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# Microstructural investigations on melt grown RE–Ba–Cu–O (RE = Y, Gd and Nd) systems

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A melt growth process has been carried out on RE–Ba–Cu–O (RE = Y, Gd and Nd) superconductors in order to fabricate grain oriented samples that support a high critical current density ($J_c$). Preliminary results on the microstructural data obtained on these samples are reported in this paper.

## 1. Introduction

The application of high temperature superconductors depends on their ability to carry a high current density ($J_c$). Low $J_c$ values in polycrystalline $YBa_2Cu_3O_7$ (Y–123) and other rare earth substituted compounds is now generally understood to be due to the presence of weak links, the lack of grain alignment and the lack of pinning in the material. It has been found that a melt growth process for Y–123 yields an oriented grain structure which enables the material to support $J_c$ values greater than $10^4$ A cm$^{-2}$ [1–5]. In this process, the superconducting Y–123 phase is produced by a peritectic reaction of $Y_2BaCuO_5$ (Y–211) and liquid phases. Using this reaction it is also possible to distribute the 211 phase in the 123 matrix so as to aid flux pinning [4].

It is known that all the lanthanide elements except Ce and Tb can fully substitute for the yttrium in the Y–123 structure. Except for Pr, all the rare earth substitutions have very little influence on $T_c$. The peritectic formation temperature of RE–123 increases with increase in ionic radius of the rare earth atoms. Hence, it is reasonable to expect microstructural variations in melt grown samples of $REBa_2Cu_3O_7$ with various rare earth elements. However, the melt processing of RE–123 superconductors other than Y–123 poses several difficulties owing to the formation of a solid solution of the form $RE_{1+x}Ba_xCu_3O_{6+y}$ [6]. Recently Murakami *et al.* [7] have reported on the fabrication of Nd–123 and Sm–123 by the melt texturing process under partial oxygen pressures that suppresses the solid solution formation. The $J_c$ values of these materials at higher fields ( > 1 Tesla) are reported to be larger than those obtained in melt processed Y–123 with Y–211 inclusions. The increase in $J_c$ at higher fields (upto 7 Tesla) in the case of melt grown Nd–123 and Sm–123 samples has been attributed to solid solution formation in the samples on a microscopic level. It has been shown that the addition of uniformly distributed fine Y–211 in the Y–123 system increases the $J_c$ value by a few orders of magnitude in the relatively lower field range upto 0.1 Tesla [8]. However, the melt grown Nd–123 and Sm–123 samples without 211 show a lower $J_c$ value than Y–123 with 211 in the low field region. It has been reported in the literature that the pinning mechanism in the case of Y–123 containing 211 inclusions has its origin in structural defects with the size of the coherence length, occurring at the 123/211 interface [9]. Similar to the Y–123 system, there is a possibility that in RE–123 systems, if we introduce homogeneously distributed fine 211 inclusions, the $J_c$ values in the lower field range can be further improved.

It is also of interest to look for similarities in the microstructure of melt grown RE–123 samples containing 211, which will have relevance to the models proposed for Y–123 melt growth [10–12]. Till now there are no detailed studies on the microstructural variations due to addition of 211 in RE–123 systems other than Y–123. It is discussed in the literature [13] that $Nd_2BaCuO_5$ which is called the 'brown' phase adopts a totally different structure from that of the 'green' phases $Y_2BaCuO_5$ and $Gd_2BaCuO_5$. $Nd_2BaCuO_5$ is tetragonal with cell parameters $a = 0.67015$ nm and $c = 0.582135$ nm, whereas $Y_2BaCuO_5$ and $Gd_2BaCuO_5$ crystallize in an orthorhombic structure. The $Nd_2BaCuO_5$ phase is built from edge and face sharing $BaO_{10}$ and $NdO_8$ polyhedra while in the green phase structure, the $Y^{3+}$ or $Gd^{3+}$ ion is surrounded by seven oxygen atoms. It is possible that the crystal structure adopted by the Nd–211 may have an effect on the superconducting properties.

In this paper, we report on a microstructural study carried out on melt grown RE–Ba–Cu–O (RE = Y, Gd and Nd) compounds and compare the results with those reported in the literature.

## 2. Experimental

The starting powders of Y–Ba–Cu–O, Gd–Ba–Cu–O and Nd–Ba–Cu–O were prepared by the nitrate

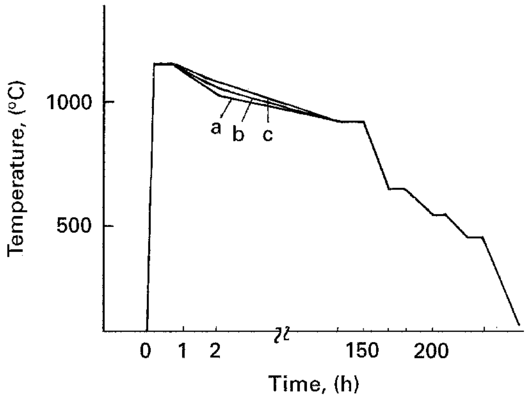

*Figure 1* Temperature–time profile of the melt growth experiments for (a) Y–123, (b) Gd–123 and (c) Nd–123 systems.

evaporation method. The composition was chosen so as to contain 0.72 $REBa_2Cu_3O_7$ (123) : 0.28 $RE_2BaCuO_5$ (211) (where RE = Y, Gd and Nd) in the starting stoichiometry. This composition has been chosen since a systematic study on the microstructural variations carried out on a melt grown Y–123 system revealed that Y–123 samples containing 28 mol % 211 composition showed finer 211 particles and a minimum crack width between the oriented 123 platelets and also large $J_c$ values ($10^4\,A\,cm^{-2}$) at 77 K [8]. Initially all the pressed compacts were sintered at 930 °C for 16 h. The sintered pellets of each compound were rapidly heated to 1130 °C and kept for 20 min. Slow cooling ($1\,°C\,hr^{-1}$) was carried out for each compound separately through the peritectic decomposition temperature. The peritectic decomposition of $REBa_2Cu_3O_7$ (RE = Y, Gd and Nd) has been reported in the literature from the differential thermal analysis (DTA) of the samples [14]. The peritectic decomposition temperatures of the 123 compounds containing Y, Gd and Nd are 1030, 1065 and 1100 °C respectively in an $O_2$ atmosphere. In the slow cooling process, the decomposed phases react to form RE–123. After slow cooling down to 930 °C the samples were kept at that temperature for 24 h and then furnace cooled to room temperature with long holds from 600–400 °C. The entire process was carried out in the presence of oxygen rather than in a partial oxygen atmosphere as reported by Murakami *et al.* [7]. The heat-treatment schedules of the melt growth process adopted in the present study are shown in Fig. 1.

Microstructural features were analysed using an optical microscope with polarized light, an ISI 100A scanning electron microscope (SEM) and a Philips EM430T Transmission Electron Microscope (TEM) with energy dispersive analysis of X-rays (EDAX) facility. Specimens for optical microscopy were prepared by polishing the samples using 1/2 μm size diamond paste with an automatic polishing machine. No etching was done to observe the microstructural features. Fractured surfaces for SEM study were prepared by cleaving the sample surface nearly parallel to the (001) plane. Thin foils for TEM study were made by ion milling of 3 mm disks of ~100 μm thickness. Microstructural features such as grain size, crack width between the grains, and particle size of the 211 inclusion were measured using standard metallographic methods. The width of the grains and crack width between the grains were measured over many grains and average values were obtained. Electrical resistivity measurement down to 77 K were performed using the 4-probe method to obtain the superconducting transition temperature ($T_c$).

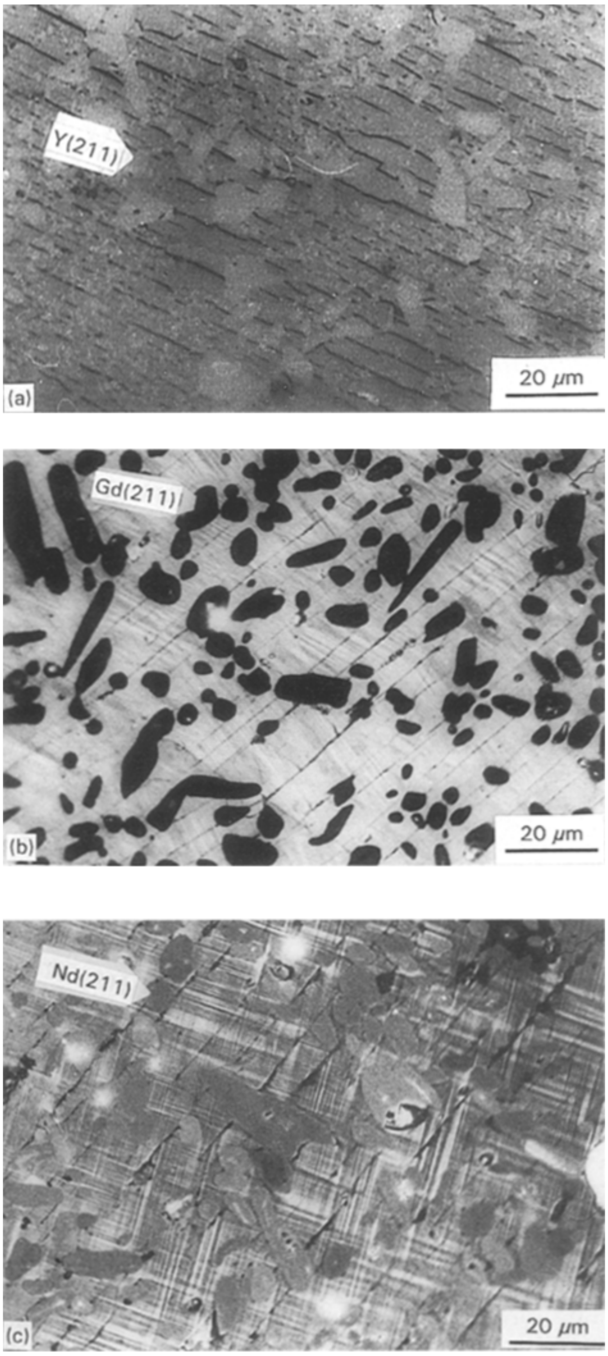

*Figure 2* Optical microstructures of melt grown samples. (a) Y(123) containing 28 mol % Y(211). (b) Gd(123) containing 28 mol % Gd(211) and (c) Nd(123) containing 28 mol % Nd(211).

## 3. Results and discussion

Fig. 2(a–c) shows the optical microstructure obtained from the melt grown RE–123 containing 28 mol % 211 of Y, Gd and Nd systems respectively. Although the microstructures show oriented RE–123 grains with 211 particles distributed in the matrix in all the samples, variations in the microstructural features can

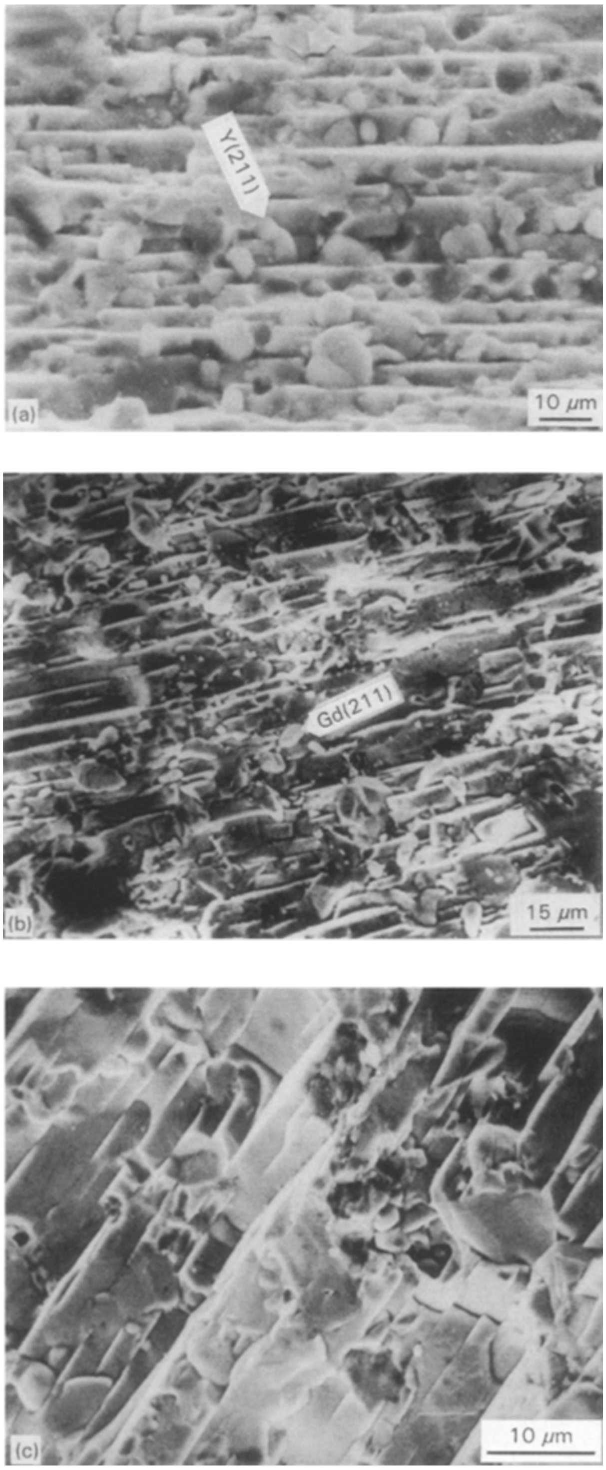

*Figure 3* SEM fractographs obtained from melt grown samples. (a) Y(123) containing 28 mol % Y(211). (b) Gd(123) containing 28 mol % Gd(211) and (c) Nd(123) containing 28 mol % Nd(211).

be noticed. The microstructures (Fig. 2(b, c)) corresponding to the Gd and Nd systems show mostly elongated 211 particles, whereas in the Y system the particles are mostly spherical and finer. Another feature to be noticed in the micrographs is the formation of a smaller volume fraction of 211 particles in the Gd and Nd samples. All the samples show formation of cracks at grain boundaries. Fig. 3 shows the SEM fractographs of the melt grown samples. It can be noticed that 211 particles are spherical in the case of the Y-system (Fig. 3a). Sawano *et al.* [15] have reported microstructural variations in melt processed RE–123 samples where rare earth elements were substituted both completely and partially for the Y of $YBa_2Cu_3O_7$. In their study most of the systems were found to form RE–123 structures, except for the Nd system in which different crystalline phases formed after quenching from the partial melting temperature. The difference in the microstructure such as the 211 size and crack formations observed in their study has been attributed to different melting behaviours of each rare earth system. We have noticed that the RE–123 grain width in the case of Gd and Nd samples was ~ 6–8 µm and 8–10 µm respectively, whereas in the Y sample it was found to be ~4–6 µm. The superconducting transition temperatures ($T_c$) of Y–123 and Gd–123 in the present study were found to be 88 K and 82 K respectively. The various microstructural parameters obtained in melt grown RE–Ba–Cu–O samples processed in the present study are listed in Table I. The values reported on various microstructural features in Table I could be reproduced in several experiments. The variations in the microstructural features observed in melt grown RE–123 samples in the present study may have their origin in differences in the growth kinetics of the RE–123 phase. It has been reported that the concentration range of the liquidus line from which the RE–123 phase is available is greater in the case of the Gd and Nd systems, whereas in the Y system it is a line compound [16–18]. This difference in the phase diagram can definitely vary the RE–123 grain growth conditions.

Figs 4 and 5 show the TEM micrographs of melt grown Y–123 and Gd–123 samples with 211 inclusions viewed along the [0 0 1] zone axis of the RE–123 matrix. Particles of 211 were identified from their electron diffraction pattern together with their EDAX spectrum. In the case of the Y system strain field contrasts were observed around 211 particles (Fig. 4a) having a radius of curvature $\leq 0.3$ µm and these

TABLE I Microstructural data on melt grown RE–123

| RE | Ionic radius $\times 10^{-1}$ (nm) | Peritectic decomposition temp. (in $O_2$) (°C) | Average grain width of RE (123) (µm) | Average crack width (µm) | Vol. fraction of RE (211) (%) | RE (211) particle size (µm) |
|---|---|---|---|---|---|---|
| Y | 0.893 | 1030 | 6 | 0.45 | 40 | 2–6 |
| Gd | 0.938 | 1065 | 6–8 | 0.40 | 25 | 4–10 |
| Nd | 0.995 | 1090 | 8–10 | 0.60 | 20 | 4–10 |

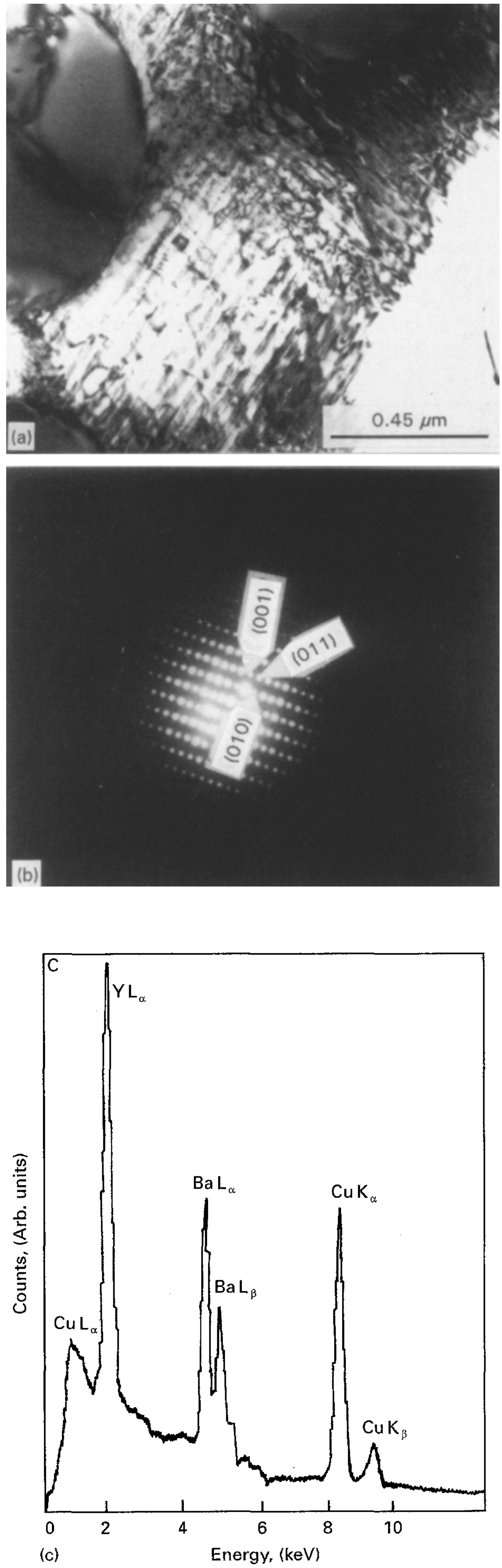

*Figure 4* (a) A TEM micrograph of melt grown Y(123) containing 28 mol % Y(211). (b) selected area diffraction obtained from a Y(211) inclusion. (c) EDAX spectrum of a Y(211) inclusion.

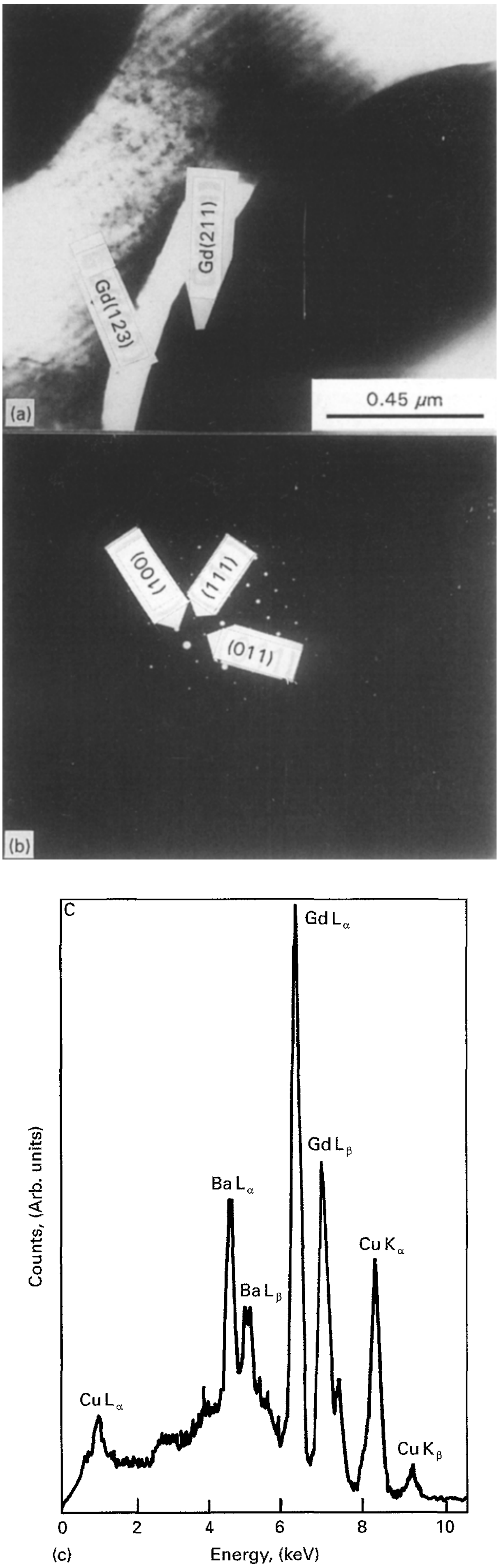

*Figure 5* (a) A TEM micrograph of melt grown Gd(123) containing 28 mol % Gd(211). (b) selected area diffraction obtained from a Gd(211) inclusion. (c) EDAX spectrum of a Gd(211) inclusion.

defects are believed to be responsible for the pinning of the magnetic flux [8]. However, no such defects could be observed around 211 particles in the Gd samples (Fig. 5a). This is probably due to the difference in the size and shape of the 211 particles formed. The variations in the microstructural features observed in melt grown RE–123 in the present work is of interest from the point of view of studying the effect of the rare earth in RE–123 on the $J_c$ improvement. It is also of interest to note that the presence of magnetic moment on the $Gd^{3+}/Nd^{3+}$ may play a role by interacting with fluxoids.

The present work has concentrated only on a preliminary microstructural study. A magnetization study would be of interest to observe the effect of the rare earth substitution on the critical current density ($J_c$).

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## References

1. S. JIN, T. H. TIEFEL, R. C. SHERWOOD, R. B. VAN DOVER, M. E. DAVIS, G. W. KAMMLOTT and R. A. FASTNACHT, *Phys. Rev. B* **37** (1988) 7850.
2. M. MURAKAMI, M. MORITA, K. DOI and K. MIYAMOTO, *Jpn. J. Appl. Phys.* **28** (1989) 1189.
3. K. SALAMA, V. SELVAMANICKAM, L. GAO and K. SUN, *Appl. Phys. Lett.* **54** (1989) 2352.
4. M. MURAKAMI, K. YAMAGUCHI, H. FUJIMOTO, N. NAKAMURA, T. TAGUCHI, N. KOSHIJUKA and S. TANAKA, *Cryogenics* **32** (1992) 930.
5. P. J. McGINN, W. CHEN, N. ZHU, U. BALACHANDRAN and M. T. LANAGAN, *Physica C* **165** (1990) 480.
6. S. A. HODOROWICZ, A. CHODOROWICZ-BAK, J. CZERWONKA, E. HODOROWICZ, W. LASOCHA and H. A. EICK, *J. Solid State Chem.* **92** (1991) 480.
7. M. MURAKAMI, S. I. YOO, T. HIGUCHI, N. SAKKAI, J. WELTZ, N. KOSHIZUKA and S. TANAKA, *Jpn. J. Appl. Phys.* **33** (1994) L715.
8. R. GOPALAN, T. RAJASEKHARAN, T. ROY, G. RANGARAJAN and N. HARI BABU, *Physica C* **244** (1995) 106.
9. P. J. KUNG, M. P. MALEY, M. E. McHENRY, J. O. WILLIS, M. MURAKAMI and S. TANAKA, *Phys. Rev. B* **48** (1993) 13922.
10. T. IZUMI, Y. NAKAMURA and Y. SHIOHARA, *J. Mater. Res.* **7** (1992) 1621.
11. C. A. BATEMAN, L. ZHANG, H. M. CHAN and M. P. HARMER, *J. Amer. Ceram. Soc.* **75** (1992) 1281.
12. M. J. CIMA, M. C. FLEMINGS, A. M. FIGUREDO, M. NAKADE, H. ISHII, H. D. BRODY and J. S. HAGGERTY, *J. Appl. Phys.* **72** (1992) 179.
13. J. K. STALICK and W. WONG-NG, *Mater. Lett.* **9** (1990) 401.
14. A. KATSUI, Y. HIDAKA and H. OHTSUKA, *Jpn. J. Appl. Phys.* **26** (1987) L1521.
15. K. SWANO, M. MORITA, K. KIMURA, K. DOI and K. MIYAMOTO, "High Temperature Superconducting Compounds II", Eds S. H. Whang, A. Dasgupta and R. Laibouitz, (The Minerals, Metals and Materials Society, Warrendale, 1990) p. 61.
16. J. E. BLENDELL, W. WONG-NG, C. K. CHIANG, R. D. SHULL and E. R. FULLER, JR. in "High Temperature Superconducting Compounds: Processing and Related Properties", (eds) S. H. Whang and A. Dasgupta (The Minerals, Metals and Materials Society, Warrendale, 1989), p. 193.
17. W. WONG-NG, B. PARETZKIN and E. R. FULLER, JR., *J. Solid State Chem.* **85** (1990) 117.
18. K. OKA, K. NAKANE, M. ITO, M. SAITO and H. UNOKI, *Jpn. J. Appl. Phys.* **27** (1988) L1065.

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