Growth conditions and properties of Y123/Y211 and Y123/Y2O3 bulks

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Abstract. The single-grain YBCO samples were prepared by TSMG process. Two nominal compositions: 1 mol. Y123 + 0.25 mol. Y2O3 + 1.0 wt.% CeO2 (Y123/Y2O3) or 70 wt.% Y-123 + 30 wt.% Y-211 (Y123/Y211) and 1.0 wt.% CeO2 and two different types of substrates were tested. It is shown that the growth rate in both systems is influenced by segregation of CuO in to the nonsolidified part of the sample what causes stop of isothermal growth. Measured melt losses are lower for ZrO2 substrate than for Y2O3/Yb2O3 substrate what influence final microstructure of prepared bulk superconductors.

1. Introduction
Currently, the number of scientific publications on REBCO bulk single-grain superconductors is focused on the details of preparation parameters to optimize technology of TSMG process [1-6]. The growth conditions are also intensively studied mainly in the systems with cheap CeO2 addition for refinement of Y211 particles [7-13]. This paper compares Y123/Y211 and Y123/Y2O3 systems with the addition of 1wt.% CeO2. It is shown that mainly the appearance of CuO due to reaction of 123 with Y2O3 and CeO2 influences growth of single-grain samples. It is also shown that higher 211 concentration in the sample with high melt losses causes difficulties at oxygenation.

2. Experimental
YBCO bulk samples with two nominal compositions: 1 mol. Y123 + 0.25 mol. Y2O3 + 1.0 wt. % CeO2 and 70 wt.% Y123 + 30 wt.% Y211 + 1.0 wt.% CeO2 were prepared in air in a chamber furnace. YBa2Cu3O7 (Solvay, particle size 30μm), Y2O3 or Y211 (Solvay, particle size 5μm) and CeO2 powders were mixed in appropriate amounts in a mixer for 30 min and then intensively milled for 15 min in a friction mill. The homogenized milled mixture of powders was uniaxially pressed into cylindrical pellets 20 mm in diameter. The samples were treated in a chamber furnace according to the following steps: heating up at the rate of 100 °C/h to 940 °C/dwell 24h, heating up at the rate of 100 °C/h to the maximum temperature, Tmax = 1040 °C (30 °C over peritectic temperature, Tp), dwell time for 1h, fast cooling to a temperature 12 °C higher than the temperature of isothermal grow, Tis, at the rate of 50 °C/h, slow cooling to the isothermal hold temperature, Tis, with cooling rate 1 °C/h and finally cooling to the room temperature with furnace. The macrostructure of the sample surfaces was studied by a stereomicroscope. Sample cuts in the a/c-plane along the cylinder axis were prepared by grinding and polishing for microscopic analyses. The microstructure details were analyzed in an optical microscope under normal and polarised light. DTA measurements of mixed nominal powder and pure YBa2Cu3O7 powder in the artificial air were applied to determine characteristic transformation temperatures. The
samples were oxygenated in flowing oxygen gas at 400°C for 150h. For trapped field measurements, the samples were field cooled in liquid nitrogen (77K) in the presence of an applied external magnetic field of 1.4T.

3. Result and discussion
The single-grain Y123 samples with different compositions were successfully grown by Top-Seeded Melt-Growth (TSMG) process. Macroscopic images of the top surface of grown single-grains are presented in Figure 1.

![Figure 1](image1.png)

Figure 1. The top surface of the sample with 60 hours isothermal dwell at 996 °C (a) and the top surface of the sample with 80 hours isothermal dwell at 992 °C (b).

The used times of isothermal dwell were long enough for the single-grain to grow fully through the sample diameter if the growth rate 0.2 mm per hour, measured in the middle of sample radius, is considered [14]. The observed growth stop is the result of CuO appearance in the system due to the reaction of Y$_2$O$_3$ and CeO$_2$ with Y123 and consequent CuO segregation into the nonsolidified rest of melt [14-15]. The presence of CuO in the Y123/Y211 system with CeO$_2$ addition is also confirmed by lower peritectic temperature of this system measured by DTA (Figure 2(a)) and high CuO concentration in the solidified melt at the sample rim (Figure 2(b)).

![Figure 2](image2.png)

Figure 2. DTA records at heating with 10°C/min. in artificial air for pure YBa$_2$Cu$_3$O$_x$ powder and mixture of Y123/Y211 with addition 1wt.% CeO$_2$ (a) and CuO phase (bright) present in the Y123/Y211 system in the solidified melt at the sample rim (b).
After oxygenation of prepared bulk superconductors the measured trapped field profiles at 77K show significant differences (Figure 3). While the sample grown from the Y123/Y2O3 system exhibits beautiful symmetric cone (Figure 3(b)), the trapped field profile of the sample prepared from the Y123/Y211 system is highly irregular with much lower maximum trapped field (Figure 3(a)).

![Figure 3](image)

**Figure 3.** Measured trapped field profiles for the 20 mm diameter samples of Y123/Y211 (a) and Y123/Y2O3 (b) systems.

The microstructure analysis done on the polished cut of the Y123/Y211 oxygenated sample helped to explain observed irregularities in the trapped field profile (Figure 4). In polarized light, it is possible to see that the Y123/Y211 sample is not fully oxygenated. The large areas along a/b-plane are still tetragonal and nonsuperconducting (Figure 4(a)). By our opinion much higher Y211 concentration observed in the Y123/Y211 sample (Figure 4(a)) than in the Y123/Y2O3 sample (Figure 4(b)) is responsible for difficult oxygenation. The sample with higher Y211 concentration has higher fracture toughness [16] and therefore formation of oxygenation cracks, which are necessary for faster oxygenation [17], is difficult.

![Figure 4](image)

**Figure 4.** Microstructure after oxygenation process 400 °C/150h of the samples Y123/Y211, where we can see orthorhombic (O) and tetragonal Y123 phase (T) (a) and Y123/Y2O3 with orthorhombic structure in entire area of the sample (b).
The reason of higher Y211 concentration in the Y123/Y211 sample is a loss of melt at the melting temperature. We tested different substrates from the point of melt losses at different melting temperatures. The results are presented in Figure 5. The lower melt loss and change in the sample diameter were observed for the substrate in the form of ZrO$_2$ bars then for the Y$_2$O$_3$/Yb$_2$O$_3$ combined substrate. The melt loss was lower for lower melting temperatures. This positive influence of ZrO$_2$ substrate is also illustrated by observed sample microstructures (Figure 6). The size Y211 particles are similar for both tested substrates. The significant difference is in the Y211 volume fraction, which is much higher for the Y$_2$O$_3$/Yb$_2$O$_3$ combined substrate where higher melt loss was observed.

![Figure 5. Melt losses (a) and changes in sample diameter (b) during growth of Y123 single-grain for different substrates (ZrO$_2$ and Y$_2$O$_3$/Yb$_2$O$_3$) at different $T_{\text{max}} = 1015$ °C, 1025 °C and 1035 °C.](image1)

![Figure 6. Microstructure of Y123/Y211 single-grain samples for different substrates and $T_{\text{max}} = 1025$°C. The size of Y211 particles is similar but concentration of Y211 is lower for ZrO$_2$ substrate (a) than for Y$_2$O$_3$/Yb$_2$O$_3$ substrate (b).](image2)

4. Conclusion
YBCO single-grain bulk superconductor with nominal composition 1 mol. Y123 + 0.25 mol. Y$_2$O$_3$ + 1wt.% CeO$_2$ and 70 wt.% Y123 + 30 wt.% Y211 + 1 wt.% CeO$_2$ were prepared by TSMG process in air. It is shown that CuO formed during the reaction of Y$_2$O$_3$ and CeO$_2$ with Y123 and segregates to the rest of melt what decreases the peritectic temperature of the nonsolidified part of the sample and causes growth stop in both studied systems. Moreover, high melt losses in the Y123/Y211 system with Y$_2$O$_3$/Yb$_2$O$_3$ substrate leads to the high volume fraction of Y211 particles and to difficult oxygenation. It is also shown that the melt losses are lower at lower melting temperature and for the ZrO$_2$ substrate.
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