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ORIGINAL PAPER

# Magnetization and Critical Current of Calcium-doped $YBa_2Cu_3O_{7-x}$ Composite Films

**Igor Rudnev[1,2] · Alexey Menushenkov[1,2] · Andrey Blednov[3] · Vsevolod Chepikov[3] · Sergey Samoylenkov[3]**

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**Abstract** The results of the study of magnetization of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ HTS films deposited on the metallic substrate are presented. The magnetization measurements were carried out in a wide temperature range 4–77 K and magnetic fields up to 14 T. Based on critical state model, the analysis of the influence of calcium concentration on the critical current was performed. It was found that the change in Ca concentration causes the decrease in value of critical current density $j_c$. The increase in temperature leads to enhancement of the observed effect. At $T = 4.2$ K and in the magnetic fields higher than 8 T, the $j_c$ reduction was found to be insignificant. This fact may indicate the possibility of $j_c$ growth in strong magnetic fields due to increase in carrier concentration caused by replacing $Y^{3+}$ by $Ca^{2+}$.

**Keywords** High $T_c$ superconductors · Ca doping · Magnetization · Critical current

## 1 Introduction

Despite the significant advances in synthesis of high-temperature superconducting films (HTSC) based on $REBa_2Cu_3O_{7-\delta}$ (where RE - rare earth element) with high critical current density values, the task of further $j_c$ increasing, especially in magnetic fields, remains relevant. A conventional way to increase in critical current is a formation in the superconducting matrix of artificial pinning centers. For HTSC $REBa_2Cu_3O_{7-\delta}$, the highly efficient pinning centers are yttrium oxide $Y_2O_3$, barium cerate $BaCeO_3$, barium zirconate $BaZrO_3$, and gafnata barium $BaHfO_3$ (see, e.g., [1–4]).

Another alternative way of critical current enhancement is an increase in concentration of superconducting carriers. Such a way may be realized either by changing of the oxygen content, or by replacing one of the cations belonging to the HTSC element by ions with lower charge. Since HTSC is a fully oxidized compound, the input of additional oxygen atoms (change in $\delta$) is impossible. One possibility of doping is to replace the ion $Y^{3+}$ by $Ca^{2+}$. Thus, extra holes are created, which may lead to growth of concentrations of superconducting carriers and, consequently, increase in $j_c$.

The possibility of increase in critical current of high-temperature superconductors $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ through doping by calcium has been widely discussed [5–9]. In particular, it was shown that the adding of Ca to the bulk polycrystalline samples leads to increased $j_c$ [5, 6]. This fact is generally attributed to excess holes introduced by bivalent $Ca^{2+}$ which substitute the trivalent $Y^{3+}$ [7]. However, polycrystalline samples that were used in these studies consist of a network of randomly oriented grains, which makes it difficult to interpret the results of experiments. The studies of films [7] also demonstrated the possibility of substitution of $Y^{3+}$ by $Ca^{2+}$ as an impurity hole. In ref. [8], it was shown that Ca is released predominantly at grain boundaries, where a replacement of yttrium by calcium takes place.

It shoud be noted that the previous studies have been performed at temperatures near 77 K. In our report, we present new results of the influence of Ca doping on magnetization

✉ Igor Rudnev
iarudnev@mephi.ru

1 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, Russia

2 International Laboratory of High Magnetic Field and Low Temperatures, Wroclaw, Poland

3 SuperOx, Moscow, Russia

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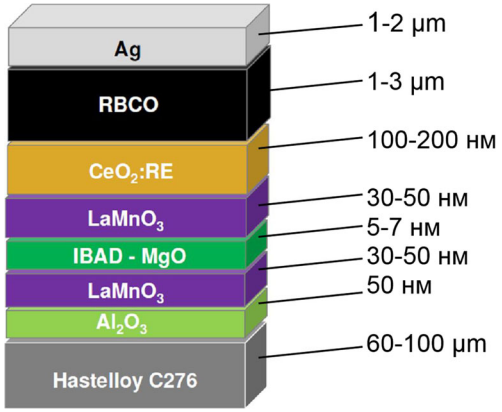


**Fig. 1** Architecture of the HTSC composites (Color figure online)

and critical current of HTSC composite film deposited on metallic substrate. A feature of our studies is that we have carried out the measurements in a wide temperature range from 4 to 77 K and in magnetic fields up to 14 T.

## 2 Experimental Details

Ca-doped YBCO films were deposited by MOCVD methods on hastelloy C276 tape covered with a system of buffer layers $CeO_2/LaMnO_3/MgO/a\text{-}Y_2O_3/a\text{-}Al_2O_3$ in a specially constructed reel-to-reel MOCVD machine. The substrate was heated up to 900 °C.

Y(thd)3, Ba(thd)2*tetraglyme, Cu(thd)2, and Ca(thd)2*tmeda were used as sources (precursors) of yttrium, barium, copper, and calcium for the film. The precursors were mixed in ratio providing stoichiometry in the obtained films, milled and pressed to a pellet. The pellet was continuously grinded during the deposition process. The grinded out material was falling down to evaporator heated to 330 °C. The vaporized precursors were carried to the deposition zone by argon flow along the tubes with hot (300 °C) walls preventing precursor condensation. Near the substrate precursors were mixed with oxygen and oxidized by it with Ca-doped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ film formation. The architecture of the film is shown schematically in Fig. 1. The concentrations of Ca were $x = 0$ for sample PZ61, $x = 0.02$ for PZ62, $x = 0.04$ for PZ63, and amount of yttrium with respect to barium and copper was reduced proportionally. For sample, PZ65 $x = 0.04$ (the same as for PZ63), but the amount of yttrium was not changed. A partial substitution of yttrium by calcium does not leads to changing of the structure of superconducting matrix. Figure 2 shows that the reflections on the x-ray phase analysis curve for the initial sample PZ61 and for the sample with the highest

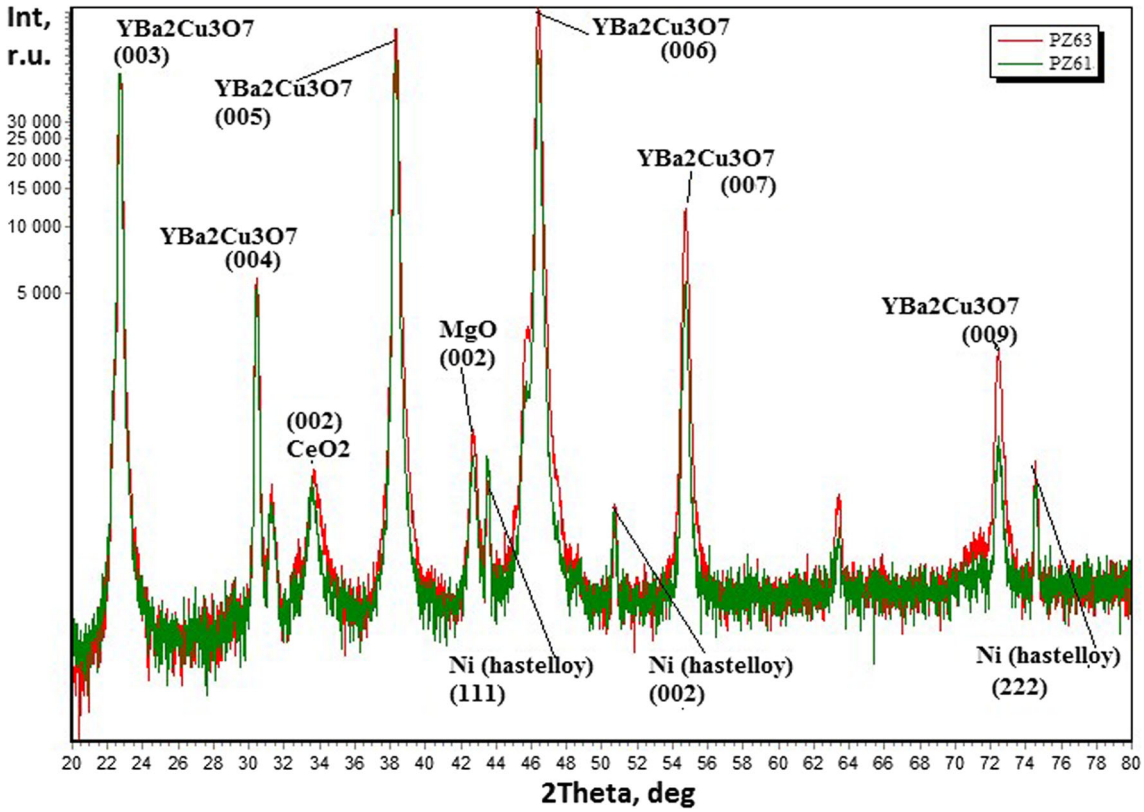


**Fig. 2** X-ray diffraction data for PZ61 (*red line*) and PZ65 (*green line*)

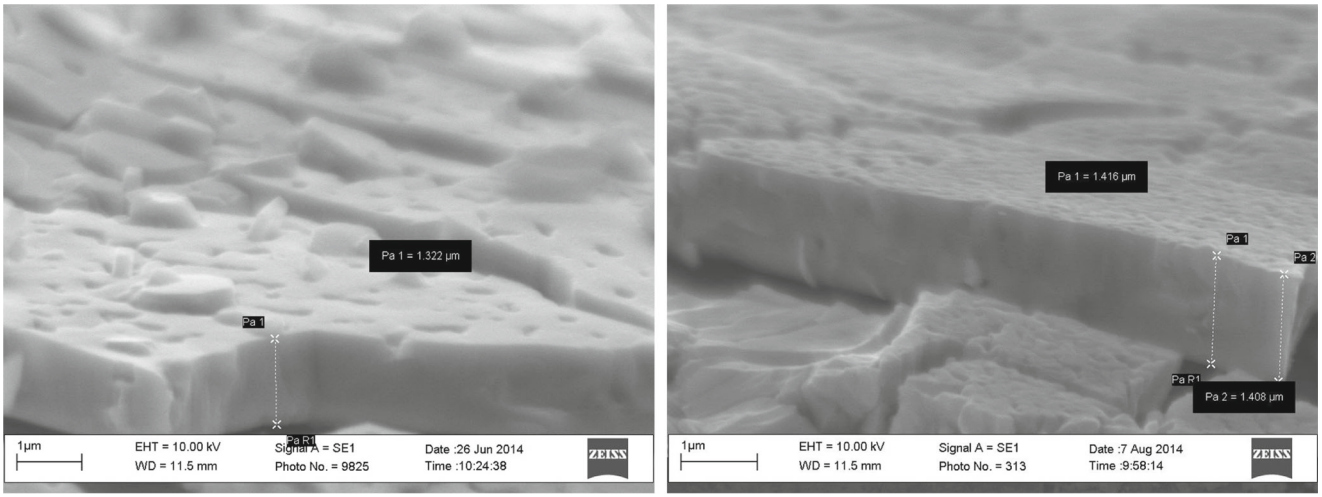


**Fig. 3** SEM images of HTSC matrix for PZ61 (*left*) and PZ65 (*right*)

content of calcium PZ64 are practically identical. There are also no significant differences in the SEM images (Fig. 3). XRD and SEM data indicate that the doping by calcium did not change the structural characteristics of the studied samples.

Magnetization measurements were performed by use of vibrating sample magnetometer in the temperature range 4–77 K and magnetic fields up to 14 T. The samples that were used for the measurements have had a form of a square with sides 12 mm. The magnetic field was oriented perpendicular to the film surface, i.e., parallel to the c axis of the HTS unit cell.

## 3 Results and Discussion

Figure 4 shows examples of the magnetization curves at minimal $T$ = 4.2 K and maximal $T$ = 77 temperatures for four samples with different content of the alloying element. From the figure, it is clear that the introducing of calcium reduce both the value of the magnetization and the width of $M(H)$ curves. The effect is enhanced as the temperature increases. The reduction of reversible hysteresis curve indicates a change of the critical current in accordance with a formula that relates the width of the magnetization loop $\Delta M$ and the critical current density for rectangular film in a perpendicular magnetic field:

$$\Delta M = \frac{bj_c}{20}\left(1 - \frac{b}{3a}\right) \tag{1}$$

Here, $\Delta M$ is the difference between the values of the magnetization with increasing external field $M^+$ and decreasing external field $M^-$:$\Delta M = M^+ - M^-$; $j_c$ - critical current density, $a$ and $b$ - the geometrical dimensions of the sample (in our case $a = b$).

Figure 5 shows the calculated from the formula (1) dependencies of the critical current density on applied magnetic field. At $T$ = 4.2 K, there is a noticeable decrease in $j_c$ for small fields, but this reduction of critical current practically vanish for magnetic fields higher than 10 T. The increase in temperature changes the picture. Thus, at

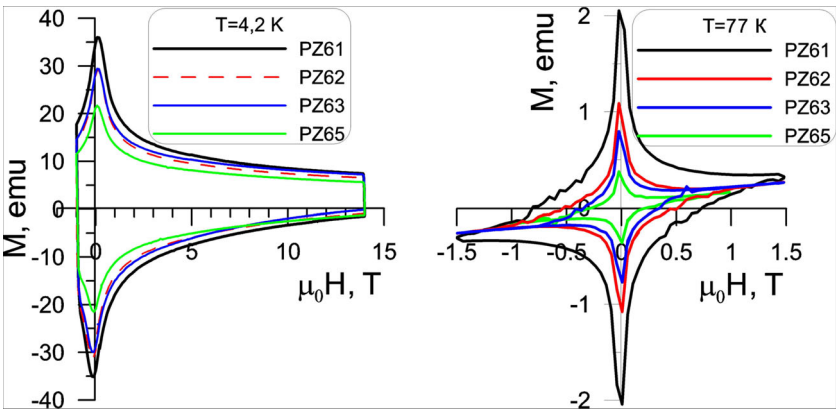


**Fig. 4** Magnetization curves of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films at $T$=4,2 K (*left*) and $T$ = 77 K (*right*)

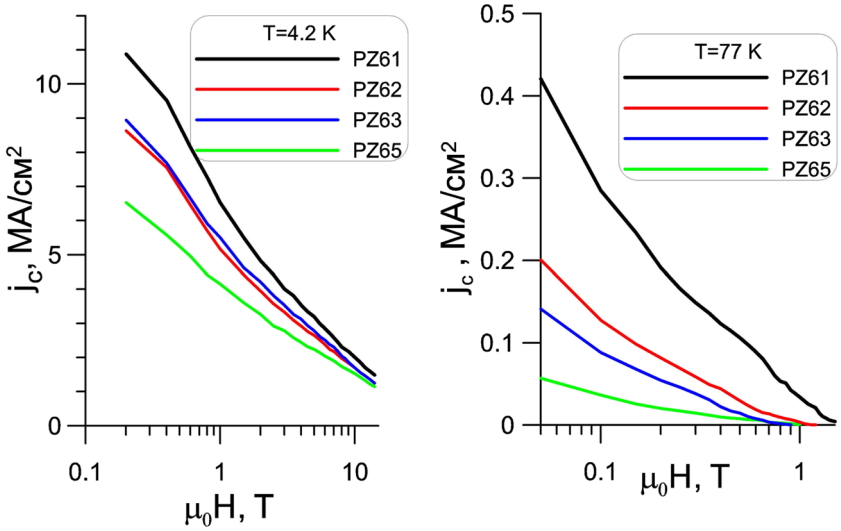


**Fig. 5** The dependencies of the critical current on applied magnetic field jc(H) for various $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films at $T$=4,2 K (*left*) and $T$ = 77 K (*right*)

$T$ = 77 K, the decrease in the critical current is observed in the entire range of non-zero critical current.

Obtained results may be analyzed based on the concept of decoupling critical current, the value of which depends on the concentration of superconducting carriers. It is easy to find that at low temperatures far from $T_c$ the critical current is expressed as follows:

$$j_c \approx \frac{n_s q_s}{\sqrt{m_s}}\sqrt{T_c} \tag{2}$$

where $n_s$, $q_s$, $m_s$ are the concentration, charge, and mass of superconducting carriers, respectively, and $T_c$ the critical temperature. Therefore, the critical current density depends on both the carriers concentration and the value of the critical temperature. Moreover, near $T_c$, according to the Ginzburg-Landau theory, the dependence of the critical current density $j_c^{G-L}$ on the critical temperature is stronger:

$$j_c^{G-L} \sim (T_c - T)^{3/2} \tag{3}$$

We can see from the expression (2) that the increase in the critical current density is possible to reach by increasing of the concentration of superconducting carriers that may be occurs at partial replacement of the trivalent yttrium by divalent calcium. Moreover, it is important whether there is a change of the critical temperature. The determinations of the $T_c$ by means of the magnetic susceptibility measurements showed a drop in $T_c$ by 3–5 K at the maximum concentration of calcium. Apparently, at $T$ = 4.2 K, the influence of the reduction of critical temperature compensate a possible increase in the carrier concentration, which ultimately did not lead to growth of the critical current. For $T$ = 77 K, a significant decrease in critical current is also explained by strong dependence of $j_c$ on $T_c$.

The question arises, why in our experiments the increase in the critical current is not observed compared to that observed in literatures. Apparently, the absence of rising of $j_c$ is due to two factors. Firstly, due to replacing of yttrium by calcium predominantly at the grain boundaries as shown in [9]. The polycrystalline samples have many grain boundaries that lead to strong effect of critical current enhancement. In our case, we deal with highly oriented epitaxial films, which have a relatively small number of grain boundaries, where calcium doping occurs. Secondly, the original composites have already initially high values of $j_c$ as a result of effective pinning in the superconducting films. Therefore, due to high initial values of $j_c$, a further additional increase in the critical current density by doping with calcium was not observed in our study.

## 4 Conclusion

It was found that the substitution of yttrium by calcium leads to a decrease of the magnetization and the critical current density. An increase in temperature leads to enhancement of the observed effect. At $T$ = 4.2 K and in magnetic fields up to 8 T, the $j_c$ reduction is slight, which may indicate the possibility of $j_c$ growth in strong magnetic fields due to increase of the carrier concentration when replacing $Y^{3+}$ by $Ca^{2+}$.

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