The Influence of the Polycrystalline State and Partial Dy Substitution on the Superconducting Properties of YBCO

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The influence of the quasi-equal partial substitution of non-magnetic (Y^{3+})/magnetic (Dy^{3+}) ions in YBa2Cu3O7 – y on the superconducting properties of the material has been investigated. To minimize the influence of the stress field induced by lattice mismatch, Dy-substituted YBa2Cu3O7 –y was studied because Y^{3+} and Dy^{3+} ions have similar ionic radii. The investigation was performed on polycrystalline and powder samples with general formula $Dy_xY_{1\_x}Ba_2Cu_3O7\_y$ (x = 0.4-0.6). Higher magnetic losses and intragranular critical current density Jc were observed for partially substituted samples in comparison with DyBCO. The strongest influence of magnetic substitution on the electrical resistivity properties was observed in the mixed state.

1. Introduction

It is well known that in the high-T_c superconductor (HTS) $YBa_2Cu_3O_{7\ y}$, the Y^{3+} ion can be replaced by most rare-earth ions, including Dy^{3+} [1], without any appreciable effects on its superconducting properties. Some authors [2] are of the opinion that the partial substitution of Y^{3+} with a rare-earth ion can lead to changes in the crystal lattice which, in turn, can result in the formation of a stress field causing local flux pinning at the unit cell level. The presence of a magnetic ion also gives rise to the appearance of a magnetic sublattice, with there being controversy as to what its contribution is to the formation of the magnetic properties of the HTS material. Investigations on partially Dy-substituted YBCO [3] showed that the Dy^{3+} ion does not influence the critical temperature Tc of the superconducting phase transition and, in the case of polycrystalline samples, the Dy^{3+} ion is manifested most strongly in what concerns the screening parameter and the hysteresis properties of the HTS with general formula $Dy_xY_{1-x}Ba_2Cu_3O_{7\ y}$ (x = 0.4-0.6). The changes in the screening properties of the DyxY1 – xBa2Cu3O7 –y samples were similar to those of polycrystalline Rb-doped YBCO with defects on the grain surface of the order of 3–4 nm [4]. In a material in a polycrystalline state, it is difficult to differentiate the magnetic ion contribution, since a whole set of defects, such as crystallographic imperfections in the crystallites, grain boundaries (more than 30% of the entire mass), size and orientation of the grain, and pores, participate in the formation of pinning centres. A substantial drawback to the magnetic behaviour is the contribution of the demagnetization factor. In order to minimize the negative effects, it would be useful to investigate powder samples of such materials consisting of grains with nearly spherical shape and with sizes smaller than that of the crystallites in polycrystalline samples.

The present paper reports on investigations of the magnetic properties of a HTS where the Y^{3+} ion is partially substituted with the magnetic rare-earth Dy^{3+} ion in $Dy_xY_{1-x}Ba_2Cu_3O_{7-y}$ in the region of substitution x = 0.4-0.6. The samples investigated were polycrystalline with controlled grain size of up to 15 mm and powders of the same material with grains of quasi-spherical shape and with average grain size of 1 mm. An attempt was made to compare the changes in the magnetic properties of samples in polycrystalline and powder states in terms of the presence of the magnetic Dy^{3+} ion in the 123 phase.

2. Experimental

Samples with nominal composition $Dy_xY1\_{}_xBa_2Cu_3O_{7}\_{}_y$ (x = 0.4-0.6) were prepared using Y2O3, Dy2O3, CuO, and BaCO3 as raw materials. The samples were obtained using classic ceramic technology, consisting of the mixing of oxides and carbonate in appropriate ratios. The powders were pressed into pellets at room temperature, sintered at 950 °C with an isothermal delay of 24 h, and milled in a vibration agate-ball mill down to a grain size of about 1 mm. The pellets were sintered at 950 °C with isothermal delays of 30 h, cooled to 650 °C with an isothermal delay of 24 h, and then cooled to room temperature. Finally, cylinders were cut from the pellets.

After a metallographic treatment of the surface, the surface grain size in the polycrystalline structure was studied using scanning electron microscopy (SEM). The average grain size was about 15 mm.

Some of the sintered samples were vibration milled to prepare fine powders of superconducting material. A highly homogeneous fraction with respect to the average particle size – 1 mm, measured by a Fritsch-analysette 23 – was separated from the powder thus obtained.

3. Results and Discussion

The samples were characterized by X-ray diffraction at room temperature using the CuKa line. The data showed that the samples consisted of single-phase orthorhombic 123-phase. The crystallographic parameters and the degree of orthorhombic distortion (b—α)⁄(α+*b)* for the limiting cases Dyo.eYo.$_4$Ba$_2$Cu$_3$O$_{7-y}$ and Dyo.$_4$Yo.6Ba$_2$Cu$_3$O$_{7-y}$ in the region investigated were compared with these for DyBCO and YBCO obtained in the authors' laboratory by the same technology and with data from the literature [3, 5]. Table 1 summarizes the data for the crystallographic parameter changes and the degree of orthorhombic distortion for these cases.

A slight change is observed in the crystallographic parameters of the polycrystalline partially substituted Dy0.6Y0.4Ba2Cu3O7 –y and Dy0.4Y0.6Ba2Cu3O7 –y samples, which gives grounds for assuming that the presence of a Dy^{3+} ion in place of a Y^{3+} ion in partially substituted samples does not provoke significant changes in the DyxY1 –xBa2Cu3O7 –y crystal cell. This can be related to the comparable ionic radii of Dy^{3+} (1.07 A) and Y^{3+} (1.06 A).

Table 1. *Structural parameters of DyxY1 –xBa2Cu3O7 –y compounds determined by X-ray diffraction*

sample	_ o _ *a* [A]	_ o _ *b* [A]	– o – *c* [A]	*(b - a)⁄(a + b)* [%]
YBa2Cu3O7 –y *)	3.824	3.891	11.681	0.882
YBa2Cu3O7 –y	3.82(7)	3.887(2)	11.680(2)	0.84
Dy0.4Y0.6Ba2Cu3O7 –y	3.825(5)	3.888(6)	11.680(8)	0.81
Dy0.6Y0.4Ba2Cu3O7 –y	3.825(9)	3.886(5)	11.672(6)	0.79
DyBa2Cu3O7 –y	3.827(2)	3.892(8)	11.683(2)	0.85
DyBa2Cu3O7 –y *)	3.829	3.892	11.692	0.816

*) Reference data for monophase samples [5].

This prompted a shift of attention to the oxygen content in the samples investigated. Figure 1 shows Raman spectra of DyBa2Cu3O7–y, Dy0.6Y0.4Ba2Cu3O7–y, Dy0.4Y0.6Ba2Cu3O7 –y, and YBa2Cu3O7 –y samples. It is seen that by using the technology discussed above one can prepare relatively easily Dy systems with stable oxygen content, which in the range investigated changes negligibly. Since the lattice parameters vary only slightly in partially substituted Dy0.6Y0.4Ba2Cu3O7 –y and Dy0.4Y0.6Ba2Cu3O7 –y, the influence of the stress field should not be as significant as it is indicated in Ref. [2].

The magnetic measurements were performed using a magnetic field in the range 0– 14 T from a water-cooled Bitter magnet at 4.2 K. A vibration sample magnetometer was used to measure the magnetization M(H). The external magnetic field was applied parallel to the long axis of the cylinder for the polycrystalline samples to minimize the demagnetizing factor [6]. The data for the magnetization measurements of DyBa2Cu3O7–y,Dy0.6Y0.4Ba2Cu3O7–y, and Dy0.4Y0.6Ba2Cu3O7 –y samples in high magnetic field (up to 14 T) at temperature of 4.2 K are shown in Fig. 2. All samples exhibited hysteresis loops. The data demonstrate that partially substituted polycrystalline samples exhibit higher hysteresis losses, as compared with DyBa2Cu3O7 –y. The sample with composition Dy0.6Y0.4Ba2Cu3O7 –y shows the highest losses, an indication that the pinning is strongest in this sample.

To minimize the influence of the polycrystalline structure, the magnetic properties of the polycrystalline material were compared with those of powder with quasi-spherical grain shape and average grain size significantly smaller than the average crystallite size in the polycrystalline samples. As can be seen from the SEM image of Fig. 3a, the Dy0.6Y0.4Ba2Cu3O7 –y sample has an average crystallite size of about 15 mm. Figure 3b shows the transmission electron microscopy (TEM) image of powder of the same composition with an average grain size of about 1 mm. A comparison of the magnetic properties is shown in Fig. 4a for the Dy0.4Y0.6Ba2Cu3O7 –y sample. At low magnetic fields one observes a diamagnetic behaviour. The minimum in the magnetization curves is observed at a magnetic field H_{min} = 0.274 T and H_{min} = 0.386 T for powder and crystalline samples, respectively. The samples exhibit hysteresis loops, with the hysteresis losses observed for the polycrystalline sample being larger than those for the powder. One can also see a closing of the hysteresis curve of the powder sample at a field of about 10 T. The magnetic data were complemented by measurements carried out using a SQUID magnetometer with fields up to 5.5 T at a temperature of 4.5 K after zero-field cooling processes. To minimize the demagnetizing factor in the case of polycrystalline samples, the external magnetic field was applied parallel to the long axis of the cylinders [6]. Figure 4b shows the magnetization curves for Dy0.6Y0.4Ba2Cu3O7 –y polycrystalline and powder samples as a function of the applied magnetic field up to 5.5 T at 4.5 K. One can observe a diamagnetic behaviour at low magnetic fields. The difference in the behaviour of the M(H) curves can be related to the characteristics of the polycrystalline state. The lower critical field was defined as the field where the low-field magnetization curves deviate from linearity. The value of Hc1 thus determined for Dy0.6Y0.4Ba2Cu3O7 –y was about 0.098 T and for Dy0.4Y0.6Ba2Cu3O7 –y about 0.112 T. Moreover, it is found that this value is not influenced by the sample state (powder or polycrystalline), while the magnetization magnitude is affected by it.

The magnetization of the Dy3$^+$ ion was extracted from the measured magnetization by averaging the hysteresis,

$$M = \frac{M^+ + M^-}{2}\ , \tag{1}$$

where M^+ and M^- are the increasing and decreasing field branches of the magnetic curve, respectively. Figure 5 shows the magnetization of the Dy3$^+$ ion for the limiting cases Dy0.4Y0.6Ba2Cu3O7 –y and Dy0.6Y0.4Ba2Cu3O7 –y (powder) compared with that for a DyBCO sample [7]. One can observe a smooth decrease of the magnetic moment values of $Dy_{0.6}Y_{0}.4Ba_{2}Cu_{3}O_{7\text{-}y}$ and $Dy_{0.4}Y0.{}_{6}Ba_{2}Cu_{3}O_{7\_y}$ with decreasing Dy^{3+} ion concentration.

The intragrain critical current density was evaluated in terms of the Bean model of the critical state: J_c = 1.5DM/Va$_0$, where DM is the difference between the magnetization for increasing and decreasing field, and V and $a0$ are the sample volume and average size of the crystallites, respectively [8]. The intragrain Jc values for the samples investigated are in the region of 10^7 A/cm^2 (10^{11} A/m^2) at 4.2 K.

The four-probe method was used for precise measurements of the electrical resistivity of the samples as described in Ref. [9]. The study of the electrical resistivity properties of the DyxY1 – xBa2Cu3O7 samples showed that $R(T)$ is strongly dependent on the degree of Y^{3+} ion substitution with magnetic Dy^{3+} ion in the area of superconducting transfer. Figure 6a shows the resistivity as a function of the temperature for the poly crystalline DyxY1 – xBa2Cu3O7 samples with a similar grain size and the electrical resistivity versus temperature variation measured at various magnetic field strengths between 0 and 0.6 T is shown in Fig. 6b for Y0.6Dy0.4Ba2Cu3O7. The absolute value of the resistivity for Y0.6Dy0.4Ba2Cu3O7 is 18 mW m/K at 100 K. In the normal state, the resistivity increased approximately proportionally to the temperature with an average rate of 0.04 mW m/K. The transition width was narrower than 3 K in the absence of an external magnetic field and became gradually broader up to 37 K at a magnetic field of 0.6 T. Even in a non-zero magnetic field the electrical resistivity dropped down to about 45% of the normal state value in a remarkably narrow interval between 85 and 88 K, which is typical for intragrain superconductivity. The intergrain processes are spread out over a much broader temperature range rising gradually with the magnetic field strength up to 25 K. The electrical resistivity behaviour observed is similar to that of the polycrystalline YBCO samples with high homogeneity of grain size and small structure defects on the crystallite surface at depths up to 4 nm, which were investigated in earlier studies [4].

4. Conclusion

Investigations were carried out on non-textured polycrystalline DyxY1 –xBa2Cu3O7 samples (x = 0.4-0.6) possessing high grain homogeneity and an average grain size of about 15 mm. To avoid the influence of the polycrystalline state, powder samples were also studied with the same composition with nearly spherical grain shape and a grain size of about 1 mm. The magnetic ion influence is clearly seen in the shift of the Hc1 value and the diamagnetic minimum toward higher magnetic fields for partially substituted samples, as compared with DyBCO. Higher magnetic losses and intragranular critical current density were observed for the $Dy_xY_{1\ x}Ba_2Cu_3O_7$ (x = 0.4-0.6) samples in comparison with DyBCO at high magnetic fields and at 4.5 K, with the Dy0.6Y0.4Ba2Cu3O7 –y sample exhibiting the highest losses. Because of the similar radii of the Y^{3+} and Dy^{3+} ions, no significant change was observed in the crystal lattice parameters for the partially substituted samples as compared with DyBCO and YBCO; therefore, the stress field, induced by the lattice mismatch between DyBCO and YBCO, should not be expected to affect significantly the superconducting properties. The results of the magnetic investigations suggest that the magnetic sublattice plays a significant part in the behaviour of the partially substituted samples studied in an external magnetic field. The investigation of the electrical resistivity showed that the presence of a magnetic Dy3$^+$ ion in YBCO affects mostly the mixed state in a HTS.

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Fig. 1. *Raman spectra of the DyxY1 –xBa2Cu3O7 –y system*

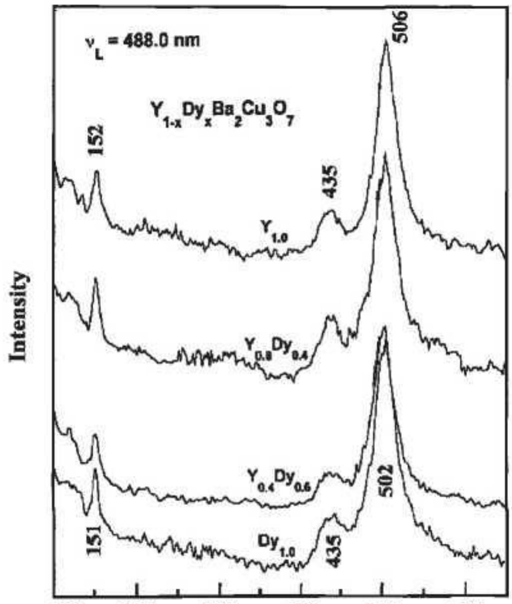


Fig. 2. *Magnetization versus external magnetic field for Dy0.4Y0.6Ba2Cu3O7, Dy0.6Y0.4Ba2Cu3O7, and DyBa2Cu3O7*

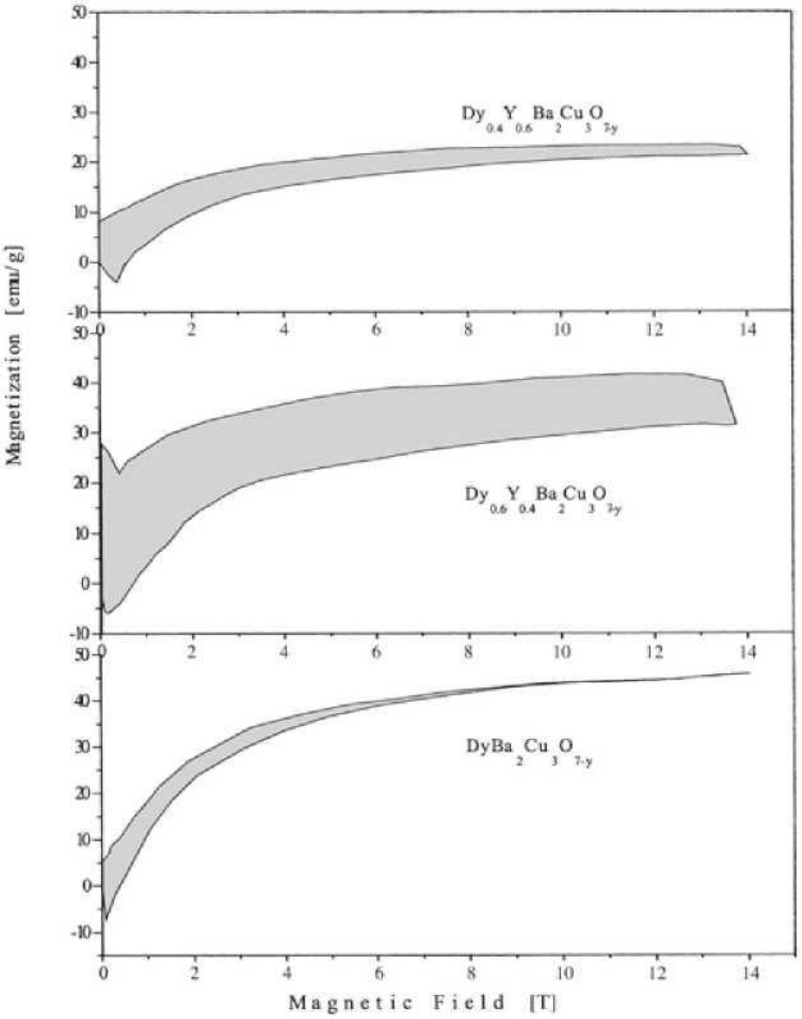
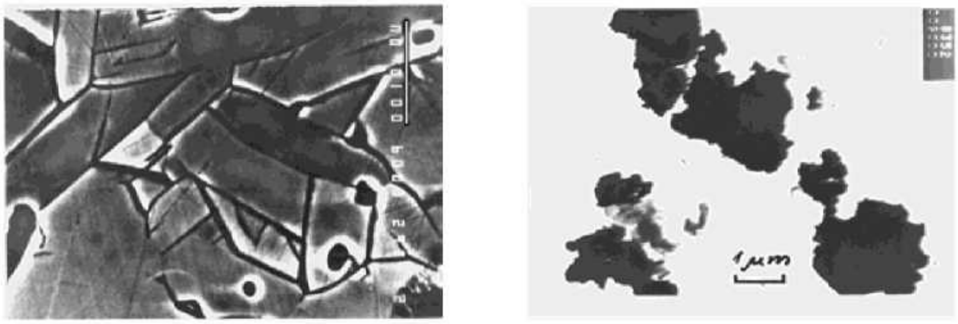
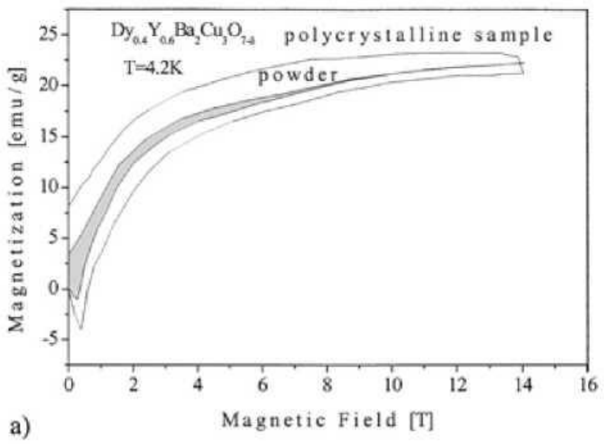


Fig. 3. a) *SEM surface image of polycrystalline bulk Dy0.6Y0.4Ba2Cu3O7 –y sample; b) TEM image of powder Dy0.6Y0.4Ba2Cu3O7 –y sample*

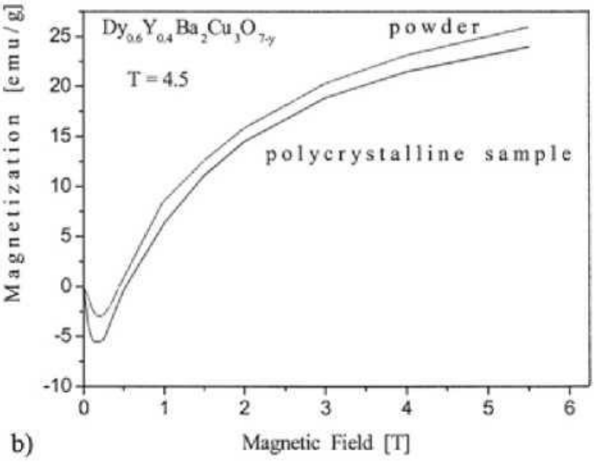


a) b)

Fig. 4. *Magnetization curves of polycrystalline and powder samples: a) Dy0.4Y0.6Ba2Cu3O7 –y in high magnetic field; b) Dy0.6Y0.4Ba2Cu3O7 –y from SQUID measurements*


Dy0.4Y0.6Ba2Cu3O7-δ
polycrystalline sample
T=4.2K
powder
Magnetization [emu/g]
Magnetic Field [T]
25
20
15
10
5
0
-5
0
2
4
6
8
10
12
14
16

a)


Dy0.6Y0.4Ba2Cu3O7-y
powder
T = 4.5
polycrystalline sample
Magnetization [emu/g]
Magnetic Field [T]
25
20
15
10
5
0
-5
-10
0
1
2
3
4
5
6

b)

Fig. 5. *Magnetization curves obtained by averaging the hysteresis for Dy0.4Y0.6Ba2Cu3O7 −y, Dy0.6Y0.4Ba2Cu3O7 −y, and *DyBa2Cu3O7 −y [7]*

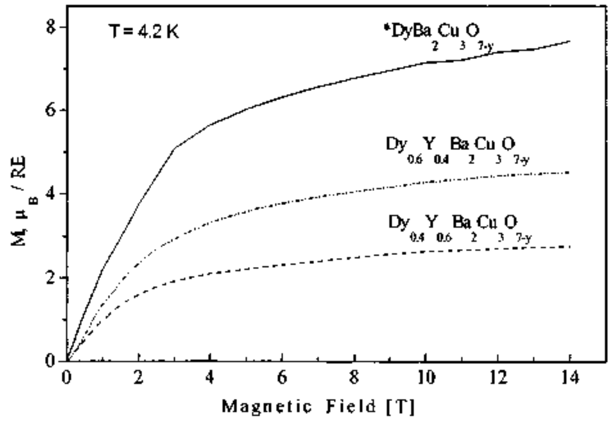


Fig. 6. *Electrical resistivity versus temperature: a) polycrystalline DyxY1 −xBa2Cu3O7; b) polycrystalline* $Y_{0.6}Dy_{0.4}Ba_2Cu_3O_7$ *at various magnetic field strengths between 0 and 0.6 T*