Influence of the Gd$_2$BaCuO$_5$ fine particles on thermoelectric power of melt-textured (Nd–Sm–Gd)Ba$_2$Cu$_3$O$_{7-\delta}$

G.S. Okram $^{a, *}$, M. Muralidhar $^b$, M. Jirsa $^b$, M. Murakami $^b$

$^a$ Inter University Consortium for DAE Facilities, University Campus, Khandwa Road, Indore 452017, MP, India
$^b$ Superconductivity Research Laboratory, ISTEC, 3-35-2, Iioka-Shinden Morioka, Iwate 020-0852, Japan

Received 28 July 2003; received in revised form 28 July 2003; accepted 4 September 2003

Abstract

Influence of Gd$_2$BaCuO$_5$ secondary phase on the $c$-axis and $ab$-plane thermoelectric power of the melt-grown ternary (Nd–Sm–Gd)Ba$_2$Cu$_3$O$_{7-\delta}$ superconductor has been studied. There is an indication of (1) a possible change of conduction mechanism from hole to electron type, (2) enhanced metallic behavior, and (3) reduced anisotropy. The latter two features would strongly enhance the high application potential of these materials.

© 2003 Elsevier B.V. All rights reserved.

PACS: 74.81.Bd; 74.25.Fy

1. Introduction

The oxygen-controlled melt-grown (OCMG) co-doped ternary rare-earth superconductors of the type (Nd–Sm–Gd)Ba$_2$Cu$_3$O$_{7-\delta}$ (NSG-123) are candidates for high-field applications [1]. They can be controllably grown as large-domain samples having nearly single-crystalline characteristics. In RE-123 (RE = rare earth) materials most important feature with respect to applications is the so-called secondary peak on magnetization loop or on the associated field dependence of the induced super-current density, $J_c$, an enhancement of $J_c$ at intermediate and high fields [2]. In melt-textured YBa$_2$Cu$_3$O$_{7-\delta}$ (Y123), the oxygen deficient clusters are responsible for the secondary peak effect. When Y is replaced by Nd, Sm, Gd, Eu, and some other light rare-earth (LRE) atoms in Y123, LRE atoms form a solid solution with Ba resulting in a compositional fluctuation of superconducting matrix. This fluctuation leads to enhanced pinning at intermediate and high magnetic fields independent of the oxygenation state [2]. Thus, the samples can be optimally oxygenated without any loss of pinning ability. $T_c$ reduction due to the excessive substitution of trivalent LRE for bivalent Ba during the melt process is circumvented by growth in a reduced oxygen atmosphere [3]. The compositional fluctuation probably leads to the spatial variation of $T_c$ that causes the $\delta T_c$ pinning [4,5].

In OCMG materials, there is always some amount of a normal secondary phase present in the form of micrometer size particles. Addition of

*Corresponding author. Tel.: +91-731-2463913; fax: +91-731-2462294.
E-mail address: okram@iucindore.ernet.in (G.S. Okram).
appropriate amount of fine secondary phase particles (SPP) in these materials can enhance pinning in low fields. It seems that the SPP can support point-like defect formation in their vicinity and participate thus on pinning enhancement at intermediate fields. Besides excellent magnetic properties of these compounds at high temperatures, these materials also possess a uniform microstructure and an excellent reproducibility. These features make these materials high potential for engineering applications.

The thermoelectric power (TEP) studies provide information on the electronic transport properties and thermoelectric phenomena. The studied materials in their pristine form are of two-dimensional nature due to the presence of CuO planes. The CuO planes cause the electronic properties of these materials anisotropic. In this paper we investigate how the two-dimensional character is affected by secondary phase particles mentioned above. For the study we chose well-oxygenated ternary (Nd–Sm–Gd)Ba2Cu3O7/Co superconductors with 10, 20, 30, 40 and 50 mol% Gd-211 grown by OCMG process. The results on the c-axis (Sc) and ab-plane (Sab) TEP studies are reported.

2. Experimental

The ternary (Nd1/3Sm1/3Gd1/3)Ba2Cu3O7−δ superconductor was prepared from high purity Nd2O3, Sm2O3, Gd2O3, BaCO3, and CuO. The starting powders were thoroughly ground, calcined at 880 °C for about 24 h with intermediate grinding, and finally pressed into pellets. The material sintering was carried out at 910 °C for 15 h under low oxygen partial pressure. This whole process was three times repeated. Finally, the sintered pellets, ground to a fine powder, were mixed with 10–50 mol% volume fraction of a high purity commercial Gd2BaCuO5 powder (<1 μm). 0.5 mol% of Pt and 1 mol% CeO2 were also added to all the samples to reduce the size of Gd-211 particles. Pellets of 20–30 mm diameter and about 15 mm thickness were compressed under a cold-isostatic pressure of 2000 kg/cm2. The NSG-123 samples were grown in a tubular furnace using OCMG process combined with a top-seeded melt-growth technique. An Nd-123 seed crystal was placed onto the top of the pellet at 20 K above the peritectic temperature and held there for 1 h. The flat surface of the pellet was found to be the ab-plane strongly disordered by extensive twining, and c-axis perpendicular to the surface [1]. Such processed pellet, cut into desired shapes, was finally annealed in flowing oxygen [1].

The thermoelectric power along c-axis, Sc (both temperature gradient ΔT and electric field ΔV parallel to c-axis) was measured using the differential dc method in the temperature range 85–300 K. The Seebeck coefficient of the copper reference material was subtracted from the measured TEP before the thermoelectric power of the sample was calculated. This procedure ensured that the TEP of the superconducting sample went to zero below its Tc. The TEP data (S = ΔV/ΔT) of the sample were recorded by a personal computer for the desired temperature step and range. Both the ΔT and T were controlled using two Lakeshore temperature controllers. The temperature stabilization time was about 7 m and the TEP data resolution was estimated to be ~50 nV/K. Similarly, the ab-plane TEP (Sab) was recorded. Details of the measurements were reported elsewhere [6].

3. Results and discussion

Composition, microstructure, and electromagnetic properties of the samples characterized by various experimental techniques were reported earlier [1]. Transmission electron microscopy showed the samples (i) heavily twinned, (ii) fine Gd2BaCuO5 particles (<1 μm) with sharp interfaces between Gd-211 and NSG-123 and (iii) no other secondary phase [1].

The c-axis (Sc) and ab-plane (Sab) thermoelectric power versus temperature curves of the melt-textured NSG-123 sample with a varying content of Gd-211 are shown in Figs. 1 and 2. The data show that all the NSG-123 samples have Tc in the range 93–95 K and a sharp superconducting transition, <1 K. This means that the Gd-211 particles do not affect Tc. This is (i) consistent with the results found by resistivity and susceptibility measurements, (ii) indicative of single-phase nature of the NSG-123
compound. These results were to some extent similar to those obtained on Y-123 single crystal [7].

The c-axis TEP data showed positive values except for the samples with 30 and 50 mol% Gd-211 that went to negative values at around 280 K (Fig. 1 inset). The positive TEP data imply holes as principal charge carriers. From Fig. 1 it follows that introduction of the Gd-211 had a striking effect on magnitude of c-axis TEP. In the sample with 10 mol% Gd-211 the TEP slope and magnitude were drastically reduced with respect to the sample without Gd-211 and behavior of NSG-123 became more metallic. This means that the SPP enhanced the overall conductivity of NSG-123. This is consistent with the enhanced $J_c$ [1] and the same conductivity of the NSG-123 matrix and the dispersed SPP [8]. Both the probable Gd magnetic transition at about 290 K and the pseudogap formation at about 115 K were smeared out [6].

In the sample with 20 mol% Gd-211, the TEP was nearly temperature independent over most of the temperature range, only above 260 K its small magnitude further decreased up to 300 K; the pseudogap-like feature was indistinguishable. In the sample with 30 mol% Gd-211 the TEP continuously decreased with increasing temperature up to the minimum value at 300 K. Also in sample with 40 and 50 mol% Gd-211, TEP exhibited similarly small magnitudes and small slopes with a slightly wavy character. However, the TEP for 30 and 50 mol% Gd-211 concentrations was negative above 280 K. We can thus conclude that addition of the SPP to NSG-123 gradually reduced hole concentration (positive TEP) and in some cases, especially at high temperatures and rather high SPP concentrations it led to partial electron conduction (negative TEP). These results are consistent with the significantly higher $J_c$ compared to the pure NSG-123 superconductor [1].

As can be seen in Fig. 2, $S_{ab}$ of the pure NSG-123 was much lower than $S_c$ but comparable to $S_c$ of the samples with different nonzero Gd-211 concentrations. The most characteristic features of all the $S_{ab}(T)$ curves were their negative slopes over nearly all the temperature range and a general tendency towards negative values. The $S_{ab}(T)$ curves did not show any clear dependence on SPP concentration, their shapes and positions seemed to be random. In the sample with 10 mol% Gd-211, $S_{ab}$ was negative for all the range of measurement. Therefore, the probable Gd ion magnetic transition at 290 K and pseudogap formation at about 115 K appear to be intake, albeit with possible electron conduction. Specimens with 20 and 30 mol% Gd-211 exhibited $S_{ab}(T)$ positive values in major part of the temperature range; only at temperatures above 170 and 225 K, respectively, the curves crossed the $x$-axis and turned to negative values. In the samples with 40 and 50 mol% Gd-211, the $ab$-plane TEP were again negative for
all temperatures, similarly as for 10 mol% Gd-211. The $S_{ab}(T)$ curve 40 mol% Gd-211 was approximately constant in the region 100–180 K and decreased above 180 K. For 50 mol% Gd-21, the curve decreased slowly in the range 100–215 K but decreased faster above 215 K.

The $S_{ab}(T)$ curves for 10, 40, and 50 mol% of Gd-211 concentration were negative while those with 20 and 30 mol% showed a positive-to-negative transition at higher temperatures (nearly 170 K for 20% and 225 K for 30%). The $S_c(T)$ curves were positive except for 30 and 50 mol% of Gd-211, which exhibited a positive-to-negative transition above 280 K. In all cases, except $S_c(T)$ of the pure sample, the magnitude was small indicating strong metallic behavior. In general we can state that the conduction by electrons sets in as the secondary phase concentration increases. The change from hole conduction in pure NSG-123 to electron conduction as the concentration of the secondary phase increases is not systematic as the change is not gradual with secondary phase concentration. This suggests a varying competition between hole and electron conduction. Depending on the temperature and secondary phase concentration, the change in the overall conduction mechanism is reflected but the conduction by electrons prevails. The anisotropy in this behavior exists (the change from hole to electron conduction along c-axis is marginal compared to that of ab-plane) but it decreases with increasing concentration of the secondary phase. This can be attractive for applications [1] because in single crystals this anisotropy is significantly larger.

4. Summary

The c-axis and ab-plane thermoelectric power of NSG-123 sample with various concentrations of Gd-211 indicate a change of conduction mechanism from hole to electron type. This change seems to be promoted by increasing SPP concentration and high temperature. Anisotropic behavior in clean NSG-123 sample was significantly reduced by addition of Gd-211. However, the change of conduction mechanism did not systematically follow concentration of the secondary phase, probably due to competition between both types of conductivity combined with nonhomogeneous distribution of SPP. The thermoelectric powers and reduction of anisotropy show a high application potential of the melt-textured superconductors.

Acknowledgements

One of us (GSO) acknowledges with thanks the support and encouragement of Dr. B.A. Dasannacharya, Prof. A. Gupta and Dr. V. Ganesan for this work.

References