



## Study and compare the effect of partial substitution on the structural and electrical properties of a lead-based compound

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### ABSTRACT

The present work includes studying the effect of partial substitution of Zinc (Zn) by Copper (Cu) on the structure properties of  $(PbBa_2Ca_2Cu_{3-x}Zn_xO_{8+\delta})$  compound, where  $(x= 0, 0.1, 0.2, \text{ and } 0.3)$ . Samples were prepared by solid state reaction (SSR) methods. Samples were sintered under a temperature of  $(800\text{ }^\circ\text{C})$  for a period of  $(48\text{ hr})$  and a heating rate of  $(10\text{ }^\circ\text{C} / \text{min})$  in order to ensure a gradual diffusion process between the atoms and obtain a bonded substance and to produce the optimal stability of high phase formation (Pb-1223). X-ray diffraction analysis was performed for the pure and partially substituted sample, and it was observed that all samples contain a high percentage of high phase (Pb-1223) in addition to some other phases with some few impurities at the end of the chart and an increase in the intensity of the high phase peaks (Pb-1223) and decrease in the intensity of the remaining phase peaks compared to the pure sample. It turns out that the sample  $(x = 0.2)$  possesses the highest percentage of the high phase (Pb-1223), which represents the ideal sample in this group in terms of the replacement ratio.

### Keywords:

Superconductors, Electrical Resistivity, Critical temperature, partial substitution

### Introduction

Many scientists and researchers have been able to prepare and manufacture compounds of various chemical elements such as yttrium compounds  $Y-Ba-CuO_{n+\delta}$ , lanthanum  $La-Ba-Ca-CuO_{n+\delta}$ , bismuth  $Bi-Ba-CuO_{n+\delta}$ , thallium  $Tl-Ba-CuO_{n+\delta}$  and mercury base  $Hg-Ba-CuO_{n+\delta}$  with different phases [1-6]. While some researchers worked on studying the effect of methods of preparing superconducting materials, as well as partial replacement of elements of these compounds in order to raise

the critical temperature to approach the room [7-10].

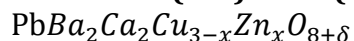
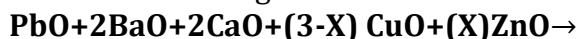
Lead compounds are described with the formula  $PbBa_2Ca_n-1Cu_nO_{2n+2}$ , where  $n = 2, 3$ , this combination includes two phases of the system (Pb-1212)  $PbBa_2Ca_1Cu_2O_6$  and (Pb-1223)  $PbBa_2Ca_2Cu_3O_{10}$ . The compounds contain from the unit cell on the boundary of two or three layers of (CuO) respectively separated by a layer of (CaO). [11,12]. It can be indicated here that the structure of the unit cell of the (1223) compound is an orthorhombic

structure [13]. Some properties of superconductors can be improved by partial substitution of Pb+2 Sb+2 Cr+ 2 and Cd+ 2 into Tl+2 La and Sr elements [8-14]. These substitutions enhance the formation of Bi-2223 and improve the superconducting properties. In the present work we have successfully to prepare  $(PbBa_2Ca_2Cu_{3-x}Zn_xO_{8+\delta})$  with  $(x=0,0.1,0.2, \text{ and } 0.3)$  polycrystalline by used solid state reaction process, we analyze the structure and study the electrical properties of Pb-Base synthesized at the optimum conditions to observe the effect of substitution on increase of high phase.

The application of high temperature superconducting (HTS) technologies can development of modern wind-mills are increasing of the output power and efficiency which leads to the increasing of their weight and sizes [ 14].

### Experimental Method

The materials were prepared in the form of pure oxides according to the system  $PbBa_2Ca_2Cu_{3-x}Zn_xO_{8+\delta}$ , which included  $(PbO_3, CaO, BaO, CuO, ZnO)$ , samples were prepared using a solid-state reaction method. Element oxides weight an according to the formula as a following:



Then each proportion of each powder was weighed using a KERN-4-digit sensor scale separately. Where the mixing and grinding process. The ingredients were mixed by hand gate mortar for a one hour, then the ingredients were mixed using an electric mixer with steel balls for two hours to obtain fine powders and to obtain the best homogeneity. The mixtures powder was formed in the form of cylindrical discs, with a diameter of (1.5 cm), using a hydraulic press, under a pressing pressure (7ton / cm<sup>2</sup>) for one minute, and an axial pressing method was used from two directions, in order to ensure the best and highest value of density.

Then, several experiments were conducted to choose the optimal conditions (Suitable electrostatic mixing time and sintering temperature) to obtain the best samples, which

included the sintering temperature and the appropriate sintering time for the compressed samples. The sintering temperature was selected (800 °C) for sintering time (48 hr) with heating rate (10 °C / min) under normal atmospheric pressure., In order to obtain coherent samples and to ensure an optimum diffusion process between the atoms, then after that the samples were cooled to room temperature at a cooling rate (10°C / min).

By use a mathematical program to calculate the lattice coefficients (a, b, c) and to calculate the lattice coefficients per unit cell from the X-ray chart (and given that the crystal structure is a rhombus) the following relationship was used [13,14].

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \dots\dots\dots (1)$$

Where: h, k, l are Miller's coefficients

Then the lattice coefficients of the cell unit (a, b, c) were calculated for each sample mathematically based on Bracke's law in X-ray diffraction. The ratio of each phase was calculated according to the following mathematical relationship: [19]

$$(V_{ph})\% = \frac{\Sigma I_o}{\Sigma I_1 + \Sigma I_2 + \Sigma I_{Other(peaks)}} * 100\% \dots\dots\dots (2)$$

Where I; represents the intensity of the peaks in each phase.

### Results And Dissection

All samples in the present investigation were subjected to gross structural characterization by X-ray diffraction. The XRD data collected from various samples (samples having various Pb, Ca, Ba, Zn, Cu and O concentration) were all polycrystalline and correspond to Pb (Zn)-1223 phases. FIGURE 1 represents the X-ray diffraction diagram (XRD), it was notice that there is a change in the intensity of the peaks as well as in their locations when increasing the value of (Zn), where we notice an increase in the intensity of some peaks and a decrease in the intensity of other peaks in addition to the presence of displacements at the sites of these peaks.

The x-ray diffraction was analyzed for the pure sample, FIGURE 1, it was observed the phases (Pb-1213, Pb- 1223) with the presence of some impurities and noticed a rise in the intensity the peaks of the higher phase (Pb- 1223) of

antimony samples compared to the pure sample with a decrease in the intensity of the peaks of the remaining phases. The appearance of different phases in the pure sample in particular and the rest of the samples in general is due to the displacement of atomic defects, lack of oxygen or irregularity of positive ions that lead to accumulation of defects in Agglutination along the (c) axis that ultimately distorts the crystal structure [10]

It was very close to the standard calculations which showed that the samples have specific orthorhombic structure.

Then the phases ratios were calculated after determining the peaks, their intensity and type by comparing them with the standard diagrams according to Equation (2), calculating the ratio (c / a) and cell unit density by using equation (3). Through the calculation of the lattice constants, which showed that all samples had a specific crystal structure present and that the values of the lattice constants change with the change of the concentration of (Zn), which consequently leads to a change in the ratio (c/a) and the size of the cell unit, which affects the change of the density values shown in the TABLE. By calculating the phases ratios of the

samples, a clear decrease in the percentage of high phase formation appeared, matched by an increase in the percentage of residual phases and impurities, in a varying manner, and this is due to the accumulation and accumulation of defects in the internal structure of the samples. (Pb-1223) compared to the phase (Pb-1213) and the impurities formed while it showed a low value for (c/a), as well as the highest value of density compared to the pure sample. From these results it becomes clear that the sample (x = 0.2) represents the ideal sample in this group in terms of the replacement ratio. The reason for these fluctuations is due to the instability of the high phase, where its thermal movements are large compared to the lower phases [12], [11]. The result showed in the TABLE. It was showed that different values, the reason for these results, which are shown in the TABLE, is due to a degree The temperature and time of sintering, as increasing both the temperature and the time of sintering gives more energy and time to the mass-transport in order to obtain interference between the particles of materials and thus reduce the large surface area of the particles at the expense of their size

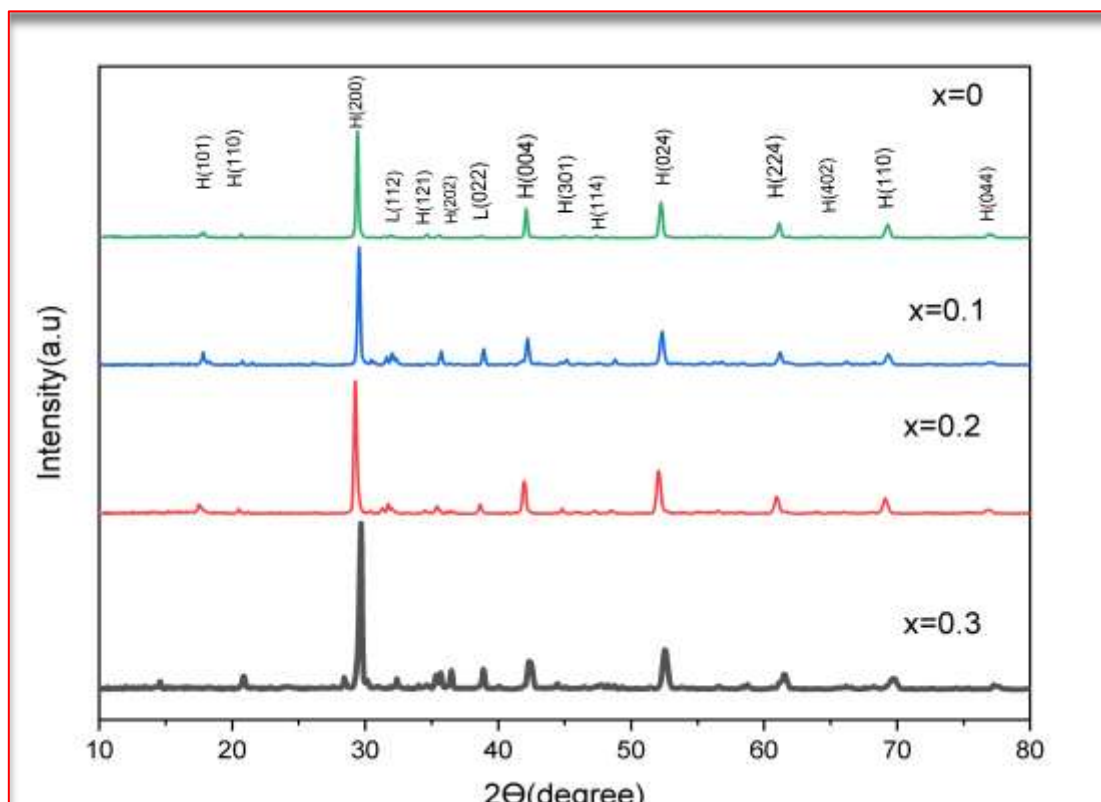


FIGURE 1. X- Ray diffraction pattern of the compound

Table 1: Demonstrates the generated samples' phase ratios, lattice coefficients, (c/a)

x	$V_{ph(H)}\%$	$V_{ph(L)}\%$	a (Å°)	b (Å°)	c (Å°)	c/a
0	86.67%	13.33%	6.123	6.093	8.597	1.404
0.1	60.00%	40.00%	6.131	6.099	8.649	1.410
0.2	86.96%	13.04%	6.103	6.093	8.717	1.428
0.3	64.52%	35.48%	6.041	6.031	8.611	1.425

Also, that the sintering time is necessary and required to obtain thermodynamically balanced phases. Whereas, a long sintering time is necessary to introduce additional layers of (CuO) and (CaO) into the low-phase structures, and this gave positive results in terms of the percentage of high phase formation in the sample [7].

Also, the substitution process may result in that some additional charges are transferred into the (CuO) layers, which leads to that some copper

atoms move from the oxidation state (Cu+ 2) to (Cu+ 3) and that this mixed state of valence leads to improvement [13].

FIGURE 2 shows the change of the ratio of lattice parameter c/a by increasing Sb concentration. Because the increasing of Zn content causes a decreasing in the percentage of oxygen, which makes them less than optimum value which gives the greatest value for the Pb-1223 phase.

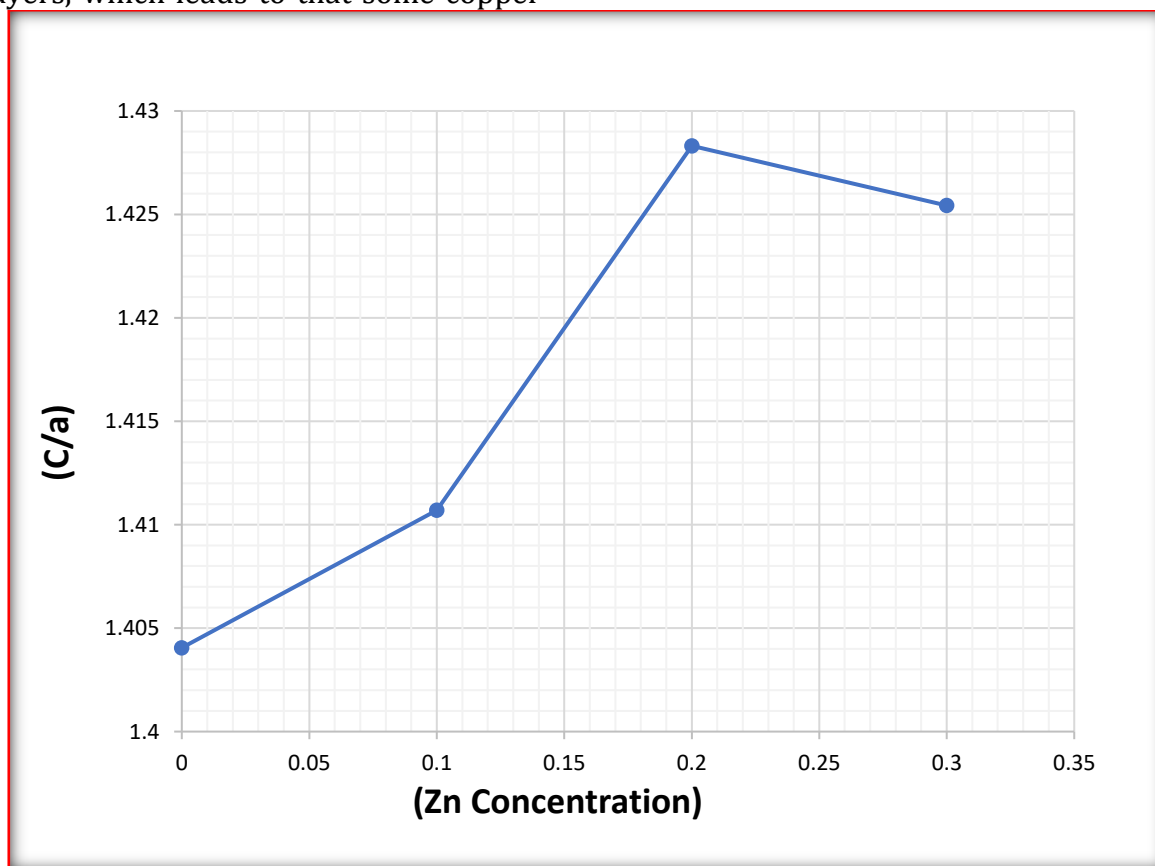


FIGURE 2. The (C/a) change as a function of the change in antimony (Zn) concentration

It is vital to understand the electrical resistance of a material as a function of temperature since it provides us with a good idea of the value of the critical transformation temperature ( $T_c$ ) as well as the nature of the interaction between the particles of the material

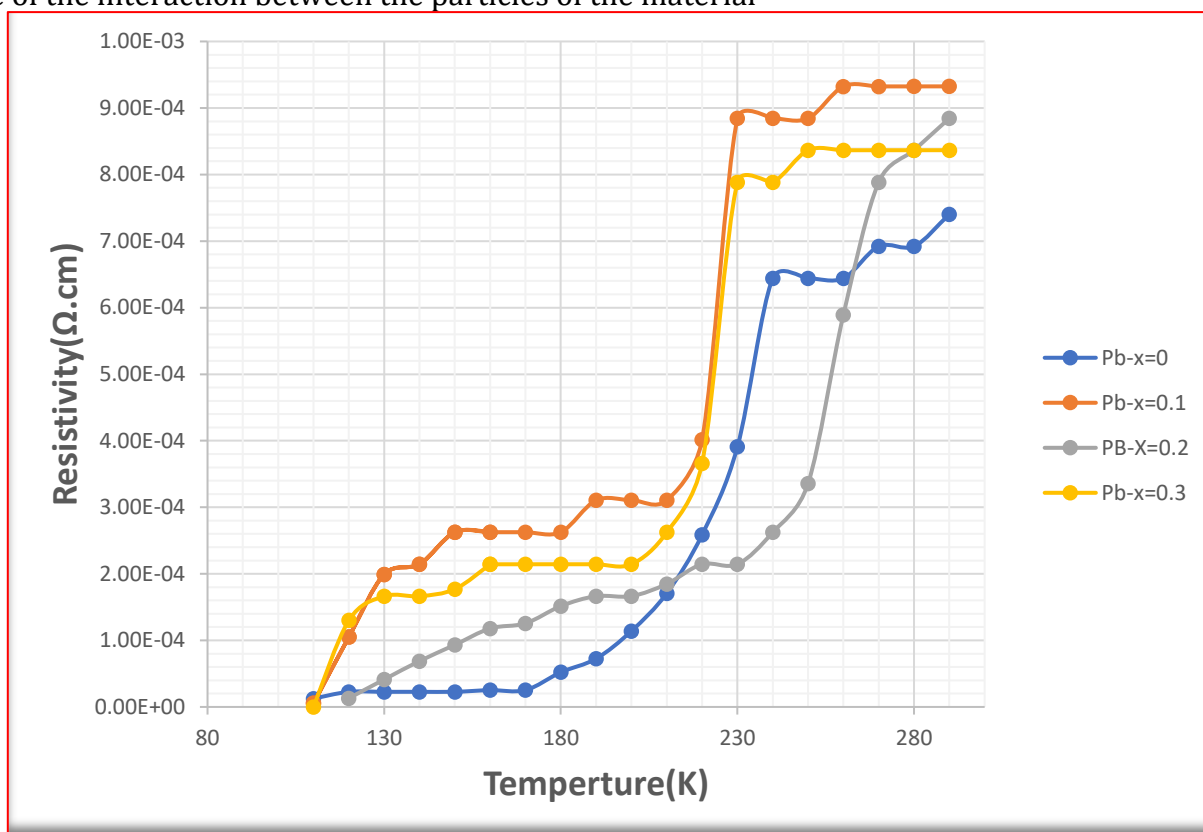


Figure (3) shows the change in electrical resistivity as a function of temperature for the group samples. In Figure (3), which represents the behavior of electrical resistance as a function of temperature in which ( $x=0, 0.1, 0.2, 0.3$ ) and in which, we note that all samples had metallic behavior in the region that precedes ( $T_{c(onset)}$ ) Which then the material turns into a superconducting state, where all samples showed

superconducting behavior with a difference in critical transition temperatures, noting the increase in the width of the transition to the superconducting state, which is attributed to the presence of impurities and low phases, as well as to the generation of some internal distortions in the crystal structure Because of the replacement process.

Table 2. Shows the ratios of phases, critical temperature, energy gap and concentration of gaps for the samples and concentration of gaps for the samples

x	Tc (K)	Tc(of) (K)	Tc(on) (K)	$\Delta T$ (K)	Tc(mid) (K)	Eg(ev)
0	104.7	104.7	119.5	14.8	112.1	0.031
0.1	109.4	109.4	120.5	11.1	114.95	0.033
0.2	110.5	110.5	129.8	19.3	120.15	0.0336
0.3	102.6	102.6	120.04	17.44	111.32	0.0312

In Table (2), we notice that the decrease in the electrical resistance in the superconducting samples was gradual. As for the transition width ( $\Delta T_C$ ), we note that it was of small values, which indicates the homogeneity of the sample, and the reason for this behavior is due to the containment. Samples have low phases and impurities in different proportions, and it is possible to explain why the critical temperature of the samples differs from the pure sample by a considerable drop in the high phase (Pb-1223) and an increase in other phases (XRD).

### Conclusions

The experimental work was studying the effect of partial substitution of Zinc (Zn) on  $(\text{PbBa}_2\text{Ca}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{8+\delta})$  compound, we were able to successfully obtain increase of high phase for the samples within the preparatory conditions. Since the long sintering time is very necessary to add layers of antimony oxide into the composition and obtain the highest percentage of the high phase, the sintering period took 48 hours. The presence of the phase (Pb-1212) in small proportions may be necessary for the growth and formation of (Pb-1223) phase and to drive the thermodynamic process and phase shift in the system (PBCCO) for greater stability at higher rates. The optimum substitution ratio was in the sample with concentration (Zn = 0.2) in which we obtained the highest phase value (86.96%) and the highest value of  $c/a$  is (8.717).

### Reverences

1. J. G. Bednorz, K. A. Moller, "Perovskite-type oxides-The new approach to high-Tc superconductivity", *Rev. Mod. Phys.* 60, (1988), 585.
2. H. Mazaki, T. Ishida, and T. Sakuma, "Superconducting Transitions of  $\text{BiSrCaCu}_2\text{O}_x$  Quenched from High Temperatures", *Jpn. J. Appl. Phys.*, 27 (1988), 811.
3. H. Kemerlingh Onnes, *Leiden commun*, (Book) 1206- 1226(1911)
4. Parkin S. S. P., Lee V. Y., Engler E. M., Nazzal A. I., Huang T. C., Gorman G., Savoy R., and Beyers, R" Bulk superconductivity at 125 K in  $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{x}$ ", (1988) *Phys. Rev. Lett.* 60 (24), 2539–2542.
5. S. N. Putilin, E. V. Antipov, O. Chmaissem, M. Marezio, "Superconductivity at 94 K in  $\text{HgBa}_2\text{CuO}_{4+\delta}$ ", *Nature*, ((1993)) 362, 226.
6. A. Schilling, M. Cautoni, J. D. Guo, H. R. Ott, "Superconductivity above 130 K in the Hg-Ba-Ca-Cu-O system", *Nature* 363, 56.(1993)
7. S.Uchida, H.Takagi, K.Kitazawa and S.Tanaka, " Superconducting Properties of  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ ", *Jpn. J. Appl.Phys* 26, L1.(1987)
8. Haider, Haider MJ, and Kareem A. Jasim. "Effect of Composition and Dielectric Properties for (YBCO) superconductor compound in different preparation methods." *Ibn AL-Haitham Journal For Pure and Applied Science* 33.1 (2020): 17-30.
9. Kareem Ali Jassim, "Structure and electrical properties of lanthanum doped  $\text{Bi}_2\text{Sr}_2\text{Ca}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{10+\delta}$
10. Kareem Ali Jassim, Tariq J. Alwan, " Effect of Oxygen Treatment on the Structural and Electrical Properties of  $\text{Tl}_{0.85}\text{Cd}_{0.15}\text{Sr}_2\text{CuO}_{5-\delta}$ ,  $\text{Tl}_{0.85}\text{Cd}_{0.15}\text{Sr}_2\text{Ca}_2\text{Cu}_{207-\delta}$  and  $\text{Tl}_{0.85}\text{Cd}_{0.15}\text{Sr}_3\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}$  Superconductors", *J Supercond Nov Magn*, 30, p3451–3457. (2017),
11. Kareem Ali Jassim, Tariq J. Alwan, " Effect of Oxygen Treatment on the Structural and Electrical Properties of  $\text{Tl}_{0.85}\text{Cd}_{0.15}\text{Sr}_2\text{CuO}_{5-\delta}$ ,  $\text{Tl}_{0.85}\text{Cd}_{0.15}\text{Sr}_2\text{Ca}_2\text{Cu}_{207-\delta}$  and  $\text{Tl}_{0.85}\text{Cd}_{0.15}\text{Sr}_3\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}$  Superconductors", *J Supercond Nov Magn*, 30, p3451–3457. (2017),
12. Haider, Haider MJ, et al. "Studying the partial substitution of barium with cadmium oxide and its effect on the electrical and structural properties of  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  superconducting compound." *AIP*

- Conference Proceedings. Vol. 2123. No. 1. AIP Publishing LLC, 2019.
13. T. Tamura, S. Adachi, X.-J. Wu, T. Tatsuki, K. Tanabe, "Critical Current Density and Irreversibility Field for  $Pb-12(n-l)n$  ( $n = 3,4$ ) Superconductors", *Physica C* 277 ,1 , .(1997)
  14. Haider MJ. Haider , Kassim M. Wadi , Hind A. Mahdi , Kareem A. Jasim, Aday H. Shaban, " Studying the partial substitution of barium with cadmium oxide and its effect on the electrical and structural properties of  $HgBa_2Ca_2Cu_3O_{8+\delta}$  superconducting compound" AIP Conference Proceedings 2123, 020033,17 July (2019).