

## Potassium substitution effects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor

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### Abstract

$\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  compound with  $x = 0, 0.1, 0.15, 0.2, 0.3, 0.5, 0.8, 1$  was prepared. The samples were characterized by XRD,  $T_c$ , oxygen content and room temperature thermopower measurements. The results shows that by increasing the potassium, the samples go to the underdoped regime. This is due to the depletion of oxygen from the samples. By post annealing of the sample with  $x = 0.2$  and  $T_c = 78$  K in oxygen, the  $T_c$  increased up to 93 K which means it is possible to put back the oxygens into the structure.

**Keywords:**  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , potassium substitution

### 1. Introduction

In high temperature superconductors anionic and cationic doping is performed to improve the superconducting properties. In anionic doping usually the oxygen content is increased. In this way the number of  $\text{Cu}^{3+}$  increases so the holes are introduced into the Cu-O planes. In cationic doping usually a univalent or divalent elements are substituted for divalent or trivalent elements. Based on the charge neutrality rule, at a fixed oxygen content, again the number of  $\text{Cu}^{3+}$  increases and the holes are introduced to the system. In some cases both methods are employed. Hume-Rothery's rules should be observed to select the best elements for substitution.

By now, many cationic substitutions in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  have been reported [1]. Among them, substitution of potassium for Barium is more interested [2]. Closeness of the ionic radius of K (1.33 Å) to that of Ba (1.35 Å) makes it the best candidate to be substituted for Ba in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

Potassium substitution for Ba in YBCO has been performed by many groups. While some groups report that  $T_c$  decrease by increasing potassium doping [1,3], some other groups have claimed  $T_c$  increases up to 124 K using KOH [4] or 135 K using  $\text{K}_2\text{CO}_3$  as the source of potassium [5]. In this study we prepared  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  with different  $x$  using  $\text{K}_2\text{CO}_3$  as the potassium source. The samples were characterized by XRD, SEM,  $T_c$ , oxygen content and room temperature thermopower measurements.

### 2. Experiment

Single phase samples of  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  were carefully

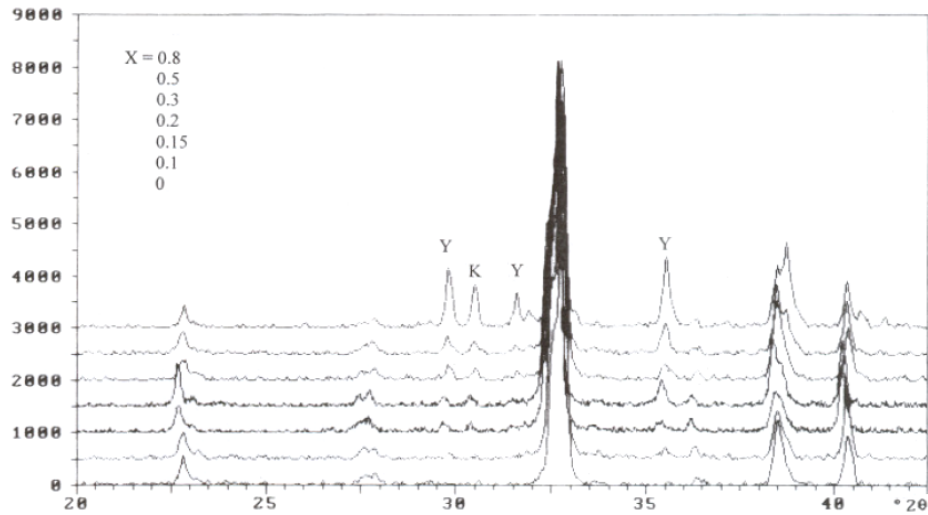
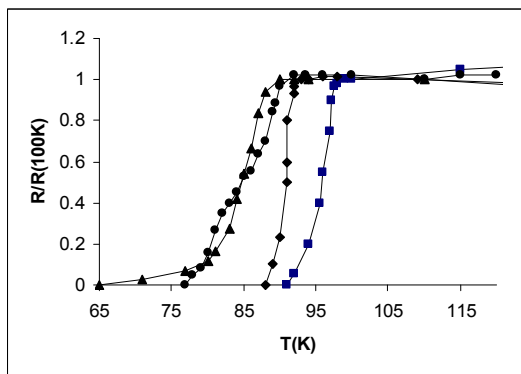
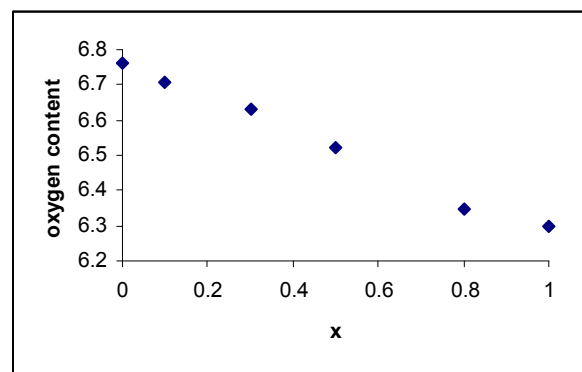
prepared with  $x = 0, 0.1, 0.3, 0.5, 0.8$  and 1 using solid-state method. Stoichiometric amount of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$  and  $\text{K}_2\text{CO}_3$  powders were mixed, grounded and pressed in the form of pellets. The pellets were calcined at  $900^\circ\text{C}$  for 4 hours and then cooled to room temperature. The pellets were reground, pressed and sintered at  $930^\circ\text{C}$  for 4 hours followed by heating at  $650^\circ\text{C}$  for 5 hours. The pellets then cooled to room temperature. Heating and cooling rates were chosen  $5^\circ\text{C}/\text{min}$ . A compact PW-1840 Phillips diffractometer was used for x-ray measurements. Lattice parameters were calculated using a computer program based on Kohen's method to minimize the systematic errors.  $R(T)$  and  $T_c$  of the samples were measured using the standard four-probe technique. Oxygen contents were determined by the iodometric titration method and a *dc* differential method was employed to measure room temperature thermopower [ $S(300\text{K})$ ]. Thermopower measurement is a powerful technique to show the doping level of samples. Based on thermopower universal rule,  $S(300\text{K})$  is related to the hole concentration of samples and is about zero for the optimum-doped superconductors. For the under-doped samples  $S(300\text{K})$  increases and for the over-doped samples  $S(300\text{K})$  crosses to the negative values [6].

### 3. Results

X-ray data shows that samples to be single phase but some trace of  $\text{K}_2\text{CO}_3$  in samples with  $x > 0.1$  is found. In order to determine the solubility limit of potassium in YBCO, we also prepared some samples with  $x = 0.15, 0.2$  and  $0.25$ . Again a trace of  $\text{K}_2\text{CO}_3$  was observed for

**Table 1.** The measured data for samples of  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  with different  $x$ .

$x$	0	0.1	0.3	0.5	0.8	1
$T_c$ [K]	91	88	77	65	-	-
$S(300\text{K})$ [ $\mu\text{V}/\text{K}$ ]	2.45	2.67	6.25	6.95	-	-
oxygen content	6.76	6.71	6.63	6.52	6.25	6.20
Lattice parameter $a$ [ $\text{\AA}$ ]	3.898	3.893	3.886	3.889	3.887	3.888
Lattice parameter $b$ [ $\text{\AA}$ ]	3.825	3.824	3.820	3.815	3.801	3.792
Lattice parameter $c$ [ $\text{\AA}$ ]	11.670	11.661	11.670	11.670	11.661	11.660

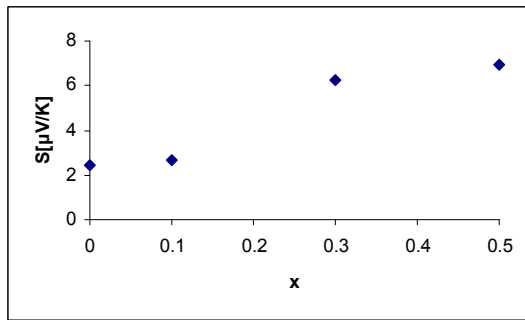
**Figure 1.** The x-ray data of different samples. Trace of  $\text{K}_2\text{CO}_3$  (K peaks) and  $\text{Y}_2\text{BaCuO}_5$  (Y peaks) are observed.**Figure 2.** (color online)  $R(T)/R(100\text{K})$  of samples with  $x = 0$  (■),  $0.1$  (◆),  $0.3$  (●) and  $0.5$  (▲).**Figure 3.** (color online) Oxygen content of samples with different  $x$ 

all of them. So in our samples the solubility limit of potassium in YBCO is 0.1. Figure 1 shows the x-ray data of different samples. The peaks which are denoted by K belong to  $\text{K}_2\text{CO}_3$  and are significant for samples with  $x > 0.1$ . The peaks grow by increasing  $x$ . Also the peaks which are shown by Y belong to the insulator phase of Y-Ba-Cu-O system ( $\text{Y}_2\text{BaCuO}_5$ ). Again by increasing of  $x$ , this impurity phase grows up.

$R(T)/R(100\text{K})$  of samples with  $x = 0, 0.1, 0.3$  and  $0.5$  are shown in figure 2. By using a nitrogen cryostat we couldn't measure the  $T_c$  below 65 K for the  $x = 0.8$  and 1 sample.

The measured data,  $T_c$ ,  $S(300\text{K})$ , oxygen content, and lattice parameters are listed in Table 1.

The data shows by increasing of potassium,  $T_c$  decreases which means the samples are either in under-doped or over-doped regimes. But the reduction of oxygen content with  $x$  (Figure 3) and the increasing of  $S(300\text{K})$  with  $x$  (Figure 4) indicate that the samples definitely go to under-doped regime. Therefore despite our expectation to have an increase in  $T_c$  by substitution of  $\text{K}^{+1}$  for  $\text{Ba}^{+2}$ , it seems that the presence of potassium causes some oxygen depletion. The reduction of the  $b$  lattice parameter with  $x$ , confirms such interpretation (Figure 5). It is to be noted in YBCO, the oxygen in the Cu-O chains are located along the  $b$  direction so depletion of oxygen causes a reduction of the  $b$  parameter. Such depletion is also observed when YBCO is doped with Co[6].



**Figure 4.** (color online)  $S(300\text{K})$  [ $\mu\text{V/K}$ ] for samples with different  $x$ .

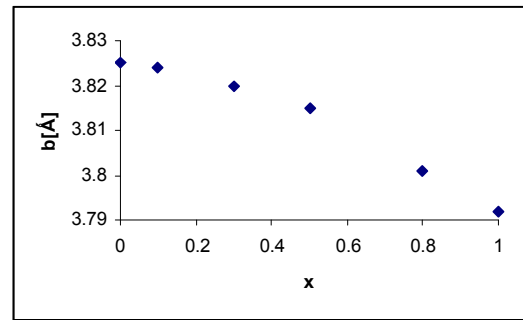
In order to see if it would be possible to put back the oxygens into the structure, post annealing of a sample with  $x = 0.2$  was performed.  $R(T)/R(100\text{K})$  of this sample is shown in Figure 6. We observed that the  $T_c$  increased from 78 K to 93 K. More annealing did not improve the  $T_c$ . This may be due to presence of the impurity phase of  $\text{Y}_2\text{BaCuO}_5$ .

#### 4. Conclusion

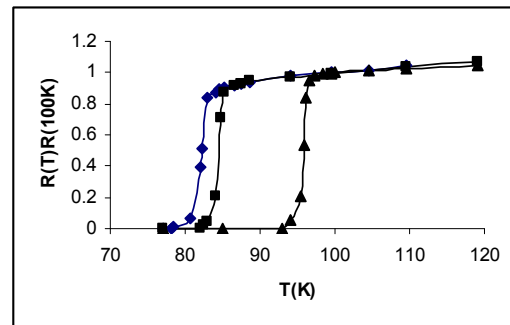
Substitution of potassium for barium was done in YBCO. It was found that the solubility limit of potassium in our YBCO samples is 0.1. By increasing of potassium, the  $T_c$  decreases and samples go to underdoped regime based on the oxygen content and  $S(300\text{K})$  measurements. So, potassium doping caused oxygen depletion. Post annealing of samples increased  $T_c$  again up to 93 K. So it is possible to put back oxygens into the structure. But in such an oxygenated sample,  $T_c$  did not increase more than 93K that could be due to growth of impurity phase of  $\text{Y}_2\text{BaCuO}_5$ .

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**Figure 5.** (color online)  $b$  lattice parameter [ $\text{\AA}$ ] against potassium doping.



**Figure 6.** (color online)  $R(T)/R(100\text{K})$  of sample with  $x = 0.2$ . As prepared sample ( $\blacklozenge$ ), annealed in oxygen for 10h( $\blacksquare$ ) and 30h( $\blacktriangle$ ).

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