Structural and Magnetization Properties of Ce doped YBa$_2$Cu$_3$O$_{7-\delta}$

[1]J. Polovková, [1]A. Cigáň, [2]T. Eslanloo Pereira,
[1]J. Maňka, [1]P. Jurdák, [1]M. Kopčok

[1]Institute of Measurement Science, Slovak Academy of Sciences,
Dúbravská cesta 9, 841 04 Bratislava, Slovakia
[2]École Polytechnique Fédérale de Lausanne, Station 16,
CH – 1015, Lausanne, Switzerland
Email: julia.polovkova@savba.sk

Abstract. *YBCO polycrystalline samples doped with CeO$_2$ up to the level of 0.25 wt% have been prepared by the solid-state reaction method at the sintering temperature of 1007 °C in flowing oxygen. The critical temperature and transition width values slightly decrease with the increasing level of doping. Results from XRD patterns indicate that if cerium enters into the YBCO phase, its solubility limit is lower than 3.76 at % (x= 1.0 wt % of CeO$_2$). Starting from the CeO$_2$ level, the Y211 and BaCeO$_3$ phases could be identified. The addition of cerium leads to an increase of the magnetization and magnetization hysteresis and therefore to an increase of the critical current density for lower doping levels.*

Keywords: High-temperature Superconductors, YBa$_2$Cu$_3$O$_{7\pm\delta}$, Cerium Oxide, Resistance, XRD, Magnetization

1. Introduction

Although cerium belongs to rare earth elements, similarly as praseodymium, it does not form the REBa$_2$Cu$_3$O$_{7-\delta}$ superconducting phase, like other elements from this group [1]. On the other hand, cerium oxide together with the 211 phase is often used at the preparation of large mono-domains of YBa$_2$Cu$_3$O$_{7-\delta}$ in order to improve their superconducting properties [2]. While the Y211 phase inclusions have been found to act as the pinning centres and thus to increase critical current densities generally, the role of cerium oxide is to refine these inclusions in textured material. Cerium oxide is usually added at 0.5 - 1.0 wt% levels. As it was found, such amount of CeO$_2$ could slightly influence the critical transition temperature T_c and transition width ΔT_c of textured samples. Previously, it has been reported too, that additions of Ce and other combinations with Ce, as Pt or Sn, have different effects on the critical current densities j_c [3]. In this respect, the pinning by the BaCeO$_3$ inclusions has been proposed to have a main influence on intergrain j_c. The studied objects in most of the works represented melt-textured samples prepared from Y123 and Y211 phases and cerium oxide. In our study, we have investigated YBCO samples with the addition of cerium oxide, to reveal an effect of cerium oxide on superconducting and structural properties of the YBCO system itself.

2. Experimental

Polycrystalline samples of YBa$_2$Cu$_3$O$_{7-\delta}$ doped with 0, 0.25, 0.5, 1.0, 1.5, 2.0 and 2.5 wt% of CeO$_2$ were synthesized by the standard solid-state reaction method using Y$_2$O$_3$, BaCO$_3$, CuO and CeO$_2$ powders of the 99.99% purity. Mixtures of Y$_2$O$_3$, BaCO$_3$ and CuO in appropriate weight amounts were well mixed in an agate mortar in acetone, carefully dried and calcined at 930 °C for 40 hours in air. The obtained precursors were again homogenized in acetone, dried, mixed with CeO$_2$ powder up to 2.5 wt% and pressed isostatically into pellets. The samples were sintered in the horizontal tube furnace in flowing oxygen (10 ml/min) at 1007

°C for 24 h, followed by cooling to 520 °C and annealing at such temperature in oxygen for 24 h.

The phase composition of the samples was identified by powder X-ray diffraction using CuKα radiation. T_c(R = 0) and ΔT_c of the samples were determined using a standard resistance four-point method and the 10-90% criterion for transition width. Volume magnetization of the samples was measured at ~77 K after zero field cooling by a compensation method using the second-order SQUID gradiometer [4]. The applied magnetic field H_a was parallel to the axis of the sample.

2. Results and discussion

Temperature T vs. resistance R curves of CeO_2 doped $YBa_2Cu_3O_{7-\delta}$ samples are shown in Fig. 1. Values of T_c are in the range of 89.0-90.8 K and values of the transition width ~ 1.2-2.0 K for all the samples except for the undoped YBCO sample, which has the worst values. We believe that the bad superconducting properties of undoped sample were caused by a somewhat lower processing temperature with regard to its utmost value. Comparing the other doped samples, we can observe an increase of normal state resistance up to 1 wt% of doping with CeO_2 followed by a decrease in resistance for higher levels of doping. This could have been caused e.g. by changes in the oxygen content at the intergrain boundaries.
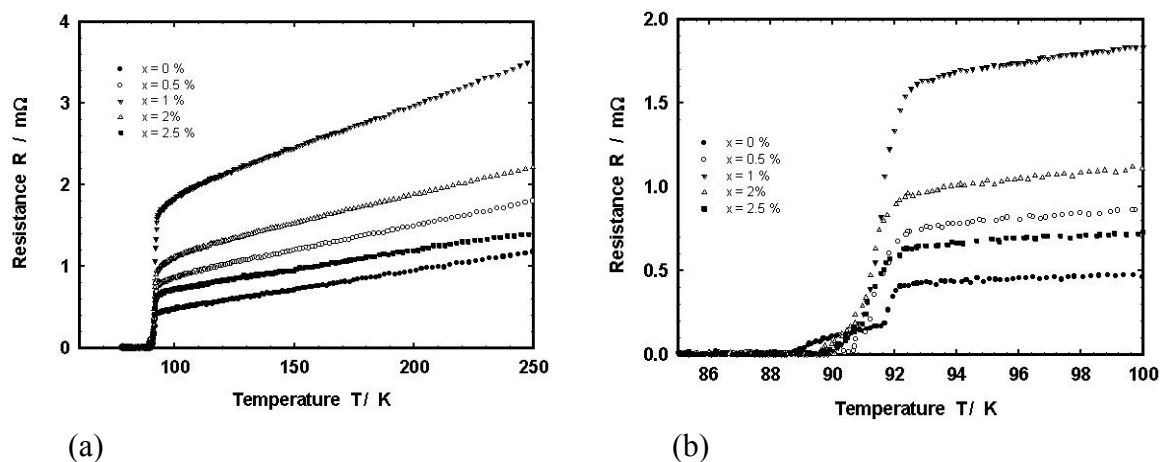

(a)   (b)

Fig. 1. R vs. T dependences of $YBa_2Cu_3O_{7-\delta}$ samples doped with x wt % of CeO_2 (a) and detail of R-T dependences in the temperature range of 85-100 K (b).

The T_c and ΔT_c dependences on increasing Ce-content in the YBCO compound are shown in Fig. 2 and 3, respectively. T_c slightly decreases with the increasing content of cerium oxide. This can be explained via the cerium atoms entering into the Y123 superconducting matrix and having mixed Ce^{3+} and Ce^{4+} valence with different ratios in the bulk and grain boundaries.

The powder XRD patterns of the undoped and doped with 2.5 wt% of CeO_2 YBCO polycrystalline samples are illustrated in Figs. 4 and 5, respectively. The diffraction patterns of undoped sample correspond to the characteristic orthorhombic Y123 phase. XRD data of the sample doped with 2.5 wt% of CeO_2, besides orthorhombic Y123 phase, show some peaks that can be assigned to green Y211 and $BaCeO_3$ phases. Tiny amounts of these phases were found already in the YBCO sample doped with 1 wt% of CeO_2. Results from XRD patterns indicate that if cerium enters into the YBCO phase, its solubility limit is lower than 3.76 at % (x = 1 wt % of CeO_2). This is also in accordance with results of Petrov et al. [5].
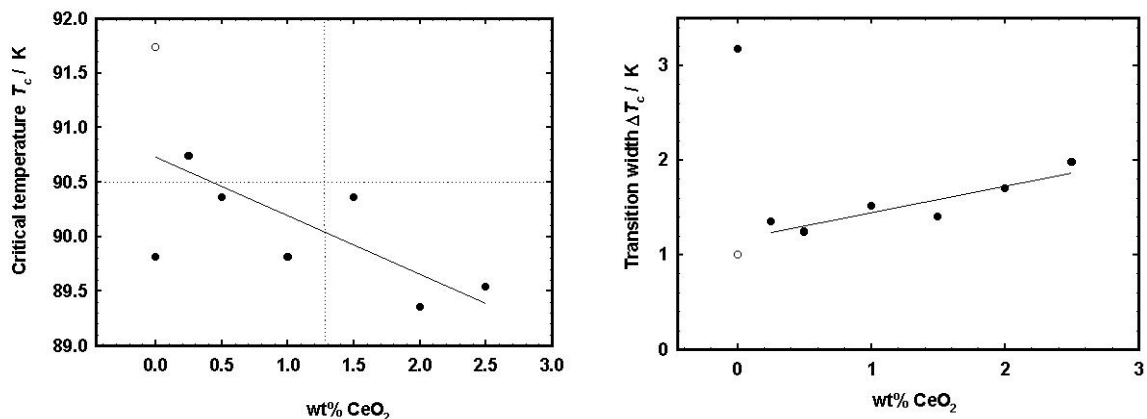
Fig. 2. and 3. T_c and ΔT_c vs. nominal content in wt% of added CeO_2 into YBCO samples, respectively. (○ – standard YBCO sample without Ce).

Changes in R vs. T dependences induced by an addition of cerium can also be explained by an entry of cerium into the YBCO matrix and formation of Y211 and $BaCeO_3$ phases.
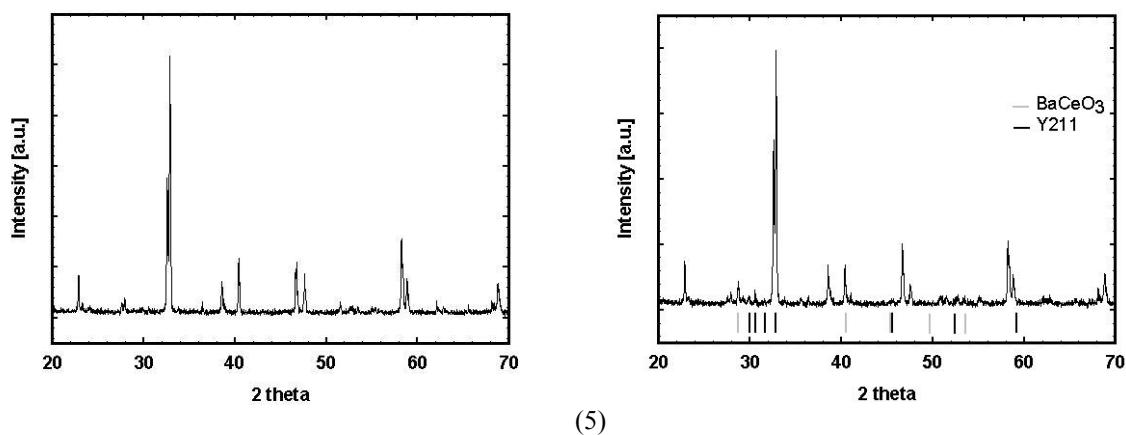

(4)   (5)

Fig. 4. and 5. Powder X-ray diffraction patterns of the undoped YBCO superconductor (4) and YBCO sample doped with 2.5 wt% of CeO_2 (5).

AC volume magnetization M vs. the applied magnetic field H_a of undoped sample and samples doped with x = 0.00, 0.25, 0.5 and 1.5 wt% of CeO_2 are shown in Fig. 6. All the samples show the Z-shape magnetization curves typical for the polycrystalline samples. In the range of a higher magnetizing field amplitude, the hysteresis of magnetization loops grows with an increase of the Ce level up to x =0.50, which is followed by a decrease of magnetization and magnetization hysteresis with the continuation of adding CeO_2. The results are in accordance with the scheme of Ce entering into YBCO at lower levels and formation of Y211 and $BaCeO_3$ phases at higher contents. Substituted Ce atoms in the YBCO matrix can act as effective point pinning centres of magnetic flux resulting in an increase of magnetization hysteresis and so in an increase of critical current density. The same is true for Y211 and $BaCeO_3$ phases, however, the formation of these phases decreases the content of the YBCO phase that results in a decrease of magnetization values, see Fig. 5. plot with x = 0.25 wt % CeO_2.
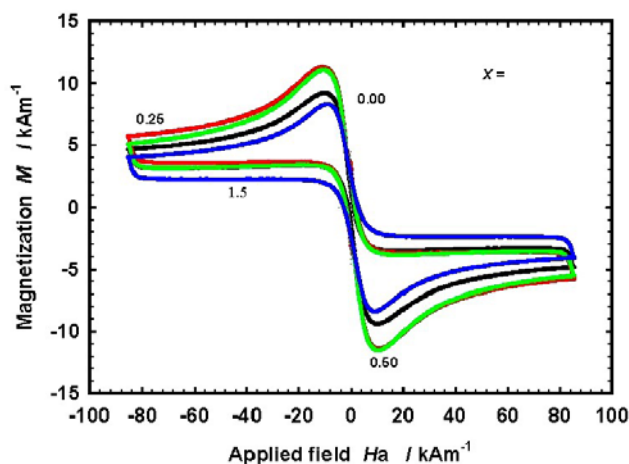
Fig. 6. AC volume magnetization M vs. the applied magnetic field H_a of undoped sample and samples doped with $x = 0.00$, 0.25, 0.5 and 1.5 wt% of CeO_2.

3. Conclusions

Effects of cerium oxide addition on the structural, transition, and magnetic properties of $YBa_2Cu_3O_{7-\delta}$ polycrystalline samples have been investigated by means of X-ray diffraction, resistance, magnetization and optical measurements. The addition of cerium causes a slight decrease in T_c from 90.8 to 89.0 K and an increase in ΔT_c from 1.2 to 2.0 K. Based on phase transition and XRD measurements, it can be inferred that cerium enters into YBCO compounds. Starting from the 1.0 wt% CeO_2, the Y211 and $BaCeO_3$ phases could be identified. The addition of cerium leads to an increase of the magnetization and magnetization hysteresis and therefore to an increase of critical current density, including significant intragrain or intergrain cluster contributions, with the maximum at $x = 0.025 - 0.05$ wt % CeO_2. Another increase causes a deterioration of the characteristics.

References

[1] Yang KN, Lee BW, Maple MB, Laderman SS. Compounds in mixed phase $CeBa_2Cu_3O_y$ and $TlBa_2Cu_3O_y$ systems. *Appl. Phys. A*, 46: 229-232, 1988.

[2] Monot I, Verbist K, Hervieu M, Laffez P, Delamare MP, Wang J, Desgardin G, Van Tendeloo G. Microstructure and flux pinning properties of melt textured grown doped $YBa_2Cu_3O_{7-\delta}$. *Physica C,* 274: 253-266, 1997.

[3] Harnois C, Hervieu M, Monot-Laffez I, Desgardin G. Relations between microstructure and superconducting properties of Ce+Sn doped YBCO. *J.Europ.Ceram. Soc.* 21: 1909-1912, 2001.

[4] Zrubec V, Cigáň A, Maňka J. Simplified fast method for magnetic characteristics measurement of the HT_c superconducting materials. *Physica C*, 223: 90, 1994.

[5] Petrov MI, Balaev DA, Gokhfeld YS, Dubrovskii AA, Shaikhutdinov KA. Effect of heterovalent substitution of rare-earth elements on the magnetic and transport properties of $YBa_2Cu_3O_7$. *Phys. Sol. State,* 11: 2047-2051, 2007.