LiF addition to (Cu,C) $Ba_2Ca_3Cu_4O_y$ superconductor

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Abstract

Samples of $(Cu_{0.6}C_{0.4})Ba_2Ca_3Cu_4O_y$ ((Cu,C)-1234) with addition of 0.1 mol LiF have been synthesized by high pressure technique. It was found that LiF promotes the formation of superconducting phases with n higher than 4 of the $(Cu,C)Ba_2Ca_{n-1}Cu_nO_y$ series. In order to obtain single-phase samples, for the same synthesis conditions, the oxygen content in the starting mixture (supplied by AgO) should be increased from 0.45 to 0.73 mol AgO, when using LiF. Samples with LiF have shown a certain morphology suggesting an enhanced 2D and suppressed 3D type of growth assisted by a liquid phase. T_c decreased from 116.5K to 113K for the sample with LiF, but at the same time the transition width also decreased and J_c has shown a fish-tail (FE) effect.

Key words: $(Cu_{0.6}C_{0.4})Ba_2Ca_3Cu_4O_y$; LiF ; morphology ; critical current density ; critical temperature

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1. Introduction

Several features of $(Cu_{1-x}C_x)Ba_2Ca_3Cu_4O_y$ ((Cu,C)-1234) [1] make this material interesting for applications; T_c is close to 117K even in the over-doped region [2], H_{irr} versus (1-T/T_c) is relatively high [3, 4] and (Cu,C)-1234 does not contain any toxic or volatile element. These advantages are shadowed by the fact that synthesis is difficult (usually under high pressure) and the absolute J_c values are not superior to other HTS (Tl-. Hg-, Y-, Bi- based systems) suggesting that in (Cu,C)-1234 there are less pinning centers [4].

Therefore, search for additions or substitutions enhancing synthesis properties and/or J_c is of interest. In this paper we present our data on synthesis and characterization of (Cu,C)-1234 with addition of LiF.

2. Experimental

Samples with starting composition $(Cu_{0.6}C_{0.4})$ $Ba_2Ca_3Cu_4O_y$ with and without addition of LiF have been prepared by high pressure method. We have used a precursor powder with composition $Ba_2Ca_{2.7}Cu_{4.6}C_xO_y$ prepared by solid-state route ($890^oC/24h/O_2$-flow) from Ba and Ca carbonates and CuO. The carbon content x in the precursor powder determined by FT-IR was 0.1. One mol of precursor was mixed with 0.3mol $CaCO_3$. For the samples without LiF, addition of 0.45mol AgO with the role of oxidizing agent was necessary in order to obtain single phase while for the samples with 0.1mol LiF the optimum amount of AgO was found to be 0.73mol. After sealing in the Au-capsules, all samples were treated at 980^oC for 2h under a pressure of 3.5GPa.

As-prepared samples were characterized by XRD, SEM (EDS) and transport measurements (R(T)). DC magnetization loops were measured (MPMS-XL, Quantum Design) up to 7T, between 20 and 102K.

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3. Results and Discussion

For the same oxygen content in the starting mixture and the same synthesis conditions, addition of 0.1 mol LiF promoted the formation of the phases with n higher than 4 of the (Cu,C)$Ba_2Ca_{n-1}Cu_nO_y$ series. This is probably due to the decrease in the local oxygen partial pressure when other elements (i.e. F and/or Li) in the vapor state are present in the system and also due to the formation of a higher amount of liquid phase (see next paragraph). As revealed by XRD and EDS, nearly single phase (Cu,C)-1234 sample with 0.1 mol LiF addition has been synthesized in the above described synthesis conditions for an optimum content of 0.73 mol AgO-oxidizer. In the following, we will limit our discussions to the two single phase samples: (Cu,C)-1234-0.45AgO and (Cu,C)-1234-0.73AgO-0.1LiF.

The two samples have different morphologies. The sample without LiF consists of plate-like grains with sharp and straight edges. Round edges of the grains in the sample with LiF, as well as big and closed pores indicate on the presence of a liquid phase. The growth mechanism was strongly affected by LiF. Although the (Cu,C)-1234 plates are of approximately the same length and width (7-20μm x 7-20μm) the height is very different: less than 1μm for the sample with LiF and usually higher then 1μm and up to 5μm for non-LiF sample. More big blocks of sintered grains, up to 40-45μm, were detected in the LiF free sample.

The critical temperature of the LiF-sample was lower, i.e. 113.1K while for the LiF-free sample was 116.4K. The transition width was decreasing from 0.55K to 0.44K when LiF was added. The J_c curves are presented in the Fig.1. The sample containing LiF exhibit a weak (FE) effect between 20 and 93-102K. The effect seems similar to the one previously reported on the samples of (Cu,C)-1234 doped with Zn [5], but stronger. Li is a pair-breaker [6] as Zn and from this point of view the explanations given in paper [5] might work in this case. On the other hand Zn and LiF are not equivalent materials from several other points of view when they are added to the (Cu,C)-1234 system. The high oxygen content in the sample with LiF makes difficult the analysis of the FE, since it is well known that, usually, in HTS materials, J_c is increasing in the over-doped state. However, the authors of ref. [2] found that it is very difficult to attain the over-doped state in (Cu,C)-1234 structure. For the over-doped (Cu,C)-1234 they reported a shrinkage in c-axis parameter and preservation of T_c at 116-117K, that was not observed in our case. More experiments are required in order to understand the fish-tail effect in (Cu,C)-1234 + LiF superconductor.

In conclusion we have succeeded in preparation of the (Cu,C)-1234 superconductor with addition of LiF. In the as-prepared samples it was found that J_c is enhanced due to fish-tail effect, while T_c is decreased with 3-4K. The FE is observed at temperatures lower than 93-102K and applied magnetic fiels higher than 0.5T.

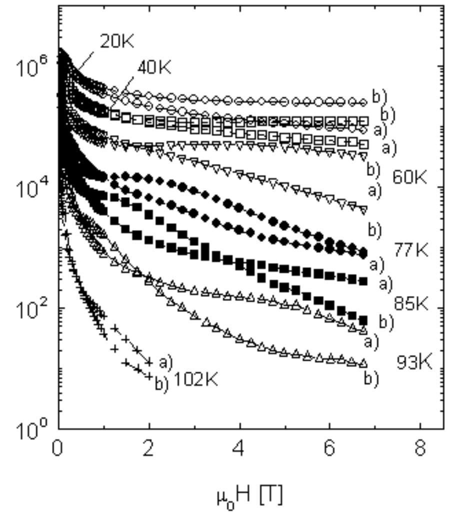

Fig. 1. Critical current density of the samples a) without LiF and b) with LiF. J_c was determined by using Beans equation and taking the grain size d=15μm.

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