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BaO$_2$-added Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$

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

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Abstract—Investigations on the effects of Ba additions in Bi-2212 superconductors are focused on compositional, microstructural, and magnetization studies. In previous studies, we showed that BaO$_2$ reacts with Bi-2212 to form second phases. Zero-field and in-field transport properties in Ag-clad BaO$_2$ 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 BaO$_2$ has a strong influence on the microstructural properties. Magnetization studies revealed that BaO$_2$ does not affect the pinning properties of optimally added Bi-2212. To estimate the potential of BaO$_2$ additions in creating possible pinning sites, TEM investigations were carried out focusing on sub-micrometer inclusions and growth defects in the superconducting phase.

Index Terms—Bi-2212, powder in tube (PIT) process, BaO$_2$ 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 BaO$_2$ additions on Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (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. BaO$_2$ 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$_2$Sr$_2$CaCu$_2$O$_{8+x}$, 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 BaO$_2$ powder, which was obtained from Alfa-Aesar and had a purity of 99.9%. A set of molar ratios of Bi-2212/BaO$_2$ 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% BaO$_2$. To remove residual carbon the powders were heat-treated under flowing oxygen at 820°C for 10 h. To minimize contamination with CO$_2$ 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 cm$^2$.

Magnetization measurements were carried out on -4 mm long sections of heat-treated tape using a Quantum Design
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 BaO$_2$ 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 BaO$_2$ 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.% BaO$_2$ 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)Bi$_2$O$_6$. 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.% BaO$_2$ were prepared and investigated, fig. 3. In the 2.38 wt.% BaO$_2$ added sample two Ba containing phases were detected by EDX, the (Ba,Ca,Sr)BiO$_3$ 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)BiO$_3$. In all samples, the (Ba,Ca,Sr)BiO$_3$ phases were found on twist boundaries of the Bi-2212 with typical sizes ≤ 5 μm.

#### 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.% BaO$_2$ 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 calculated from magnetic relaxation data applying
\[ S = \frac{1}{M_0} \frac{dM}{d(\ln T)} = \frac{d(\ln M)}{d(\ln T)} = \frac{k_B T}{U_{\text{eff}}}, \]
where \( S \) is the normalized relaxation rate of the magnetic decay and \( U_{\text{eff}} \) 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 \( B \parallel ab \). The recorded values were normalized with respect to the maximum \( I_{\text{c}} \) and plotted versus \( \theta \), 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 \( J_c = 1.1 \times 10^5 \text{ A/cm}^2 \) for undoped tapes, \( J_c = 1.2 \times 10^5 \text{ A/cm}^2 \) for 3.17 wt.% BaO₂ added composition and \( J_c = 2.1 \times 10^5 \text{ A/cm}^2 \) 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
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 \( I/\Delta I \) 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 \( \geq 1.0 \) 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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