



Stability of barium oxides in REBa₂Cu₃O_y superconductors

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ABSTRACT

We have investigated the stability of BaSnO₃, BaZrO₃, BaTiO₃ and BaNb₂O₆ in the ErBa₂Cu₃O_y (Er123) matrix by mixing and sintering powders of Er123 and barium oxides. The degradation of T_c due to the addition of barium oxide was the lowest in the case of BaSnO₃ (BSO). BSO-added samples exhibited a T_c above 90 K even for 15 vol% addition and an improved J_c under a magnetic field. XRD and SEM results indicated that BSO was very stable in the Er123 matrix. The dependence of T_c on BSO addition showed similar trends for the sintered samples and Er123 thin films. It was found that the most stable barium oxide in Er123 superconductors was BaSnO₃.

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1. Introduction

Enhancement in the critical current density (J_c) is essential for the application of REBa₂Cu₃O_y (RE123) superconductors to high-current-carrying wires and high magnetic field engineering. Introduction of artificial pinning centers (APCs) into RE123 superconducting phases is well known to be very effective for improving J_c . Significant improvements in J_c have been achieved for melt-textured RE123 by adding fine RE₂BaCuO₅ (RE211) particles as APC material [1]. In addition to RE211 materials, several Ba-related APC materials, such as BaZrO₃ [2], BaCeO₃ [3] and BaSnO₃ [4], have been studied. It has recently been reported that the introduction of nanometer-sized BaZrO₃ [5–6], BaSnO₃ [7] and BaNb₂O₆ [8] into RE123 thin films results in the enhancement of J_c in high magnetic fields. This suggests that it is very important for high- J_c thin films to exploit the new APC material. However, it involved a lot of time and difficult problems to search new APC materials in thin films.

In the present study, we investigated the stability of various barium oxides reported as effective pinning centers for REBCO thin films, viz., BaSnO₃ (BSO), BaZrO₃ (BZO), BaTiO₃ (BTO) and BaNb₂O₆ (BNO), in RE123 superconducting phases and their effects on the superconducting properties using sintered samples easy to prepare. Furthermore, we compared the results on the sintered samples with the dependence of the superconducting properties on the barium oxides content in the RE123 thin films prepared by pulsed laser deposition (PLD) using REBCO targets containing the barium oxides.

2. Experimental

Er123 samples were prepared from Er₂O₃ (99.9%), BaCO₃ (99.95%), and CuO (99.99%) using a standard solid-phase reaction technique. Appropriate amounts of the reagents were thoroughly ground and calcined at 1173 K for two periods of 12 h in air, with intermediate regrinding. The resultant Er123 powder was pressed into pellets and sintered at 1233 K in air for two periods of 12 h, with intermediate regrinding. High-purity (99.9%) BSO, BZO, BTO and BNO powders were then added to the pulverized Er123 pellets

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in concentrations of 0.5–25 vol%. The barium oxide-added Er123 powders were thoroughly ground, pressed into pellets and then sintered at 1233 K in air for 12 h. All samples were subsequently annealed in flowing oxygen at 1183 K for 12 h, cooled to 773 K with a 12 h stay, and then cooled to room temperature in a furnace.

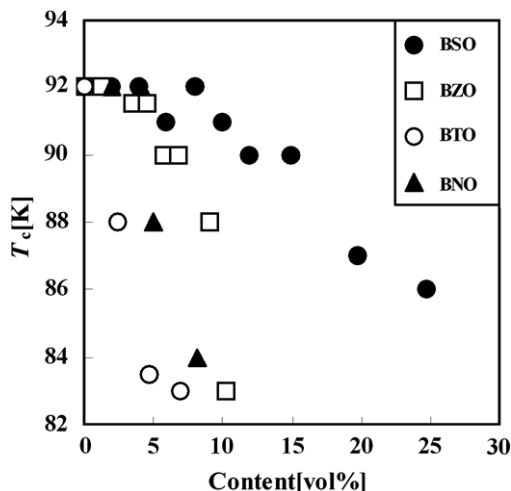


Fig. 1. Addition dependence of T_c for various barium oxides (BSO, BZO, BTO and BNO)-added ErBCO sintered samples.

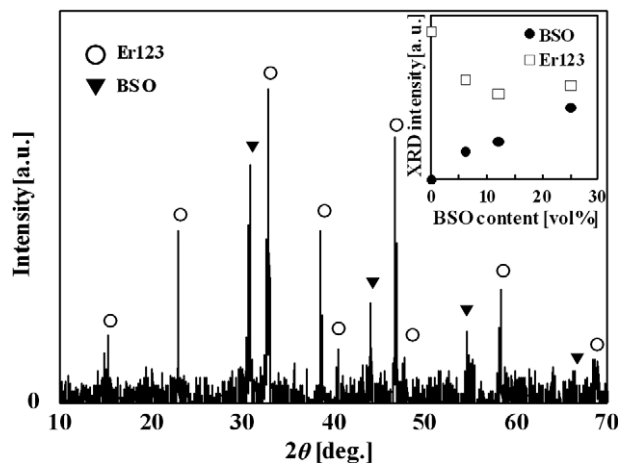


Fig. 2. XRD θ - 2θ spectrum for a 25 vol% BSO-added Er123 sintered sample. The inset shows the peak intensity of BSO (110) and Er123 (103).

The electrical resistivity of the samples was measured by the standard four-probe technique to determine the critical temperature (T_c) values. The J_c of the samples at 77 K was calculated from B - M curves measured by a superconducting quantum interference device at magnetic fields of 0–1.0 T. X-ray diffractometry (XRD) was employed to identify the phases in the samples. The surface of the samples was characterized using a scanning electron microscope (SEM). The chemical composition of the samples was determined by energy-dispersive X-ray spectroscopy (EDX).

3. Results and discussion

Fig. 1 plots the T_c of the various barium oxide (BSO, BZO, BTO and BNO)-added ErBCO sintered samples as a function of the amount of addition. The degradation of T_c in the sintered samples was the lowest for BSO addition. The BSO-added samples showed a T_c of above 90 K even for 15 vol% addition. BSO has been reported to be a stable APC material in the melt-textured RE123 bulk [4]. BZO, which is well known as an APC material suitable for coated conductors [5–6], was relatively stable among the barium oxides studied. BSO, BZO and BTO have a perovskite structure, while BNO has a bronze structure. Our previous [8–9] and present results on APC materials suggest that barium oxides with a perovskite structure tend to be most stable in the superconducting phase. Among the barium oxides with a perovskite structure, BSO is the most stable in the superconducting phase, presumably owing to its high thermal stability and low reactivity with the superconducting phase.

Fig. 2 shows an XRD pattern for 25 vol% BSO-added Er123 samples. No diffraction peaks except BSO and Er123 was observed for the BSO-added samples. As can be seen in the inset, the main peak intensity of the BSO (110) diffraction increased with increasing BSO content, while the intensity of the Er123 (103) diffraction remained constant. These results indicate BSO was stable in the Er123 matrix up to a sintering temperature of 1233 K. The main peak intensity of BTO and BNO decreased upon addition to Er123 due to the reaction with the Er123 phase. The decrease in T_c for BNO addition was much lower than that for BTO addition (see Fig. 1). This is possibly because BNO transforms into $\text{BaEr}_{0.5}\text{Nb}_{0.5}\text{O}_3$ with a perovskite structure upon reacting with Er123, as reported for BNO-doped Er123 thin films [10].

Fig. 3 shows the SEM image and result of Sn concentration mapping by EDX analysis for Er123 samples with 8.0 vol% BSO addition. Fine BSO particles with a size of 0.5–1.0 μm and their agglomerates with a size of around 5 μm were observed on the Er123 grain. In addition, many BSO particles embedded in the Er123 grain were observed near the grain surface. These observations agree with the XRD results. In order to study the stability of barium oxides in the RE123 phase, we investigated the reactivity of the barium

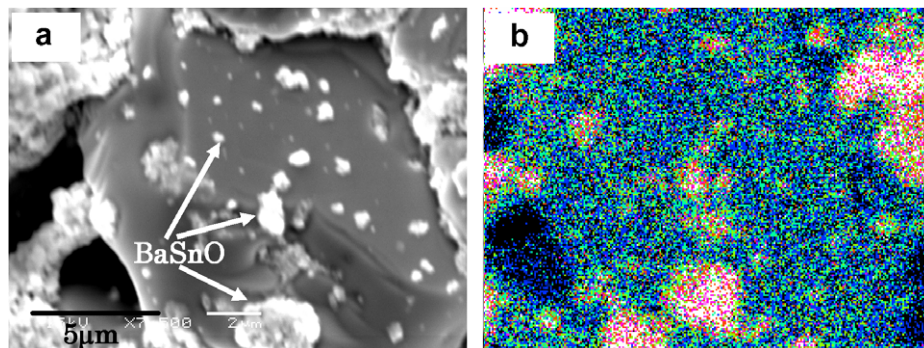


Fig. 3. SEM image (a) and Sn concentration mapping by EDX (b) of an 8.0 vol% BSO-added Er123 sample.

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