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Influence of annealing in oxygen and argon on the superconducting properties of Li-doped YBCO single-grain bulks

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ABSTRACT

$YBa_2(Cu_{1-x}Li_x)_3O_{7-\delta}$ single-grain bulk superconductors with different Li concentrations were grown using the top-seeded melt growth process. Structural analysis of the samples and magnetisation measurements showed that substitution of the Cu atoms by the Li atoms took place in the $YBa_2Cu_3O_{7-\delta}$ crystal lattice. This substitution was accompanied by the formation of effective pinning centres, which improved the pinning properties of the samples and increased the critical current density. Additional annealing and reannealing in oxygen and argon showed that the superconducting transition temperature displays substantially more suppression, when the Li-doped $YBa_2Cu_3O_{7-\delta}$ samples were annealed in argon, that was associated with different distribution of the Li atoms between the CuO chains and the CuO_2 planes in comparison to annealing in oxygen. Investigation of the critical current densities showed that the pinning properties of $YBa_2(Cu_{1-x}Li_x)_3O_{7-\delta}$ single-grain bulk superconductors did not depend on the arrangement of the Li atoms in the $YBa_2Cu_3O_{7-\delta}$ crystal lattice. It was also observed that the crystal lattice parameters and the mean diameter of the non-superconducting Y_2BaCuO_5 particles systematically change with Li concentration.

1. Introduction

The properties of high-temperature superconducting materials [1], can be significantly enhanced by creating nanosized non-superconducting regions, which interact with the flux line lattices and are effective pinning centres. Chemical substitution of the atoms in $YBa_2Cu_3O_{7-\delta}$ (Y123) bulk superconductors is one of the most promising ways to create nanosized point-like pinning centres. However, the concentration of dopants must be optimal in order to prevent a considerable reduction in the superconducting properties. It should be noted that the flux lines interact not only with the pinning centres created by the substitution of the atoms in the crystal lattice of high-temperature bulk cuprates, but also with various inhomogeneities and crystal lattice distortions such as twin planes, subgrain boundaries, secondary phases, nanoparticles, oxygen vacancies and pinning centres introduced by neutron irradiation [2–6].

Shortly after the discovery of Y123 [7], it was shown that the univalent chemical element Li could substitute for the Cu atoms in the Y123 crystal lattice [8]. A high critical current density [9] and trapped magnetic field [10] were successfully obtained in Li-doped Y123 bulks. This confirmed that Li was a suitable dopant for enhancing the superconducting properties of Y123. In earlier investigations of Li-doped Y123 samples, it was considered that Li firstly substitute for the Cu atoms in the CuO chains and after reaching a certain concentration limit in the chains Li substitutes for the Cu atoms in the CuO_2 planes [11–13]. Other investigations observed substitution of the Cu atoms by Li only in the CuO_2 planes [14,15]. Using neutron powder diffraction measurements, Maury et al. [16–18] showed that during chemical substitution, the arrangement of the Li atoms in Y123 depends on the fabrication process or on post-growth thermo-chemical treatments. It was shown that in Li-doped Y123 samples synthesised in oxygen, the Li atoms substitute for the Cu atoms in the CuO_2 planes, whereas in samples prepared in air or annealed in argon, the Li atoms can substitute for the Cu atoms in both the CuO_2 planes and the CuO chains. However, only about 20%–25% of the Li substitutes for the Cu atoms in the CuO chains after the preparation of Li-doped Y123 in air or annealed in argon, the rest of the Li substitutes for the Cu atoms in the CuO_2 planes.

The superconducting properties of Li-doped Y123 single-grain bulk superconductors, such as the pinning properties and the superconducting transition temperatures, have not yet been compared between samples where Li is arranged in both the CuO chains and the CuO_2 planes, and where it is arranged solely in the CuO_2 planes. According to the neutron powder diffraction results from Maury and colleagues [16–18] the first task of the cur-

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rent work was to prepare a series of Li-doped Y123 single-grain bulks with different Li concentrations, in which the Li atoms substitute for the Cu atoms only in the CuO_2 planes, and series of Li-doped Y123 single grains with Li atoms that substitute for the Cu atoms in both the CuO_2 planes and the CuO chains. To achieve this, we used post growth high-temperature annealing of Li-doped Y123 single grains in oxygen and argon. The second task after sample preparation was to investigate how the arrangement of Li influences the superconducting transition temperatures and the pinning properties of the prepared samples. Additionally, the possible reversibility of the Li arrangement and its influence on the superconducting properties were investigated after high-temperature reannealing of the same Li-doped Y123 samples, in oxygen if the samples were initially annealed in argon, and in argon if they were initially annealed in oxygen.

2. Experimental details

Y123 single grain-bulk superconductors were fabricated using the top-seeded melt growth (TSMG) process in a chamber furnace with $SmBa_2Cu_3O_{7-\delta}$ seeds [19] in an air atmosphere. As a nominal composition for the crystal growth we used a mixture of 1 mol Y123, 0.25 mol Y_2O_3 and 1 wt.% CeO_2. A part of Y123 reacts with Y_2O_3 to form an excess of Y_2BaCuO_5 (Y211) particles and small amounts of CuO below 940 °C in a solid state prereaction [20]. After the TSMG process the Y211 particles are trapped in the Y123 matrix and they play an important role for improving of the pinning properties of Y123 and this is a reason why Y_2O_3 or directly Y211 powder is mixed with Y123 before the TSMG process [21]. However, the size of Y211 particles has to be a few micrometers in order to be effective pinning centres. CeO_2 addition is commonly used for obtaining as small as possible Y211 particles. The growth of Y211 particles is stipulated by Oswald ripening and the growth rate could be slow down in some way by presence of solved Ce in the melt [22]. In the case of the Li-doped Y123 samples, the nominal composition was enriched with different amounts of Li_2CO_3 (0.04–0.8 wt.%), corresponding to five different concentrations: x = 0.0025, 0.005, 0.01, 0.02 and 0.05 of Li in $YBa_2(Cu_{1-x}Li_x)_3O_{7-\delta}$. Precursor powders were carefully blended, milled for 15 minutes in a friction mill, sieved and pressed into cylindrical pellets of 20 mm diameter with a thickness of 12 mm. The samples were treated in a chamber furnace with the time/temperature program optimised for high Y123 crystal quality [23].

The powder mixtures after blending and milling were taken (about 100 mg) for differential thermal analysis (DTA). DTA measurements were carried out by NETZSCH STA 449 *Jupiter* F1 thermal analyser. The temperature calibrations and the baselines were done for further correct measurements. DTA measurements were performed from 35 °C to 1100 °C under air flow with a heating rate of 10 K/min using Al_2O_3 crucibles.

X-ray diffraction (XRD) analyses of Li-doped and undoped Y123 powdered samples were performed using a Rigaku Ultima IV X-ray diffractometer with CuKα radiation. These X-ray diffraction analyses were performed at room temperature and the crystal lattice parameters were determined using Rietveld refinement calculations.

For the annealing processes we used small samples, which were cut 0.5 mm below the top surface of the *a*-growth sector [24] of as-grown bulks, at a distance of 3 mm from the seed, in order to prevent possible contamination from Sm in the Y123 lattice in the vicinity of the seed [25]. Small samples had the shape of a slab with dimensions $1.55 \times 1.55 \times 0.55\ mm^3$, where the smallest dimension was parallel to the *c*-axis of the crystal.

Small samples of all Li concentrations were annealed in oxygen and argon gases using two annealing processes. During the first annealing process, one series of the samples was slowly heated to 800 °C in flowing oxygen ("oxygen annealing"), annealed for two hours and slowly cooled down to room temperature. The second series of the samples was annealed also at 800 °C for two hours, this time in flowing argon ("argon annealing") and slowly cooled down to room temperature. After both annealing processes at 800 °C, the samples were oxygenated in a tubular furnace at 410 °C for 200 h in order to obtain an orthorhombic structure of Y123.

After the oxygenation process, the field dependence of the magnetic moment was measured for all samples at 77 K using the commercial Magnetic Property Measurement System MPMS3, a product of Quantum Design with a magnetic field of up to 7 T at a constant sweep rate of 100 Oe/min. During the magnetisation measurements, the applied magnetic field was parallel to the *c*-axis of the crystal. The critical current densities, J_c, were calculated from the magnetic hysteresis loops using the Bean model [26] for rectangular samples, $J_c(B) = \{\Delta m(B)/V\}\{2/[b(1-b/3a)]\}$, where Δm is the difference in magnetic moments between the ascending and descending branches of the magnetic hysteresis loops, and V is the sample volume, $a \times b \times c$. The superconducting transition temperatures were determined from the magnetic moment transition curves taken after zero-field cooling in an applied external magnetic field of 10 Oe

The second annealing process followed the first magnetisation measurements. The samples that were annealed in oxygen in the first annealing process were annealed in argon during the second annealing process ("oxygen-argon annealing") and the samples annealed in argon at the first annealing process were annealed in oxygen during the second annealing process ("argon-oxygen annealing"). All temperature conditions during the second annealing processes were the same as in the first annealing processes and the oxygenation process was applied at 410 °C for 200 h. Following the second annealing processes and oxygenation, magnetisation measurements were performed under the same conditions as after the first annealing processes.

3. Results and Discussion

3.1. Sample characterisation

Top views of the TSMG-prepared Y123 single-grain bulk superconductors are presented in Fig. 1. Before the TSMG-process, DTA measurements were performed for all powder compositions in order to investigate the influence of Li on the thermal reactivity of $YBa_2Cu_3O_7$, Y_2O_3, and CeO_2 powder mixture. The results of DTA measurements are shown in Fig. 2. Both undoped Y123 and Li-doped Y123 powder mixtures displayed only two endothermic peaks on DTA curves in the whole measured temperature range. It is well known for the system of our nominal powder composition that the first peak at about 940 °C corresponds to the thermal reaction $aYBa_2Cu_3O_{7-\delta} + bCuO \leftrightarrow cY_2BaCuO_5 + dL(p1) + eO_2$ where CuO was formed during the solid state prereaction of Y123 with Y_2O_3. The second endothermic peak corresponds to the peritectic-like reaction where a rest of Y123 phase melted according to the reaction $YBa_2Cu_3O_{7-\delta} \rightarrow aY_2BaCuO_5 + bL(m1) + cO_2$. Composition of L(p1) and L(m1) consists of 3.7 mol.% $YO_{1.5}$, 22.3 mol.% BaO, 74 mol.% CuO and 4 mol.% $YO_{1.5}$, 36.5 mol.% BaO, 59.5 mol.% CuO, respectively [20]. It was observed from the DTA results that the highest concentration of Li ($x = 0.05$) reduces the second endothermic peak temperature by about 9 °C, from 1025 °C (undoped Y123) to 1016 °C, whereas the other Li concentrations had almost negligible influence on the peritectic melting temperature in comparison to the undoped Y123 sample. From the obtained DTA results it was evident that the temperature segments (where the crystals growth)