Microstructures and superconducting properties of melt-processed (RE(RE′)–Ba–Cu–O

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Abstract

We have studied the microstructures and superconducting properties of melt-processed (RE(RE′)–Ba–Cu–O composite bulks (RE and RE′ are two different rare earth elements selected from a group of Nd, Sm, Eu, Gd and Y). It was found that the peritectic decomposition temperatures \( T_d \) of the (RE(RE′)–Ba–Cu–O composites increased linearly with increasing the average ionic radius between two different rare earth elements. Large grain growth was observed in almost all the (RE(RE′)–Ba–Cu–O bulks except those containing Y, when they were melt-processed in a reduced oxygen atmosphere. Compositional analyses revealed that the ratio of RE to RE′ in the (RE(RE′)BaCuO\(_{2+\delta}^{-}\)) matrix phase was almost the same as that of the nominal composition, showing that the mixture of the two different rare earth elements was very uniform. All the samples showed onset superconducting transition temperatures \( T_c \) exceeding 93 K with a sharp transition, and exhibited a secondary peak effect in the \( M-H \) loops.

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1. Introduction

Melt-processed Y–Ba–Cu–O superconductors exhibit a high critical current density \( J_c \) at liquid nitrogen temperature, and thus a number of bulk type applications have been proposed and tested by many groups [1]. Those applications are magnetic bearing, superconducting fly-wheel, transport system and trapped field magnet. Recently the application of bulk Y–Ba–Cu–O superconductor as a trapped field magnet attracts worldwide attention, because such bulk magnet can generate magnetic fields much larger than those of a permanent magnet. In addition, it is attractive that there is no theoretical limit for the trapped field, which is proportional to \( J_c d \) where \( d \) is the current loop or the size of the superconductor without weak links. This shows that even when \( J_c \) is constant, the trapped field can be increased simply by increasing the size of the superconductor. How-
ever, in that case, the irreversibility field \(B_{irr}\) determines the maximum trapped field. It should also be noted that bulk samples can trap large fields only when the field is applied parallel to the \(c\)-axis, because the weak-links are always introduced along the \(ab\)-plane or between \(CuO_2\) planes for large dimension samples during the tetragonal to orthorhombic transformation. In most bulk \(Y\)-Ba-Cu-O samples, the \(B_{irr}\) values determined by DC magnetization measurements were in the range of 3–5 T at 77 K for the field parallel to the \(c\)-axis \((B||c)\). Therefore, the enhancement of \(B_{irr}\) of \(Y\)-Ba-Cu-O for this field direction has been one of the critical issues for the trapped field application. Ren et al. \(2\) have achieved a significant improvement of both \(B_{irr}\) and \(J_c\) through heavy ion irradiation and they recorded a trapped field of 10 T at 49 K.

Recently, high \(B_{irr}\) values have been achieved in \(RE\)-Ba-Cu-O \(RE: Nd, Sm, Eu, Gd\) melt-processed in a reduced oxygen atmosphere \([3–6]\) and \(B_{irr}\) reached 9 T even at 77 K for \(B||c\). Further enhancement of \(B_{irr}\) to 12 T \((B||c)\) was also reported for \(RE\)-Ba-Cu-O samples subjected to high pressure oxygen annealing \([7]\). These results suggest that \(RE\)-Ba-Cu-O superconductors have a high potential as trapped field magnets. In order to achieve high trapped fields, however, it is also important for bulk superconductors to exhibit large \(J_c\) values in high magnetic fields. It is interesting to note that all \(RE\)-Ba-Cu-O superconductors melt-processed under low oxygen partial pressure \((pO_2)\) exhibit the secondary peak effect, which leads to high \(J_c\) in a high field region. Such peak effect is ascribed to finely dispersed \(RE\)-rich 123 phases with depressed \(T_c\), which act as field-induced pinning centers \([3–5]\).

It is also important to note that the secondary peak field is not only dependent on the processing conditions but also on the kind of \(RE\) elements \([6]\). Thus, it is interesting to study how superconducting properties of \(RE\)-Ba-Cu-O are affected by mixing different rare earth elements in the \(RE\) site in combination with the effect of processing conditions.

Matthews et al. \(8\) have successfully melt-textured \((Y, Nd)\)-Ba-Cu-O in air by applying a relatively large temperature gradient and they have reported high \(J_c\) values at 77 K. Schatzle et al. \(9\) have also fabricated high \(T_c\) \((Sm,Y)\)-Ba-Cu-O by melt-texturing in air. Recently, we have reported that the \((RE,RE')\)-Ba-Cu-O composites show onset \(T_c\) exceeding 95 K when they are melt-processed in low \(pO_2\) \([10]\).

In the present paper, we have studied how the mixing of two different rare earth elements affects the peritectic decomposition temperature \((T_m)\), microstructure and superconducting properties of \((RE,RE')\)-Ba-Cu-O \((RE\ and \ RE' \ are \ selected \ from \ a \ group \ of \ Nd, Sm, Eu, Gd \ and \ Y)\).

2. Experimental

\(RE_2O_3\) \((RE, RE': Nd, Sm, Eu, Gd and Y), BaCO_3\) and \(CuO\) powders were mixed to have the nominal compositions of \(RE:Ba:Cu = 1:2:3\) \((RE123)\) and \(2:1:1\) \((RE211)\). The materials were first calcined at 880°C for 24 h in air and subsequently calcined at 950°C for 24 h in 0.1% \(O_2\) + 99.9% \(Ar\) \((pO_2 = 10^{-3}\ \text{atm})\) with intermediate grinding.

The peritectic decomposition temperatures \((T_m)\) of \(RE123\) were determined by differential thermal analysis \((DTA)\) in air and flowing mixed gas \((pO_2 = 10^{-2} \text{ and } 10^{-3}\ \text{atm})\).

For the melt-texturing process, the calcined materials of \(RE123, RE'123, RE211\) and \(RE'211\) were mixed to have \(RE:RE':Ba:Cu = 0.9:0.9:2.4:3.4\), and pressed into pellets of 20 mm in diameter with a cold isostatic press \((CIP)\) under a pressure of 20 MPa. The pellets were then subjected to the oxygen-controlled-melt-growth \((OCMG)\) process, the details of which are described elsewhere \([3–6]\). The heating profiles were scheduled as follows, based on the \(T_m\) values determined by DTA measurements. Samples were heated to \(T_m + 40\ °C\) in 3 h and held for 10 min, cooled to \(T_m + 5\ °C\) in 1 h, and then cooled at a rate of 0.5°C/h from \(T_m - 95\ °C\) and finally cooled in the furnace. The melt-process was performed in flowing mixture gas of \(O_2\) and \(Ar\) \((pO_2 = 10^{-2} \text{ and } 10^{-3}\ \text{atm})\). All the OCMG-processed samples were post-annealed in flowing oxygen with the following schedule: heating to 600°C for 2 h, cooling to 200°C in 300 h, and furnace cooling. The whole heating schedule is schematically shown in Fig. 1.

Microstructural observation and compositional analyses were performed with a scanning electron microscope \((SEM)\), an electron probe microanalyzer \((EPMA)\) and an X-ray diffractometer \((XRD)\). \(T_c\) and
Fig. 1. Schematic illustration of the heating schedule for the OCMG-process.

$J_c$ values were measured with a Quantum design SQUID magnetometer.

3. Results and discussion

3.1. Peritectic decomposition temperature

Fig. 2 shows a plot of $T_m$ value vs. the average ionic radius of RE and RE' elements for all the RE123 and (RE,RE')123 binary composites under $pO_2 = 10^{-2}$ and $10^{-3}$ atm. Here, the average ionic radius is an averaged ionic radius of two different RE and RE' elements. The ionic radii of all rare earth elements are from the Shannon’s data [11], assuming the coordination number is eight. It is clear that $T_m$ has a good correlation with the average ionic radii, in that $T_m$ of both RE123 and (RE,RE')123 linearly increased with increasing the averaged ionic radius of rare earth elements. These results suggest that (RE,RE')123 composites form a complete solid solution, which then enables us to control $T_m$ simply by changing the ratio or the kind of rare earth elements. It was also found that $T_m$ decreased by about 30°C in a 1% $O_2 + 99%$ Ar atmosphere and decreased by 60°C in a 0.1% $O_2 + 99.9%$ Ar atmosphere compared to that measured in air.

3.2. Grain growth

Well developed large grains of the RE123 phase about 10 mm in diameter were obtained for almost all the (RE,RE')123 composites both in $pO_2 = 10^{-2}$ and $10^{-3}$ atm, except those containing Y. It is known that the solubility of RE elements in the liquid is lowered by decreasing $pO_2$, which may hinder the grain growth of RE123. However, it has been confirmed that even in a reduced oxygen atmosphere, the grain growth rate of (RE,RE')123 for
RE = Nd, Sm, Eu, and Gd is fast enough for producing a well-textured structure, thus the fabrication of a large single domain (RE,RE')123 sample will be possible, which is extremely important for future applications of a trapped field magnet. For the samples containing Y, the textured grain size is very small, which might be due to the very limited solubility of Y in the liquid. It is also probable that the formation temperature of BaCu$_2$O$_2$ is higher than that of (RE,Y)123 in low $p$O$_2$ so that the presence of BaCu$_2$O$_2$ prevents a preferential grain growth of the (RE,Y)123 phase, as already proposed in Dy123 by Takahashi et al. [12].

### 3.3. Microstructural characterization

Fig. 3 shows XRD patterns for (RE,RE')–Ba–Cu–O composites OCMG-processed in a 0.1% O$_2$ + 99.9% Ar atmosphere. It is clear that the samples are mainly composed of the RE123 phase with a small amount of the second phase RE422 for Nd,Sm–Ba–Cu–O and RE211 for other composites. It is also important to notice that no other trace of an impurity phase is present, which shows that the peritectic reaction was completed for all the samples.

Figs. 4 and 5 show the results of microstructural observations with EPMA compositional mapping for the (Nd,Sm) and (Nd,Gd) composite bulks. It can be seen from both figures that the RE123 matrix of the (RE,RE')–Ba–Cu–O composites is homogeneous. Compositional analyses with EPMA revealed that the ratio of Nd:Sm and Nd:Gd is close to unity with

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**Fig. 3.** X-ray patterns for the (RE,RE')–Ba–Cu–O composite samples OCMG-processed in a 0.1% O$_2$ + 99.9% Ar atmosphere.

**Fig. 4.** Micrographs of the (Nd,Sm)–Ba–Cu–O composite OCMG-processed in a 0.1% O$_2$ + 99.9% Ar atmosphere.
Fig. 5. Micrographs of the (Nd,Gd)-Ba-Cu-O composite OCMG-processed in a 0.1% O₂ + 99.9% Ar atmosphere.

Fig. 6. Magnetization vs. temperature for (RE,RE) composite samples OCMG-processed in a 0.1% O₂ + 99.9% Ar atmosphere.
relative standard deviations less than 2% for the whole area of each grain, indicating that RE elements in the RE site form a perfect solid solution, which was also supported by the results of XRD analyses presented in Fig. 3. In contrast, we could find an inhomogeneous compositional distribution in RE422 or RE211 particles in almost all the samples. We believe that such inhomogeneity is closely related to the sample preparation process. We used a mixture of RE211 (or RE422 for RE:Nd) and RE123 as starting materials. When these powders are heated to the partial melting temperature, two kinds of RE211 (or RE422) particles are present in the liquid, one decomposed from RE123 and the other added as the starting powder. Some of these RE211 particles will dissolve into the liquid and grow as new RE211 phases, when the samples are held in the RE211 + L region, and as a result we can observe inhomogeneous RE211 along with homogeneous RE211 in which the RE to RE' ratio is unity. However, the fact that we can observe homogeneous RE211 demonstrates that mixing of different RE elements is uniform even in the RE211 (or RE422) phase. Here it is also interesting to note that the RE422 phase is produced from the (Nd,Sm)–Ba–Cu–O composite, which may imply that there is a critical ionic radius for the RE element that determines the crystal structure of the second phase, since the second phase is always 422 for Nd and 211 for Sm. Further study is necessary to confirm this fact.

3.4. Superconducting property

Fig. 6 shows the temperature dependence of DC magnetization for (Nd,Sm)–Ba–Cu–O, (Sm,Eu)–Ba–Cu–O and (Sm,Gd)–Ba–Cu–O composites OCMG-processed in 0.1% O₂ + 99.9% Ar. All the samples showed an onset $T_c$ of 93 K with a relatively sharp transition. However, these $T_c$ values are lower than the 95 K reported for Nd–Ba–Cu–O in the previous report [10]. This may be attributable to the improper calcination conditions. Unlike Y–Ba–Cu–O, the 211–123 tie line is not a single line for RE–Ba–Cu–O (RE: Nd, Sm, Eu, Gd) so that when 211-rich compositions are used as starting material, the RE-rich 123 phase may preferentially be formed even in a reduced oxygen atmosphere, resulting in relatively low $T_c$.

Fig. 7 shows $J_c$–$B$ curves for (Nd,Sm)–Ba–Cu–O, (Sm,Eu)–Ba–Cu–O and (Sm,Gd)–Ba–Cu–O composites OCMG-processed in 0.1% O₂ + 99.9% Ar. The peak effects commonly observed in single

Fig. 7. $J_c$–$B$ curves for (RE,RE') composite samples OCMG-processed in a 0.1% O₂ + 99.9% Ar atmosphere.
rare earth element–Ba–Cu–O are also observed in all the samples. We believe that the source of the peak effect is identical and RE-rich 123 clusters are responsible for the peak effect. Here, it should be noted that the peak field is also different depending on the kind of RE, such that the peak field is higher with a smaller average ionic radius, which may allow us to control the desired peak field by changing the ratio of the RE mixture.

4. Conclusions

We have studied the superconducting properties of (RE,RE′)–Ba–Cu–O composite bulks. It was found that the $T_m$ of the (RE,RE′)Ba–Cu–O composite increased with increasing the average ionic radius of the (RE,RE′), which shows that $T_m$ is controllable simply by changing the kind and the ratio of rare earth elements.

It was also found that the $T_m$ decreased in a reduced oxygen atmosphere. In addition, the $T_m$ decreased by about 30°C in a 1% $O_2$ + 99% Ar atmosphere and decreased by 60°C in a 0.1% $O_2$ + 99.9% Ar atmosphere compared to that measured in air.

Microstructural observations and compositional analyses revealed that the 123 matrix of the (RE,RE′)–Ba–Cu–O composite is homogeneous and the ratio of RE:RE′ is almost the same with that of the nominal compositions. In contrast, some of the second phases were not homogeneous, which can be explained by the fact that two kinds of RE211 (or RE422) are present in the partial melting regions.

Like OCMG-processed Nd123, (RE,RE′)-Ba$_2$Cu$_3$O$_y$ composite bulks exhibit high $T_c$ with a sharp transition and show the peak effects in $M$–$H$ loops, indicating that the source of pinning are RE-rich 123 clusters like single RE element–Ba–Cu–O superconductors.

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