Melt processing of high-$T_c$ Nd–Ba–Cu–O superconductors in air

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Abstract

We have succeeded in fabricating Nd–Ba–Cu–O bulk superconductors, which exhibit high $T_c$ and a sharp superconducting transition, by the melt process in air without additional high temperature annealing in a reduced oxygen atmosphere. The key to this achievement is the use of Ba-rich Nd$_{4-2x}$Ba$_{2+2x}$Cu$_{2-y}$O$_{10-y}$ as a precursor. Fabricated bulk samples exhibit onset $T_c$ values of 94–95 K and the secondary peak effect in the $M$–$H$ loop like the case of Nd–Ba–Cu–O superconductors produced by melt processing in a reduced oxygen atmosphere. The peak position and the irreversibility field for the best sample were about 1.2 T and 5 T at 77.3 K, respectively, and the estimated $J_c$ at the peak field was about $2.3 \times 10^4$ A cm$^{-2}$.

Keywords: Superconductor; Melt process; Nd–Ba–Cu–O; Critical current density; Solid solution; Phase diagram

1. Introduction

Unlike YBa$_2$Cu$_3$O$_y$, which forms only a stoichiometric compound, large rare earth elements (RE: La, Nd, Sm, Eu and Gd) are known to form a RE$_{1+y}$Ba$_{2-y}$Cu$_3$O$_{7+y}$ solid solution (RE123ss) because the ionic radius of RE$^{3+}$ is close to that of Ba$^{2+}$. The superconducting transition temperature ($T_c$) is depressed when RE$^{3+}$ substitutes on the Ba$^{2+}$ site, since the carrier concentration is decreased. Owing to the presence of the RE–Ba substitution, REBa$_2$Cu$_3$O$_{7+y}$ (RE123) samples melt-processed in air exhibit low $T_c$ with a broad transition. Such substitution can largely be suppressed by employing low oxygen partial pressure $pO_2$ during the solidification of the RE123 phase, which is the oxygen-controlled-melt-growth (OCMG) process [1–3].

OCMG-processed RE–Ba–Cu–O (RE: Nd, Sm, Eu, Gd) superconductors exhibit high $T_c$ and a sharp transition. Furthermore, they are very promising for practical applications since the critical current density $J_c$ and the irreversibility field were higher than those of melt-processed Y–Ba–Cu–O. The OCMG process, however, has the disadvantage that $pO_2$ must be controlled during the process, which adds to the cost and will require a complicated system to seed the crystal for the fabrication of large grain samples. To avoid these problems melt processing in air has greatly been favoured.

Recently, Obradors et al. [4] and Hu et al. [5] have reported that Nd–Ba–Cu–O superconductors melt-processed in air exhibit high $T_c$ of 95–96 K. It should be noticed, however, that in both cases add-
tional Ar annealing at high temperatures above 900°C is indispensable to the achievement of high $T_c$. We suppose that during such treatment RE-rich phase with depressed $T_c$ will decompose into Nd$_2$Ba$_2$Cu$_2$O$_{10}$ (Nd422) plus the liquid phase, and then the phase with enhanced $T_c$ solidifies from Nd422 and the liquid, leading to the recovery of high $T_c$.

In the present paper, we show that Nd–Ba–Cu–O superconductors exhibiting $T_c$ of 94–95 K and a sharp transition can be fabricated by the melt process in air without additional high temperature annealing in low $pO_2$.

2. Experimental

Four batches having different nominal compositions were prepared using precursors of Nd$_{0.9}$Ba$_{2.1}$Cu$_{1.8}$O$_{7-\delta}$, Nd$_{0.9}$Ba$_{2.1}$Cu$_{1.8}$O$_{7-\delta}$, Nd$_{3.6}$Ba$_{2.4}$Cu$_{1.8}$O$_{10-\delta}$ and Nd$_{3.6}$Ba$_{2.4}$Cu$_{1.8}$O$_{10-\delta}$, which were independently prepared by the solid state reaction. Nominal compositions for the samples are shown in Table 1. Chemical compositions of the Nd422 and Nd$_{3.6}$Ba$_{2.4}$Cu$_{1.8}$O$_{10-\delta}$, which were analyzed by inductively coupled plasma (ICP) spectrometry, are also displayed in the table. The results of powder X-ray diffraction (XRD) analyses for the precursor materials suggested that all the precursors were phase-pure at least on the X-ray level except Nd$_{0.9}$Ba$_{2.1}$Cu$_{1.8}$O$_{7-\delta}$ which contained a small amount of BaCuO$_2$ phase. Although the solubility limit of Ba in Nd422ss was reported to be $z = 0.1 - 0.15$ [6,7], an XRD pattern for Nd$_{3.6}$Ba$_{2.4}$Cu$_{1.8}$O$_{10-\delta}$ indicates that a single phase is formed even when $z = 0.2$, suggesting that the solubility limit is higher than the reported values.

Well-mixed precursor powders were uni-axially pressed into pellets of 20 mm diameter, and subjected to cold-isostatic pressing under a pressure of 200 kg/cm$^2$. For the melt growth in air, the samples were placed on yttria-stabilized zirconia plates and ramped to 1120°C in 3 h, held for 30 min, cooled to 1080°C at a rate of 10°C/min, slowly cooled to 1010°C at a rate of 1°C/h, and then furnace cooled.

Melt-grown samples were composed of many textured Nd–Ba–Cu–O grains of 5–10 mm diameter. Small samples with a rectangular cross section of $1.5 \times 2.0$ mm$^2$ and 0.5–0.8 mm thickness were cut from textured domains, and then annealed in flowing pure O$_2$ gas at a rate of 300 ml/min with the following temperature schedule: heated to 500°C in 3 h, held for 1 h, cooled to 300°C in 25 h, held for 200 h and finally furnace-cooled.

DC magnetization measurements were performed with a Quantum design MPMS SQUID magnetometer. A zero-field-cooled warming procedure was used for the $T_c$ measurement with the applied field of 10 Oe. The magnetization hysteresis loops were also obtained with the SQUID magnetometer for fields parallel to the $c$-axis. The $J_c$ was estimated using the extended Bean model [8].

3. Results and discussion

Fig. 1 shows the temperature dependence of magnetization for the samples. The sample D, synthesized using stoichiometric Nd422 powder as the precursor, exhibits onset $T_c$ of 90 K with a broad transition width of 10 K. In contrast, the samples A to C, synthesized using Ba-rich Nd422ss as the precursor, exhibit relatively high onset $T_c$ values of 94–95 K with the transition width of 4–7 K. It is
clear that the $T_c$ and transition were greatly improved when the Ba-rich Nd422ss was used, although the transition is still broad compared to those of OCMG-processed Nd–Ba–Cu–O samples [2,3]. It should also be noted that even batch D shows much-improved superconducting properties compared with the previous result [2,3]. It is probable that the formation of Nd-rich Nd123ss could be suppressed in the present experiment, since we used separately sintered Nd123 and Nd422 powders.

The formation of high-$T_c$ phase in air can be explained in terms of phase compatibility. The composition $x$ of Nd$_{1+y}$Ba$_{2-x}$Cu$_3$O$_{y+4}$, which is solidified through the peritectic reaction of Nd422ss and the liquid phase, is determined by the liquid phase composition which is compatible with the Nd$_{4-z}$Ba$_{2+z}$Cu$_{2-z}$O$_{10-z}$ at just above the peritectic temperature. As shown in Fig. 2, which is the schematic subsolidus NdO$_{1.5}$–BaO–CuO ternary phase diagram in air, the tie line of high-$T_c$ Nd123 phase is connected to the Nd422ss, in which Ba content lies at the solubility limit. Therefore, the composition of the liquid phase which is compatible with high-$T_c$ Nd123 phase should also be compatible with Ba-rich Nd422ss, although the exact number of $z$ could not be determined in the present experiment. It is also probable that the presence of Ba-rich Nd422ss in the liquid will maintain Ba-rich liquid component, which also favours the formation of high-$T_c$ Nd123 with suppressed Nd–Ba substitution.

We confirmed that $T_c$ of 94–95 K could also be obtained using Nd$_{3.3}$Ba$_{2.2}$Cu$_{1.9}$O$_{10-\delta}$ instead of Nd$_{3.6}$Ba$_{2.4}$Cu$_{1.8}$O$_{10-\delta}$, but the transition was broader. This suggests that the excess Ba in the solid solution of $z = 0.1$ is not sufficient to achieve the preferential formation of high-$T_c$ phase. It might also be possible to simply prepare the Ba-rich liquid phase, however, for the melt-textured process, the reaction of the liquid phase with the substrate or the crucible will easily shift the liquid composition toward Ba-poor direction. It is thus concluded that the present success in growing high-$T_c$ Nd123 phase in air is ascribed to the use of Ba-rich solid phase, that is, Ba-rich Nd422ss.

For comparison, the $J_c$–$B$ curve of a Nd–Ba–Cu–O bulk with 20 mol% excess Nd422, which was OCMG-processed in 1% $O_2$, is also displayed. While the absolute values of $J_c$ for the samples A to C are still lower than that of OCMG-processed sample, they are much improved compared to the batch D. The peak effect, which is commonly observed in OCMG-processed RE123 superconductors is also observed in batches A to C, suggesting that the field-induced pinning center, which was first proposed by Murakami et al. [9] and later verified as the
clusters of Nd–Ba substituted phase with lower $T_c$ finely dispersed in the Nd123 matrix [10–12], also exists in the samples melt-processed in air.

4. Conclusions

The utilization of Ba-rich Nd$_{4-2x}$Ba$_{2+2x}$Cu$_{2-z}$O$_{10-\delta}$ solid solution (i.e. large $z$) as the precursor is the key to growing high-$T_c$ phase of Nd$_{1+y}$Ba$_{2-x}$Cu$_{2}O_{7+\delta}$ solid solution with small $x$ ($0.0 < x < 0.1$) in air, which implies that the fabrication process for Nd–Ba–Cu–O superconductors can be much simplified. Further improvement in both $T_c$ and $J_c$ is expected by the optimization of the processing conditions.

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**References**