Pinning behavior of Al, Mn and Ag substitutions in YBCO TSMG bulk superconductors

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Abstract. Peak effect in dependences of critical current density on applied magnetic field caused by nanosize chemical pinning centers was studied in $Y_{1.5}Ba_2(CuM)_3O_y$, for $M = Ag$, Mn, and Al with CeO$_2$ technological addition. The behavior of Mn, Ag and Al dopants was analyzed in relation to sample microstructure and oxygenation heat treatments respectively. It is shown that formation of $Cu_2Mn_3Ba_6O_y$ compound and low negative partition coefficient of Ag between the solid and melt are responsible for declination from expected pinning behavior for Mn and Ag substituents.

1. Introduction

As a consequence of low coherent length ($\approx 3$ nm at 77 K), the most effective pinning centers in RE123 superconductors should have nanosize dimensions. For example optimally irradiated Y123 bulk superconductors can reach 3 times higher trapped fields due to effective nanosize pinning centers induced by irradiation damage [1]. There are successful attempts to introduce nanosize pinning centers in the form of ex-situ [2] or in-situ [3] created nanoparticles or through introduction of nanosize pinning centers by chemical substitutions in the RE123 lattice [4]. In the case of RE123 bulk superconductors the most problematic step in the incorporation of nanoparticles is the pushing of the particles with the size smaller than critical by the growing crystal. It seems therefore sensible to create nanosize pinning centers in these bulks through substitution of atoms in the RE123 lattice. It is characteristic for TSMG RE123, especially for Y123, that small technological addition of Pt or Ce is necessary for their successful fabrication. These elements can react with added substitutions and consequently misrepresent their influence on the pinning behavior. For example in the TSMG Y123 bulks with Pt or Ru addition the phase $Ba_4Cu_2PtO_y$ type is formed and this phase can incorporate Cu substituents [5, 6]. All reported studies on TSMG YBCO bulks with Cu substitutions were done on the systems with Pt addition [4, 7, 8]. Therefore in our program we used Ce addition where no reaction with Cu substitutions has been reported.

2. Experimental details

YBCO bulk single-grain samples with a nominal composition $Y_{1.5}Ba_2(CuM)_3O_y$, for $M = Ag$, Mn and Al were fabricated by top-seeded melt-growth process (TSMG). The stoichiometry of the M elements in $Y_3Ba_2(Cu_{1-x}M_x)O_7$ was chosen in the range $x = 0.0025$ to 0.05. YBa$_2$Cu$_3$O$_7$, $Y_2O_3$, CeO$_2$ and M-oxide powders were mixed in appropriate amounts, milled in a friction mill and pressed in to
cylindrical pellets 20 mm in diameter. The as grown samples were cut in two halves along the \{100\} plane. The microstructure of the sample was analyzed by an optical microscope and by scanning electron microscope (SEM). For magnetization measurements, the plate-like samples (2 x 2 x 0.5) mm$^3$ in size were cut from the a-growth sectors of the single-grain bulks in a distance 1 mm from the seed. The samples were oxygenated in flowing oxygen at 400 °C for 150 hours. Magnetization properties of the samples were measured at 77 K by a vibrating sample magnetometer under fields applied parallel to the c-axis. The critical current density, $J_c$, was calculated from the width of magnetization hysteresis loops based on the extended Bean model. The critical temperatures, $T_c$, were determined from the zero field and field cooling curves with an applied external magnetic field 2 mT. The transition temperatures were obtained from the mid-point of the magnetization transition curves (50% magnetization) from the superconducting state to the normal state.

3. Results and discussion

In the case of Al dopant the peak effect appeared from the lowest used dopant concentration $x = 0.0025$ while for Mn the strongest peak effect was observed for $x = 0.02$ and for Ag the peak effect was observed only at the highest dopant concentration $x = 0.05$ (Figure 1). According to Ishii [8] in the

![Fig. 1. Dependences of critical current densities, $J_c$, on applied magnetic field, $B$, and transition temperature, $T_c$, on dopant concentration. Peak effect appears at the lowest Al concentration, starts at higher Mn concentration and is observed only at the highest Ag concentration. Decreasing of $T_c$ with dopant concentration evidences substitutions in Y123 lattice.](image)

RE123 melt processed samples with RE element, which do not substitute Ba (for example Y and Dy) the peak effect should be observed at concentration of dopant leading to the distance between randomly distributed dopant atoms in the CuO$_2$ plane equal to 2 coherent lengths what is about 6 nm at 77 K. In our case this distance between substituents is reached for $x = 0.0013$ when they substitute Cu.
in CuO chains. This level of doping can correspond to our lowest used concentration as some dopant atoms can substitute also in Y211 phase what will decrease their concentration in Y123 phase. The decreasing of $T_c$ with dopant nominal concentration confirms that Cu atoms in Y123 crystal lattice were partially substituted. Some differences in $T_c$ decreasing in comparison with polycrystalline ceramics may be caused by redistribution of dopants between Y123 and Y211 phases, inhomogeneous distribution of dopant caused by solidification process as well as due to formation of secondary phases rich in dopant.

The peak effect caused by Al and Mn was not observed so far in the TSMG bulk YBCO superconductors and Ag and Mn behavior is different because both these elements exhibit peak effect at concentrations higher than expected. Further we will analyze more in detail Ag, Mn and Al doping separately.

**Ag substitution.** The peak effect caused by Ag addition in TSMG YBCO was reported by Nakashima [9] but the concentration of Ag in the sample with peak effect was not given. Important information, which can explain why the peak effect in our case was observed at much higher nominal dopant concentration, was obtained from conducted microstructural observation. We found that in the middle of the samples, at the beginning of solidification, the microstructure does not contain any Ag phase at any Ag nominal concentration and consists only from Y123 crystal and Y211 particles and well developed gray barium cerate phase (Fig. 2 (a)).

![Fig. 2. SEM micrographs of a/c-cross section of Ag doped samples. Besides Y123 and Y211 phases only grey barium cerate, BaCeO$_2$, rectangular particles were present at the beginning of solidification (a). Later, white globular Ag particles are trapped (b) but the most Ag is concentrated as separated phase at the sample rim (c).](image)

After some distance from the beginning of solidification the Ag phase start to appear in the structure in the form of globular particles (Fig. 2 (b)) as it was confirmed by EDAX analysis. The distance from the seed, when the first Ag particles appeared, was longer for the samples with lower nominal Ag concentration. At the lowest nominal Ag concentration the Ag particles were observed only at the end of solidification, at the rim of the sample where they solidified together with the rest of melt (Fig. 2 (c)). This experimental result confirms that there is some partition coefficient controlling ratio of Ag concentration between the solid Y123 crystal, $C_{AgS}$, and the nominal Ag concentration in melt, $C_{Ag0}$.

$$k_{Ag} = \frac{C_{AgS}}{C_{Ag0}}$$  \hspace{1cm} (1)

From the ratio between nominal Ag concentration at which the peak effect was observed ($x = 0.05$) and the Ag concentration in the Y123 crystal at which the peak should appear ($x = 0.0013$) we can
conclude than the Ag distribution coefficient, $k_{Ag}$, is somewhere around 0.026 (0.0013/0.05). During solidification of the system with negative partition coefficient the dopant element is distributed inhomogenously with the lowest concentration in the solid, $C_{AgS}$, at the beginning of solidification and increasing concentration with the relative distance from the beginning of solidification, $\lambda$, according to equation [10]:

$$C_{AgS} = k_{Ag} C_{Ag0} (1-\lambda)^{k_{Ag}^{-1}}$$

Dependence of Ag concentration on the relative distance from the seed calculated from equation (2) for used starting nominal Ag concentrations is presented in Fig. 3.

Fig. 3. Calculated Ag concentration in the Y123 crystal, $C_{AgS}$ versus relative distance from the seed, $\lambda$.

We measured magnetization and $T_c$ of the samples separated at the beginning of solidification where much lower concentration of Ag was substituting Cu in the Y123 lattice than the nominal Ag concentration. Only at the nominal concentration $x = 0.05$ the concentration of Ag solved in the Y123 crystal at the beginning of solidification reached value which generated the effective distance of Ag atoms for pinning. As the solubility of Ag in the Y123 phase is limited [11] after some solidification length the Ag concentration in the Y123 crystal exceeds this limit and all the rest of Ag diluted in the melt is pushed by growing crystal. When the Ag concentration in the melt overcomes the solubility limit, Ag rich phase star to precipitate in the form of droplets in the melt. These droplets are trapped by growing Y123 crystal and later, during cooling from the crystal growth temperature, they solidify [12].

**Mn substitution.** Microstructure analysis revealed that in the studied system with Mn addition the compound with composition close to Cu$_2$Mn$_3$Ba$_6$O$_y$, measured by EDAX, was formed (Fig. 4). Formation of this compound consumes a part of added Mn, but some Mn also substitute Cu in the Y123 lattice what is evidenced by the influence of Mn addition on transition temperature as well as appearance of peak effect at higher Mn concentrations (Fig. 1).

**Al substitution.** $T_c$ decreasing with Al concentration which was measured (Fig. 1) is comparable with that measured on polycrystalline ceramics [13]. Microstructure analysis has shown that Al addition does not form any compound with Y, Ba, Cu or Ce in the system, therefore we can suppose that the Al partition coefficient is close to one and Al is mostly diluted in the Y123 phase. The peak effect, which we observed at the lowest Al concentrations (Fig. 1), also confirms that Al substitution in the Y123 lattice is close to nominal concentration. Al$^{3+}$ substitutes CuO chains in the Y123 lattice and should behave similarly to Fe and Co substitutions. Both these elements prefer higher coordination number than two and therefore at annealing in Ar at higher temperatures they shear deficit oxygen atoms and
form clusters [14]. Additional heat treatment of the samples with Al doping in argon at 800 °C for 1 hour caused significant changes in both \( T_c \) and pinning behavior. In the concentration range for \( x \) from 0.0025 to 0.02 we observed recovery of transition temperature to the values found in the sample without Al substitution (Fig. 5) as well as extinction of peak effect and

![Image](image-url)

**Fig. 4.** Y211 particles and particles of \( \text{Cu}_2\text{Mn}_3\text{Ba}_6\text{O}_y \) phase in the Mn doped sample with \( x = 0.05 \) and EDAX spectrum of Mn rich phase.

its appearance at the highest Al concentrations (Fig. 5). If we suppose clustering of Al atoms and effective mean distance between Al clusters 6 nm we can expect about 20 Al atoms in the cluster.

![Image](image-url)

**Fig. 5.** Critical temperature, \( T_c \), recovered and peak effect shifted to the highest Al concentration after preannealing in Ar at 800 °C.

### 4. Conclusions

The study of Cu substitutions in TSMG YBCO bulk superconductors with CeO\(_2\) technological addition showed that the peak effect can be induced by Al, Mn or Ag doping. In the case of Al, the peak effect appeared from the lowest used dopant concentration \( x = 0.0025 \). We suggest that Al behaves similarly as Fe and Co e.g. under annealing in low oxygen atmosphere it has a tendency to form clusters. Mn
addition is partially bound by \(\text{Cu}_2\text{Mn}_3\text{Ba}_6\text{O}_y\) phase and only partially substitutes Cu in the Y123 lattice. Ag is distributed highly inhomogenously in the sample due to low Ag partition coefficient between solid and melt, which was estimated to be about 0.026. Very low Ag partition coefficient causes that peak effect appeared only at the highest nominal Ag concentration \(x = 0.05\).

**Acknowledgements**

This work has been supported by VEGA project No. 2/7052/27, APVV projects No. 51-061505 and LPP-0334-06, EU network NESPA, and by the Centre of Excellence of Slovak Academy of Sciences NANOSMART.

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