Magnetoresistance studies of PbO addition in YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor

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Abstract. The effect of PbO addition on the superconducting properties of YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123) polycrystalline phase has been investigated through samples with x wt.% PbO (x = 0 - 4.5) addition prepared using standard solid state reaction method. Electrical transport measurements indicate that samples with x = 1-3 have their current density, at self magnetic field, $J_0$, increased about 50%. Their magnetic field dependent $J_c(H)$ has been measured in liquid nitrogen, and the activation energies have been determined using the TAFF model which shows an enhanced flux pinning proprieties. TEM and EDX analyses have shown that Pb reacts with Y-123 phase to form nanometric Pb-rich phase intergrown in Y-123 superconductors matrix. These inhomogeneities may be the origin of strong pinning.

1. Introduction

Y-123 superconductor is one of the most promising for high temperature (liquid nitrogen) applications due to its lower anisotropy and its higher coherence length than Bi-2223 superconductor. However, its poor performance under magnetic field, arising from the weak pinning of vortex lattices leads to dissipation which prevents its extensive high field utilization. The interaction between pinning centers and flux lines determines the $J_c(H)$ as maximum zero-resistance current density. Pinning may be intrinsic, caused by the layered crystal structure itself, or extrinsic generated by defects with a size matching the coherence length as effective pinning centers. At around 77 K, the layer spacing becomes too small compared to the flux line diameter leading to less intrinsic pinning [1]. Around this temperature, relatively large-sized extrinsic pinning centers such as twins, stacking faults [2,3], interfaces between Y$_2$BaCuO$_5$ (Y-211) and Y-123 [4,5] columnar defects [6], normal nano particles inclusion [7] … are thought to be more efficient.

Chemical dopants may also be able to modify the crystalline structure and generate defects. Some defects such as chemical inhomogeneities…, can be an additional effective pinning centers. For bismuth based superconductors, lead (Pb) is the most important doping element that influences their microstructure, phase compositions and related electrical transport properties $J_c(H)$ and $T_c$ [8-10].

To our knowledge, only one paper has been published about the PbO addition effects on the Y-123 system [11]. The authors show that the addition of Pt together with SnO$_2$ or PbO using the melt-
powder-melt growth Y-123 phase results in various shapes and non uniform distribution of Y-211 are not beneficial to the enhancement of $J_c$. The central aim of the present work is to analyse the pinning properties of PbO addition in the Y-123 system.

2. Experimental
Polycrystalline samples of x wt.% (0.0, ..., 4.5) of PbO addition in YBCO were prepared by the standard solid state reaction route. Previously, a Y-123 phase was prepared from stoichiometric quantities of pure Y$_2$O$_3$ (99.99%), BaCO$_3$ (99.99%), and CuO (99.99%) mixed in an agate mortar and uni-axially cold pressed in pellets at 200MPa. The pellets were placed in alumina crucibles and calcined in furnace for 8 hours at 950°C, with a heating rate of 12°C/min. After cooling down at room temperature, they were reground with appropriate amounts of PbO (99.99%) addition before pressed and annealed as above.

The transport properties were measured using the four probe technique with samples cut in rectangular shape in typical dimensions of $5 \times 1.5 \times 0.3$ mm$^3$. To determine their current densities in liquid nitrogen, a criterion of 5$\mu$V/cm is used. Their magnetoresistance graphs, as a function of temperature were obtained via lock-in detection with ac current at 0.13mA at 36Hz, under fields from 0 to 300mT, perpendicular to samples surface. The magnetic field is applied when cooling from 110 K.

The powder x-ray diffraction analyses were performed with a Philips 1710 diffractometer with CoKα radiation on the $20^\circ \leq 2\theta \leq 60^\circ$ range with 0.02° ($2\theta$) step size. Refinement of the x-ray diffraction data was carried out by the Rietveld method using the FULLPROF program with multiphase capability. The structural parameters of YBCO were used as a starting model for the refinement. The positional, thermal, and occupancy parameters were varied in addition to scale factor, zero angle, half-width and background parameters. The microstructure of samples was characterized by scanning (Jeol JEM-5510) and transmission (Technai G2) electron microscopy. Their chemical composition was determined by energy dispersive x-ray (EDX) analysis.

3. Results and discussions
The x-ray diffraction patterns do not show the presence of any secondary phases and the negligible lattice parameters change, reported in Table 1, permits to say that Pb does not substitute any element in Y-123 structure.

| x PbO | 0.0 | 1.0 | 2.5 | 3.5 |
|-------|-----|-----|-----|-----|
| a (Å) | 3.81672 | 3.81662 | 3.81834 | 3.81761 |
| b (Å) | 3.88018 | 3.88002 | 3.88050 | 3.88094 |
| c (Å) | 11.67266 | 11.67266 | 11.67439 | 11.67407 |

In figure 1, a slight amount of lead is observed in x-ray diffraction patterns with 3.5 wt % PbO-added sample indicating that the Pb-inclusions increase drastically.
Figure 1. Powder x-ray diffraction patterns of PbO added samples showing a slight amount of lead with 3.5 wt. % of PbO addition.

Figure 2. shows the $J_c$ curve versus PbO content and its enhancement by 50% compared to the free sample implying the better grains connectivity, namely weak links through the passivation of Josephson junctions [14,15].

To investigate the PbO pinning effect, three samples (x = 0.0, 2.5, 3.5) were used and measurements of $J_c$ dependence on the applied magnetic field, $J_c(H)$, were performed with the field direction perpendicular (H⊥) and parallel (H∥) to the sample surface. To isolate the flux pinning improvements, the measured $J_c(H)$ values in magnetic field can be instead normalised to the $J_c(0)$ at zero-field value. PbO added samples exhibit the slower $J_c$ decrease compared to the free one as indicated in figure 3. Strong flux pinning ability is observed in sample with x = 2.5 and an “anomalous” second peak appears when magnetic field is parallel to PbO-added sample surface in low field domain (10mT).
In the weak links region, where the $J_c$ drops suddenly from his higher value at $H=0$, the flux pinning improvement due to grains connectivity is enhanced with 2.5 wt. % PbO-added sample. In fact, C. H. Cheng and Y. Zhao [12] found that the self-field $J_c$ value increases at 77 K indicating that grains boundaries are strongly coupled and, their rapid decrease with an increasing applied magnetic field may be attributed to their degradation in the grains boundaries region. The intergranular current is rather small, and the intragranular current is dominant.

As shown SEM micrographs in figure 4. and figure 5., it is thought that PbO leads to Y-123 phase melting temperature decrease allowing the small plates melting near and near, which in cooling agglomerate to a big one.

Melting process induced by PbO addition leads to a better intergranular connectivity with improvement of the area of connectivity, increases the density of sample and decreases the angle between grains boundaries, as shown in SEM micrographs.
To further investigate flux pinning enhancement, the samples temperature dependence of the in-plane resistivity out of and under various magnetic fields perpendicular to their surface are measured. The magnetoresistance curves show in the region of the superconducting transition two sections, a steep part associated with the onset of the superconductivity in the individual grains and transition tail due to weak links coupling the grains [13]. The superconducting transition width of the initially steep of each sample becomes wide with increasing magnetic field. The tail part moves considerably to lower temperature and the slope of the normalized resistance $\log(R/R_{110K})$ versus $1/T$ close to $T_c$, in the Thermal Activated Flux Flow (TAFF) model, shown in figure 5., is related to the activation energy [14].

![Magnetoresistance curves](image1)

**Figure 6.** Magnetoresistance curves of (a) 0.0 wt. %, (b) 2.5 wt. %, (c) 3.5 wt. % of PbO addition on Y-123 for various magnetic fields applied perpendicular to sample surface.

The activation energy plotted in figure 7. shows the pinning ability of 2.5wt. % PbO-added sample due to the better intergranular connectivity associated to the presence of the Pb-rich phase in the superconducting matrix observed by transmission electron microscopy (figure 8.)

![Activation energy](image2)

**Figure 7.** Enhancement of pinning energies induced by PbO addition on Y-123. Their convergence to a fixed point seems to be a result of plastic deformation.
4. Conclusion
The superconductor properties of Y-123 phase have been enhanced by PbO addition. The optimum rate of best improvement in magnetic field is found to be 2.5 wt.%. Y-123 phase electrical properties enhancement is thought to be the consequence of its grains size increase and their best connectivity induced by PbO ability to reduce materials melting temperature. In the other hand, the improvement of critical current density behaviour under applied magnetic field can be also attributed to the intra-granular flux pinning enhancement, due to the pinning centers introduced by the Pb-rich phases embedded in the superconducting matrix.

5. References
[1] Yamada H, Yamasaki H, Develos-Bagarinao K, Nakagawa Y, Matawatari Y and Obara H 2003 Physica C 392-396 1068-1072.
[2] Feng Y, Wen J G, Pradhon A K, Koshizuka N and Zhou L 2002 J. Phys.: Condens. Matter 12 5843-5845.
[3] Plain J, Sandiumenge F, Rabier J, Proult A, Stretton I, Puig T and Obrodars X 2005 Supercond. Sci. Technol. 18 5184-5187.
[4] Zhang H, Liu Y, Li H L, Qu J F, Li X G and Feng Y 2005 Supercond. Sci. Technol. 18 1317-1322.
[5] Muralidhar M, Jirsa M, Sakai N and Murakami M 2003 Supercond. Sci. Technol. 16 R1-R16.
[6] Kang S, Leonard K J, MartinP M, Li J and Goyal A 2007 Supercond. Sci. Technol. 20 11-15.
[7] Varanasi C V, Barnes P N, Burke J, Brunke L, Maartense I, Haugar T J, Stintzian E A, Dunn K A and Haldar P 2006 Supercond. Sci. Technol. 19 L37-L41.
[8] Ben Azzouz F, M’chirigu A, Yangui B, Boulesteix C and Ben Salem M 2001 Physica C 356 83-96.
[9] Hua L, Yuan G, Yoo J, Kim H, Chuang H and Qiao G 2000 Physica C 341-348 2021-2012.
[10] Pu M H, Song W H, Zhao B, Wu X C, Sun Y P and Du J J, 2001 Supercond. Sci. Technol. 14 299-304.
[11] Cai C –B, Gong S -M, Fu Y –X and Zhang H 1997 Physica C 282-287 499-500.
[12] Cheng C H and Zhao Y 2003 J. Appl. Phys. 93 4.
[13] Gamchi H S, Russell G J and Taylor K N R 1994 Phys. Rev. B 50 17.
[14] Plastra T T M, Batlogg B, Van Dover R B, Schneemeyer L F and Waszczak J V 1990 Phys. Rev. B 41 10.