

## Superconducting Properties of Electrochemically $\text{Li}^+$ Intercalated $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Films

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### Abstract

We have intercalated c-axis oriented  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  thin films with  $\text{Li}^+$  ions. Undoped films were grown by a pulsed laser deposition technique. A strong correlation was observed between the superconducting properties of  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  and the number of inserted  $\text{Li}^+$  ions. A maximum  $T_c$  of 92.5 K was measured for intercalation with one  $\text{Li}^+$  ion per unit cell.

### 1. Introduction

The recently discovered high temperature superconductor (HTS)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) has a layered structure with multiple  $\text{CuO}_2$  planes connected by Cu-O chains and by Y and Ba atoms. The structure is very open, and one can expect it to be a good host for different intercalants [1-3]. Intercalation is a process of ion-insertion for which no strong chemical bonds are broken in the reaction; the kinetic barrier to the reaction is usually very small. An intercalation process is also usually reversible if an electrochemical driving force is applied. Intercalation has been shown to be an effective method to modify the electronic properties of layered materials [4]. Rechargeable high-energy-density batteries and electrochromic devices are based on materials with good intercalative properties. Lithium intercalation into bulk YBCO samples was investigated with regard to its potential as a cathode material for rechargeable lithium batteries by Chen et al. [5]. In their work, however, no superconducting properties of the YBCO material were considered.

The mechanism of superconductivity in HTS materials still remains unclear. However, a strong correlation between the superconducting transition temperature ( $T_c$ ) and the distance between the  $\text{CuO}_2$  planes has been established [6]. Recently it was shown that iodine intercalation in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  causes a decrease in  $T_c$  [1,2] as a result of an increase of the distance between the  $\text{CuO}_2$  planes. The coupling between the  $\text{CuO}_2$  planes can be adjusted by ion-intercalation, and thereby one can expect to observe a tuning of the superconducting properties of the material.

In this paper we report on intercalation of lithium ions into the structure of YBCO thin films and on superconducting properties of the intercalated material at different density of  $\text{Li}^+$  ions.

### 2. Experiment

Thin YBCO films were grown by a pulsed laser deposition technique [7]. Films were c-axis oriented perpendicular to the substrate. The film thickness was 250 nm. Our experiments used films deposited mainly on  $5 \times 5 \text{ mm}^2$   $\text{SrTiO}_3$  substrates; however the use of other substrates like MgO and Y-ZrO<sub>2</sub> gave similar results. The critical temperature was measured by a standard four probe method. Films were examined by x-ray diffraction spectroscopy (XRD) and by microwave surface resistance measurements. The microwave surface resistance ( $R_s$ ) was measured by a parallel plate resonator method at 22 GHz as described elsewhere [8].

The samples were studied by XRD and  $T_c$  measurement in as-deposited state and after  $\text{Li}^+$  intercalation to different ion contents. For two samples, we measured  $R_s$  before and after the intercalation.

#### 2.1. Electrochemical Intercalation

Lithium ion intercalation was accomplished by a constant current method in a standard electrochemical three-electrode set-up. The current was held constant at 10  $\mu\text{A}$ , corresponding to approximately 50  $\mu\text{A}/\text{cm}^2$ . The potential was monitored during the intercalation, and prior to each intercalation or deintercalation step the open circuit potential (OCP) was recorded. A lithium foil served both as a counter electrode and a reference electrode. The electrolyte was 1 M  $\text{LiClO}_4$  in propylene carbonate. The electrochemical experiments were done in an argon atmosphere glove-box-system with less than 1 ppm of humidity. A SOLARTRON 1286 electrochemical interface served as a galvanostat in the experiments. The sample was withdrawn and exposed to normal atmosphere before  $T_c$  and XRD measurements.

A current of 10  $\mu\text{A}$ , applied during 520 s, gave a  $\text{Li}^+$  intercalation corresponding to approximately one ion per unit cell. The proper charge insertion was

calculated from the area of the film ( $0.5 \times 0.5 \text{ cm}^2$ ), its thickness (250 nm), and the size of the unit cell ( $0.38 \times 0.39 \times 1.168 \text{ nm}^3$ ). No porosity was assumed in the calculation. All films were intercalated under the same conditions. YBCO is known to be very sensitive to chemical reagents and therefore we checked the influence of the electrolyte on the superconducting properties. First the sample was dipped in water free propylene carbonate (PC) for 10 min, and in a second step it was dipped into the electrolyte (1 M LiClO<sub>4</sub> + PC) for 10 min. No degradation of the superconducting properties was observed, but instead a slight increase in  $T_c$  (see Table 1, steps 1 and 2). We conclude that the electrolyte by itself does not influence the sample quality negatively.

### 3. Results and discussion

We investigated YBCO thin films with  $T_c$ 's between 80 and 90 K. Films with high  $T_c$  (>89 K) and low  $T_c$  (<86 K) showed different behaviour and are treated separately below.

#### 3.1 Intercalated YBCO thin films with $T_c > 89$ K.

Films with  $T_c$  above 89 K are considered first. The Full Width at Half Maximum (FWHM) of the (005) peak in the x-ray diffractograms was less than  $0.2^\circ$ . The (007) peak was slightly shifted towards higher diffraction angles

corresponding to increased c-parameter values in intercalated sample.

Table 1 describes the intercalation procedure (steps 1-8) for one of the samples studied in most detail. For all other samples, we applied a simplified procedure with an intercalation of 1 Li<sup>+</sup> ion and subsequent deintercalation of 1 Li<sup>+</sup> ion. The open circuit potential (OCP) was recorded prior to each intercalation step (see steps 3-8 in Table 1), except for step 5. In this case, we had problems with the electrical contact to the film, but since the OCP changed as expected (see step 6) we believe that the intercalation took place as shown. The constant current intercalation occurred with no plateaus in the potential curve, i.e. only a monotonic change in potential during the intercalation was measured (Fig. 1). The OCP vs. Li was 2.50 V before any forced intercalation took place. Chen et al. [5] recorded a value of 3.4 V at this point and the potential decreased rapidly towards 2 V upon intercalation. Our value of 2.50 V can be an indication of Li<sup>+</sup> being introduced into the material already at step 2, i.e. when the sample was dipped into the electrolyte. Hence one can expect that we started with a material composed of Li<sub>y</sub>YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>. It can be noted that the OCP goes towards the Li potential upon Li<sup>+</sup> intercalation and in the opposite direction upon deintercalation. The reversibility of the OCP is interpreted as an evidence of the reversibility of the intercalation process. We observed

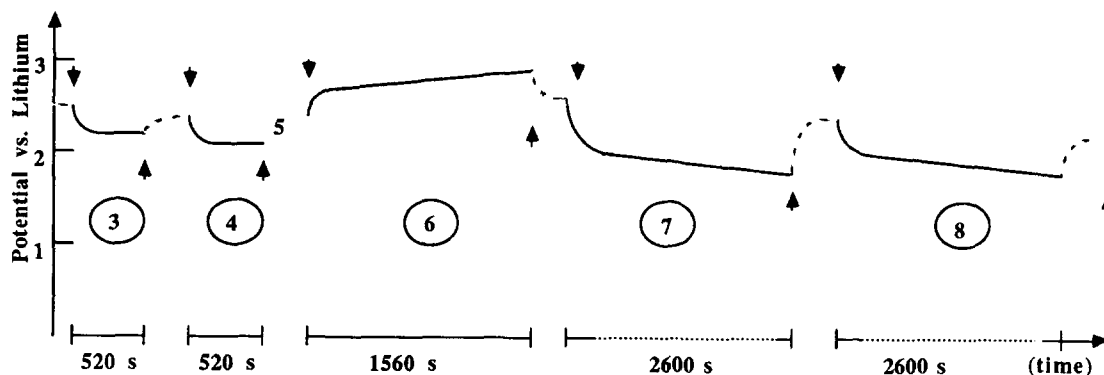


Figure 1. Potential versus time during constant current Li<sup>+</sup> ion intercalation of a YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> film. All current steps were + or - 10 μA and 520 s corresponds to 1 Li<sup>+</sup> ion per unit cell. Arrows denote where a current step starts ↓ and ends ↑. Encircled numbers indicate the intercalation step according to Table 1. Step 5 is missing since OCP in step 5 (marked by \* in table 1) was not measurable because of contact problems. Note the nonlinear timescale between steps and in steps 7 & 8.

Table 1. Experimental steps 1-8 for a sample with an initial  $T_c$  of 89.3 K. In step 1 the sample was dipped into pure propylene carbonate(PC), and in step 2 it was dipped into the electrolyte consisting of 1 M LiClO<sub>4</sub> in PC. The values in the second row denote the charge densities transferred sequentially to the material. (Note that both intercalation and deintercalation have been performed). OCP denotes open circuit potential.

Intercalation step nr.	1	2	3	4	5	6	7	8
Li <sup>+</sup> /unit cell	in PC	in LiClO <sub>4</sub> +PC	+1	+2	+4	+1	+6	+11
OCP vs. Li	X	X	2.50	2.40	*	2.38	2.54	2.38
$T_c$ [K]	89.7	91.1	92.5	92.1	91	91.8	91.6	90.7
c-parameter [Å]	11.669	11.681	11.686	11.700	11.710	11.695	11.705	11.710

a strong metalization of the film surface at steps 7 and 8 which correspond to  $y$  up to 11.

We observed a strong correlation between  $T_c$ , c-parameter, and the number of Li<sup>+</sup> ions inserted into the material (Fig. 2). After step 2,  $T_c$  rose to 91.1 K even when no electrical potential was applied. As discussed above, this is consistent with the low intercalation potential of the YBCO film. During step 3 we intercalated 1 Li<sup>+</sup> ion, and  $T_c$  reached 92.5 K, which is the maximum value observed in YBCO materials. At the same time the c-parameter was equal to 11.68 Å, a value typical for YBCO with this  $T_c$ . Further intercalation of the sample with 3 Li<sup>+</sup> ions led to a degradation of  $T_c$  (steps 4 and 5). However, a deintercalation with 3 Li<sup>+</sup> caused an increase in  $T_c$  and a decrease of the c-parameter (see step 6). In terms of Li<sup>+</sup> ions per unit cell, the sample after step 6 should be equivalent to that after step 3. The observed values of  $T_c$  and the c-parameter however were different after the two steps. Nevertheless the tendency of increasing  $T_c$  and c-parameter during intercalation, and opposite changes during deintercalation, give clear evidence for a reversible intercalation behaviour. The reversible intercalation was investigated for two other samples, and we observed an analogous behaviour.

There are two possible explanations of the effect on  $T_c$  and c-parameter. In principle, the changes can be caused either by an intercalation of Li<sup>+</sup> in the crystal structure or by a withdrawal of oxygen from the film during the electrochemical process. Measurements of microwave surface resistance can discriminate between these two mechanisms. The data indicated an increase of  $R_s$ , which was interpreted as a result of an inclusion of Li<sup>+</sup> in the YBCO structure, which as a metallic lithium causes dissipation of the microwave power and correspondingly give an increase of  $R_s$ . After a deintercalation with 1 Li<sup>+</sup>,  $R_s$  decreased but it did not

reach the value it had before the intercalation. The behaviour of  $T_c$ , c-parameter and  $R_s$  is consistent with the hypothesis that during the intercalation process Li<sup>+</sup> enters into the crystal structure of YBCO.

### 3.2 Intercalated YBCO thin films with $T_c < 86$ K.

Films with  $T_c$ 's less than 86 K are considered next. The intercalation behaviour for these films differed significantly from the one described above. The potential during intercalation was not smooth, but a step-like character could be observed. The voltage varied comparatively steeply with the intercalation level, and the required intercalation voltage was close to the Li potential.

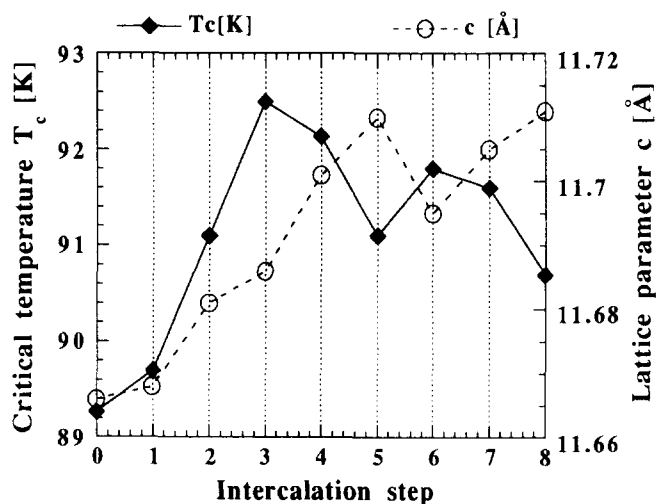


Figure 2.  $T_c$  and c-parameter at different intercalation steps for a sample with a starting  $T_c$  of 89.3 K.

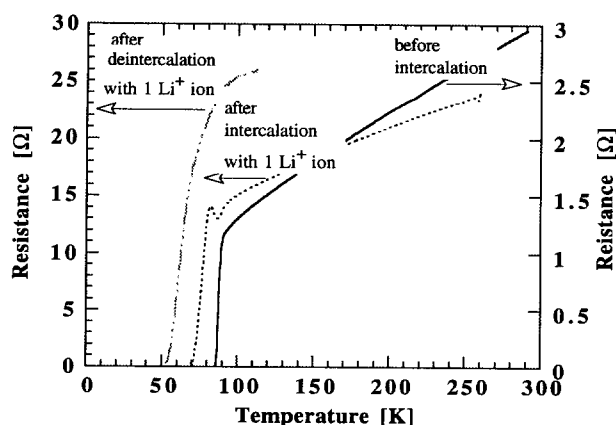


Figure 3. Resistance vs. temperature for an YBCO thin film before intercalation (full line), after intercalation with 1  $\text{Li}^+$  (dotted line) and after deintercalation with the same amount of charge (mixed line). The degradation of high  $T_c$  is obvious. The initial  $T_c$  was 86 K.

We investigated three samples which all showed a similar degradation of their superconducting properties upon intercalation as well as deintercalation. After a first intercalation step, the resistivity at room temperature increased by about five times, the resistance ratio  $R(300\text{K})/R(100\text{K})$  decreased from 2.3-2.8 to 1.5-1.8, and  $T_c$  dropped to 60-70 K (see Fig. 3). The FWHM of all (00l) peaks in the diffractograms were considerably broadened and the value of the diffraction angle for the (007) peak was shifted towards lower values, corresponding to a higher c-parameter. When a negative current was applied, in order to withdraw one  $\text{Li}^+$  ion per unit cell, a further degradation of resistivity,  $T_c$  and crystal structure was observed.

#### 4. Concluding remarks

We have demonstrated that electrochemical intercalation can be applied to modify the superconducting properties of YBCO thin films. It was shown that YBCO has an open structure (i.e. it serves as a good host material for  $\text{Li}^+$  ions) with a very low potential for intercalation. We observed a strong correlation between superconducting properties and the number of  $\text{Li}^+$  ions intercalated per unit cell. In the case of high quality films with  $T_c$  of 89 K, adding of 1  $\text{Li}^+$  ion increased  $T_c$  to the maximum value observed for YBCO materials, 92.5 K. These results can be explained by introducing  $\text{Li}^+$  ions in the YBCO crystal structure. However, the exact place of lithium in the YBCO is not yet known and is a subject of further studies.

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