Effect of Li-Halides on the Morphology of Cuprates Ceramics and Their Properties under Neutron Irradiation

V Sandu, G. Aldica¹, S. Popa¹, and E. Sandu²

¹ Department of Low Temperature Physics and Superconductivity, National Institute of Materials Physics, Magurele, Ilfov, 077125 Romania;
² National Institute of Nuclear Physics and Engineering "Horia Hulubei", Magurele, Ilfov, 077125 Romania

E-mail: vsandu@infim.ro

Abstract. Superconducting YBa₂Cu₃O₇₋δ ceramics were prepared with small addition (2-10 mol%) of lithium halides (LiF and LiCl). In all cases, the sample structure became less compact but the grains got better connected. Therefore, there is an optimal content of Li halide, around 4 mol%, which provides the best transport properties and the highest critical temperature. When submitted to neutron irradiation, the normal state resistivity shows an overall increase while the critical temperature slightly increases (δTc ≤ 1 K) in the more homogeneous samples and decreases in the stronger Li-doped samples (δTc ≤ -2.8 K).

1. Introduction

The exciting advantage of cuprate superconductors of carrying supercurrent at high temperatures has a fundamental drawback arising from the nature of vortex pinning in these materials. The small coherence length ξ of these materials, of order of few nanometres, restricts the efficient pinning centres only to defects of extension comparable to ξ, i.e., to small structural defects like vacancies or interstitials. Naturally, in cuprate superconductors, the most frequent defects are the oxygen vacancies that provide a pinning relief where the vortex lines meander in order to minimize their total free energy. Some special defects, with one extended size (twin boundaries, point defect loops, particle tracks, etc) but keep the others of order ξ, provide very strong pinning force as the vortex is aligned along the longer size. As expected, the density of this kind of defects is extremely low; hence, a functional amount of such strong pinning centres requires special processes of fabrication. Therefore, the first challenge for these materials is the creation of artificial pinning centers with increased pinning strength.

A way to create strong pinning centres is particle irradiation but only the use neutrons is effective in bulk samples because the charged particles are promptly stopped in the matter. The main drawback of neutron is the low effective cross section, of order unity, of the atomic species in cuprates. It is possible to overcome this shortcoming by the use of Li-based additives to cuprates because the isotope ⁶Li has an effective cross section σ = 936 barn, a natural abundance of 17%, and is not poisonous for superconductivity [1]. Appropriate vectors (additives) for Li were found to be Li-halides [2] because both Li and the halogen have beneficial effects on superconductivity when used in reasonable amount. However, the morphology of the ceramic sample stays sensitive to the amount of the halide which in turn controls the defect accumulation during neutron irradiation. In this paper, we present the effects...
of lithium halides on the structural and superconducting properties of virgin and neutron irradiated YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123) ceramic samples.

2. Experimental

YBa$_2$Cu$_3$O$_{7-\delta}$(LiX)$_x$ ceramic samples X = F and Cl, $x = 0.02; 0.04; 0.08$, and $0.10$, were prepared by solid state reaction from high purity reagents: Y$_2$O$_3$, CuO, BaCO$_3$, and LiX. The preparation is already trivial and involves calcinations and sintering processes in flowing oxygen for 24 h at temperatures in the range of 940-960°C.

The samples were further submitted to complex investigations regarding the magnetic and transport properties. Transport investigation was made using the four points method whereas the ac-susceptibility was measured with a homemade susceptometer. The morphology of the samples was investigated with a Hitachi S-2600N scanning electron microscope.

The irradiation of the samples was performed at the INR Pitesti 14MW TRIGA reactor at a fluence of $5 \times 10^{17}$ neutrons/cm$^2$. The samples were sealed in quartz ampoules and suspended in the reactor core. After irradiation, the samples were stored for one month to reduce the residual activity at the level accepted for public (1 mSv/year).

3. Result and discussion

X-ray diffraction investigation revealed only single phase Y-123 for all concentrations of Li-halide, in agreement with other reports [3]. The investigations by scanning electron microscopy revealed a continuous diminish of the sample compactness as the amount of Li-halide is inserted. The most homogeneous and compact structure is displayed by the samples with $x = 0.02$ (see Fig. 1a for LiF and Fig. 1b for LiCl) that have polyhedral grains but their size is clearly larger in the sample with LiCl (Fig. 1b), possible due to the lower melting temperature of LiCl that provides local flux for growth.

The pores have size of about one micron and are situated both between and within grains.

![Figure 1. SEM micrograph of YBa$_2$Cu$_3$O$_{7-\delta}$(LiF)$_{0.02}$ (a) and YBa$_2$Cu$_3$O$_{7-\delta}$(LiCl)$_{0.02}$ (b) (×3000).](image)

The increase of the halide contents decreases the degree of homogeneity with predominantly smaller grains (about 2.5 μm). Grains of size of 10-25 μm are also frequent. The inhomogeneity is emphasized by an increased density of voids of order of 10 microns. However, the intergrain contacts are perceptibly improved. Some grains appear to be almost soldered in clusters (see Fig. 2 for $x = 0.04$). As the halide content increases, the samples get almost porous, but display different characteristics. The sample with LiF has large voids (10-30 μm) and often large grains (up to 25 μm) but also molten areas (Fig. 3a for $x = 0.08$). Contrarily, the grains of the sample YBa$_2$Cu$_3$O$_{7-\delta}$(LiCl)$_{0.08}$ are tiny (about 5 μm), of nonuniform shape and size, like at the incipient stage of growth (Fig. 3b).
The morphology of the samples has, in turn, influence on the transport properties as reflected in the resistivity \( \rho \) vs. temperature \( T \) measurements. At low temperatures, both types of doping induce similar behaviour, i.e., an improvement of the transition characteristics (\( T_{c0} \) and transition width) for \( x = 0.04 \) followed by a depression at higher halide content.

![Figure 2. SEM micrograph of YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\)(LiF)\(_{0.04}\) (a) and YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\)(LiCl)\(_{0.04}\) (b) (×3000).](image1)

At high temperatures \( T > 140 \) K, the evolution is different. The doping with LiF decreases the normal state resistivity (with the minimum for \( x = 0.04 \)), whereas for LiCl the doping increases continuously the resistivity. A reason would be the better intergrain contacts which visible for the YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\)(LiF)\(_{0.04}\) sample (Fig. 2a). An enhanced critical temperature was also previously reported [4]. It is considered that F substitutes O atoms mainly at O(4) sites [5, 6] increasing the ionic contribution within the Cu(1)-O(4)-Cu(2) bond, hence, the decrease of the latter and the increase of the free carrier density in the CuO\(_2\) planes. The occupancy of O(2) and O(3) sites is also possible [7]. For chlorine, the increase of the critical temperature suggests a similar mechanisms though extended Hückel tight binding calculations indicate the O(2) sites as preferred within the CuO\(_2\) plane [8]. Additionally, the larger size of chlorine not only limits the possibility of occupation of different oxygen sites but also induces mechanical strains and dislocations promoting granular behaviour (see Fig. 3b) [9]. On the other hand, the substitution of Li for Cu reduces the hole doping. Therefore, there
is an optimal value for $x$ that we find to occur at $x \approx 0.04$, for which superconducting properties display optimal values.

![Graph](image1)

**Figure 4.** Temperature dependence of the resistivity of the virgin samples of YBa$_2$Cu$_3$O$_{7-\delta}$ doped with Li via LiF.

![Graph](image2)

**Figure 5.** Temperature dependence of the resistivity before (empty symbols) and after neutron irradiation at $5 \times 10^{17}$ cm$^{-2}$ (filled symbols). a) YBa$_2$Cu$_3$O$_{7-\delta}$ (LiF)$_x$, $x = 0.02$ and 0.04; b) YBa$_2$Cu$_3$O$_{7-\delta}$ (LiF)$_{0.08}$ and YBa$_2$Cu$_3$O$_{7-\delta}$ (LiCl)$_{0.04}$

After irradiation, the samples with a higher structural homogeneity show a 0.9 K increase of the post-irradiation critical temperature (Fig. 5a) accompanied by a slight decrease of the transition width.
The residual resistivity doubles up, as well as the slope $\rho/dT$. The improvement of the superconducting transition after irradiation in the more homogenous samples is not in contradiction with the general increase of the resistivity in normal state. In a ceramic sample, both the grains and the intergrain area contribute to the resistivity. Usually, the resistivity of the grain is lower than the intergrain space. The two contributions behave differently under neutron irradiation. The border area that has the largest resistance plays the role of a sink for the irradiation defects, hence, it always increases. The transition, however, is controlled by the grain. Therefore, the improvement of $T_c$ and of the transition width is a grain effect. The sample with LiF for $x \geq 0.08$ and the sample with LiCl for $x \geq 0.04$ have a different dependence on irradiation. The normal state resistivity is multiplied by two after irradiation whereas the critical temperature is noticeably depressed ($\Delta T_c = -2.8$ K for YBa$_2$Cu$_3$O$_{7-\delta}$ (LiF)$_{0.08}$ and 1.2 K for YBa$_2$Cu$_3$O$_{7-\delta}$ (LiCl)$_{0.04}$) (Fig. 5b). The degradation of the transition temperature suggests that even the mechanisms of superconductivity are disturbed by the energy deposited by neutron irradiation.

![Figure 6](attachment:image.png)

Figure 6. Temperature dependence of the imaginary part of $ac$-susceptibility before (empty symbols) and after neutron irradiation at $5 \times 10^{17}$ cm$^{-2}$ (filled symbols). a) YBa$_2$Cu$_3$O$_{7-\delta}$ (LiF)$_{x}$, $x = 0.02$ (circles) and 0.08 (triangles); b) YBa$_2$Cu$_3$O$_{7-\delta}$ (LiCl)$_{x}$, $x = 0.02$ (circles) and 0.04 (triangles)

This response to neutron irradiation is the result of the interplay between defect generation, their diffusion, capture, release and recombination in the complex landscape of the ceramic sample. All the above processes have a rate that dependent on the defect size and density. It was demonstrated that, for a low density of network dislocations, the uniform distribution of defects may become unstable relative to the pattern formation [10]. The pattern formation is enhanced in the anisotropic systems most likely in the basal planes where the mobility of the interstitial is larger. They consist in walls made of clusters of dislocations separating dislocation free areas. When the wavelength of the pattern is of the order of the grain size, the grain remain almost defect free expelling the walls in the vicinity of the grain border. The effect is important in the samples with good and large grains, i.e., at low LiX content, where it is expected that defect self-organization occurs within grains. The shape and size of the grains impose the position of the walls where the defects build up, most likely at the grain border. The presence of the walls increases both the residual and normal state resistivity (Fig. 5). Collecting the defects, these walls leave intragranular defect-free areas where superconductivity gets improved. In addition, the defects within wall strongly pin the flux lines. These assumptions are confirmed by the
evolution of the imaginary part of the \( \chi' \)-susceptibility. The intragranular peak narrows and shifts to higher temperatures (Figs. 6).

For higher content of LiX, the grains are smaller, more disordered, with a high density of defects. These samples do not satisfy the requirements for self-organization of the irradiation induced defects. Therefore, the latter get evenly distributed within sample and disturb the basic interactions responsible for superconductivity. The critical temperature is depressed (Figs. 6), but the defect accumulation allows an increase of the intragranular pinning.

In summary, we have found that the addition of small amounts of LiF or LiCl to the YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\), controls the sample morphology (shape, size, and size distribution of the grains, size and density of the voids, etc) which, in turn, influences the transport and magnetic properties of the sample after neutron irradiation. When the amount of pre-irradiative defects is small enough the irradiation produces an enhancement of the intragrain superconductivity due to a self-organization of the defects. At high density of defects (larger LiX amount), the density of pre-irradiative defects is high and the defects density is uniformly distributed within grain, the superconducting properties are depressed, but the pinning properties remain sensitively enhanced.

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