Study of light nonstoichiometry in Eu-Ba-Cu-O systems

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Abstract. We studied effects of light Eu-Ba nonstoichiometry in Eu-Ba-Cu-O superconducting compounds on their transition, structural, and magnetic properties. Two series of Eu1+xBa2-xCu3O7+δ and Eu1-xBa2+xCu3O7+δ samples with \( x = 0, 0.01, 0.02, 0.04, 0.05, 0.07 \) and 0.1 were synthesized by the solid-state reaction method from Eu2O3, BaCO3 and CuO precursors and sintered at 1050 °C for 72 h in flowing oxygen. Structural, transition, and magnetic properties were investigated by means of X-ray diffraction, resistance, mutual inductance, magnetization and optical measurement methods. The Eu-Ba nonstoichiometry in the two series results in different effects on transport, magnetization, grain, intergrain and microstructure properties of the samples in relation to the substitution level of \( x \). All the samples show the values of critical temperature \( T_c \), volume density \( \rho \), and maximum volume magnetization \( M_{\text{max}} \) higher than 91 K, 6.4 g cm\(^{-3}\) and 10\(^4\) Am\(^{-1}\), respectively.

1. Introduction

Up to now, it seems that RE-123 systems are the only candidate materials for high-field power applications at high temperatures, especially advantageous for the synthesis of superconducting bulks. The systems, where RE represents the so-called light rare-earth elements (LRE) like La, Nd, Sm, Eu, are particularly interesting. It is well-known that in the LRE-123 systems, the LRE\(^{3+}\) ions can occupy the Ba\(^{2+}\) sites because the ion radius of the elements is nearest to the ion radius of Ba ion. It was reported that the increasing occupation of Ba\(^{2+}\) sites resulted in a sharp deterioration of some superconducting properties, e.g., critical transition temperature \( T_c \) mainly at high RE-Ba substitution levels \([1, 2]\). It was also observed that the LRE-Ba substitution led to local composition fluctuations, known as nanostripes that had a size ranging from several to several tens of nanometres \([3, 4]\). For example, Wu Ting. et al. \([3]\) reported that the bright regions observed in Nd-123 single crystals by STM were more conductive than that of the stoichiometric Nd123 matrix, and that it was possible that these regions corresponded to the regions, where Ba was replaced by Nd. In addition, they reported that the more conductive regions could act as new magnetic flux pinning centres. So, it is interesting to study nonstoichiometric LREBa2Cu3O7+δ systems, namely in the range of light substitution levels. All the more, the systematic study of the systems has not been performed yet and their properties are strongly dependent on technological procedure parameters.

In this paper, we presented results of a study of light Eu-Ba nonstoichiometry in two series of samples of a nominal composition of Eu1+xBa2-xCu3O7+δ (A) and Eu1-xBa2+xCu3O7+δ (B), respectively.
2. Experimental

Samples of A and B series, where $x = 0, 0.01, 0.02, 0.04, 0.05, 0.07$ and 0.1 were prepared by a standard solid-state reaction method from Eu$_2$O$_3$, BaCO$_3$ and CuO precursors. The mixture in appropriate weight amounts was homogenized in an agate mortar and calcined in air at 930°C for 40 h. The obtained precursors were again homogenized, pressed into pellets (with the diameter of 12 mm and mass of 1.28 g), and sintered in a horizontal tube furnace in flowing oxygen (10 ml/min) at 1050°C for 72 h; then cooled to 580°C and held at this temperature for 24 h, and thereafter cooled in the furnace to room temperature. For every group, parallel samples were prepared in the same thermal cycle for every value of $x$. The critical temperature $T_c(R = 0)$ of the samples was determined by a standard resistance four-point method and the transition width $\Delta T_c$ was characterized by the 10-90% criterion. The distance of the voltage contact points of all samples was approximately the same. The temperature measurement uncertainty was less than 0.1 K. In addition, transition dependences of the induced voltage vs temperature were measured using contactless mutual inductance method [5]. The phase composition was studied by X-ray diffraction measurements (CuKα radiation) from powdered samples. Microstructure was studied by optical polarization microscopy. AC and virgin volume magnetization characteristics were measured by a compensation method using the second-order SQUID gradiometer [6]. All magnetization characteristics of the samples were measured at ~77 K after zero-field cooling. The applied magnetic field $H_0$ was parallel to the axis of the sample. The demagnetising factor was determined from the geometry of the sample. The first penetration magnetic field $H_{pl}$ characterising the intergran weak link network, and the magnetic susceptibility $\chi$ were determined from the linear behaviour of the virgin magnetization curves in the region of the full Meissner shielding of the entire sample.

2. Results and discussion

The resistance $R$ vs. temperature $T$ dependences of A and B samples are shown in Figures 1 and 2, respectively. All the samples show the linear temperature dependence of $R$ in a broad temperature range. The A samples with excess Eu show a trend of a decrease in the normal state resistance at the lower $x$ followed by an increase in the resistance for higher $x$.

[Figure 1. $R$ vs. $T$ dependences of A samples.]

[Figure 2. $R$ vs. $T$ dependences of B samples.]

This is consistent with the observed increase in the oxygen content, if LRE$^{3+}$ ions substitute Ba$^{2+}$ ions [7]. With respect to a small change in $T_c$, it is probable that additional oxygen enter into the plane of the chains for low values of $x$. We deduce that local structure disordering effects start to dominate at higher substitution levels of $x$. They could cause also an increase in the resistance and decrease in the magnetization of samples. Series of B-samples with Ba excess show a rather opposite trend of an increase in $R$ with $x$. The values of $T_c$ and $\Delta T_c$, corresponding to the relevant substitution nominal level of $x$ of A and B samples, are shown in Figures 3 and 4, respectively.
The trends of a significant decrease in $T_c$ and increase in $\Delta T_c$ with increasing $x$ were seen for A samples beyond the initial increase in $T_c$ for $0.1 \leq x \leq 0.04$. For B samples, similar trends were also observed. However, $T_c$ of all the samples was still higher than 91 K, even for the substitution level of $x = 0.1$.

From powder X-ray diffraction data, it can be concluded that single-phase samples were obtained for all samples in A and B groups, as shown in Figure 4 for some samples from A and B series. It was impossible to identify any impurity phase within the limit of the resolution.

The hysteresis curves of the volume magnetization $M$ vs. applied field $H_0$ for A samples and B samples are shown in Figures 6 and 7, respectively. A part of the increasing amplitude of $H_0$ was omitted in these figures. All the samples show the Z-shape magnetization curves typical for polycrystalline samples. The $M$ vs. $H_0$ hysteresis loops of A samples with Eu excess show a tendency of a significant decrease in $M$, starting from $x \geq 0.05-0.07$, shown in Figure 6. In addition, the increasing magnetization hysteresis of A samples in the range of higher $H_0$ fields (significant grain magnetization or grain clusters) can be observed up to $x = 0.04-0.05$. It corresponds to a growth of the
value of the grain- and/or cluster grain critical current density $j_{c}^{g}$. The magnetization $M$ vs. $H_{0}$ loops of the B samples with excess Ba are shown in Figure 7.

They show no significant trend with a change in $x$ as well as their maximum values of the magnetization hysteresis loops ($M_{\text{max}}$), corresponding to the so-called low field (central) peak, shown in Figure 8, unlike A samples.
concentrations of $x = 0.0$ (on the left) and $x = 0.05$ (on the right). Excess Eu has some positive effect on intergrain properties for lower substitution level of $x$. There is a trend of increasing the penetration magnetic field $H_{pl}$ with $x$ from zero to $x = 0.04-0.05$ followed by a significant decrease. The penetration magnetic field $H_{pl}$ grows from the value of 600 Am$^{-1}$ for $x = 0$ to the value of 1200 Am$^{-1}$ at $x = 0.5$. Samples with an excess in Ba show a weak, if any, opposite trend of a decrease in $H_{pl}$ in the whole $x$ range, see Figure 9.

The above-stated results are in line with the optical polarization microscopy results shown in Figures 10 and 11. The trend of a grain size growth was observed for A samples in the substitution range of $x$ from zero to 0.04-0.05, which also corresponds to the $H_{pl}$ growth, whereas for the B samples, their grain size quite significantly decreases in line with their $H_{pl}$.

Figure 11. Optical polarization micrographs of Eu$_{1-x}$Ba$_{2+x}$Cu$_3$O$_{7+δ}$ (on the left) and Eu$_{1-x}$Ba$_{2+x}$Cu$_3$O$_{7+δ}$ (on the right) samples with the same nominal concentration of $x = 0.1$.

3. Conclusions

We studied effects of nonstoichiometry in Eu$_{1-x}$Ba$_{2+x}$Cu$_3$O$_{7+δ}$ (A) and Eu$_{1-x}$Ba$_{2+x}$Cu$_3$O$_{7+δ}$ (B) of the systems in the substitution range of $0 \leq x \leq 0.1$. The single-phase polycrystalline samples were sintered at 1050 °C for 72 h in flowing oxygen. The initial increasing nominal substitution level up to $x = 0.04-0.05$ results in an improvement of intergrain properties such as $T_c$, $H_{pl}$, and grain critical current density $j_c$ in the A-system. A further growth of $x$ causes their degradation. Values of $T_c$, $H_{pl}$, and $j_c$ decrease as well as volume magnetization $M$.

In the B-system, an increase in the Ba excess content results in the trend of a degradation of intergrain properties, decrease in $T_c$, $H_{pl}$ values with $x$, and grain sizes, however, $H_{pl}$ values do not change so significantly as in A-samples. The same applies also to magnetization $M$ in the B system, despite a significant grain disintegration effect of the Ba excess. In the whole substitution range in both systems, values of critical temperature $T_c(R=0) > 91$ K and the corresponding values of characteristic temperature $T_{c}^{\text{ln}}$ determined by the inductance method were, for samples with an excessive Eu content, within the interval from 92 to 93.5 K and for systems with an excessive Ba content, within the interval from 93 to 93.7 K.

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