

# Pinning Enhancement by Heterovalent Substitution in $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$

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**Abstract.** The intragrain pinning in high- $T_c$  superconductor compounds  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$  with low concentration of RE (La, Ce, Pr) was investigated. Magnetic and transport measurements reveal that the pinning is maximal for the concentration of heterovalent RE such that the average distance between the impurity ions in the plane of rare-earth elements close to the diameter of Abrikosov vortices in YBCO.

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## 1. Introduction

Improvement of critical current of YBCO materials is attained by a creation of additional defects acting as pinning centers. Irradiation, incorporation of nanoparticles and doping [1, 2, 3, 4, 5] are the main ways to increase the pinning. In last case the partial substitution of rare earth elements (RE) for Y is favorable [3, 6, 7, 8, 9] that results in a local distortions of crystal structure and electron density.  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$  was earlier investigated in most cases with the concentration  $x$  about a few tens of atomic percents. It is found that the pinning depends on valence and size of RE ions. The doping ions with valence 3+ do not change superconducting properties of YBCO greatly unlike ions with larger valence [10]. Increasing of pinning in  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$  films with small concentrations of RE ( $x < 0.1$ ) was observed in article [8]. Authors of [8] were interested mainly by a relative influence of different doping elements to the flux pinning. They found the pinning enhancement by a minute doping with different RE especially Tb and Nd. The dependence of critical current density in polycrystalline  $Y_{1-x}Pr_xBa_2Cu_3O_7$  on  $x$  was investigated in article [9]. The maximal critical current density was reached for  $x = 0.08$ .

To study the concentration dependence of pinning we suggest to choose  $x$  connecting with parameters of the crystal structure. The concentration of RE can be correlated with the average distance between impurity ions in the rare-earth plane,  $D$ . Atoms of Y arrange the planes in YBCO such that the connection between  $x$  and  $D$  is given by  $x = a^2/D^2$ , where  $a$  is the lattice constant in the rare-earth plane. It can be written

as  $x = a^2/(na)^2 = 1/n^2$ , where  $n = D/a$ . Thus one can choose  $x$  to obtain integer  $n = 2, 3, 4, 5, 6, 7, 8, 9, 10, \infty$ , i.e.  $D$  is divisible by  $a$ . The compound with  $n = \infty$  corresponds to classical  $YBa_2Cu_3O_{7-\delta}$ . Such choice of  $x$  reveals the pinning dependence on the average distance between the pinning defects.

To prove an influence of the heterovalent substitution on the pinning we investigate YBCO doped by Ce and Pr. Ions Ce and Pr have valence equal 4+ and 3÷4+ correspondingly and should strongly modify superconductivity near their location. Ions La have the same valence as Y but the larger radius. The doping by La is chosen to examine the influence of a lattice distortion without the distortion of electron density.

Earlier we published the first results for  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$  with the above-stated concentrations  $x$  [11, 12]. Here we report about comparative study of the magnetic and transport characteristics of  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ,  $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$  and  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$ . Measurements of magnetization and resistance were carried out. It allows comparing the intragrain pinning in the compounds with different  $x$ .

## 2. Experiment

Three series of compositions  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$  were prepared for  $RE = Ce, Pr, La$ . The series ( $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$ ,  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  and  $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ ) were synthesized separately by the standard solid-phase technique. The starting reactants were  $Y_2O_3$ ,  $CeO_2$ ,  $Pr_6O_{11}$ ,  $La_2O_3$ ,  $CuO$ ,  $BaCO_3$ . The corresponding amounts of reagents were mixed thoroughly in an agate mortar, pelletized, and annealed at 930 °C. The synthesis, including seven intermediate crushings and pressings, lasted 160 h. Long procedures favor ordering of RE elements and cerium substitution in yttrium positions. The synthesis completed, the samples were annealed at a temperature of 300 °C for 3 h and cooled slowly in the furnace to room temperature to reach oxygen saturation.

Each series contain 10 samples with  $x = 0.25, 0.11, 0.0625, 0.04, 0.0278, 0.0204, 0.0156, 0.0123, 0.01$  and 0 which were synthesized simultaneously at the same conditions. The chosen concentrations of RE correspond to  $n = 2, 3, 4, 5, 6, 7, 8, 9, 10$  and  $\infty$ . In such a way the composition with  $x = 0$  ( $YBa_2Cu_3O_{7-\delta}$ ) was synthesized for each series.

The temperature dependence of resistance  $R(T)$  was measured by the standard four-probe technique with the bias current 10 mA. Samples have rectangular cross section (2 mm × 1 mm), the distance between the potential contacts being 2 mm.

Magnetic characteristics were measured by a vibrating sample magnetometer. The samples were cut out in the shape of cylinders with height  $\approx 5$  mm and diameter  $\approx 0.5$  mm. The temperature dependence of magnetization is measured at the samples cooled without external field ( $M_{ZFC}$ ) and in magnetic field 100 Oe ( $M_{FC}$ ). The measurements were carried out during heating with speed 0.8 K/min from 77.4 K to 100 K for  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$  and  $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$  and from 55 K to 100 K for  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ . The magnetic field  $H = 100$  Oe was applied parallel to the cylinder axis. The temperature of intragrain superconducting transition  $T_c$  was determined from  $M_{ZFC}(T)$  (criterion is  $dM/dT = 0$ ). The temperature of disappearance

of resistance  $T_{c0}$  was determined from  $R(T)$  (criterion is voltage drop on sample = 1  $\mu$ V cm).

### 3. Results and Discussion

The x-ray diffractions patterns show that most of samples are single-phase and have YBCO structure. There are small distortions of crystal lattice for  $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$  with high concentrations of La ( $x = 0.11, x = 0.25$ ). For  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$  the phase  $BaCeO_3$  precipitates when  $x > 0.024$  (see details in [12]) because Ce dissolves in YBCO at low concentrations only.

Figure 1 displays the temperature evolution of the resistance  $R(T)$  normalized to  $R(100\text{ K})$  for a few samples. The measured  $R(T)$  dependences are typical for polycrystalline superconductors and exhibit a sharp drop of the resistance at  $T_c$  and a smooth part till  $T_{c0}$  reflecting the transition of Josephson media formed by the intergrain boundaries. Above  $T_c$  most of dependences  $R(T)$  are metallic like. The exception is  $Y_{0.75}La_{0.25}Ba_2Cu_3O_{7-\delta}$  ( $n = 2$ ) having a quasi-semiconductor like  $R(T)$  above  $T_c$ . It is probably because La occupies partially Ba sites for high  $x$  [13]. The dependences  $R(T)$  demonstrate that Pr depresses superconductivity stronger than Ce or La. The remarkable tail from  $T_c$  to  $T_{c0}$  on  $R(T)$  of  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$  for  $n = 3$  shows that the intergrain boundaries thickness is increased due to a precipitating of nonsuperconducting phase (see the article [14] concerning the composites YBCO + nonsuperconducting compounds).

Figure 2 demonstrates that  $T_c$  of  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$  depends weakly on RE concentration for  $x < 0.0625$  ( $n > 4$ ). To reveal the influence of RE impurities to the intergrain boundaries we compared the width of superconducting transition ( $T_c - T_{c0}$ ) of samples. These were normalized to  $T_c$  for a correct comparison of the samples with different  $T_c$ . Figure 3 plots the normalized width of superconducting transition  $(T_c - T_{c0})/T_c$  for the samples as a function of  $n$ . The dispersion of  $(T_c - T_{c0})/T_c$  is  $\approx 4\%$  for the compositions with  $x \leq 0.04$  ( $n \geq 5$ ). It follows that there is no remarkable influence of RE concentration on intergrain currents at these concentrations.

Magnetization loops of samples are typical for polycrystalline superconductors. Dependences  $M(H)$  of sample  $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$  with  $x = 0.0156$  ( $n = 8$ ) measured up to different  $H$  are presented in Figure 4. There is the method [15] separating the intergrain and intragrain critical currents from curves  $M(H)$  measured up to low and high magnetic fields. However the width of loop  $M(H)$  at zero field is practically the same for curves measured up to 200 Oe and 1000 Oe. Also the observed asymmetry of loop  $M(H)$  at high  $H$  is a sign of strong influence of the edge barriers [16, 17]. For such case application of Bean model and the method [15] is incorrect [18].

The temperature dependences of magnetizations  $M_{FC}(T)$  and  $M_{ZFC}(T)$  of the samples at  $H = 100$  Oe are plotted in Figure 5 *a, b, c*. Data for  $Y_{0.75}Pr_{0.25}Ba_2Cu_3O_{7-\delta}$  ( $n = 2$ ) are lost unfortunately. It is clearly seen that the absolute values of  $M_{ZFC}(T)$  are sensitive to the concentration of RE. The sample  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  with  $x =$

0 ( $n = \infty$ ) has somewhat smaller absolute values of  $M_{ZFC}(T)$  at any fixed  $T$  than  $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$  and  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$  with  $x = 0$ . The different oxygen content in the different series of samples is possibly reason for this mismatch.

The dependences  $M_{FC}(T)$  and  $M_{ZFC}(T)$  give information about the pinning in samples. The difference between  $M_{FC}(T)$  and  $M_{ZFC}(T)$  depends monotonically on the pinning energy in a type II superconductor [19]. Influence of the intergrain pinning is small here due to the strong depinning in intergrain boundaries [20]. Thus the value  $\Delta M = M_{FC} - M_{ZFC}$  is concerned with the intragrain pinning. Figure 6 displays  $\Delta M$  at 77.4 K as a function of  $n$ . The character of dependence  $\Delta M(n)$  and the position of maximum do not change at other  $T < T_c$ . For  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$  and  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ,  $\Delta M$  has a maximal value at  $n = 8$  ( $x = 0.0156$ ). This position of maximum corresponds to the average distance between the impurity atoms  $D = 8a$ . For YBCO  $a = 0.382$  nm, so  $D = 3.06$  nm. Such value of  $D$  is comparable to the coherence length in YBCO ( $\xi_0 \sim 1.5$  nm,  $\xi(77\text{ K}) \sim 4$  nm [21]). We believe that the pinning is maximal then the defects spaced at the average distances close to the diameter of Abrikosov vortex. Here the pinning defects are the local distortions of electron density formed by the RE ions with valence higher than 3+. The pinning defects created by RE doping can also be associated with a formation of oxygen vacancies in  $CuO_2$  planes [9].

The discrepancy between our result for maximal pinning concentration and the result of article [9] ( $x = 0.08$ ) is possibly found because the technique of synthesis used in investigation [9] differs from ours. In the samples [9] the doping Pr partially goes to intergrain boundaries modifying them. This leads also to decreasing of the actual concentration of Pr in the granules.

$Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$  does not demonstrate a clear maximum of  $\Delta M$  for any  $n$ . The distortions of crystal structure which arise from larger size of La ions probably do not pin vortices. Therefore the doping by RE elements with valence higher than 3+ is preferable for the high pinning.

#### 4. Conclusions

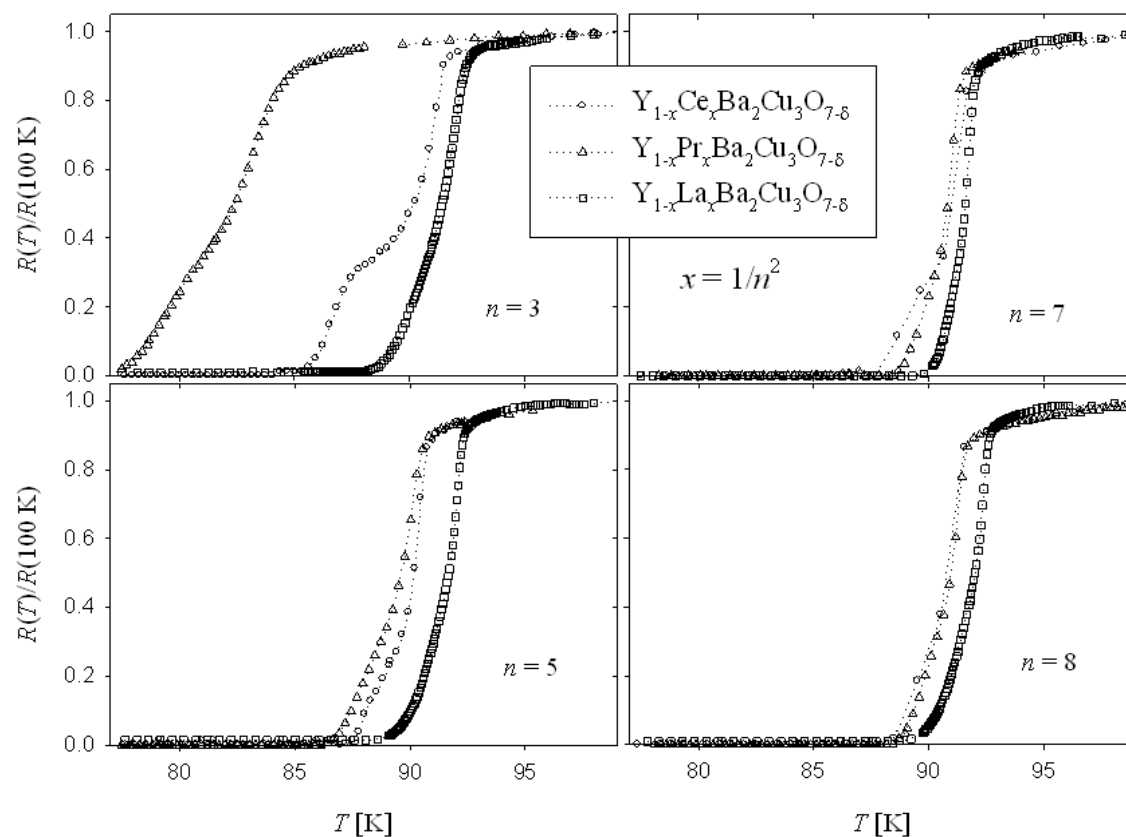
The resistance dependences on temperature of  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$  demonstrate that the RE impurities do not modify the intergrain transport while  $x < 0.04$ . The remanent magnetization of the samples reveals that the doping of the RE elements with valence higher than 3+ in small amounts increases the intragrain pinning. The doping of YBCO by the homovalent RE (La) does not increase the pinning. Concentration of the heterovalent RE for the maximal pinning,  $x = 0.0156$ , is the same for both tested elements (Ce and Pr). This concentration corresponds to the average distance between the impurity atoms equal to 3.06 nm ( $\sim 2\xi_0$ ).

## Acknowledgments

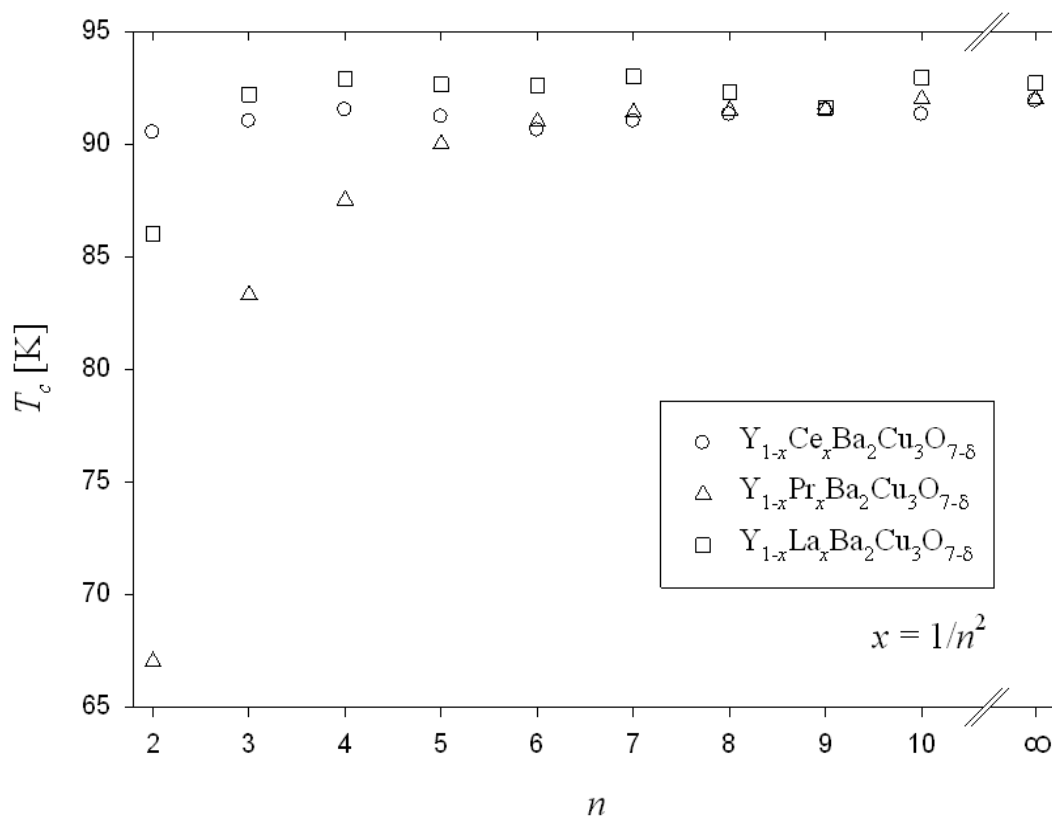
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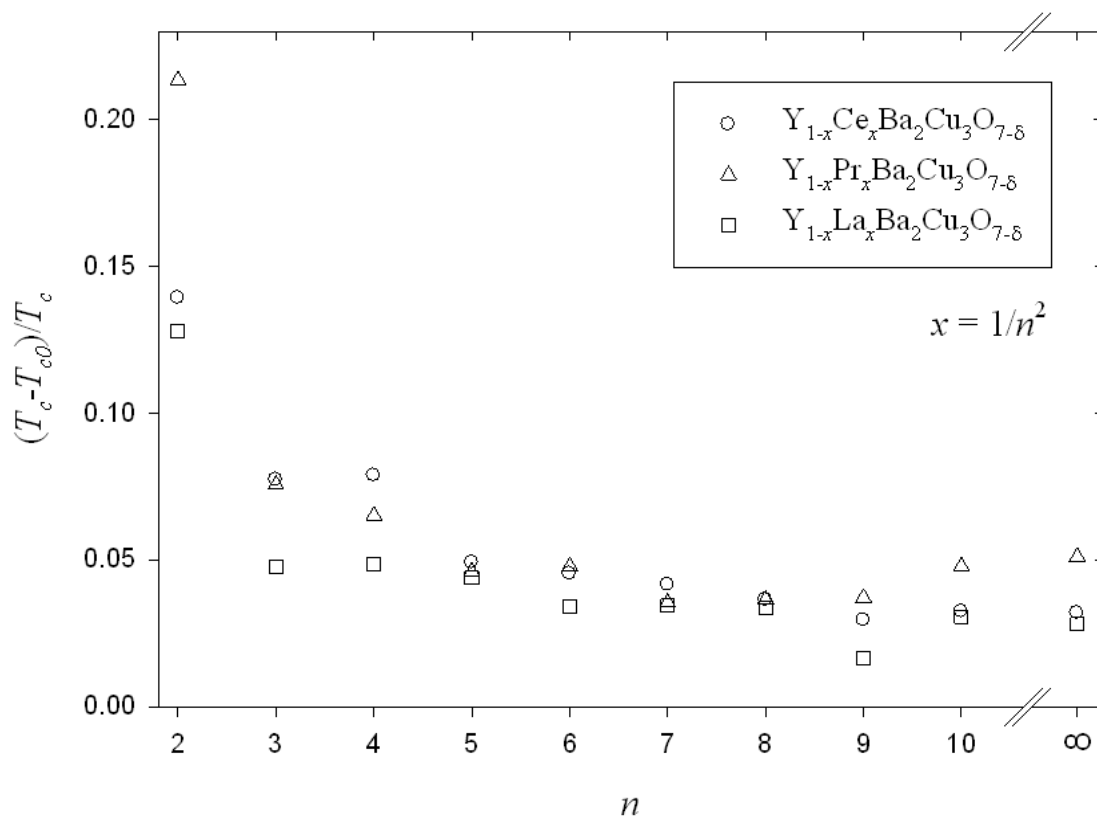
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**Figure 1.** Temperature dependence of normalized resistance  $R(T)/R(100\text{ K})$  of samples  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$ .

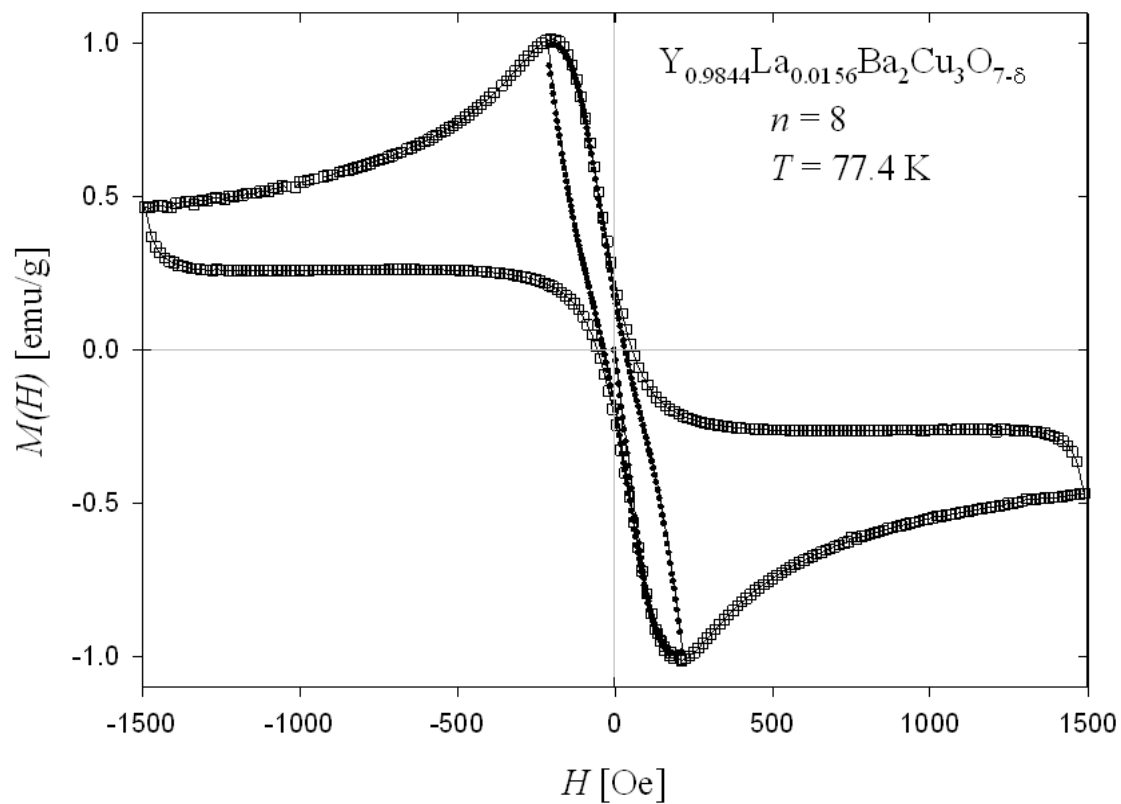


**Figure 2.** Intragrain critical temperature  $T_c$  of  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$ .

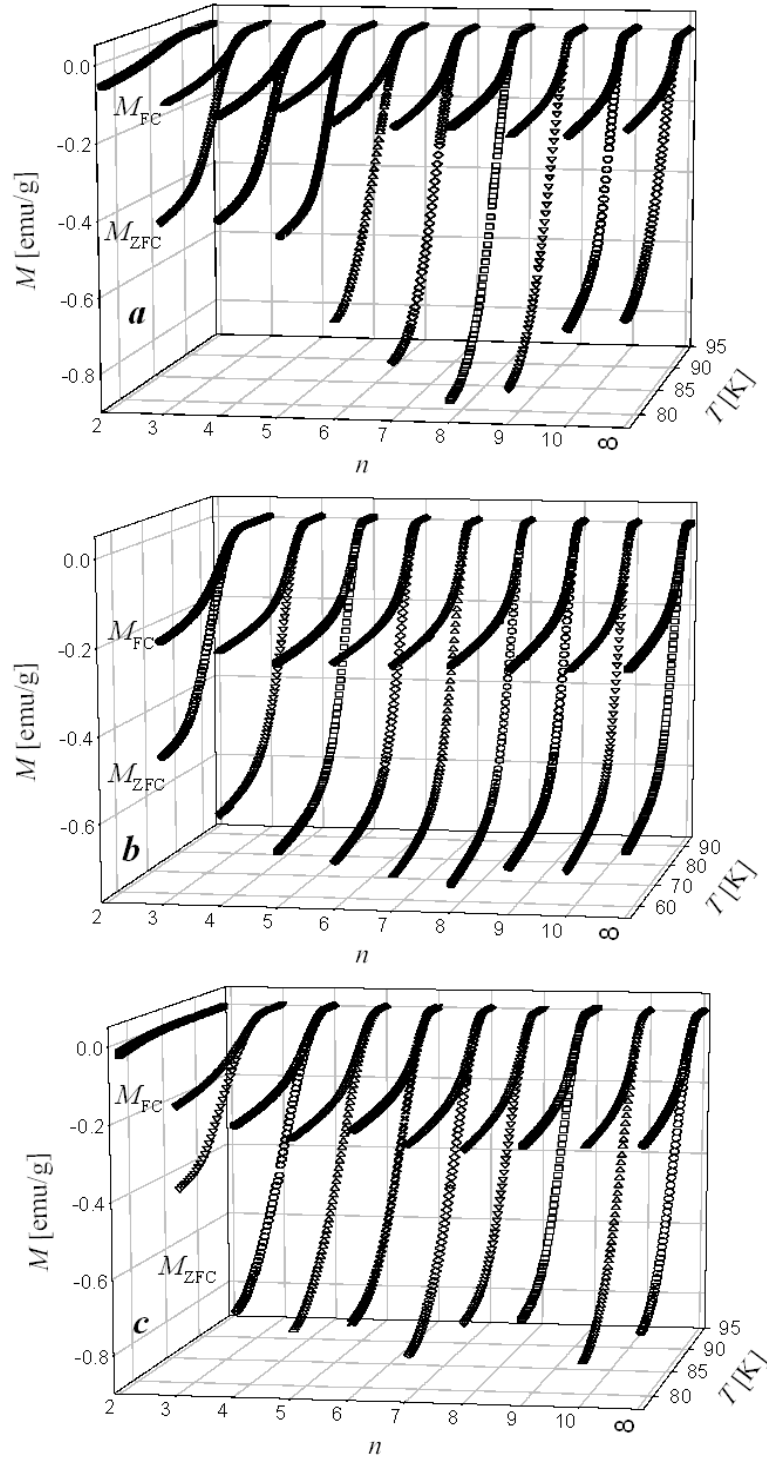


**Figure 3.** Normalized width of superconducting transition  $(T_c - T_{c0})/T_c$  for  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$ .

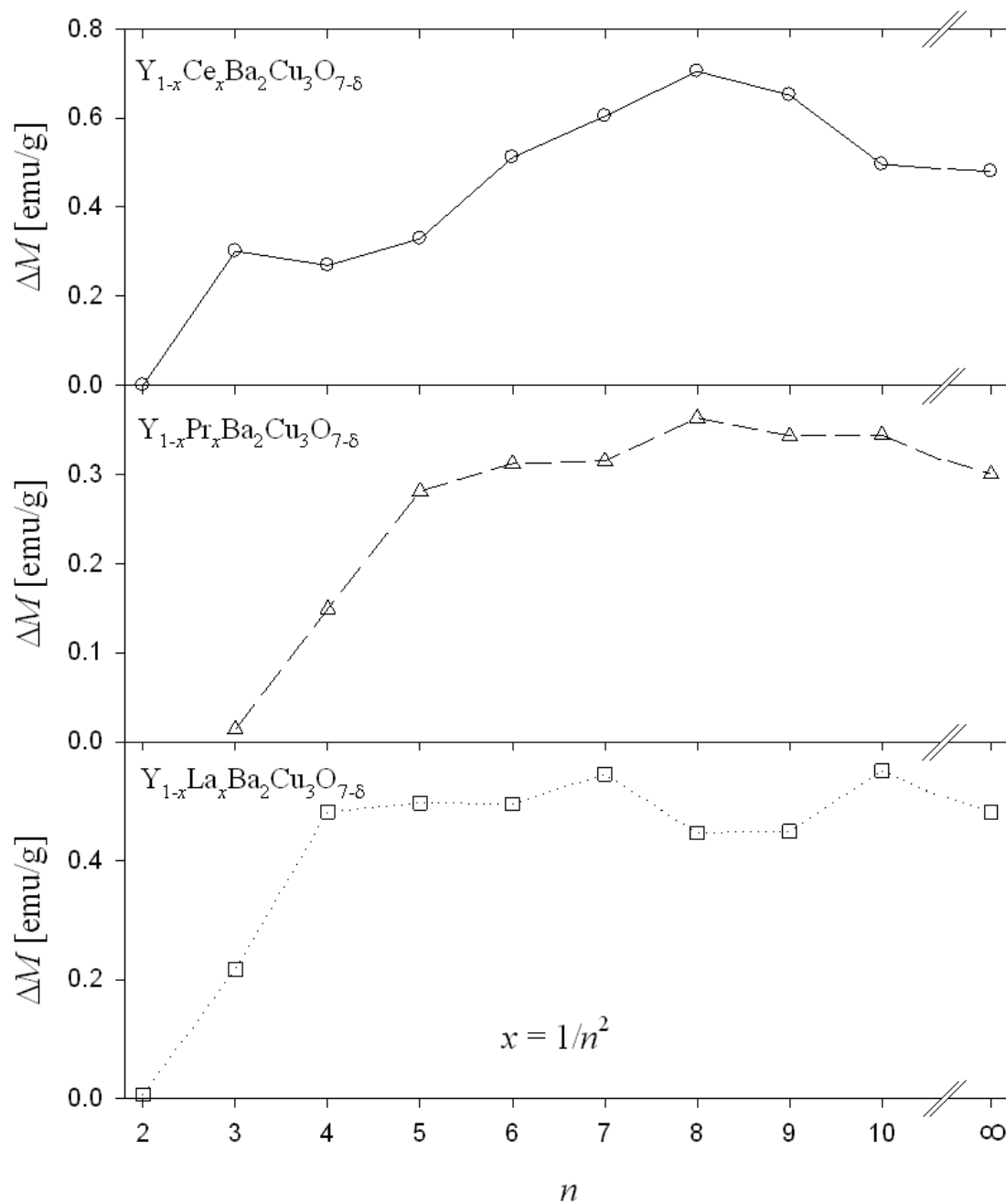




**Figure 4.** Magnetization of sample  $Y_{0.9844}La_{0.0156}Ba_2Cu_3O_{7-\delta}$  vs. magnetic field up to 200 Oe (black dots), 1500 Oe (squares).



**Figure 5.** Temperature dependence of zero field cooled  $M_{ZFC}(T)$  and field cooled  $M_{FC}(T)$  magnetization of a)  $Y_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$ , b)  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ , c)  $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ .



**Figure 6.** Difference of field cooled and zero field cooled magnetization  $\Delta M$  of  $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$  at 77.4 K.