Transport and Low Field Magnetic Properties of $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ Superconductors with Gadolinium Excess

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Abstract. *A series of single-phase samples of $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ with slight gadolinium excess x from the stoichiometric value of 0 to 0.1 were synthesized by the solid-state reaction method and their structural, transition, and magnetic properties were studied. The samples with $x \leq 0.01$ show critical temperature T_c above 93 K. DC and AC magnetization measurements confirm the control role of the gadolinium overdoping in Gd-Ba-Cu-O compounds to tailoring temperature and magnetic field application parameters as critical current density.*

Keywords: High-T_c Superconductor, $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$, Nonstoichiometry, Critical Temperature, Mass Magnetization, Paramagnetic

1. Introduction

High temperature oxide superconductors, namely of the RE-123 type, are promising materials for high-field power applications at high temperatures. The systems, where RE is represented by so-called light rare-earth element (LRE) like La, Nd, Sm, Eu or Gd, 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 deterioration of superconducting properties, e.g. critical transition temperature, T_c, mainly at high LRE-Ba substitution levels [1-2]. On other hand, for the melt-textured samples or single crystals, local composition fluctuations were observed, known as nanostrips or nanoclusters, consisting of the $LRE_{1+x}Ba_{2-x}Cu_3O_y$ phase. The 10-50 nm dimension nanoclusters may work as highly effective pinning centers at higher magnetic fields [3-4].

H. Shimizu at al. [5] investigated $Gd(Ba_{2-x}Gd_x)Cu_3O_{6+\delta}$ polycrystalline samples for x from 0.00 to 0.25 and refer decreasing T_c and the orthorhombicity with increasing the Gd concentration, marked for $x > 0.1$ K. Miyachi et al. [6] investigated the $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ thin film prepared by PLD using the targets with changing the composition x from 0 to 0.4.The highest T_c of 91.5 K and critical current density j_c at 77 K were measured for $x = 0.04$. C. Xu et al. [2] studied a series of compounds of melt textured samples of $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ with x ranging from -0.1 to 0.2. They show that solubility was limited to 0 - 0.1 and onset T_c decreases with increasing x.

In our former works [7, 8], we studied nonstoichiometric bulk sintered $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$, and $Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ compounds with x from 0 to 0.1. In this work we prepared a series of slight non-stoichiometric bulk samples of $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ and investigated composition deviation effects on their structural, superconducting and magnetic properties.

2. Subject and Methods

The $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples, where nominal x = 0, 0.01, 0.02, 0.04, 0.05, 0.07 and 0.1, were prepared by a standard solid-state reaction method using commercial 99.99 % purity oxide powders of Gd_2O_3, CuO, and $BaCO_3$. Prior to weighing and mixing, the Gd_2O_3, CuO, $BaCO_3$ powder was pre-annealed at 950 °C for 8 h in air to release contaminations, e.g., moisture. Thereafter, the powders were carefully weighed in appropriate weight amounts, homogenized in acetone in an agate mortar for five minutes, put into alumina crucibles and calcined at 950 °C for 40 hours in air. The precursors were then homogenized, pressed into pellets (with the diameter of 12 mm) and sintered in a horizontal tube furnace in flowing oxygen 20 ml/min) at about 1000 °C for 72 h, cooled to 450 °C and held at this temperature for 24 h, and thereafter cooled in the furnace to room temperature. The critical temperature, $T_c(R = 0)$ was determined by a standard resistance four-point method and the transition width ΔT_c was characterized by the 10-90 % criterion. The uncertainty of temperature measurements was less than 0.2 K. The phase composition was studied by X-ray diffraction measurements (CuKα radiation). AC (0.1 Hz) low field magnetization at 77 K was measured by a compensation method using the second-order SQUID gradiometer [9] and DC magnetization at the higher field and lower temperature by Quantum Design SQUID magnetometer MPMS XL-7.

3. Results

From X-ray diffraction data, it can be concluded that all samples of series are single-phase. It was impossible to identify any impurity phase within the limit of the resolution. The XRD patterns of some samples of $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ series are shown in Fig. 1.

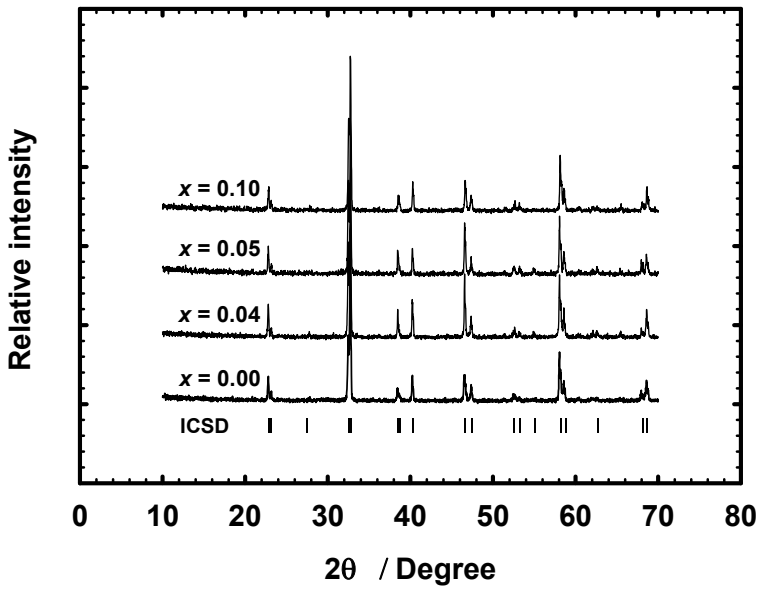

Fig. 1. Comparison of the powder X-ray diffraction patterns of four sample series $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ for shown x and position of main peaks of $Gd_1Ba_2Cu_3O_{6.99}$ of ICSD #78456.

Changes of T_c and ΔT_c of the samples vs. x are shown in Fig. 2 and Fig. 3, respectively. The values of T_c and ΔT_c of the samples change slightly except for that with x = 0.1. The results are consistent with corresponding results in [1].

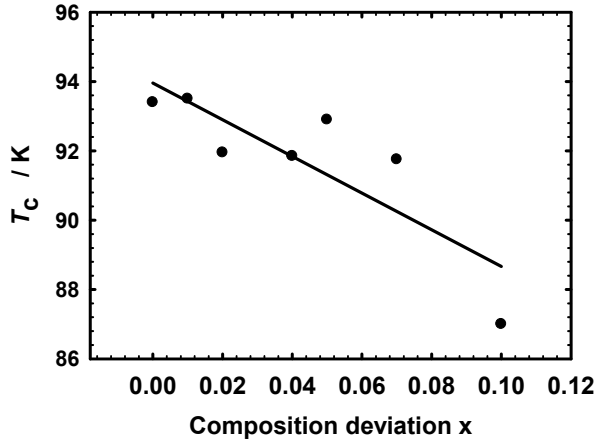

Fig. 2. T_c vs. x of the $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$.

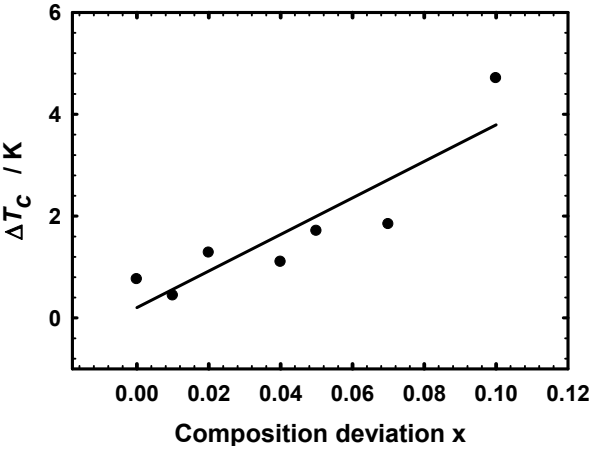

Fig. 3. ΔT_c vs. x of the $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$.

We think that local structure disordering effects start to dominate at higher composition deviations of x as a result of the Gd substitution for Ba. It is in accordance with the model proposed by M. J. Kramer et al. and J. Chen et al. [10, 11], according to which the increase of the Gd content of x results in an increase of the total oxygen content and a decrease in the hole concentration in Cu-O_2 planes by donate electrons of the substitution of Gd^{3+} entering Ba^{2+} sites. The effects together determine the superconducting properties of samples, e.g. T_c, ΔT_c and their degradation for higher levels of x.

Mass magnetization hysteresis curves of M vs. H of samples at 77 and 20 K are shown in Figs. 4 and 5, respectively.

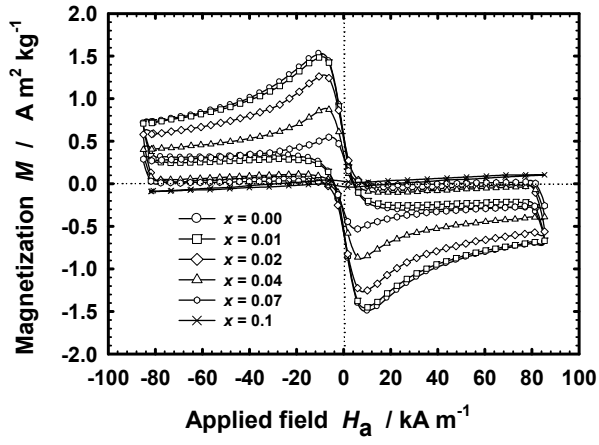

Fig. 4. M vs. H_a dependences of $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ at 77 K.

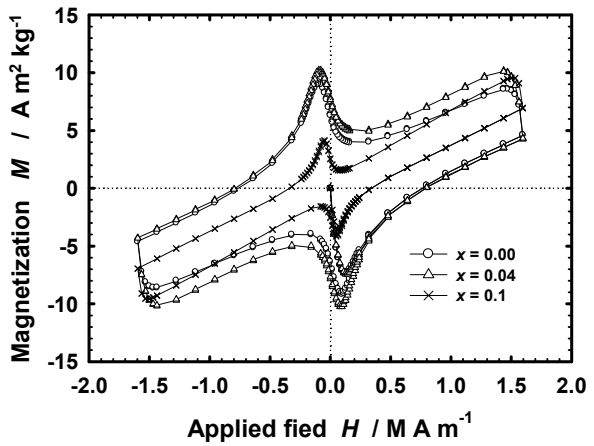

Fig. 5. The same as in Fig. 4 at 20 K.

The AC magnetization $M(H)$ curves at the low field to ~85 kA m^{-1}for the x = 0, 0.01, 0.02, 0.04, 0.07 and 0.1 (Fig. 4) show superconducting hysteresis field dependences (diamagnetic, sitting in the second and forth quadrants). The increase of the Gd content results in a decrease in magnetization except for similar curves with x = 0.01 - 0.02 with the best one, where x = 0.01. All the samples show the Z-shaped magnetization curves typical for polycrystalline samples except for that with x = 0.1. The curve with the highest Gd content shows paramagnetic behavior (sitting in the first and third quadrants).The situation is different if the effect of magnetic moment of Gd^{3+} ions is increased. It can be done by increasing temperature (considering the Curie–Weiss law) or by applied field. The result is shown in Fig. 5 where the DC mass magnetization curves with x = 0.00, 0.04 and 0.1 are shown at 20 K and at H ~ 1.59 MA m^{-1}.The curves include a superconducting component (diamagnetic behaviors at

low field and hysteresis) and paramagnetic one - slope of the curves points to the first and third quadrants. In this case, the best superconducting properties belong to composition deviation $x = 0.04$.

We believe that slight Gd/Ba non-stoichiometry x supports composition fluctuations (like nanoclusters in grains) and thus magnetic flux pinning is increased. On the other hand, the entering of Gd into Ba sites results in a certain degradation of superconductivity, e.g. T_c and ΔT_c, however at higher substitution levels. These two effects compete to each other. We note that similar results were reported for non-stoichiometric thin films too. K Miyachi et al. [6] investigated an effect of the substitution of Gd into the Ba site in $Gd_{1+x}Ba_{2-x}Cu_3O_{6+\delta}$ thin film samples ($0 \leq x \leq 0.4$). The highest values of $T_c = 91.5$ K and $j_c = 3$ MAcm^{-2} were observed for $x = 0.04$. Of course, our results have to be verified on monodomain or single crystal samples.

4. Conclusions

We studied slight Gd excess doping effects in a series of single-phase $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples with a composition deviation x from 0 to 0.1. The samples were synthesized by the solid-state reaction method at ~ 1000 °C for 72 h in flowing oxygen. The samples, up to $x \leq 0.07$, show values of $T_c > 91$ K and still $\Delta T_c \leq 1.8$, whereas the slight excess Gd doping x can be used for tailoring critical current density with respect to temperature and magnetic field application range.

Acknowledgements

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