

# Investigation of Pb doping on electrical, structural and superconducting properties of $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-\delta}$ superconductors

S. Ezzatpour\*, L. Sharifzadegan, F. Sarvari, H. Sedghi

Superconductivity Research Center (Sc.R.C), Physic Departments, Urmia University, Sero Road, Urmia, Iran



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## ABSTRACT

In this study the high temperature superconductor  $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-\delta}$  with doping  $x = 0, 0.05, 0.1, 0.15$  were prepared by the standard solid-state reaction method. The effect of Pb substitution on Ba site of YBCO superconducting system, structural, electrical and superconducting properties of Y-based superconductor has been investigated. The measurements of dc resistivity were performed on all samples with four-probe method using low frequency/low AC current (4 mA). The superconducting temperature,  $T_c$ , were determined from the resistivity versus temperature (R-T) curves. Results show that Pb doping reduced the critical temperature ( $T_c$ ) and superconductivity properties of our samples. The maximum and the minimum  $T_c$  were observed for the samples with  $x = 0.15$  and  $x = 0.1$  respectively. The structure and phase purity of samples were examined by the X-ray powder diffraction technique (XRD) performed by means of D8 Advance Bruker diffractometer with  $\text{Cu K}\alpha$  radiation. The grain morphology of surface of the samples was analyzed by scanning electron microscopy (SEM). XRD patterns of polycrystalline materials of composition  $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-\delta}$  revealed that all prepared samples are orthorhombic. All of the peaks of YBCO and  $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-\delta}$  have been used for the estimation of volume fractions of the phases and ignored the void peaks.

## 1. Introduction

Since the discovery of Cu-O based superconductors, the effects on their physical properties of doping with different elements have been extensively studied as a practical method for obtaining information on their superconducting mechanisms [1–3]. The analysis of impurity effects in high temperature (HTSC) gained additional interest upon confirmation that this subject could provide a crucial test for d-wave symmetry of the order parameter in high  $T_c$  copper oxides [4,5]. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  the carrier concentration in the  $\text{CuO}_2$  planes can be changed isovalent substitutions at Y-site, but is unaffected by isovalent substitutions. Nonisovalent substitutions in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  influence the redistribution of the oxygen atoms in the lattice which is, on the whole, the combination of two effects: influence of the impurity itself and the oxygen content change. It is well known that the oxygen content affects the crystal structure electronic transport and superconducting properties in YBCO. It is also realized that the superconducting transition temperature,  $T_c$ , sensitively depends on both the hole concentration in the  $\text{CuO}_2$  planes and the relative electric charge of the oxygen within the planes [6,7]. The level of this charge can be controlled either by manipulating the oxygen stoichiometry in the Cu–O chains, by application of pressure or by ionic substitution [8,9]. The study of non-

magnetic cation substitution in HTSC has generated a thoroughly interest in the last years due to the observation of a very high efficiency in depressing  $T_c$  in these materials. This is now to be an indication primarily of the d-wave symmetry of the superconducting order parameter [10,11]. The most interesting substitution effects are those where the impurities occupy the  $\text{CuO}_2$  planes.

In this study, Pb were substituted in the Ba site of YBCO samples. XRD analysis reveals that such substitution does not lead to changes in the structural symmetry of YBCO, but a decrease in the orthorhombicity of the system with doping Pb is observed. However, in the fully-oxygenated  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , Pb doping will decrease  $T_c$ . The reason is that Pb doping is accompanied by a reduction in oxygen content. Oxygen deficiency could increase the coherence length value in C direction [12].

## 2. Material and methods

Polycrystalline  $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-\delta}$  samples were prepared by a conventional solid-state reaction method using  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$  and  $\text{PbO}$  3N powders. The components were thoroughly mixed in the required proportions for each sample and calcined at 910 °C in air for 30 h. This process was repeated twice, with intermediate grinding and pressing into pellets at each stage. The samples were synthesized at 930 °C for

\* Corresponding author.

E-mail address: [s.ezzatpur@urmia.ac.ir](mailto:s.ezzatpur@urmia.ac.ir) (S. Ezzatpour).

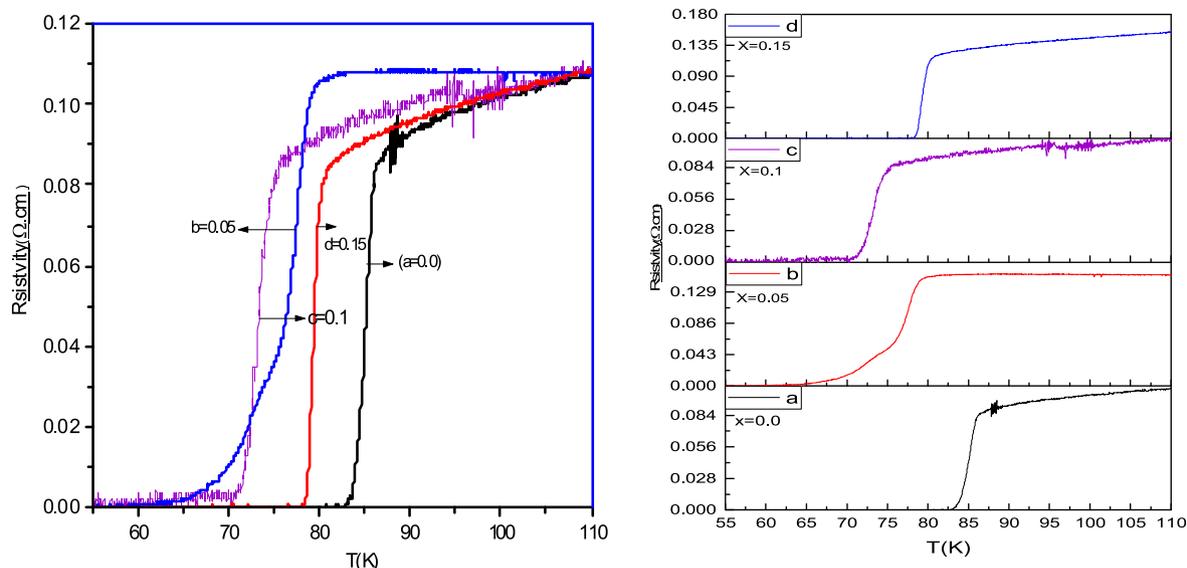


Fig. 1. R-T curves of the  $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-\delta}$  ( $x = 0.0$ (a),  $x = 0.05$ (b),  $x = 0.1$ (c),  $x = 0.15$ (d)).

20 h in an oxygen atmosphere, the sample temperatures were reduced to room temperature by furnace cooling. The resistivity measurements were carried out by standard four-probe method using low frequency /low AC current over the temperature range 50–290 K. Electrical contacts were made using conducting silver paint and the structures of the samples were analyzed by X-ray diffractometer (XRD) with a Cu K $\alpha$  source. Finally the grains morphology of surface of the samples was analyzed by scanning electron microscopy (SEM).

### 3. Results and discussion

#### 3.1. Temperature dependence of resistivity

The normal state resistance was studied to investigate the effect of substitution Pb in Ba location on superconductivity properties. It is clearly seen from the curves (Fig. 1) that all lead-contaminated samples have a transition to superconducting phase at temperatures above 60K. For all the values of the contamination, the critical temperature is reduced to the pure state (without the contamination). According to Table 1, the lowest transition temperature is related to the sample  $x = 0.1$  and the highest transition temperature is related to the sample  $x = 0.15$ . The results show with increasing Pb doping  $T_C^{\text{Onset}}$  increases. All samples in normal state ( $T > T_C$ ) show a metallic behavior. It is easily seen from the curves that the sample  $x = 0.15$  has the lowest resistance of the normal state and the highest transition temperature of 83.1 K compared with other lead-contaminated samples. Improve weak inter-granular communication and reduced inter-granular resistance due to the formation of SNS bond between superconducting inter-granular by Pb can lead to a decrease in the normal state. In general, the reduction of transition temperature to the pure sample (base state) is due to the destruction of the superconducting state due to the substitution of lead and the change of the sample structure and increasing the weak inter-granulars. (Figs. 2 and 3).

Table 1  
Characteristic temperatures and lattice parameters for all samples.

Nominal value of x	$T_C^{\text{mf}}$	$T_{C0}$	$\delta T_C$	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$
0.0	92	82.36	9.64	3.82	3.88	11.655
0.05	80.8	64.6	15.9	3.965	3.683	11.049
0.1	79.7	70.1	9.6	2.564	4.573	13.716
0.15	83.1	78.3	4.8	3.955	3.691	11.070

#### 3.2. Phases identification

In order to investigate the structure of the samples and ensure the formation of the desired phase, the x-ray diffraction spectrum was investigated. It was observed from the comparison of the spectrum of contaminated samples with Pb by the pure sample ( $x = 0.0$ ) that in some of the contaminated samples were removed a number of peaks related to the optimal phase 123, and instead of that, the unwanted phase peaks of 211, along with the secondary peaks of the lead impurity, appeared in the samples spectrum of diffraction patterns. In high temperature superconductors, the appearance of secondary phases with different transition temperatures or phases that exhibit metal or insulator properties play an important role in transition temperature changes. The visible change seen in diffraction patterns is related to the severity and location change of the peaks, the intensity of the peaks depends on the nature of the atoms, the number of atoms, and how they are distributed in crystalline solids. And shifting the peaks and shifting them to higher angles indicates a decrease in the parameter c. In Table 1, the variations of the lattice parameters of all samples are given based on the amount of the x-contamination. It was concluded from Table 1, none of the lattice parameters 'a', 'b' are equal. In samples with values of  $x = 0.05$ ,  $x = 0.15$ , 'a' lattice parameter increases and b, c parameters decreases. Since most of the oxygen positions are occupied along the direction b in the Cu-O chain, Excess oxygen is placed on the a-axis instead of oxygen deficiency, which increases 'a' and structural distortion; also, in these samples, the c lattice parameter decreased, but in the sample  $x = 0.1$  the c parameter was increased. The small c-parameter is a valuable quantity for examining the superconducting property because the copper atoms that produce the load carriers are larger in number along the axis c. In these samples, the composition also has orthorhombic structure for all levels of contamination.

#### 3.3. SEM measurements

Images related to SEM show: The sample (b) has a non-uniform surface in which the grains are randomly oriented and bonded between grains is weak. The number of fine grains in the sample and the reduction in grain size indicate increased strength and hardness of the contaminated samples. This behavior can be attributed to the decrease in the amount of liquid phase in the contaminated samples during the growth process [13]. High temperature superconductors include known internal boundaries which is called grain boundaries. When the sample is made, the atoms inside each growing grain are regulated with a

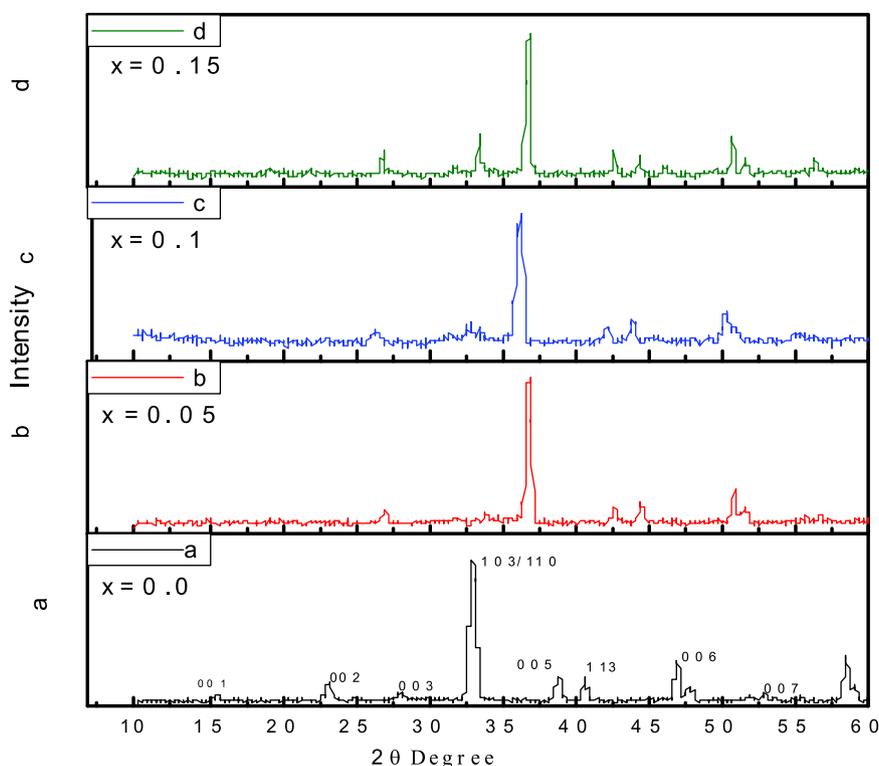


Fig. 2. XRD patterns of  $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-s}$  samples with (a)  $x = 0$ , (b)  $x = 0.05$ , (c)  $x = 0.1$ , (d)  $x = 0.15$ .

particular pattern that depends on the crystalline structure of the specimen and during the growth process of each grain, affects the other grains and the connecting line that atoms are oriented on it in different shapes. The strength and hardness of the ceramic samples can be changed depending on the reversed root square of the grain size. From the micro-structural analysis, it was found that the last two samples

have a uniform appearance with less porosity and larger grain size, crystallization, and better inter-granular bonding. As it can be seen from the figures, with increasing the amount of Pb doping, grain size and inter-granular interactions have increased, and the porosity of the samples has decreased. In fact, by increasing lead-contamination, the growth of the grains improves, which is responsible for good connection

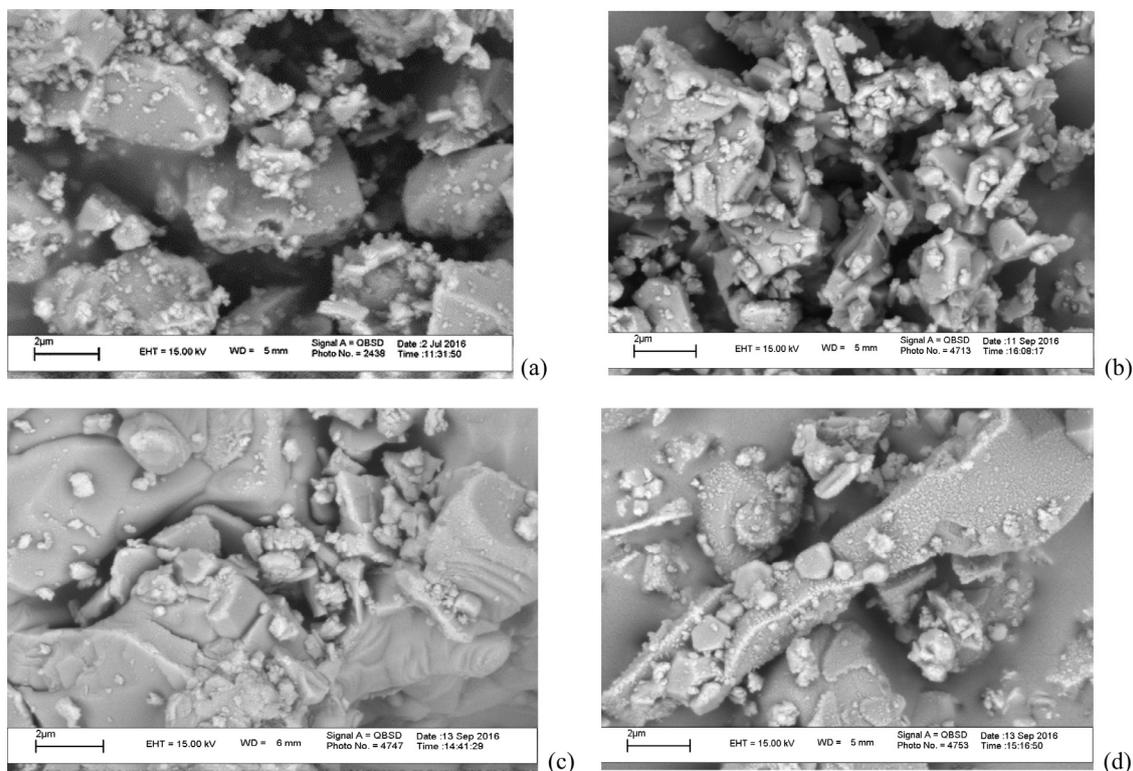


Fig. 3. The SEM photographs of samples with (a)  $x = 0$ , (b)  $x = 0.05$ , (c)  $x = 0.1$ , (d)  $x = 0.15$ .

between the grains and homogeneity of the superconducting phase. Improvement of grain boundaries can predict that the critical density of these samples will increase with increasing lead-concentration.

#### 4. Conclusion

We investigated the effects of lead on the crystalline structure and superconducting properties of the  $\text{YBa}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{7-\delta}$  system. XRD diffraction patterns showed that a number of peaks related to optimal phase 123 were eliminated, and instead of that has appeared unwanted phase peaks of 211 with the peaks of the secondary phases of the lead impurity; also, changes have been created in the location of the peaks and cause their shift to higher angles which indicates a decrease in the C parameter. In these samples, the composition has an orthorhombic structure for all amounts of contamination. Also, it is derived from thermal electrical resistance diagrams that superconducting transition temperature is reduced by increasing the amount of substituted lead and all samples in normal mode ( $T > T_C$ ) show a metal behavior.

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