiment, the precursor powder used for MTG method is a mixture of 70%wt. YBa2Cu3Ox (aka Y123), 30%wt. Y2BaCuO5 (aka Y211) and 0.15%wt. PtO2 (equivalent to 60%mol Y211 addition) [11]. The PMP precursor is a mixture of Y2BaCuO5, BaCuO2, and CuO. Its composition is Y: Ba: Cu: O= 1.8:2.4:3.4:7-x, and 1%wt CeO2 addition. The samples of MTG or PMP are pressed into pellets of 20 mm in diameter and 18 mm in height. They are put in the ISSM-furnace with 8T magnetic field. For our investigation, the heat treatment schedule is the same for the MTG and PMP samples. The sample is heated from 200°C to 900°C quickly at 240°C/h, up to 1060°C at 60°C/h, kept at this temperature 2 hours, and cooled from 1060°C to 1020°C at 60°C/h, then from 1020°C to 980°C at the very low cooling rate of 1°C/h, and fast cooled to 200°C at 240°C/h. The susceptibility signal of the sample is measured every second, but data are recorded only every 30 seconds.

For PMP method, experiments were also performed with heating rates of 240°C /h and 10°C /h during the heating period 900°C-1060°C in order to compare the effect of different heating rates.

The drilled sample was machined by a drilling robot after being pressed. Both the plain- and drilled- samples are prepared by PMP method and were submitted to ISSM. The weight loss was also recorded by doing again the experiment in the ISSM set-up without magnetic field applied.

3. Results and Discussion
3.1. ISSM measurement applied to an MTG- YBCO bulk sample
The principle of ISSM is that the susceptibility \( \chi \) changes not only with temperature (Curie-Weiss law), but also with the material composition and phase. So, it is a method to reveal the phase transition of bulk material, especially for YBCO bulk. In the precursor powders of YBa2Cu3O7-x (Y123), Y2BaCuO5 (Y211), BaCuO2 and CuO, the valence of ions are as Y^{3+}, Ba^{2+}, Cu^{2+} and O^{2-}. Ions of Y^{3+}, Ba^{2+}, O^{2-} and Cu^{2+} are not magnetic, but the Cu^{2+} ion is paramagnetic. In the melting of YBCO, CuO decomposes after 1035°C, as CuO \( \rightarrow \) Cu_{2}O+O_{2}. Only the susceptibility of magnetic ions will yield a signal, so the susceptibility of YBCO derives from the paramagnetism of Cu^{2+}. Except at the phase transitions, the susceptibility \( \chi \) of YBCO changes depending on the temperature and abides by a Curie-
Weiss law. In the interpretation, we have to take into account the weight change in the magnetic signal and the fact that we are working with mixture of compounds.

From results of MTG-YBCO by ISSM, as shown in figure 1.a and b, it is observed that the susceptibility abides by a Curie-Weiss law in the temperature range from 200°C to 900°C. From point A (995°C), the Y123 phase begins decomposing into Y211 and liquid phase, until the temperature point B (1052°C). The reaction is \( \text{Y123} \rightarrow \text{Y211} + \text{L} \). The melting region is the A-B part. During overheating, i.e., the curve part above the melting point B, the susceptibility does not abide by a Curie-Weiss law. This is due to oxygen flowing out of the sample because of the reaction \( \text{CuO} \rightarrow \text{Cu}_2\text{O} + \text{O}_2 \) [7]. As well, oxygen uptake occurs in the cooling range. The oxygen loss appears more clearly as a step at the overheating dwell and the oxygen uptake at the beginning of the slow cooling ramp. At point C (1009°C), small tiny crystals can be seen at the sample top surface and the susceptibility changed quickly as the solidification of the bulk is triggered, as shown in figure 1.b. The solidification region is the C-D part.

![Figure 1.](image1.png)

Figure 1. Susceptibility curve of a MTG YBCO bulk showing the sample melting (A-B) and solidification (C-D) temperature range. Figure b is a zoom in of figure a.

3.2. ISSM measurement in PMP–YBCO bulk

The results of susceptibility of PMP-YBCO bulk vs. temperature are shown figure 2.a and b. Before 900°C, the susceptibility \( \chi \) abides by a Curie-Weiss law. After 900°C, Y123 particles appear as the following reaction occurs: \( \text{Y211} + \text{BaCuO} + \text{CuO} \rightarrow \text{Y123} \). From point A to point B, as seen in figure 2.b, the Y123 decomposes into Y211 + L (1000°C-1011°C). Oxygen loss and uptake are seen as well in the melted part of the curve, a similar phenomenon as in MTG. At point C, tiny YBCO crystals appear on the surface. From point C to D, the Y123 crystals grow. Thereby, the melting and solidification range of PMP are 1000°C-1011°C (A-B) and 1004°C-980°C (C-D) respectively.

![Figure 2.](image2.png)

Figure 2. Susceptibility curve of a PMP YBCO bulk Showing the melting (A-B) and the solidification (C-D) temperature range. Figure b is a zoom in of figure a.
Comparing the results of ISSM, it is found that the melting and solidification steps are different between MTG and PMP method. The melting temperature (1052°C) of MTG sample is much higher than that of PMP sample (1011°C). It can be explained by the different melting route. The PMP sample has less formed Y123 phase and this phase is in contact with CuO. Decomposition of Y123 in presence of CuO is known to occur around 940°C [13]. The MTG sample has a higher melting temperature because it corresponds to the classical melting of Y123 around 1020°C. The melting or solidification temperature observed in this work represents a real process taking into account out of equilibrium mechanisms (heat and chemical diffusions) in the bulk.

The solidification onset temperature of MTG sample (1009°C) is higher than that of PMP sample (1004°C). Here we suggest that some Y123 nuclei or impurities exist in the high temperature even after Y123 melting, and these nuclei or impurities serve as seed so that nucleation occurs at a smaller undercooling. In PMP sample, the different route avoiding Y123 formation may be more efficient to reduce these possible seeds.

3.3. ISSM measurement of PMP-YBCO bulks with different heating rate
We investigated with PMP samples different heating rates (240°C/h, 60°C/h and 10°C/h) over the 900°C-1060°C temperature range. The melting behaviour of PMP sample is found different along with the heating rate as shown in figure 3. The fast heating rate 240°C/h does not yield any obvious melting step (curve 1). We assume that the Y123 phase has not enough time to form. For the heating rates of 60°C/h and 10°C/h, the temperatures corresponding to the melting range (point A to B in curve 2, and in curve 3) are 1000°C-1012°C and 980°C-1006°C respectively. The slow heating rate (10°C/h) gives more time to form the Y123 phase in the range of 900°C-1000°C. This results in a large volume of Y123 particles in the PMP sample. As a matter of fact, the melting behaviour of this sample is close to the one of the MTG sample. The volume of Y123 phase in the PMP samples is different with different heating rate according to the existence and amplitude of the melting step. The heating rate has an influence on the melting state of the PMP sample.

![Figure 3. Susceptibility curves of PMP samples with heating rates of 240°C/h, 60°C/h, and 10°C/h.](image)

The solidification onset temperature of PMP sample with different heating rate is listed in the table 1. They are marked as point C at 1006°C, 1004°C, and 1001°C on the curves 1, 2 and 3. A lower heating rate yields a lower nucleating point in the PMP sample. It is supposed that the nuclei size...
becomes smaller since the sample with slow heating rate stays more much time at higher temperature, so as to decrease the nucleation temperature according to the theory of heterogeneous nucleation by Turnbull [12].

| No | Heating rate between 900°C -1060°C R (°C/h) | Start Melting A (°C) | Finish Melting B (°C) | Start solidification C (°C) | Finish solidification D (°C) |
|----|---------------------------------------------|----------------------|----------------------|-----------------------------|-----------------------------|
| 1  | 240                                        | --                   | --                   | 1006                        | 980                         |
| 2  | 60                                         | 1000                 | 1012                 | 1004                        | 980                         |
| 3  | 10                                         | 980                  | 1006                 | 1001                        | 980                         |

3.4. Oxygen diffusion in plain- and drilled- samples in PMP

The behavior of bulk YBCO samples was investigated with drilled- and plain- geometry. Both samples are treated with the same PMP process with a seed placed on their surface prior to the heat treatment. Their pictures are shown in figure 4 and the ISSM results are shown in figure 5.a and b. The samples have been cut along c-axis (figure 4c and d). The drilled sample has grown as a single domain, but not the plain sample. The single domain is regularly cracked along the ab-plane as can be seen on figure 4c. The section of the plain sample shows many grains. In its center, grains are mixed with Y211 particles and liquid phase.

![Figure 4. Morphology of drilled and plain YBCO bulk made by PMP method with seed.](image)

Comparing the ISSM results in drilled and plain bulk sample as shown in the figure 5.b, we observed that the shapes are very different. The ISSM curve of the drilled sample has a similar value at point B (heating) and at point C (cooling), but not the one of the plain sample. It means they have different oxygen content before solidification. The higher surface to bulk ratio of the drilled sample can be assumed to be more beneficial for thermal as well as for oxygen diffusion. Figure 6a is the corresponding thermogravimetry of drilled and plain PMP samples. We assumed that the change of weight is only related to oxygen loss or uptake. We note more oxygen loss for the drilled sample during heating, which is in agreement with this hypothesis. We observe that the drilled sample start to uptake oxygen from the onset of solidification while the plain sample seems to keep losing oxygen to stop only at the end of solidification (D, 980°C). And this trend stops when the first nuclei appear (1010°C) in the drilled sample.

During cooling, there is a susceptibility jump at 1025°C both in drilled and plain samples as shown in figure 5.a. This phenomenon exists in MTG sample (as shown in figure1.b) at 1020°C and is explained by the contribution of the Cu\(^{2+}\) ion susceptibility based on the reaction Cu\(_2\)O+O\(_2\) → CuO, in MTG sample [7]. But in PMP samples, the calculated increase of oxygen mass that should correspond to this susceptibility jump (about 2.2 mg/g in the plain sample - “blue curve” shown in figure 5.a) is one order larger than the observed mass increased in thermogravimetry (0.4mg/g - figure 6.b ). We believe it is linked to the composition in the PMP route. For instance, the oxygen may be kept in the sample in association with other compounds. Further investigations are underway to find an explanation to this discrepancy.
The nucleation starts at the same temperature for both samples. It is a surface event, while the growth itself is bulk related. Since we obtained a far better growth in the case of the drilled sample, we postulate that oxygen promotes the growth of YBCO bulk. It is noticed in [12] that, as a general tendency for CuO and Cu (II) cuprates, the oxygen content in the liquid is remarkably less that in the solid phase in equilibrium. Therefore, oxygen is required to grow the solid phase, here the Y123.

Figure 5. a. Susceptibility curve of drilled and plain bulk of PMP. It shows obvious that melting A-B and solidification C-D range of its magnetic signal change versus temperature. Figure b is a room in of drilled sample.

Figure 6. a. Thermogravimetry of drilled and plain PMP samples. Figure b is a room in of figure a. At 1025°C, there is a weight jump in plain sample and a convex curve in drilled sample. It is corresponding to figure 5 that there is an oxygen uptake around 1025°C.

4. Conclusion
Using ISSM technique, phase transitions of bulk YBCO can be clearly evidenced whatever the route, MTG or PMP method. But the route has a strong influence on the way phase transitions occur. The susceptibility behaviour shows noticeable difference in solidification and melting, which is explained by the fact that in MTG, Y123 exists prior to the melting, while in PMP, the formation of the Y123 phase during heating depends on the heating rate. Presence of CuO phase in PMP route can also explain lower melting temperature. The sample geometry is shown to have a strong influence on the growth of PMP YBCO bulk samples. The growth is enhanced by the thin wall geometry. It is assumed to be linked to the improved oxygen diffusion.

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