Optimization of ternary LRE–Ba–Cu–O materials for use at liquid oxygen temperature

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Abstract

The paper refers on advances in fabrication of mixed LREBa₂Cu₃O_y (LRE: Nd, Sm, Eu, Gd; combinations NEG-123, NSG-123, and SEG-123) composites developed for bulk applications at liquid oxygen temperature. In order to enhance flux pinning over 90 K, we introduced to the 123 systems a ball-milled Gd₂BaCuO₅ powder in various average sizes ranging from 200 to <70 nm. In all these compounds Zr-rich nanoscale particles were formed that improved magnetic performance up to 90 K. As a result, levitation experiments with these ternary systems cooled by liquid oxygen were performed.

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1. Introduction

Significant progress in technology of LREBa₂Cu₃O_y (LRE-123, LRE = Nd, Sm, Eu, Gd) materials represented introduction of the oxygen controlled melt growth (OCMG) process [1–4]. The OCMG process substantially reduced amount of LRE/Ba solid solution content in LRE₁₋ₓBa₂₋ₓCu₃O_y compounds to a reasonable level and enabled variation of the LRE/Ba ratio in a controlled manner. As a result, a controlled pinning performance at 77 K and high magnetic fields was achieved [5]. Recently, (NEG)Ba₂Cu₃O_y “NEG-123” system with significantly reduced size of Gd₂BaCuO₅ (Gd-211) particles exhibited an enhanced flux pinning at temperature as high as 90.2 K [6]. The critical current density was improved by one order of magnitude as compared to the other LRE-123 materials. This achievement is due to changes in microstructure. The TEM by EDX analysis revealed small secondary phase particles and additional nanometer-size Zr-rich NEG–Ba–Cu–O formation in the NEG-123 matrix [6]. The new pinning medium enabled realization of
the old dream to shift the operating temperature of bulk high-$T_c$ superconductors above liquid nitrogen temperature. Field trapping capability of the new composite at 90.2 was good enough to enable levitation experiments with liquid oxygen cooling [7]. All these results motivated us to test other ternary systems with respect to the Zr-rich LRE–Ba–Cu–O and investigate their ability for levitation at liquid oxygen. In this study, we show that the strong size effect is possible with various ternary LRE-123 systems with a ball-milled Gd-211 addition.

2. Experimental

NEG-123, NSG-123, SEG-123 powders were prepared by OCMG process described [2–4]. Gd-211 powder added to the ternary LRE-123 systems was ball milled by means of Y$_2$O$_3$–ZrO$_3$ balls in acetone, for 0.3–8 h. Subsequently, the milled particles were sieved off from the balls and dried for several hours at room temperature. The average size of the ball-milled particles was 200 to $<$70 nm, in dependence on the milling time. The size was estimated by Brunauer–Emmet–Teller (BET) specific area measurements [8].

Sintered LRE-123 and ball-milled Gd-211 powders were thoroughly mixed. In order to suppress the coarsening of Gd-211 particles during melt processing, 0.5 mol% Pt and 1 mol% CeO$_2$ was added. Then the material was pressed into pellets 2 cm in diameter and 1 cm in thickness by applying cold isostatic pressing (CIP) of 200 MPa. After placing a MgO (1 0 0) seed crystal on the top centre, the pellets were subject to the OCMG process in a commercial 1% O$_2$–Ar gas mixture flowing through the furnace at the rate of 300 ml/min. The heat treatment profiles in the melt process for various ternary materials were scheduled on the basis of the DTA results. The details of the heat treatment scheduled can be found elsewhere [3,4,9].

For magnetic measurement and microstructure study, small specimens with dimensions of $a \times b \times c = 1.5 \times 1.5 \times 0.4$ mm$^3$ were cut from the as-grown pellets and oxygenated in a separate oxygenation process details of which were reported in Refs. [3,4,9]. Magnetization hysteresis loops (MHLs) were measured by SQUID magnetometer (Quantum Design, model MPMS7) at 77 K in magnetic fields up to 7 T applied parallel to $c$-axis of the sample. The magnetic $J_c$ values were estimated by means of the extended critical state model [10]. Some of the samples were tested at liquid oxygen temperature.

3. Results and discussion

Fig. 1 shows field dependences of critical current densities, $J_c(H_a)$, of four SEG-123 samples with 40 mol% of Gd-211 with the starting average particle size ranging between 200 and $<$70 nm. All samples were measured first of all at 77 K (left). It can be seen that the remnant critical current density increases with decreasing particle size as in the NEG-123 system [11]. The highest remnant $J_c$ value of 142 kA/cm$^2$ was achieved in the sample with starting average particle size $<$70 nm. The irreversibility field was similar in all four samples. The critical current density enhancement with decreasing the particle size extended up to moderate magnetic fields. This observation needs a more detailed study as Gd-211 particle even in size below 70 nm are still too large to be associated with point-like disorder pinning. Fig. 1 (right) shows that similarly as in the previous study on the NEG-123 system [11], also in the present sample the flux pinning strongly increased at 90 K. $J_c(H_a)$ behavior was similar as at 77 K. Again, $J_c$ increased with decreasing initially added Gd-211 particle size. The (highest) remnant critical current density of 25 kA/cm$^2$ was observed in the sample with the particle size less then 70 nm.

Fig. 2 presents critical current densities of four NEG-123 samples with 30 mol% Gd-211 of various sizes measured at 77 (left) and 90 K (right). Although the initially added Gd-211 content, 30 mol%, was less than that of the previous case and still not optimal for the NEG-123 system [11], all the NEG-123 samples had better properties in the whole field range than the SEG-123 ones. The NEG-123 sample with starting average particle size $<$70 nm exhibited record remnant $J_c$ values of 190 and 38 kA/cm$^2$ at 77 and 90 K, respectively. Both SEG-123 and NEG-123 systems with the Gd-211
average particle size <70 nm showed dramatically improved critical current density, especially at zero field, with respect to the same composites with addition of commercial secondary phase powders. The $J_c(H_a)$ data of two NSG-123 samples with addition of 30 mol% Gd-211 with various initial sizes derived from $M–H$ loops at 77 K are presented in Fig. 3. Again, critical current densities notably increased with decreasing size of the initially added Gd-211 particles from 200 to 70 nm, however, the enhancement was slightly less than for SEG-123 samples. Thus, the strongest size effect was found in the NEG-123 system.

The high $J_c$ values at zero applied magnetic field and systematic improvement in all three systems with decreasing Gd-211 particle size corresponds to the models of surface [12] or volume pinning [13] by large non-superconducting particles. However, for
the $J_c$ improvement in high magnetic fields the Gd-211 refinement is still too coarse. Microstructure analysis of NEG-123 samples made by transmission electron microscope (TEM) and dynamic force microscopy (DFM) indicated formation of a special 20–50 nm particle dispersion of Zr-rich NEG–Ba–Cu–O particles in the NEG-123 matrix [6]. More details on the chemical composition of these nanoparticles can be found in Ref. [11]. Evidently, these new defects were formed during melt growth from the Gd-211 contaminated by Zr during its ball milling. These new pinning sites were smaller than initially added secondary phase and could enhance $J_c$ not only at low fields but their effect could extend up to intermediate fields (Figs. 1 and 2).

The supercurrent density at 90 K reached high enough values (Figs. 1 and 2) to enable levitation experiment with liquid oxygen temperature. This is documented in Fig. 4 where a permanent Fe–Nd–B magnet is shown stably levitating above the NEG-123 superconductor at 90.2 K (Fig. 4(a)) and, in opposite, the NEG-123 superconductor cooled by liquid oxygen (99.2 K) is suspended below the permanent magnet (Fig. 4(b)). Quite similar as the levitation with Y-123 materials cooled by liquid nitrogen [14].

Fig. 3. Field dependence of critical current density for (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ sample with 40 mol% Gd-211 refined by ball milling for 0.3 and 4 h (200 and 70 nm average particle size). Both samples were measured at 77 K, $H_0 || c$-axis.

Fig. 4. A permanent Fe–Nd–B magnet stably levitates over an NEG-123 + 30 mol% Gd-211 <70 nm in size superconductor at liquid oxygen temperature (90.2 K), after the superconductor had been magnetized by stray field of the permanent magnet and cooled down to 90.2 K (top figure); The same type of NEG-123 pellet is cooled to 90.2 K and suspended below the Fe–Nd–B magnet (bottom figure).

4. Summary

The recently observed effect of size reduction of the initially added Gd-211 powder on magnetic properties of melt-processed NEG-123 was verified in other ternary systems, SEG-123 and NSG-123. Comparison of the results indicates that NEG-123 system is superior, both at 77 and 90 K. In the NEG-123 sample with 30 mol% of <70 nm size the highest remnant critical current densities of 190 and 38 kA/cm$^2$ at 77 and 90 K, respectively, were observed. The analogous SEG-123 and NSG-123 systems were slightly worse but also good enough for realization of levitation at 90 K.

The key to the successful levitation at liquid oxygen temperature was a combination of submicron secondary phase particles with nanometer
size Zr-rich NEG–Ba–Cu–O clusters. The present data suggest that a further improvement of electromagnetic properties via reduction of the pinning defect size is possible.

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References


