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Growth and characterization of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ bulk single crystals

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Single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ ($x=0$, $x=0.10$, $x=0.15$ and $x=0.20$) were grown in oxygen atmosphere using the Travelling Solvent Floating Zone (TSFZ) method. The as grown rods were analyzed by Electron Probe Micro Analysis (EPMA), x-ray diffraction and neutron diffraction techniques. EPMA results showed the correct phase with homogeneous strontium distribution. Neutron diffraction revealed single crystalline grains with sizes up to 200 nm^3 . The onset of the superconducting transition temperatures of crystals with composition $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_{4-\delta}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ determined from ac susceptibility were 25K and 35K with 90% of the transition within 3K. A full report is given on preparation method of the starting materials and growth parameters. Additionally, single crystals of La_2NiO_4 , Nd_2CuO_4 and Sm_2CuO_4 were grown. Diamond saw and spark-erosion were used to separate the crystals from as grown boules. Experience with spark-erosion technique to shape samples for physical measurements is reported.

1. INTRODUCTION

Because of the large anisotropy and complexity of high temperature superconductors research on single crystals is of a great importance. For the same reasons the growth of large high quality single crystals is not trivial, so many different methods are being used [1]. Tanaka and Kojima proved the Travelling Solvent Floating Zone (TSFZ) method to be the most successful for growing large and contamination free crystals of the incongruently melting system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ [2,3]. The main problem of this method is to keep the travelling zone procedure running for the extremely long period [4]. We have succeeded in keeping the experiment stable for weeks and continue the growth until the feed was finished. Grown crystals are of very good quality.

2. EXPERIMENTAL PROCEDURE

Starting materials were prepared using 99.99% pure powders of La_2O_3 , SrCO_3 and CuO . Stoichiometric amounts of the powders were mixed in acetone for 30 minutes, dried at 200°C for 3 hours and then calcinated at 920°C for 48 hours in air. After this first calcination the, still soft, material was reground and calcinated a second time, now at 940°C for 48 hours in air. The powders were

reground and formed in a cylindrical shape of 6 mm diameter and 9 cm length by pressing at an isostatic pressure of 6 kbar. Finally, the obtained feed rods were vertically sintered, using Pt wire, at 1100°C for 24 hours in air. Crystal growth was performed with a NEC SC-N35HD double ellipsoidal type (Nichiden Machinery Ltd.) image furnace with two 1.5 kW halogen lamps as the heat source in a static ambient atmosphere of 200 kPa oxygen pressure. Feed and seed were counter rotated at rates of 35 rpm and 30 rpm respectively, growth speed was 0.2 mm/hour. The as grown boules were checked on composition, homogeneity and single-crystallinity by electron probe micro-analysis (EPMA), X-ray Laue back-scattering and neutron diffraction techniques. The superconducting transition temperature was determined from AC-susceptibility measurements in an AC magnetic field of 3 Gauss and a frequency of 90 Hz.

3. RESULTS AND DISCUSSION

It is found that during the growth procedure the loss of CuO from the floating zone, by evaporation and penetration of the floating material in the feed, causes the melting temperature to increase and the growth procedure to stop [4]. Using feed material with one percent excess of CuO improved the

Figure. 1. Grown boule of $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_{4.5}$, the arrows point to the places where the Sr/La ratio was measured by EPMA: 1 corresponds to the feed rod, 2, 3 and 4 correspond to the crystal: 5, 30 and 53 mm from the end of the growth.

growth conditions considerably. For the growth with $x = 0.10$ a nominal feed composition with the ratio $\text{La}_{1.90}\text{Sr}_{0.10}\text{O}_3/\text{CuO}$ of 49/51 and a nominal solvent composition with the ratio $\text{La}_{1.90}\text{Sr}_{0.10}\text{O}_3/\text{CuO}$ of 20/80 were used. Figure 1 shows a picture of the grown boule of $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_{4.5}$ with frozen solvent and feed rod. At the end of the grown boule two facets, perpendicular to the growth direction, were observed. Laue X-ray photographs of the facets displayed sharp diffraction spots and revealed a clear 4-fold rotation axis. The growth direction was found to be about 15 degrees tilted from the a-direction. EPMA analysis showed the correct phase with no contamination or inclusions of second phases. On some parts of the grown boule a thin skin of pure CuO could be found. A single crystalline boule of $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_{4.5}$ grown from a 48/52 feed did contain inclusions of CuO, indicating that the solvent became too rich in CuO. The Sr/La ratio as indicated in figure 1 is constant over a long part of the grown boule and equal to the amount in the feed, which shows that the system was in equilibrium for a large part of the growth. This is confirmed by figure 2, showing the ac-susceptibility of two feed rods with $x=0.10$ and two crystals, one with $x=0.10$ and one with $x=0.15$. The onset of the superconducting transition temperature of feed and crystal are the same, for $x=0.10$ $T_c=25\text{K}$ and for

Figure. 2. Normalized ac-susceptibility of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4.5}$: $\diamond$ crystal $x=0.15$, 200 mg; $\square$ crystal $x=0.10$, 186 mg; $\triangle$ feed $x=0.10$, 49/51; ∇ feed $x=0.10$, 48/52.

$x=0.15$ $T_c=35\text{K}$. The amount of strontium in the frozen solvent turned out to be about a factor of two higher than in the feed and crystal. Neutron diffraction revealed that the end of the boule contains several large single crystalline grains up to 200 mm^3 in size.

We have found that for the doped (conducting) material spark-erosion can be used to cut the crystals. Although the surface layer is melted by this technique the crystals remained stable and T_c showed no change.

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