Effects of Europium–Barium Nonstoichiometry in EBCO123 Systems on Transition and Magnetization Properties

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We studied the effects of Eu–Ba nonstoichiometry in two series of $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ and $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ samples on transition, structural, and magnetic properties. The samples with the nominal composition of $0 \leq x \leq 0.07$ were synthesized by the solid-state reaction method from Eu_2O_3, $BaCO_3$, and CuO precursors and sintered at $1050°C$ for 72 h in flowing oxygen. All the samples show the values of critical temperature T_c, volume density ρ, and maximum volume magnetization M_{max} higher than 90 K, 6.3 g cm^{-3} and 10^4 Am^{-1}, respectively, except for $x = 0.07$ samples. The Eu–Ba nonstoichiometry in the two series shows different effects on transport, magnetization hystereses, and intergrain properties of the samples.

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1. Introduction

High-T_c $LREBa_2Cu_3O_{7-\delta}$ superconductors, where LRE is a light rare element such as Nd, Eu, Sm, are known to exhibit higher T_c, critical current density j_c, and irreversibility field than $YBa_2Cu_3O_{7-\delta}$. However, while the last system is stoichiometric, in the former systems, $LRE_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ solid solutions can be formed. In this systems, LRE-Ba substitution can take place due to a small difference in the ionic radius between LRE^{3+} and Ba^{2+} ions. The increasing occupation of Ba^{2+} sites by LRE^{3+} ions results in a sharp deterioration of some superconducting properties, e.g., T_c, j_c at higher LRE-Ba substitution levels. Nevertheless, the LRE-Ba substitution leads also to local composition fluctuations, which can play a positive role in formation of the so-called ∂T-pinning centres of magnetic field, increasing j_c [1]. On the other hand, an addition of Ba-containing precursors is one of the ways of preventing the LRE-Ba substitution [2]. For the

above reasons, it is interesting to study nonstoichiometric $LRE_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ systems.

In addition, a systematic study of the systems has not been performed yet and their properties are strongly dependent on parameters of technological procedures.

In this paper, we present results of a systematic study of Eu–Ba nonstoichiometry in two series of samples, one series $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$, and another one $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$, where $0 \leq x \leq 0.07$.

2. Experimental

Samples with nominal composition $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ and $Eu_{1-x}Ba_{2+x}$-$Cu_3O_{7-\delta}$, where $0 \leq x \leq 0.07$, have been prepared by a standard solid-state reaction method from Eu_2O_3, $BaCO_3$, and CuO precursors. The mixture in appropriate weight amounts has been homogenized in an agate mortar and calcined in air at $930°C$ for 40 h. The obtained precursors have again been homogenized in the agate mortar, pressed into pellets (with the diameter of 12 mm) under the pressure of 200 MPa and sintered 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 a furnace to the room temperature. The mass of sintered samples was about 1.28 g. The critical temperature $T_c(R=0)$ of the samples was determined by a standard resistance four-point method and the transition width ΔT_c, was characterized by the 10–90% criterion. The phase composition was studied by X-ray diffraction measurements (CuK_α radiation) from powdered samples. AC volume magnetization characteristics were measured in detail by a compensation method using a second-order SQUID gradiometer [3]. All magnetization characteristics were measured at 77.3 K after the zero-field cooling in applied magnetization field H_a with the frequency of 0.1 Hz and amplitude ranging from 10^{-1} to 10^5 Am^{-1}. H_a was parallel to the axis of the sample. The demagnetizing factor was determined from the geometry of the sample. The first penetration magnetic field H_{pl} of the intergrain weak link network and the magnetic susceptibility χ were determined from the first deviation from the linear behaviour of the virgin magnetization curves.

3. Results and discussion

The resistance R vs. temperature T dependences of the $Eu_{1+x}Ba_{2-x}$-$Cu_3O_{7-\delta}$, and $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ samples with $x = 0.0$, 0.01, 0.04 0.05, and 0.07 are shown in Fig. 1a and b, respectively. All the samples show the linear temperature dependence of R in a broad temperature range, except for the Ba-rich sample ($x = 0.07$). The values of T_c and ΔT_c are in the intervals of 91.4–93.4 K and 1.6–1.2 K, respectively for the $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples and 90.2–92.4 K and 1.6–1.2 K, respectively for $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ samples, except for the sample with $x = 0.07$ with T_c and ΔT_c of 87.5 K and 1.9 K, respectively.

For the systems with excess Eu and Ba, there are evident opposed trends of a decrease resp. increase in the zero temperature resistance R_0 extrapolated from the linear part of $R(T)$ dependence and normal resistances (Fig. 1) with a growth of x. From powder X-ray diffraction data, it can be concluded that single phased samples were obtained for all x values in $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ compounds. This applies also to $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples. However, an impurity phase was detected from $x = 0.05$, which was quite unexpected since the forming of a solid solution in air in the system was reported up to $x \sim 0.4$ [4]. In the near future, we want to verify or identify the presence of the impurity phase in repeated syntheses.
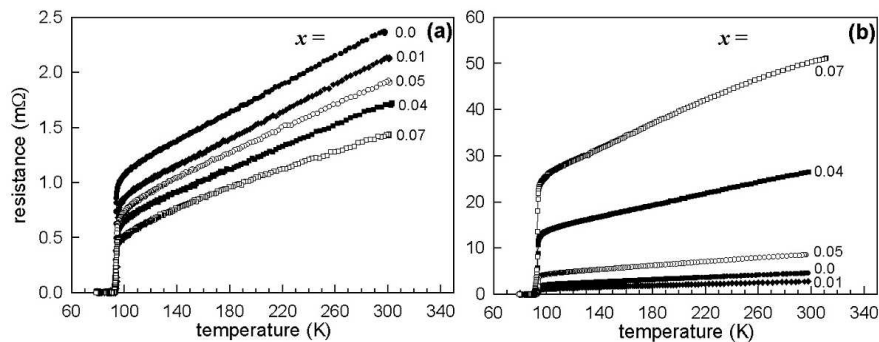

Fig. 1. R vs. T dependences of $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (a) and $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ (b), samples with $x = 0$, 0.01, 0.04, 0.05, and 0.07.

The hystereses curves M vs. H_a of samples with the nominal composition of $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ and $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ for $x = 0$, 0.05, and 0.07 are shown in Fig. 2a and b, respectively, for given amplitude of H_a. All the samples show the Z-shape magnetization curves typical of polycrystalline samples. $M-H$ curves are approximately the same and M_{max} is higher than 10^4 Am^{-1}, except for the Eu-rich sample with $x = 0.07$, which shows an already significantly lower value. On the other hand, magnetization hystereses of the $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples increase with x up to $x \leq 0.5$; see also Fig. 2a. The increasing magnetization hysteresis supports a growth of values of the grain- and intergrain j_c. The former could be related to the creation of new pinning centres by the composition fluctuations for lower x and/or forming of the impurity phase for $x \geq 0.05$. Adding an excess Eu has also a positive effect on intergrain properties. There is a trend of increasing the penetration field H_{pl} from 450 Am^{-1} to 1110 Am^{-1} with x from zero to $x = 0.05$. Samples with excess of Ba show an opposite trend of a decrease in H_{pl} from 580 Am^{-1} to 120 Am^{-1}. Results of optical polarization microscopy show no significant effect of Eu doping on the microstructure of $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples. On the contrary, an increasing Ba-content leads to a structure disintegration and an increase in small-sized grains.

Generally, it seems that excess Eu leads to a structural ordering, e.g., the filling-up vacancies in the Cu-O chains using excess oxygen [5], better homogeneity, and tight distribution of intergrain links contrary to Ba-excess samples.
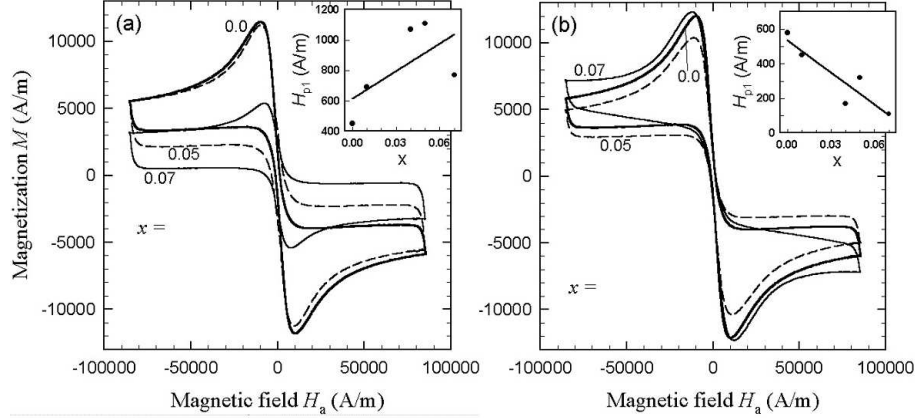

Fig. 2. M vs. H_a dependences of $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (a) and $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ (b) for the samples with $x = 0$, 0.05, and 0.07.

4. Conclusions

We studied the effects of nonstoichiometry in $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ and $Eu_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ systems, $0 \leq x \leq 0.07$. Increasing x leads to different behaviours in the two systems. In the former system, evident trends of a decrease in the extrapolated resistance R_0, improvement of normal resistances, and intergrain properties, (e.g., H_{p1}) are observed with x up to $x = 0.05$, and vice versa in the last system, while T_c is still above 90 K.

Acknowledgements

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