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# Effect of CeO<sub>2</sub> addition on microstructure and magnetic properties in (Nd,Eu,Gd)–Ba–Cu–O

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## Abstract

Morphology of Gd<sub>2</sub>BaCuO<sub>5</sub> (Gd-211) secondary phase particles in an oxygen-controlled-melt-growth processed (Nd<sub>0.33</sub>Eu<sub>0.33</sub>Gd<sub>0.33</sub>)Ba<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> + 0.5 mol% of Pt (NEG-123) was studied as a function of varying amount (0–3 mol%) of CeO<sub>2</sub>. Optical and scanning electron microscopy revealed that sub-micron Gd-211 particles were distributed uniformly throughout the NEG-123 matrix for additions of up to 2 mol% of CeO<sub>2</sub>. With increasing CeO<sub>2</sub> content the critical current density,  $J_c$ , increased particularly at low magnetic fields. The maximum value of  $J_c$  was achieved for 1 mol% CeO<sub>2</sub> and reached 100 kA cm<sup>-2</sup> at zero field and 77 K. The improved low-field critical current density is attributed to the refinement of Gd-211 particles. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Recent experiments performed on a variety of NEG-type superconductors have demonstrated that magnetic properties of these compounds are superior to other known RE-123 materials [1–4]. Furthermore, in the NEG-123 system doped with the secondary phase NEG-211 we found that sub-micron-sized particles were formed during the oxygen-controlled-melt-growth (OCMG) process [1]. Interestingly, transmission electron microscopic analyses with energy dispersion spectroscopy revealed that extremely small Gd-211 particles precipitated in the NEG system, while most of larger

particles consist of NEG-211. We then prepared NEG-123 samples with an addition of Gd-211 alone. As a result, fine dispersion of Gd-211 could also be achieved in the NEG-123 matrix [5]. Some of our recent results demonstrated that a combined addition of Pt and CeO<sub>2</sub> is effective in refining NEG-211 particles in NEG-123 matrix [6]. In order to further refine Gd-211 particles, we added 0–3 mol% of CeO<sub>2</sub> to the samples of NEG-123 with 30 mol% Gd-211 and 0.5 mol% Pt. In this paper, we will report on the effect of CeO<sub>2</sub> content on the size of Gd-211 and  $J_c$ – $B$  performance at 77 K.

## 2. Experimental

Precursor powders of (Nd<sub>0.33</sub>, Eu<sub>0.33</sub>, Gd<sub>0.33</sub>)-Ba<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> were prepared by repeated calcination

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and grinding using a mixture of  $\text{Nd}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$ . The details of the NEG powder preparation have been reported elsewhere [1]. NEG-123 bulk samples with 30 mol% of Gd-211 were prepared using a mixture of sintered NEG-123 and commercial Gd-211 powders. Commercial Gd-211 powders with diameter less than 1  $\mu\text{m}$  were used to make the initial 211 particles as small as possible. In order to clarify the  $\text{CeO}_2$  effect on the microstructure and critical current density of the NEG-123 system, various concentrations of  $\text{CeO}_2$  (0, 1, 2, and 3 mol%) were added. Since a combined addition of  $\text{CeO}_2$  and Pt is known to be the most effective in reducing the size of LRE-211, 0.5 mol% of Pt was also added to all samples. The peritectic decomposition temperature obtained from the DTA measurements was used to determine the heat treatment schedule of the OCMG process for different NEG samples. The melt growth was performed in flowing a mixture gas of 0.1%  $\text{O}_2$  and 99.9% Ar. The details of the heat treatment schedule and oxygen annealing process can be found elsewhere [1].

Microstructural observations were performed on the polished surfaces of the samples with a

scanning electron microscope (SEM). Magnetization hysteresis loops (MHLs) were measured at 77 K in applied fields up to 7 T using a commercial SQUID magnetometer (Quantum Design, model MPMS7). The external magnetic field was always applied parallel to the  $c$ -axis of the samples.  $J_c$  values were evaluated from the MHL data using the extended Bean critical state model [7].

### 3. Results and discussion

#### 3.1. Microstructural analysis

Fig. 1(a)–(d) shows SEM micrographs of NEG-123 samples with 30 mol% of Gd-211, 0.5 mol% Pt, and 0–3 mol% of  $\text{CeO}_2$ . It is evident that the secondary phase particles are homogeneously dispersed in the NEG-123 matrix. In the samples with 1 and 2 mol% of  $\text{CeO}_2$  a high concentration of sub-micron Gd-211 particles appeared, indicating that an excellent particle refinement can be achieved in this way. An increase of  $\text{CeO}_2$  content over 2 mol% did not result in further particle refinement.

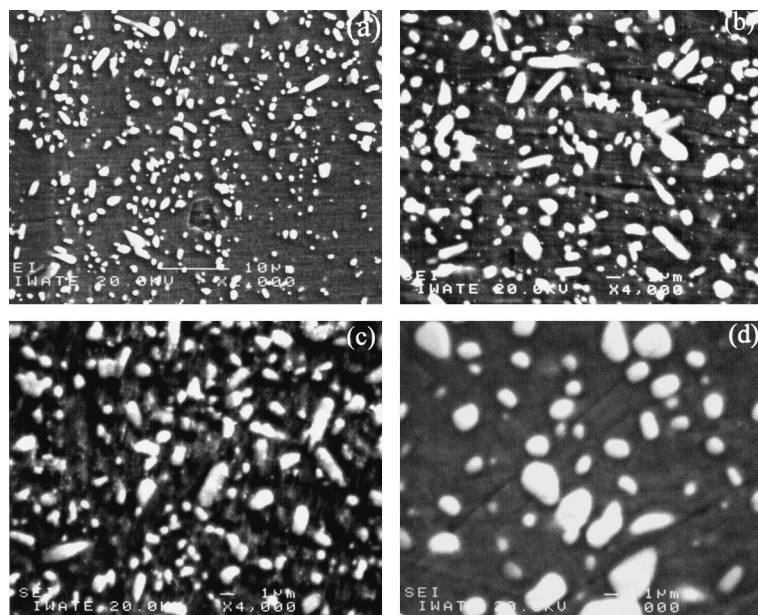


Fig. 1. Scanning electron micrographs of NEG-123 with 30 mol% of Gd-211 and 0.5 mol% of Pt prepared in 0.1%  $\text{O}_2$ : (a)  $\text{CeO}_2$  free; (b) 1 mol%; (c) 2 mol%; (d) 3 mol%  $\text{CeO}_2$ .

Fig. 2 shows the volume fraction of the secondary phase trapped in the NEG-123 matrix for the sample with 1 mol% CeO<sub>2</sub>. The values were determined using an image processing system from SEM micrographs. The average particle size was around 0.1 μm.

### 3.2. Magnetic characterization

Fig. 3 shows the critical current density ( $J_c$ ) as a function of applied field for various contents (0–3 mol%) of CeO<sub>2</sub>. In the CeO<sub>2</sub> free sample, the highest remnant value of  $J_c$  was 75 kA cm<sup>-2</sup> and the secondary peak value recorded at 3 T was 50 kA cm<sup>-2</sup>. In the sample with 1 mol% of CeO<sub>2</sub> a higher  $J_c$  at zero field was observed. With increasing the CeO<sub>2</sub> content,  $J_c$  values were first increased but decreased above 2 mol% of CeO<sub>2</sub>.

Fig. 3(b) shows the field dependence of the  $J_c$  normalized by the current density at zero field,  $J_c$

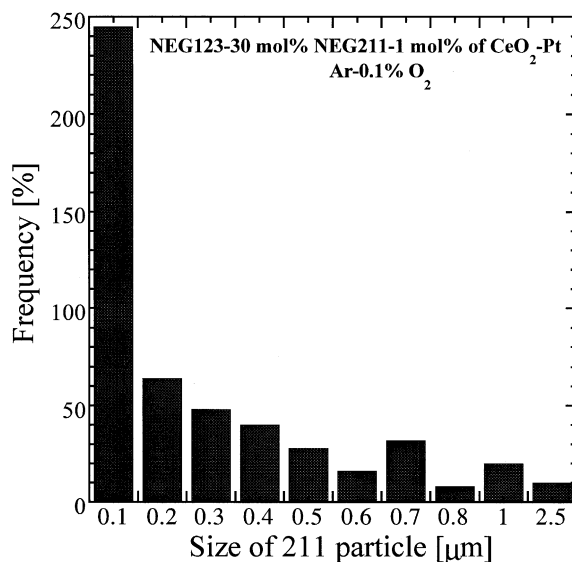


Fig. 2. Size distribution of Gd-211 secondary phase in OCMG-processed NEG sample fabricated with an addition of 1 mol% CeO<sub>2</sub>.

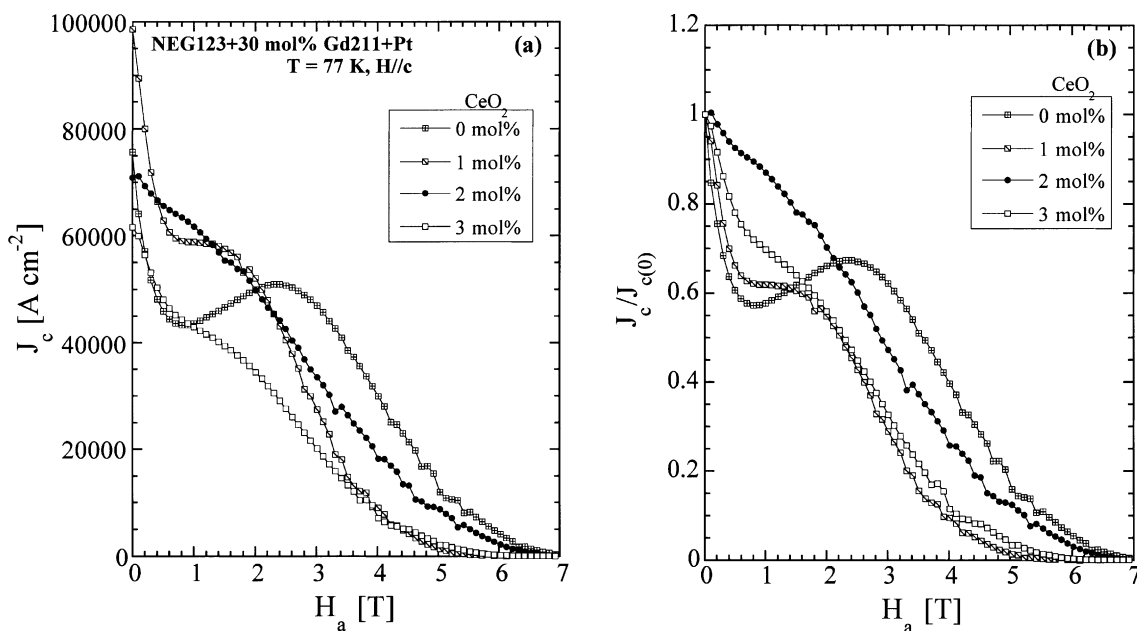


Fig. 3. Field dependence of the critical current density ( $T = 77$  K,  $H_a \parallel c$ -axis) for NEG-123 + 30 mol% Gd-211 + 0.5 mol% Pt with different amounts of CeO<sub>2</sub>. (a)  $J_c$  data of samples with varying contents of CeO<sub>2</sub>. (b) Plot of  $J_c$  normalized by the current density at zero field (self-field),  $J_c(0)$  (0 T).

(0). From this graph, one can see the  $J_c$  enhancement in low fields, however at higher magnetic fields the normalized  $J_c$  values decreased with increasing  $\text{CeO}_2$  addition. Similar behavior was observed in the YBCO system, in that such deterioration was linked to the contamination caused by cerium doping [8,9]. We believe that the superconducting properties were also degraded in our samples with  $\text{CeO}_2$  addition.

#### 4. Conclusion

We studied the effect of  $\text{CeO}_2$  addition on the microstructure and field dependence of the  $J_c$  at 77 K for OCMG-processed NEG-123 composites with 30 mol% of Gd-211. The SEM observations confirmed that a combined addition of Pt and  $\text{CeO}_2$  is effective in reducing the size of the secondary phase particles. However, when the content exceeded 2 mol%,  $J_c$  decreased in a wide temperature range. The best results with respect to both microstructure and  $J_c$  were achieved with an addition of 1 mol%  $\text{CeO}_2$ .

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