

# Effect of Pb Doping in $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ synthesized via Co-precipitation method on superconducting properties

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**Abstract**— Pb-doped  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was successfully prepared via coprecipitation method using acetate salts as a starting material. The acetates were precipitated in alcoholic media using oxalic acid as a precipitating agent. Heat treatment of the oxalate precursor happened in an oxygen environment where it was calcined and sintered at 900 °C and 920 °C, respectively, for 24 hours. The XRD patterns show a secondary phase of  $\text{PbO}_2$  and  $\text{Pb}_3\text{O}_4$  accompanied with the orthorhombic structure. The  $T_{C(R=0)}$  for samples has a slightly changed compared with the amount of dopant where the changing was lower than 7 K and the samples show a good superconducting behavior at liquid nitrogen temperature. The SEM microstructure shows large grain size with a highly compacted. These results show that the Pb may get a significant change in the superconducting properties at different concentrations.

**Index Terms**— Doping; ErBCO; Magnetism; Superconductor; Resistivity.

## 1 INTRODUCTION

THERE are many procedures known during the past years in preparation of the superconducting materials. The conventional solid-state reaction is widely used due to the easy controlling the proportional amount of the content, but there are some disadvantages such as long calcinations and sintering duration, high temperature (940-1000 °C) and intermittent grinding to get an improved final product [1-4]. Co-precipitation method (COP) is one of the favorable method in preparation of superconductor. This technique has been used during the last few years due to the homogeneity and short time of calcinations and sintering [5-10]. The main role of using COP depends on the solubility product constant,  $K_{sp}$ , of the starting salts produced, where the precipitation occurred as the concentrations of the ions reached the value of  $K_{sp}$ [11]. On the other hand, the pH has an important character in the precipitation process where it controls the ions content in the solution according to the dissociation factor of the weak acids,  $pK_a$ , in the mixture. However, the mixture of acetic acid and acetates works as a puffer to control the changing of pH in the solution to keep the value in the range of 3.7-6.5 where the precipitation is likely to occur.

In this paper, we reported the doping effect of Pb in Er-123 system synthesized via coprecipitation method. The doping site was at Er site according to the stoichiometry composition in the preparation procedure.

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## 2 MATERIALS & METHODS

Er-123 was doped with lead at the weight percentages of 5, 10, 15 and 20. Doped samples were prepared using  $\text{Pb}(\text{CH}_3\text{COO})_2$ ,  $\text{Er}(\text{CH}_3\text{COO})_3$ ,  $\text{Ba}(\text{CH}_3\text{COO})_2$  and  $\text{Cu}(\text{CH}_3\text{COO})_2$  as the starting materials. Metals' acetate was dissolved in glacial acetic acid to form a homogenous solution (A). Precipitating agent used is 0.5 M oxalic acid which dissolved in alcoholic solution of water iso-propanol (1:1.5) solution (B). A blue slurry of metal acetates, was precipitated with mixing solution (B) with the solution (A). The slurry was dried for eight hours and then calcined at 900 °C for 24 hours followed by 3 hours calcinations at 600 °C as a second calcinations time. The calcined powder was ground and pressed into  $\approx 13$  mm diameter pellets under 4 ton/cm<sup>2</sup> force. Pellets obtained were then sintered under oxygen for 24 hours at 920 °C as a first sintering, followed by 5 hours sintering at 600 °C. Heating rate was 2 °C/min while the cooling rate was 1° C/min. The sintered pellets were characterized by a Shimadzu X-ray diffractometer (XRD) with Cu K $\alpha$  radiation at 40 KV and 30 mA with a step of 0.02 ° over the range 4-60°. Microstructure of the samples was studied by a Phillips XL30 ESEM scanning electron microscope. The electrical resistance temperature was measured by a DC four-point probe with 30 mA constant current, the range of temperature was 50-250 K using a Closed Cycle Helium Cryostat.

## 3 RESULTS & DISCUSSION

Figure 1 shows the XRD pattern of pure and Pb-doped Er-123 superconductor. It is clear that by the first doping of Pb in Er-123 superconductor, ( $x= 0.05$ ), there is a change in the peak intensities, positions, and generate new peaks. This changing increased proportionally with increasing the amount of Pb in the sample.

XRD results analyzed by an XPert program version 1.0 show that there is a decreasing in intensities of the major peaks of

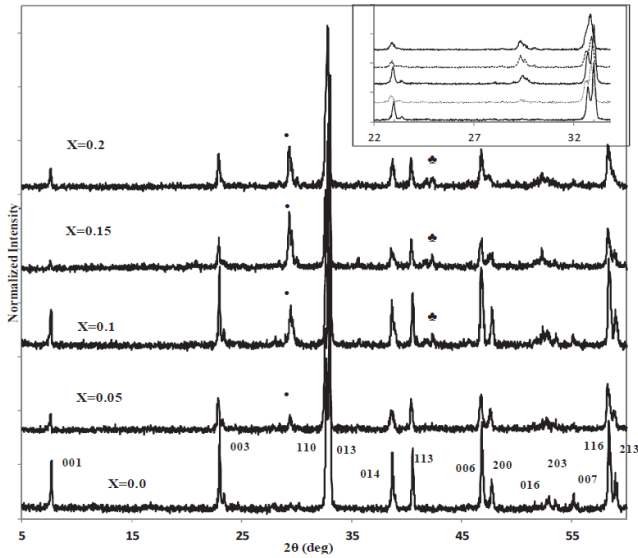


Fig.1. XRD patterns of pure and doped Pb samples, \* and • indicated  $Pb_3O_4$  and  $PbO_2$  phase respectively. The inset shows the enlarged image of diffracted patterns at the range of  $26^\circ - 36^\circ$

Er-123 superconductor, in consequence, with appearing of two indexed compounds,  $PbO_2$  and  $Pb_3O_4$ , at  $2\theta \approx 29.3$  and  $2\theta \approx 42.4$ , respectively.

The peak of  $PbO_2$  appeared at the first doping content of Pb in Er-123 superconductor; a cubic crystal with a Pa-3 space group indexed by reference ICDD 00-050-1430. The peak intensity is proportionally increased by the Pb increase in the sample. The peaks of  $Pb_3O_4$  appeared at two minor positions;  $2\theta \approx 42.3$  and  $2\theta \approx 52.29$ , the first peak is indexed at  $x \geq 0.1$  mole of Pb content, while the second peak is indexed at the lower doping of Pb with less than 12% intensity.  $Pb_3O_4$  were indexed by reference ICDD 00-065-2851 as a tetragonal structure with P42/mbc space group.

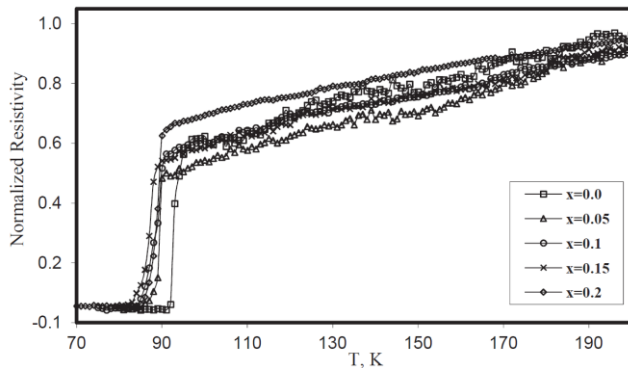


Fig.2. Normalized DC electrical resistance (R) against temperature (K) of pure and doped Lead samples.

The volume of polycrystalline structure (Table 1), had no significant change by the doping of Pb in the Er-123, where lattice parameters have no change, in which it can be concluded that the sample has another phase in the perovskite structure. In addition, the decreasing of the major peak intensities of Er-123 superconductor with increasing the porosity led to conclude that the sample going to form a

mixed phase of  $ErPbBaCuO$  compound. The orthorhombicity distortion presented in Table 1 of Pb-doped samples shows that the sample still orthorhombic with close value to the Pb-free sample.

TABLE 1  
LATTICE PARAMETERS, VOLUME AND ORTHORHOMBICITY DISTORTION OD OF PURE AND DOPED Pb SAMPLES

Mole of dopant	a	Lattice Parameters A	b	c	Volume	OD
P0	0.00	3.811(3)	3.887(4)	11.648 (7)	172.55	$10^3(b-a)/(a+b)$ 9.8727
P1	0.05	3.832(4)	3.899(4)	11.600(2)	173.32	8.6664
P2	0.10	3.811(4)	3.885(4)	11.638(8)	172.31	9.6154
P3	0.15	3.814(6)	3.880(9)	11.630(2)	172.10	8.5781
P4	0.20	3.811(4)	3.893(4)	11.649(9)	172.83	10.6438

A superconducting behavior observed in all samples with slight change in the critical resistance temperature,  $T_C$  (Fig. 2). In general, all doped Pb samples have lower  $T_C$  value compared with the free Pb sample. The determined  $T_C$  of pure and Pb-doped Er-123 were, 92, 85, 84, 84, and 85 K for  $x = 0.0, 0.05, 0.1, 0.15,$  and  $0.2$ , respectively. The degradation of  $T_C$  values may refer to present a new phase of  $PbO_2$  and  $Pb_3O_4$  in the doped system.

TABLE 2  
RESISTIVITY, DENSITY AND RELATIVE POROSITY OF PURE AND DOPED Pb SAMPLES

Mole of dopant	$T_{Conset}$ , K	$T_{C(R=0)}$ , K	Density, $g/cm^3$	Porosity	
P0	0.00	96	92	7.14	7.00
P1	0.05	93	85	6.27	10.39
P2	0.10	92	84	5.91	16.99
P3	0.15	91	84	5.39	22.80
P4	0.20	91	85	5.12	27.59

Furthermore, the rising of the critical resistance temperature,  $T_C$ , at  $x=0.2$  was interesting to study at higher doping content of Pb in Er-123 perovskite superconductor. In addition, there is a decreasing in density at the same addition content at variance of the consequence of other results of Pb content

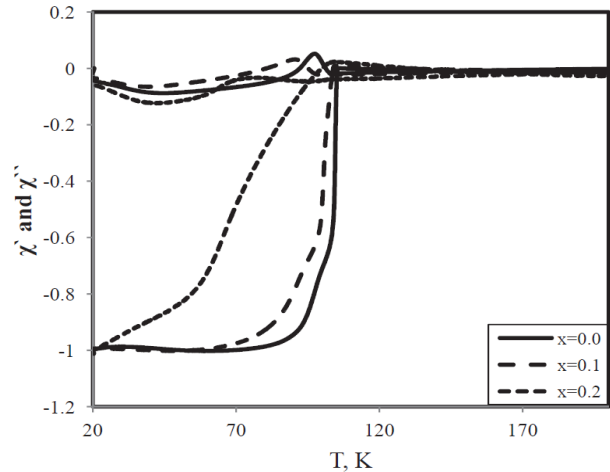


Fig.3. AC susceptibility data of pure and doped Pb samples

(Table 2).

The steady effect of lead in Er-123 transport properties at different content of Pb in the sample may refer to the superconducting property of Pb as a member of several structures of BSCCO and LSCO systems dopant. Selective Pb-doped samples were characterized by ACS device. Fig. 3 displays the real ( $\chi'$ ) and imaginary ( $\chi''$ ) parts for

the complex AC susceptibility as a function of temperature for  $Er_{1-x}Pb_xBa_2Cu_3O_{7-\delta}$  ( $x=0.0, 0.1$  and  $0.2$ ) with applied magnetic

pores appeared in all doped Pb samples, while the grain size changes do not have a significant effect. The presence of pores in the sample led to resist the current flow between the grains due to air pocket's effect. At  $x=0.1$ , the pores disappeared, in which it can be related to the presence of  $Pb_3O_4$  in the XRD

TABLE 3

THE CRITICAL RESISTANCE TEMPERATURE, MAXIMUM JOSEPHSON CURRENT AND JOSEPHSON COUPLING ENERGY OF PURE AND DOPED Pb SAMPLES CALCULATED FROM THE AC SUSCEPTIBILITY DATA

Mole of dopant	$T_C$	$T_{Cj}$	$I_o$	$E_j$	
P0	0.0	105	101	$4.33 \times 10^{-05}$	$2.28 \times 10^{-39}$
P2	0.1	103	87	$1.04 \times 10^{-05}$	$5.49 \times 10^{-40}$
P4	0.2	101	87	$1.14 \times 10^{-05}$	$6.03 \times 10^{-40}$

field of 2.5 Oe at a frequency 1 KHz. The experimental AC susceptibility data  $\chi'$  (T) and  $\chi''(T)$  were normalized to  $|\chi'|$  at the lowest temperature.

The real ( $\chi'$ ) and imaginary ( $\chi''$ ) parts data show a decrease of the superconducting properties of Er-123 superconductor by the increase of the Pb content. The onset temperature,  $T_{Conset}$ , for  $x=0.0, 0.1$  and  $0.2$  recorded were 105.3, 103.8 and 101.7 K, respectively (Table 3). The transition of superconducting properties shows that the grains still superconducting, as the current can flow between the grains.

In addition, the sample  $Er_{0.9}Pb_{0.1}Ba_2Cu_3O_{7-\delta}$ , shows a similar behavior of free-Pb sample, in which the transition of the properties went to lower temperature. On the other hand, for  $Er_{0.8}Pb_{0.2}Ba_2Cu_3O_{7-\delta}$  sample, the superconducting properties still appeared with a change in behavior towards the applied magnetic field, which may be due to the poor coupling among the grains by increasing the Pb content in the sample.

The degradation of estimated maximum Josephson current,  $I_o$ , and Josephson coupling energy,  $E_j$ , presented in Table 4, show that as the amount of Pb increased, support the poor coupling

TABLE 4

THE TRANSITION TEMPERATURES FOR PURE AND Pb-DOPED SAMPLES

Mole of dopant	$T_{C.on}$	$T_{C.off}$	$\Delta T_C (T_{C.on}-T_{C.off})$	
P0	0.0	105.30	76.20	29.10
P2	0.1	103.80	60.91	42.89
P4	0.2	101.71	12.95	88.76

among the grains in the sample. Furthermore, the transition temperature  $\Delta T_C$  increased as the amount of Pb increased in the sample where the resistance increased due to the inter-grain boundaries.

TABLE 5

THE EDX ELEMENTAL ANALYSIS FOR  $Er_{1-x}Pb_xBa_2Cu_3O_{7-\delta}$  ( $x=0.0, 0.05, 0.1, 0.15$  and  $0.2$ )

x, mole	Er%	Ba%	Cu%	Pb%	
P0	0.00	0.86	2.01	3.12	0.00
P1	0.05	0.87	2.14	2.99	0.01
P2	0.10	0.85	2.04	2.97	0.13
P3	0.15	0.84	2.05	2.97	0.15
P4	0.20	0.86	1.95	2.97	0.21

Microstructural surface study for pure and Pb-doped Er-123 superconductor was taken by SEM device presented in Fig. 4. All sample's picture was taken in 1500x magnification. The samples show a highly compact randomly distribution. The

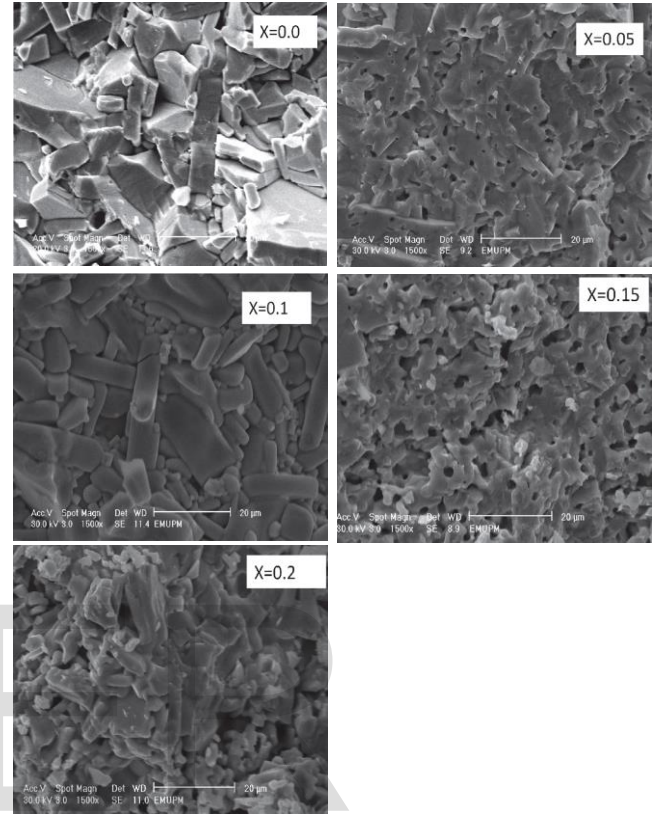


Fig. 4. SEM micrographs for  $Er_{1-x}Pb_xBa_2Cu_3O_{7-\delta}$

patterns. In addition, the presence of pores in the sample may refer to the increasing of  $PbO_2$  content in the samples. Furthermore, the increase of the pore's size by adding Pb into the Er-123 system has a proportional relation with the porosity as measured in Table 2.

Elemental analysis using EDX device was summarized in Table 5. The elements show a homogeneous distribution over the structure due to using a self-control preparation method of homogeneity, COP. It is shown that the content of Pb in the sample is proportionally increased by an increase in the dopant content of Pb in the stoichiometry calculation in the preparation method. On the other hand, the content of Er has no change, where the effect is happened in the Ba site.

The Pb addition is going into Cu and Ba site. Meanwhile, the decreasing of the electrical properties and critical resistance temperature,  $T_C$ , in the first doping of Pb in the Er-123 system may be due to the replacing of Pb into the Cu site, the responsible on the transition of the current between the grains. In addition, the replacing of Pb in the Ba site at higher content of  $Pb \ x \geq 0.1$ , explains the stability of the critical resistance temperature,  $T_C$ , in the other doped sample.

## 4 CONCLUSION

Pb-doped  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was successfully prepared via coprecipitation method. All doped samples show a secondary phase of  $\text{PbO}_2$  increased with the dopant content in the XRD pattern. The doped samples show a good superconducting properties, where the  $T_C$  decreased with less than 7 K. The samples show a highly compact with randomly distributed in the SEM and EDX microstructure, where the current flow easily between the grains and show a good superconducting behavior.

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