Microstructural Development and Superconducting Properties of
 BaO_2 -added $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ *

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Microstructural Development and Superconducting Properties of BaO₂-added Bi₂Sr₂CaCu₂O_{8+x}

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Abstract—Investigations on the effects of Ba additions in Bi-2212 superconductors are focussed on compositional, microstructural, and magnetization studies. In previous studies, we showed that BaO₂ reacts with Bi-2212 to form second phases. Zero-field and in-field transport properties in Ag-clad BaO₂ added Bi-2212 tapes had been improved at 4.2 K [1]–[3].

SEM micrographs, pole figures, and transport critical currents versus magnetic field orientation suggest that BaO₂ has a strong influence on the microstructural properties. Magnetization studies revealed that BaO₂ does not affect the pinning properties of optimally added Bi-2212. To estimate the potential of BaO₂ additions in creating possible pinning sites, TEM investigations were carried out focussing on sub-micrometer inclusions and growth defects in the superconducting phase.

Index Terms—Bi-2212, powder in tube (PIT) process, BaO₂ addition, texture, transport critical current, artificial pinning center (APC).

I. INTRODUCTION

Several studies have been conducted on dopants and additions in high temperature superconductors in the recent past to improve the microstructure and superconducting properties. This investigation focuses on the influence of BaO₂ additions on Bi₂Sr₂CaCu₂O_x (Bi-2212). Besides its well-understood and straightforward thermo-mechanical processing parameters, Bi-2212 has some important advantages relative to other high temperature superconductors. Bi-2212 is stable in a wide range of stoichiometries and is more stable than the other conductors in the HTS-family. Bi-2212 achieves reasonable texture in a partial melt process, is compatible with metallic interfaces, and shows high transport properties in wires and tapes. One drawback, however, is the lower irreversibility line compared to the other high temperature superconductors due to weak flux pinning, which can be overcome by further texturing and

the introduction of pinning centers via dopants or additions. In an earlier study, the effects of MgO additions, applied as nanosized MgO powder, were investigated. It was shown that the pinning properties were improved. Transport properties of MgO doped Bi-2212, however, suffered [4], [5]. This investigation focuses on the effects Ba exerts on the properties of Bi-2212. BaO₂ reacts with Bi-2212 creating non-superconducting second phases which can influence microstructural, pinning, and transport properties.

II. EXPERIMENTAL PROCEDURE

Bi-2212 monofilament tapes produced in the powder-in-tube process were used in this investigation. Bi-2212 powder, which was produced in a coprecipitation process, was obtained from Superconductive Components Inc. (SCI). The powder had a nominal stoichiometry of Bi_{2.1}Sr_{1.7}CaCu₂O_x, which is slightly off the ideal chemical composition, but has been proven to optimally suit processing purposes, [6], [7]. The Bi-2212 powder was added with BaO₂ powder, which was obtained from Alfa-Aesar and had a purity of 99 +%. A set of molar ratios of Bi-2212/BaO₂ were produced for the samples: 10/1, 8/1, 6/1, which correspond to weight ratios of 1.9, 2.38, and 3.17 wt% BaO₂. To remove residual carbon the powders were heat-treated under flowing oxygen at 820 °C for 10 h. To minimize contamination with CO₂ during processing, most of the tape manufacturing steps were carried out under oxygen atmosphere in a glove box. Fully processed monofilament tapes had typical widths of 3.2 mm and thickness of 0.2 mm. The core widths were about 60 μm and the density was about 75 % of the theoretical density of Bi-2212. The heat treatment schedule, described in detail elsewhere, was modified for each composition to optimize the Bi-2212 phase formation and superconducting properties, [8], [9]. Polished cross sections of heat-treated tapes were slightly etched in 1 part of 60 % perchloric acid plus 99 parts of 2-butoxy-ethanol to reveal the microstructure. These samples were then observed under the ESEM. Tiny pieces of tape were milled down to about 100 nm thickness to expose their transverse cross sections for TEM analysis. For pole figure analysis, a x-ray texture goniometer operating in Schultz reflection mode was used. The Ag sheaths of the samples were removed by etching and strips of the remaining core material were mounted with their flat side on a glass plate to cover an area of about 4 cm².

Magnetization measurements were carried out on ~ 4 mm long sections of heat-treated tape using a Quantum Design

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SQUID magnetometer operating in a range up to 5 T. Typical sample weights used for magnetization measurements were around 30 mg. Irreversibility lines were determined from field cooled (fc) and zero field cooled (zfc) magnetization measurements.

Activation energies were determined from magnetic relaxation measurements. After the samples were zero-field cooled to temperatures between 10 - 40 K, magnetic field was applied. The magnitude of the applied field was estimated from hysteresis loop measurements and set to a value between the first field of full penetration and the irreversibility field. The field was held for several seconds before it was switched off and the measurements were started.

Transport measurements were carried out at 4.2 K using the conventional four-point method. To measure the orientation dependence of critical current in field, a rotating sample holder was used.

III. RESULTS AND DISCUSSION

A. Microstructural Properties:

Cross sections of tape with BaO₂ additions of 0.0 wt.%, 2.38 wt.%, and 3.17 wt.% were investigated under the ESEM, fig. 1. Among these samples, the 2.38 wt.% added tape showed improved microstructure. Bi-2212 grains grew visibly larger and were well-aligned. At 3.17 wt.%, however, high angle grain boundaries occurred more often and in spots all over the tape Bi-2212 spikes grew into the Ag-sheath. Additionally, an increased amount of Cu-rich phase was visible. The spike-like growth suggests that additional mechanisms, like local changes of the BaO₂ concentration [1]-[3], supersede the growth direction enforced by the constrained volume of the growth-channel within the tape. Differences in the microstructure of the *a*,*b*-planes of the samples were not found in any sample and all samples showed a similarly high amount of high-angle grain boundaries in the *a*,*b*-planes.

Pole figure analysis, which was mainly done to analyze a larger area of sample material, supported the observations made on small sections under the ESEM, fig. 2. All samples revealed uniform and pronounced *c*-axis texture. The 2.38 wt.% BaO₂ added sample, however, showed the highest degree of *c*-axis texture within the set, indicating the existence of an optimum of the addition, above which the microstructural properties deteriorate.

In our earlier study it was found that the additional phase that forms in the reaction of Bi-2212 with the addition is a solution consisting of (Ba,Sr,Ca)BiO. The Ba containing phases, however, could not be detected clearly under the ESEM because of the limited resolution of the instrument and small amount of the addition. To study where Ba-containing precipitates form and how big they grow in Ag-clad tape-conductor, TEM analyses were carried out. Samples made from pieces of tape containing 2.38 wt.% and 3.17 wt.% BaO₂ were prepared and investigated, fig. 3. In the 2.38 wt.% BaO₂ added sample two Ba containing phases were detected by EDX, the (Ba,Ca,Sr)BiO₃ solid solution and a Ba and Sr containing phase which was most probably a solid solution

consisting of (Ba,Sr)O. These inclusions, however, were less often visible and always located close to the (Ba,Ca,Sr)BiO₃. In all samples, the (Ba,Ca,Sr)BiO₃ phases were found on twist boundaries of the Bi-2212 with typical sizes $\leq 5 \mu\text{m}$.

Figure 1. ESEM micrographs of polished and surface-etched cross sections of tapes with 0.0 wt.% (a), 2.38 wt.% (b), and 3.17 wt.% (c) BaO₂ additions. The white bars correspond to 10 μm in (a) and (b), and 20 μm in (c). The 2.38 wt.% added sample shows a tendency of longer and better-aligned grain growth compared to the undoped specimen. At 3.17 wt.% more high angle grain boundaries and Cu-rich phases were clearly visible.

B. Magnetic Properties:

In our earlier studies it was shown that the magnetization varied with the amount of the addition. Hystereses of bulk and tape samples with 2.38 wt.% BaO₂ were the widest. A similar trend was also seen in the irreversibility line measurements on tape sections, fig. 4. Towards high temperatures, however, the curves coincided indicating that the pinning centers in Bi-2212 created by Ba-doping are only

effective at low temperatures below 20 K. To quantify the strength of pinning in the samples, activation energies were

Figure 2. Pole figures of (a) 0.0 wt.%, (b) 2.38 wt.%, and (c) 3.17 wt.% BaO₂ added tape samples. The plots show uniform and pronounced c-axis texture in all samples. The 2.38 wt.% added sample, however, shows the highest degree of c-axis texture within the set.

Figure 3. TEM images of two regions (a), (b) inside a 2.38 wt.% BaO₂ added tape sample. The regions marked with the labels were related to following phases: 1: Bi-2212, 2: (Ba,Ca,Sr)BiO₃, 3: (Ba,Sr)O.

Figure 4. Irreversibility lines of tape samples with BaO₂ additions between 0.0 – 3.17 wt.%. The orientation of the tape samples was $B \parallel c$. A spread in both curves at low temperatures is visible. At temperatures above 40 K, all curves are more or less identical.

calculated from magnetic relaxation data applying

$$S = \frac{1}{M_0} \frac{dM}{d(\ln t)} = \frac{d(\ln M)}{d(\ln t)} = -\frac{k_B T}{U_{eff}},$$

where S is the normalized relaxation rate of the magnetic decay and U_{eff} is the effective pinning energy. The results of the relaxation measurements did not show the clear difference between the undoped and 2.38 wt.% added sample visible in the irreversibility measurements. The 3.17 wt.% added sample, however, appears to show slightly lower activation energies in a temperature range between 10 – 40 K, fig. 5.

C. Transport Properties:

Transport critical currents versus field angle were measured in fields up to 4 T. To avoid hysteresis effects due to flux trapping, the measurements were taken at increasing angle for each direction, starting with $B \parallel a, b$. The recorded values were normalized with respect to the maximum J_{c0} and plotted versus θ , fig. 6. Clearly visible in all diagrams is the flat maximum around low angles caused by the average misorientation of crystallites in the tape leading to averaged critical current values at small angles. Significant differences in the transport critical current ratios at high angles are visible above 1.0 T, indicating a higher degree of anisotropy in the 2.38 wt.% BaO₂ added tape. The 3.17 wt.% added sample showed the highest transport critical currents at high angles, indicating inferior crystallinity.

The highest zero field critical current density achieved at 4.2 K after heat treatment optimization was $J_c = 1.1 \cdot 10^5$ A/cm² for undoped tapes, $J_c = 1.2 \cdot 10^5$ A/cm² for 3.17 wt.% BaO₂ added composition and $J_c = 2.1 \cdot 10^5$ A/cm² for 2.38 wt.% BaO₂ added tapes, fig. 7. A conspicuous feature in the heat treatment optimization curves is the change in the width of the temperature plateaus for which high critical current densities are achieved. For BaO₂-added tapes the width of these plateaus was between 3 – 4 °C, whereas undoped samples showed a broad plateau of about 10 °C width before J_c dropped significantly. This feature suggests that BaO₂-added Bi-2212 decomposes in a different way compared to pure Bi-2212 during partial melt. It appears that at high processing temperatures, BaO₂-additions alter the

Figure 5. Activation energies, calculated from magnetization decay data, for undoped and 2.38 wt.%, and 3.17 wt.% BaO₂ added tape. The curves are almost identical, indicating no change of the pinning behavior in BaO₂ added Bi-2212.

composition of the partial melt, so that it can not completely react back into Bi-2212 on cooling.

Figure 6. Ratios of the transport critical currents I_c/I_{90} of an undoped, 2.38 wt.%, and 3.17 wt.% BaO_2 added tape sample versus orientation angle of the applied magnetic field. Significant differences of the transport current ratios are clearly visible for fields ≥ 1.0 T at 90° indicating a higher degree of anisotropy in the 2.38 wt.% BaO_2 added tape.

Figure 7. Critical current density vs. peak temperature for (a) 0.0 wt.%, (b) 2.38 wt.%, (c) 3.17 wt.% BaO_2 -added Bi-2212 tape conductor.

IV. CONCLUSIONS

BaO_2 additions significantly influence melting characteristics, phase formation and microstructure in Bi-2212. BaO_2 additions result in finely distributed precipitates. The sizes of precipitates measured under the TEM, however, were too large to directly promote pinning in BaO_2 added Bi-2212. Irreversibility line and activation energy measurements on the other hand indicated no adverse effect on pinning properties within low amounts of BaO_2 . An improvement in texture was seen in micrographs and pole figure measurements. These observations were clearly reflected in improved J_c and increased dependence of J_c towards field angle found in BaO_2 added Bi-2212 tapes.

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