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Crucible free Techniques in $YBa_2Cu_3O_{7-x}$ - Crystal Growth

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Abstract

We present new techniques for $YBa_2Cu_3O_{7-x}$ (YBCO)- crystal growth. One method allows a much faster growth of single crystals than the standard techniques. A porous ceramic sucks up the flux and causes a constant material flow at a cooled tip where growth takes place. During 24 hours a bundle of single crystals is formed standing freely at the cool tip. The crystals are superconducting with a T_c of 90 K and reach a size of 3 x 2 x 0.5 mm^3. An other technique is quasi crucible free. A flux/YBCO mixture is partially melted and grain growth takes place. We also introduce a setup for seeded growth of YBCO - crystals out of a self crucible.

1. Introduction

The phase diagram Y - Ba - Cu - O [1] shows, that the growth of high quality $YBa_2Cu_3O_{7-x}$ single crystals (YBCO, 123) is only possible by techniques based upon the flux method. In addition to the conservative slow cooling technique which yields crystals of a quality sufficient for many purposes we develop new growth techniques in order to overcome the typical difficulties of the YBCO synthesis. The melting behaviour is pronouncedly incongruent, mixtures in the primary crystallization field contain only 10% YBCO. The maximum growth rate is strongly anisotropical. In c-direction it does not exceed 4 μm/h at diffusion controlled growth and 15 μm/h upon stirring [2]. These arguments require a low growth rate i.e. a long duration of the growth experiments.

On the other hand the reactivity of the flux with all available crucible materials calls for short times of contact between the flux and the crucible. Otherwise corrosion products like $YBa_3Al_2O_{7.5}$ in the case of alumina crucibles or $BaZrO_3$ for zirconia crucibles change the properties of the liquid and may even be incorporated in the crystals. Furthermore the melt composition can change due to selective material flow over the crucible wall and the crystals are difficult to remove from the solidified melt.

A solution of these problems are crucible free or quasi crucible free methods. In our approach the growth rate is increased by supplying the growing crystals with fresh saturated flux.

2. Flux growth with vertical flux flow

The flux is prepared from Y_2O_3, BaO_2 and CuO. First BaO_2 and CuO are mixed and prereacted at 875 °C twice to obtain a $BaCuO_2$/CuO - flux mixture containing Ba and Cu in a molar ratio of 3 to 7. YBCO - powder is added in a molar ratio of 1/10 flux : 1/6 YBCO = 90.9 : 9.1. This composition according to [1] shows a liquidus temperature of 970 °C under air. A reduced oxygen pressure changes the situation markedly [3]. The ball milled powder is filled into an alumina or yttria stabilized zirconia crucible. To melt the powder completely it is heated to 972 °C in a resistance furnace. Temperature oscillations could be suppressed to less than 0.5 °C peak to peak. A double walled alumina tube with streaming air provides a spot slightly cooler than the surroundings. The tube is embedded in porous ceramic mass to thermally isolate the cooling air from the furnace (Fig. 1).

The growth process is initiated by touching the melt surface with the cooled tip. Au-leads submerged in the flux and attached to the tip allow to observe the persistence of contact between the tip and the melt. During the next hours the flux creeps up the tube into the ceramic mass which sucks up the flux like a sponge. Simultaneously the temperature is decreased by 0.6 °C/h and the tip is withdrawn from the melt by 0.2 mm/h. In the first experiment the contact between melt and tip was lost several times after at most 10 hours. In sum the contact had been maintained for 24 hours. By starting the withdrawal 12 hours after the

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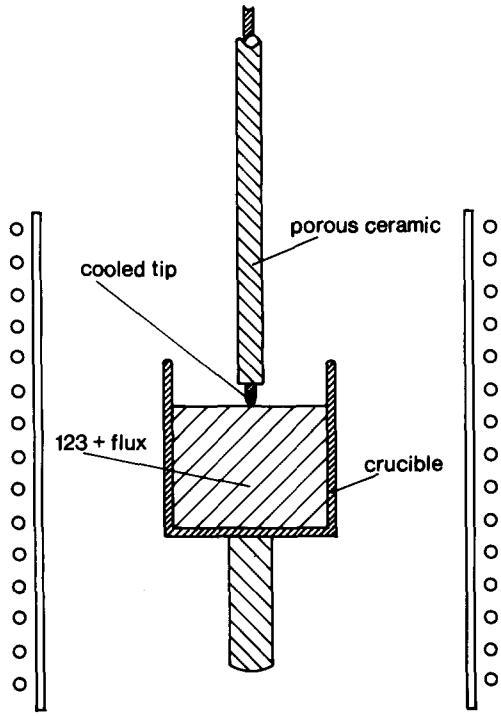

Figure 1: Experimental setup for gowth with vertical flux flow

first contact when the temperature had reached 967 °C we could avoid a premature loss of the contact to the melt.

After the growth process the tip is covered with YBCO single crystals which are up to 3 x 2 x 0.5 mm^3 in size (Fig. 2). Some of them are removed from the tip manually under the microscope and show no great pollution by residual flux.

To characterize the crystals we used the Laue technique, EDX, AC-susceptibility and optical polarized hot stage microscopy. After oxygenating at 570 °C for 65 hours they show a sharp transition at 90 K. EDX analysis shows an Al content in the crystals which is close to the detection limit and well below the value for conventionally flux grown crystals when alumina crucibles are used. During 24 hours the crystals reached a thickness of 0.5 mm. So the average growth rate was 20 µm/h, a value close to 15 µm/h which is observed in stirred melts [2]. This means that the flux flow has the same positive effect on the growth rate as stirring.

3. The Self Crucible Method

To avoid the possibility of melt pollution we designed a setup employing a crucible made of dense isostatically pressed YBCO-powder (Fig.3).

It should be possible to replace the Alumina or Zirconia crucibles in the method described in section 2. We expect a real improvement by an other procedure which is related to the Travelling Heater Method. The crucible is filled with saturated flux

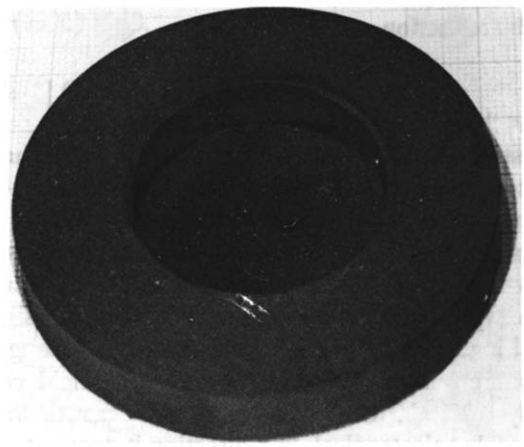

Figure 3: The Self crucible (in cooperation with HOECHST AG, Frankfurt/Main, Germany)

Figure 2: Crystals standing freely on the tip - two different runs

heated to the liquidus temperature and a seed is dipped into the flux. At equilibrium no material transport will take place between the crucible and the seed. Slowly reducing the seed temperature will cause a local supersaturation and YBCO crystallizes on the seed. A decrease of the overall YBCO-content in the flux will be compensated by dissolving material from the crucible. To avoid depleting the crucible via flux creep up the seed holder a creeping barrier needs to be employed. We experiment with ZrO_2 single crystals but MgO is already mentioned to be applicable for this purpose [4].

To obtain a stable melt position inside the crucible the wall must be cooled. In the resulting temperature field the position of the liquidus isotherm and the solvent concentration assume an equilibrium value. Together with the cooled seed the resulting lateral temperature profile across the crucible will be 'M'-shaped. In the depth there must also be a temperature maximum. Model caculations prove the achievability of these conditions with a resistance furnace (Fig. 4).

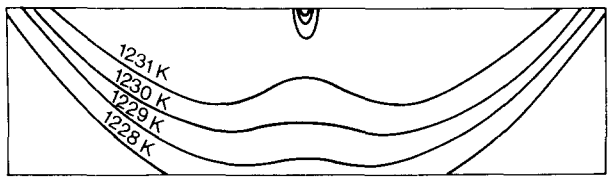

Figure 4: Calculated isotherms in the self crucible heated from above and cooled from the side and the bottom

4. Quasi crucible free grain growth

An ingot of oversaturated flux/YBCO mixture is heated to a point at which it melts partially. Upon cooling the bigger grains grow at the expense of smaller ones. The mechanism involves only short range material transport through the liquid between the grains. Especially the crystals at the top of the ingot are very clean, because the reaction products with the support have to pass a long distance across the ingot. This method is described in detail elsewhere [5].

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