Barium Overdoped $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ Superconductors – Transport and Low Field Magnetic Properties

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Abstract. *We studied effects of slight Ba overdoped in $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ superconducting compounds on their transition, structural, and magnetic properties. A series of samples of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ with Gd/Ba composition deviation x from stoichiometric value from 0 to 0.1 were synthesized by the solid-state reaction method. All the samples in the studied composition range show the critical temperature T_c and the transition width ΔT_c around 93 K and 1 K, respectively. AC magnetization measurements confirm a slight deterioration magnetization and magnetization hysteresis at low magnetic field and 77 K from x= 0.01 to 0.1. Magnetization measurements at 20 K and higher field show a stabilization effect of Ba excess to magnetic flux pinning properties for $x \geq 0.04$, however, there is an evidently worse magnetization hysteresis compared to the stoichiometric sample.*

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

1. Introduction

In LRE-123 family superconductors with a light element (LRE) like La, Nd, Eu or Gd, with the ionic radius close to Ba, the solid solutions with the LRE-Ba substitution can be formed. This usually leads to a reduction of the superconducting properties, e.g., critical transition temperature T_c mainly at high LRE-Ba substitution levels [1-3]. To avoid this, the synthesis method in the atmosphere with a decreased or controlled oxygen content is usually used, and/or an addition of Ba-excess (in the form of precursors such as BaO, BaO_2, $BaCuO_x$, or Ba-rich phase as $GdBa_6Cu_3O_y$, etc.) to effectively suppress the substitution and therefore the formation of solid solutions of the $LRE_{1+x}Ba_{2-x}Cu_3O_y$ type [4]. In the last case of the Gd, it was observed that superconducting properties of the single grain bulk Gd-123 were not degraded even when they were fabricated in air, however, Ba excess compositions were used [5]. However, for nonstoichiometry Gd-123 thin film, opposite results were also observed. T. Kakeshitaet et al. [6] reported the worst superconducting properties (T_c, j_c) for Ba-rich thin films. Moreover, it is seen that Ba excess results in a different effect on critical temperature T_c and critical current density j_c. In addition, no systematic study of the systems has been performed yet and it must be noted that the compound properties are strongly dependent on technological processing parameters. In our former works [7, 8], we studied light non-stoichiometric bulk sintered samples of the Eu-123 and Sm-123 composition. In this work, we prepared a series of light non-stoichiometric bulk samples of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ and investigated composition deviation x effects on their superconducting, structural, and mainly magnetic properties.

2. Subject and Methods

Samples of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ with the nominal composition deflection 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 obtained precursors were again homogenized, pressed into pellets (with the diameter of 12 mm) and sintered in a horizontal tube furnace in flowing oxygen of 20 ml/min) at about 1000 °C for 72 h, then cooled to 450 °C and held at this temperature for 24 h and thereafter cooled in the furnace to room temperature. The series of samples were prepared in the same thermal cycle. $T_c(R=0)$ was determined by a standard resistance four-point method and the transition width, ΔT_c, was characterized by the 10-90 % criterion. The inaccuracy of temperature measurements was less than 0.2 K. The phase composition was studied by X-ray diffraction measurements (CuKα radiation). AC low field magnetization at 77 K was measured by a compensation method using the second-order SQUID gradiometer [9] and DC magnetization at higher field and lower temperature by the Quantum Design SQUID magnetometer MPMS XL-7.

3. Results and Discussion

From X-ray diffraction data, it can be concluded that the samples are single-phase, however, for higher contents of Ba some new peaks for 2θ in the range of 28°-29° could be ascribed to the excess Ba-Cu-O phase. The XRD patterns of some samples of $Gd_{1-x}Ba_{2+x}Cu_3O_y$ series are shown in Fig. 1.
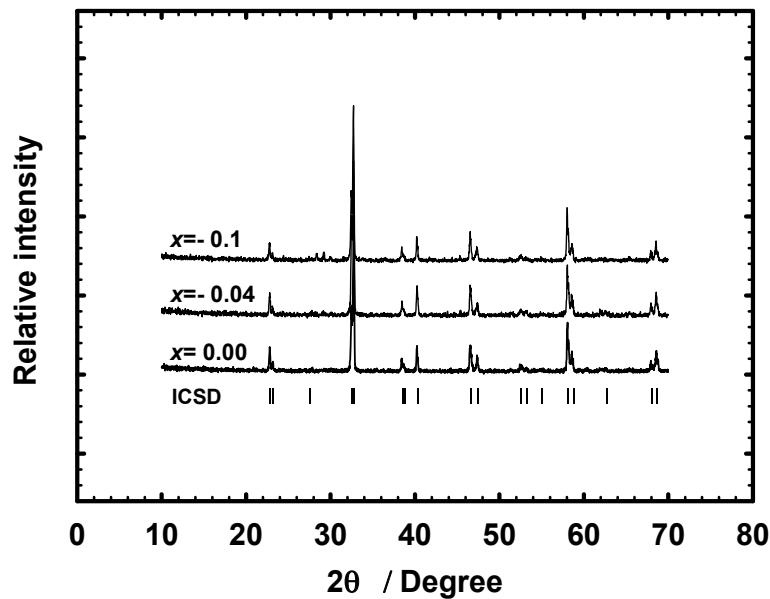

Fig. 1. XRD patterns of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ samples with shown x values.

Dependences of T_c and ΔT_c vs. x are shown in Fig. 3 and Fig. 4, respectively. As awaited, they confirm a positive effect of the barium excess on T_c and ΔT_c as a consequence of depressing of Gd entering into the Ba position. T_c and ΔT_c change slightly only. However, there is a weak trend of worsening both T_c and ΔT_c with an increasing x, whereas the values of T_c are still mostly about 93 K and ΔT_c about 1 K.
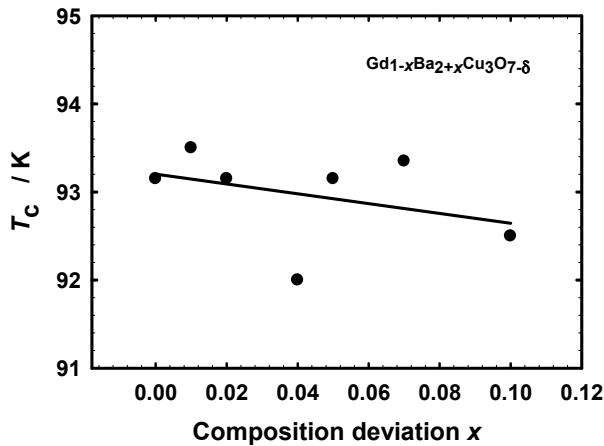
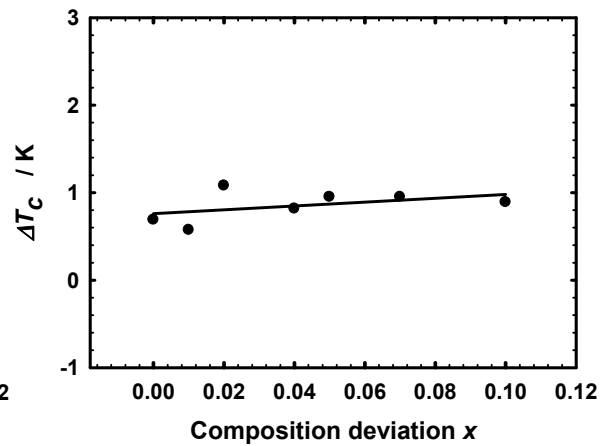Fig. 2. T_c vs. x for $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$.

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

Hysteresis curves of mass magnetization M vs. applied field H for a series of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ samples at 77 K and low applied field are shown in Fig. 4, for samples with $x = 0, 0.04, 0.05$ and 0.1 at 20 K and at higher field in Fig. 5.
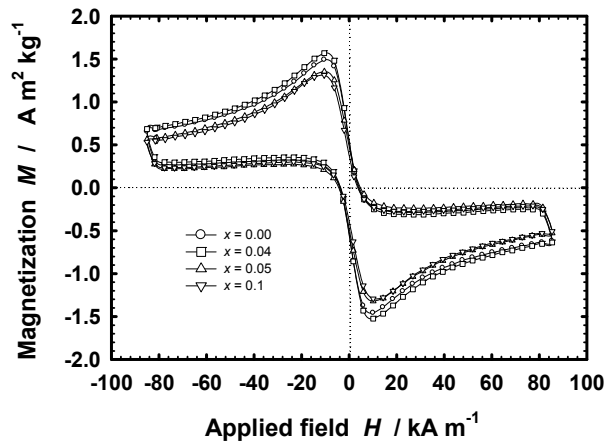

Fig. 4. M vs. H dependences of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ at 77 K.
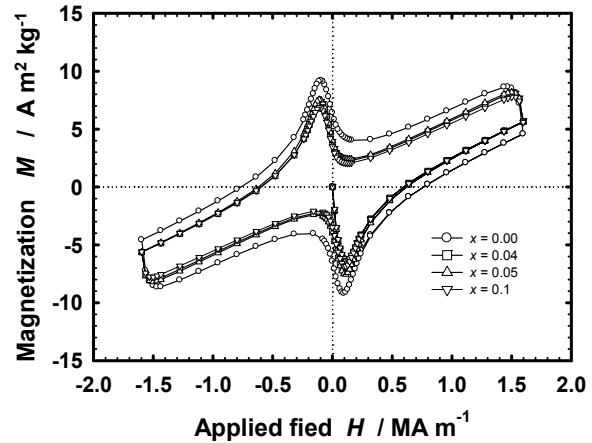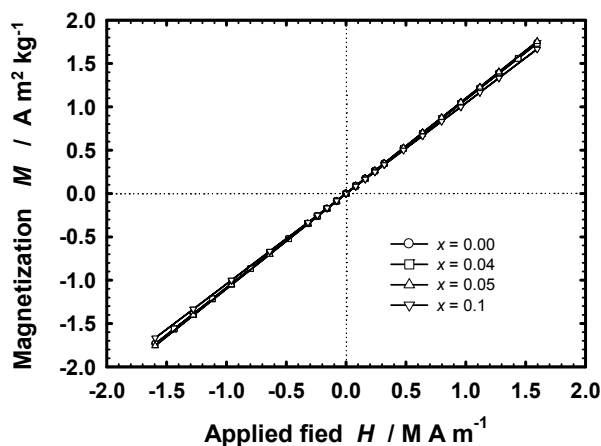

Fig. 5. The same as in Fig. 4 at 20 K.

Fig. 6. M vs. H dependences of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ at 100 K.

All the samples at 77 K show Z-shaped magnetization curves typical for polycrystalline samples at a weak applied field. We can see that magnetization curves are approximately the same. The best hysteresis properties and thus critical current density belong to the samples with the 0.01 Ba excess. The next hysteresis slowly continues to decrease with x. When

compared with this at 20 K, the form of magnetization curves is diametrically different. The curves involved a superconducting component (diamagnetic slope at low field and hysteresis) and paramagnetic contribution - slope of the curves point to the first and third quadrants. The presence of the paramagnetic component is clearly displayed at a temperature higher than critical temperature. Fig. 6 shows dependences of mass magnetization on the applied field at 100 K, where the superconducting component is absent. It is accepted that magnetic properties in the Gd-123 superconductors are mainly determined by magnetic moment of Gd cations. A weak decrease in magnetization for the sample with the lowest value of Gd content ($x = 0.1$) is in line with this. However, it is presently still questionable, whether or how the magnetic ordering RE cations affect superconductivity in the RE-123 type superconductors [10].

4. Conclusions

We studied transport and magnetization properties in a series of $Gd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ 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 obtained results supported a positive effect of slight Ba excess doping on stabilization of T_c and ΔT_c and magnetization hysteresis at low field and 77 K. T_c and ΔT_c of the samples is about 93 K and 1 K, respectively. We can see that magnetization hysteresis at 77 K and low field is approximately the same. The best hysteresis properties and thus critical current density belong to the samples with the 0.01 Ba excess. In addition, magnetization hysteresis measurements at a higher field and lower temperature indicate that the slight excess Ba doping x can be used for tailoring critical current density with respect to the temperature and magnetic field application range, namely, e.g. the second peak effect.

Acknowledgements

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