Optimization of the Pr concentration in Y$_{1-x}$Pr$_x$BCO films prepared by pulsed laser deposition

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Abstract. A series of studies has been carried out on thin films which were prepared by pulsed laser deposition from micro-grained targets of Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ (Y$_{1-x}$Pr$_x$BCO) to determine the doping effect of Pr (at Y site) in concentrations between $x = 0 - 0.20$. Earlier results on bulk materials show that the Pr substitution can significantly enhance the value of $J_c(B)$ at cost of $T_c$. Our X-ray diffraction results confirmed the good quality of the films without any impurity phases. Magnetometric studies show the systematic decrease of $J_c(B)$ when the Pr concentration is increased.

1. Introduction
Since the discovery of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) and other high temperature superconductors (HTS), cationic substitutions (such as Pr, Ca, Ni, etc.) have been widely studied, because the response of the normal and superconducting state to the substitutional disorder has given new insights and information about these materials (see e.g. [1]).

The interest in such studies has recently risen, because despite the decrease of the superconducting critical temperature, $T_c$, other superconducting properties such as critical current density, $J_c(B)$, can be improved [2, 3, 4, 5, 6]. The doping concentrations for the improving superconducting effects are, however, relatively small. For example, Zn, Ni, Co, Ga, Er and Ho, when doped in small concentrations of 0.1 - 5% depending on the sites they occupy, can enhance $J_c(B)$, which is important for high magnetic field and critical current applications.

Pr presents an intriguing case, because it isostructurally replaces Y in YBCO over the entire range from $x = 0$ to 1, giving rise to a dramatic depression in $T_c$ [7, 8, 9], and at $x \geq 0.55$, no superconductivity is observed. Moreover, the magnetic insulator PrBa$_2$Cu$_3$O$_{7-\delta}$ is a compound which has a single orthorhombic 123 structure, but it does not show superconductivity [10, 11, 12, 13]. Nevertheless, Pr has been found to increase the value of $J_c(B)$, e.g. in bulk [14, 15, 16] and melt-textured samples [17]. In the bulk samples [16], $J_c(B)$ increases with increasing Pr concentration up to $x = 0.08$ and decreases beyond this level. Because of the similarity of the ionic radii between Y and Pr, there is no remarkable change in the lattice parameters between pure and doped samples. It is proposed that the reason for the enhanced
\( J_c(B) \) for Pr-doped bulk samples is due to formation of rows of oxygen vacancies in CuO\(_2\) planes, which provide strong pinning interaction with pancake vortices formed in the same planes [16].

In this paper, we report the effect of Pr\(^{3+}\) substitution at the Y\(^{3+}\) site in Y\(_{1-x}\)Pr\(_x\)BCO (x = 0 - 0.20) thin films, prepared by pulsed laser deposition (PLD), whereas earlier studies on films have been made on samples with small concentrations (x \( \leq \) 1\%) [18].

2. Experimental details

The Y\(_{1-x}\)Pr\(_x\)BCO (x = 0 - 0.20) films were deposited on SrTiO\(_3\) (001) substrates with PLD. The deposition targets were prepared as described previously [19, 20, 21, 22, 23]. Detailed description of the deposition process can be found in [24].

The crystallinity of the film samples was characterized by x-ray diffraction measurements (XRD), using CuK\(_\alpha\) radiation for 29 scans and texture measurements with Shultz geometry. The grain size, surface roughness and thickness of the films were measured by atomic force microscopy (AFM).

Magnetic measurements were performed with a Physical Properties Measurement System (PPMS), at temperatures between 10 - 300 K in fields up to 8 T. The critical current densities \( J_c = 3\Delta M/2R \) of the films were calculated from the opening of the hysteresis loop by using the Bean’s critical state model for disc-shaped samples [25, 26].

3. Results and discussion

The first optimization of the PLD parameters was done with films deposited from pure YBCO target. The substrate temperature was varied from 620\(^\circ\)C to 730\(^\circ\)C and the best film quality was obtained at 670\(^\circ\)C. Other deposition parameters, such as laser fluence, atmosphere, cooling process of films etc. were unchanged due to earlier optimization [24].

All the films were highly c-axis-oriented, and they had the amount of the a-axis-oriented material less than 2\% without any clear dependence on the Pr content. The Y\(_{1-x}\)Pr\(_x\)BCO (212)/(022) XRD peaks show no effect of Pr on twinning and straining of the films. Also 29 scans show only typical YBCO (001) peaks without any signs of impurities. Therefore, it is clear that Pr replaces Y in the lattice over the whole range of x \( \leq \) 0.20 and the structural quality of the samples is good. The AFM data showed that on the contrary to the unaligned polycrystalline pellets prepared using the solid state method [15], grain size in the films and the surface roughness did not have correlation with the Pr concentration.

As shown in figure 1, the values of \( J_c(B) \) decreased at all the measured temperatures (a) and in external magnetic field densities (b) when the Pr concentration was increased. The insert in figure 1(a) shows the decrease of \( T_c \) with the increasing Pr concentration. The values of \( T_c \) are roughly the same as in the sintered bulk samples [16]. However, the \( J_c(B) \) does not behave as in the earlier studies on different type of samples [14, 17, 15, 16], where \( J_c(B) \) was found to increase at some specific Pr concentrations. The same tendency is also seen in figure 2, where the \( J_c(B) \) values decrease as the Pr concentration increases in all fields.

The accommodation field, \( B^* \), defined with the criterion \( J_c(B^*)/J_c(B(0)) = 0.9 \) [27, 28] was found to decrease as the Pr concentration was increased, giving the highest value of 35 mT in a pure sample at 10 K. This value agrees with those obtained from similar targets [29]. The \( B^* \) values decrease with increasing doping, reaching 14 mT for x = 0.20 sample at 10 K. This behaviour is similar at all measured temperatures. The field dependence of \( J_c \) above \( B^* \) is often described by a power law expression \( J_c(B) \sim B^\alpha \) with \( \alpha \) varying from -0.50 to -0.60 [30, 29, 31]. The values of \( \alpha \) are in the typical range for all the samples up to 70 K, varying from -0.40 to -0.60 without any dependence on the Pr concentration, excluding the case of x = 0.20 where \( \alpha \) decreases rapidly from -0.45, observed at 10 K to -0.72 at 60 K, indicating a rapid decrease of \( J_c(B) \) with temperature.
Because doping with Pr did not improve the superconducting quality of the $Y_{1-x}Pr_xBCO$ films, we performed a second optimization, using the $Y_{1-x}Pr_xBCO$, $x = 0.08$ PLD target. Though this dopant level gave the highest $J_c(B)$ for bulks [16], we did not come up with a 8% film sample holding greater $J_c(B)$ than the pure YBCO film. E.g., at 10 K and 0 T the pure film sample has $J_c(B) = 4.2 \cdot 10^{11}$ A/m$^2$ and the best $x = 0.08$ film sample (deposited at the substrate temperature 710$^\circ$C) has $J_c(B) = 2.8 \cdot 10^{11}$ A/m$^2$, whereas in the $x = 0.08$ bulk samples $J_c(B)$ was three times higher than in the pure sample [16].

It is possible that the clear difference in the SC properties on the dopant level, between the polycrystalline bulk samples and the epitaxial thin films, can be explained by the effect of surface pinning [32]. Due to the formation of defects at the interior of thin films, they become rough on the atomic scale, and since the coherence length is small, the barriers for flux entry and flux expulsion are broken or weakened. This gives rise to decrease in $J_c(B)$ of thin films when doped with Pr. Anyhow, our structural measurements did not indicate any dependence between surface roughness and Pr concentration. Thus, we propose that this difference is at least partly due to the grain boundary critical current density $J_{gb}^c(B)$, which is due to increased misorientation angle between the grains. This effect has been reported many times [33, 34] and Ca$^{2+}$ doping is well known to increase $J_{gb}^c(B)$. Furthermore, the ionic radii of Pr and Ca are roughly the same, and it has been suggested lately that the ionic radius is more important than the valence of the dopant in creation of high $J_{gb}^c(B)$ [35]. This is in agreement of the enhancement of $J_c(B)$ only in the polycrystalline samples, but lacks from our epitaxial thin film samples.
4. Conclusions
In this work, we optimized Pr-doped YBCO films. Even though the structural quality of the samples was good and the dependence of \(T_c\) on Pr concentration was as expected, neither \(J_c(B)\) nor \(B^*\) increased in the doped films. We suggest that this is at least partly due to the grain boundary critical current effect, which increases \(J_c\) in the polycrystalline samples and is absent in thin film samples.

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