

The structural properties of $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ superconductor compound

A. H. Shaban^a, L. A. Mohammed^b, H. S. Hussein^c, K. A. Jasim^{b,*}

^aCollege of Science, University of Baghdad, Baghdad, Iraq

^bDepartment of physics, college of Education for pure sciences Ibn Al-Haitham, University of Baghdad, Iraq

^cGeneral Directorate of Karbala Education, Karbala, Iraq

The effect of partial substitution for lanthanum (La) on the structural properties of the compound $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ were studied. The variation of (x) are x=0.1, 0.2 and 0.3, which was synthesized by solid state reaction method. The mixed powder was pressed with pressure (7 ton / cm²) as a disc (1.5 cm) diameter and a thickness of (0.25 to 0.3 cm). The samples were sintering by 120 °C / hour with a changing rate from room temperature to 850 ° C through 72 hours. XRD analysis using to calculate crystal size, strain and degree of crystallinity. It was found all samples have orthorhombic structure and change of structure with increasing lanthanum concentration. It was shown that the change lanthanum concentrations of all our samples produce a change in the crystal size, strain, degree of crystallinity and lattice parameters.

(Received January 9, 2022; Accepted April 12, 2022)

Keywords: Crystal size, Strain and degree of crystallinity, X-ray diffraction, Lanthanum concentration and partial substitution

1. Introduction

The superconductors are classified into two types with respect to temperature as high and low temperature superconductors. The high superconductor RE-Ba-Cu-O [(RE) BCO], where RE = Sm, Y, and Gd, have the ability to trap more magnetic fields than those produced by the permanent magnet field [1, 2]. These materials will be important in high speed trains, medical, industrial, trapped flow devices, rotating electrical machines and energy storage systems [3-5]. Loose superconductors are characterized by their brittle nature and are often described as being similar to ceramics in their physical and chemical properties. In addition, it often limits the extent to which it can be exploited in applications as a superconducting material due to its poor mechanical properties, especially in higher field fields [6, 7]. Partial addition or substitution of certain chemical elements, especially those of a metallic quality, such as silver, lead, copper, cadmium, and nickel in the crystalline structure will greatly improve the properties of the bulk sample, such as fracture and bending toughness [8-15]. It does not tend to minimize Characteristics of single grain superconductivity, unlike many other alloys [16-18]. To prevent the creation of grain boundaries, superconductors should be created as single grains for practical applications that significantly limits the ability of these materials to produce massive magnetic fields and significantly inhibits the high critical current [17]. After more than 30 years of study into the production of these materials in form of massive single grains [19].

The top melt growth technique is now commonly used to produce single granules with large sizes to produce a variety of superconducting formulations [20]. The $YBa_2Cu_3O_{7-\delta}$ superconducting phase (Y-123) is decomposed into secondary solid phase Y_2BaCuO_5 (Y-211) non-superconducting and the remaining Ba-Cu liquid phase by heating the pressurized sample powder to the temperature of geometric decomposition [18, 19]. Slow cooling with a temperature controller with a suitable solid seed crystal in place, allowing it to nucleate and expand grain of

* Corresponding author: kareem.a.j@ihcoedu.uobaghdad.edu.iq
<https://doi.org/10.15251/DJNB.2022.172.519>

large single made up of a continuous Y-123 phase matrix. This approach includes distributing separate non-superconducting Y-211 phase contents in addition to the superconducting phase [21].

The top melt growth technology is one of the most basic production methods for these products, but it is focused on optimizing a large number of interfering processing parameters and variables. As a result, applying chemical agents to alloying makes deciding the best manufacturing conditions [16, 19]. In some cases, it can be very difficult to successfully grow one single grain. Although the original material is chemically stable in nature within the phase matrix of Y-123, the incorporation of the elements increases the temperature of the architectural decomposition to form the precursor [20]. Recent advancements in dissolution treatment have made it possible to consistently and repeatedly manufacture big single YBCO-Ag pellets [13]. In order for these single pellets to be useful, their superconducting properties must be comparable to those of the top melt growth technology fabricated normal conductivity YBCO [5, 6].

In the present work, $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ polycrystalline compound were prepared by use solid state reaction process. We will analyze the $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ structural properties and study the effect partial substitution of lanthanum concentrations on crystal size, strain and degree of crystallization by using different methods.

2. Experimental

Four Samples with formula $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ were prepared by solid reaction technique where $x = 0.1, 0.2$ and 0.3 . The purity of primary ingredients was taken care of: the basic content of Y_2O_3 was 99.99%, BaO, 99.99%, and CuO was 99.99%. Additives were introduced in the form of highly pure alkaline oxides (LaO more than 99.9% by weight). The ingredients were weighed and mixed with an electric magnetic stirrer for 45 minutes, and then pressed into tablets with a diameter of 1.5 cm and a thickness of 3 mm with a pressure of 9 ton/cm². Samples were sintering by 120°C / hour rate from room temperature to a reaching 850°C and they were kept at 850°C for 90 hours and then were cooled with same rate to 400 ° C, then stays at this temperature for 4 hours with oxygen injected into furnace. After that temperature of furnace was decreased from 400 to 25 °C at same rate. The structure of prepared samples was obtained using X-ray diffraction measurements in θ -2 θ arrangement, in the 20 to 60 degrees range.

3. Results and discussion

XRD was examined for $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ bulk polycrystalline samples where $x=0.1, 0.2, 0.3$ and 0.4 , for a deflection angle ranging between (20° to 80°), which were illustrated in Figure 1. The results shows a polycrystalline structure for all samples have with a structure of an orthorhombic. The pattern of the (XRD) for doped sample illustrated the existence of Y-147 in high rate with less phases of (Y-211 and Y-123) and some impurity phases appearing [22]. By substitution of La concentration, the fluctuation of the intensities for the phases (Y-211 and Y-123) and the accumulated of impurities could be refer to the defect in the internal structure of the samples. The substitution process will lead to a very small shift in the (XRD) chart angle and peaks intensities. XRD analysis using to calculate crystal size, strain and degree of crystallinity. The crystal size was calculated by different methods, the Shearer method, Williamson-Hall, and the Size-strain plot method.

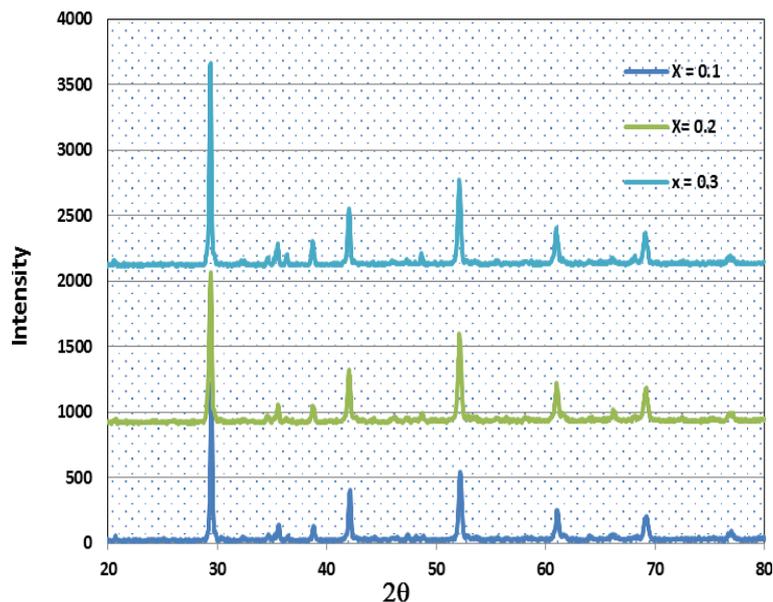


Fig. 1. X-ray diffraction for $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ bulk polycrystalline samples where $x=0.1, 0.2$ and 0.3 .

3.1. Scherrer Method

The Scherrer equation is a formula that relates the average crystal size in solids to a peak expansion in the X-ray diffraction pattern, and is mainly based on the values obtained from X-ray diffraction. It is named by the scientist (Paul Scherrer) put it. Scherrer formula is used to calculate the average crystal size in the vertical direction of the crystal. $D=K\lambda/(\beta \cos\theta)$, where K =constant, λ is the X-ray wavelength and d = Full width at half maximum peak intensity (in Rad). Average crystal size can calculate using the Origin software. The Figure 2 shown a graph of $\cos\theta$ as a function of $1/\beta_{hkl}$ for $Y_{0.9}La_{0.1}Ba_4Cu_7O_{15+\delta}$ bulk polycrystalline, the Scherrer crystalline size can be calculated from the slope which is found as 5.2043 nm. In the same way, the crystal size of $Y_{0.8}La_{0.2}Ba_4Cu_7O_{15+\delta}$ and $Y_{0.7}La_{0.3}Ba_4Cu_7O_{15+\delta}$ was calculated when $X=0.2$ and 0.3 was found, as it was found to be 261.3091 and 281.3589 nm, respectively and their values are indicated in the table.

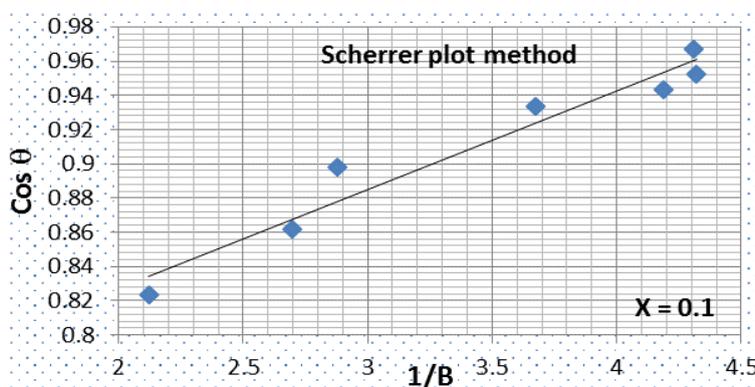


Fig. 2. Graph of $\cos\theta$ as a function of $1/\beta_{hkl}$ for $Y_{0.9}La_{0.1}Ba_4Cu_7O_{15+\delta}$ bulk polycrystalline slope presented to Scherrer crystalline size.

3.2. Williamson-Hall method

Williamson-Hall method is it method for finding crystal size and crystal strain. The curvature of the XRD peak physical line occurs due to the magnitude [23]. So the total anxiety induced by strain and size crystal at a given peak having hkl value can be expressed from the

Williamson-Hall relationship [24, 25]. From this relationship and with the aid of an X-ray diffraction diagram, a line equation is possible to draw a graph between $\cos\theta$ versus to $4\sin\theta$ of the $Y_{0.9}La_{0.1}Ba_4Cu_7O_{15+\delta}$ bulk polycrystalline as shown in Figure 3, where the X axis represents $4\sin\theta$ and the Y axis represents $\cos\theta$. This diagram gives the slope of the straight line has an intrinsic strain value of 0.00236. Pinna gives the average crystal size of the compound found to be 50.056 nm [12, 23]. In the same way, the crystal size of $Y_{0.8}La_{0.2}Ba_4Cu_7O_{15+\delta}$ and $Y_{0.7}La_{0.3}Ba_4Cu_7O_{15+\delta}$ was calculated when $X = 0.2$ and 0.3 , was found to be 45.514 and 258.9426 nm, while the strain 0.0017 and 0.00209 respectively, their values are indicated in the table.

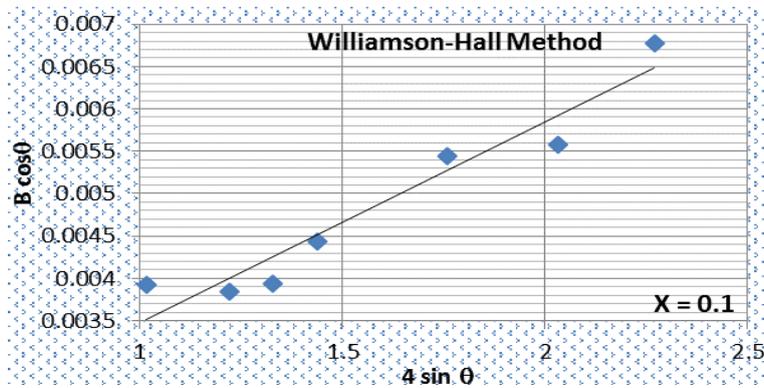


Fig. 3. $B_{hkl} \cos\theta$ versus $4\sin\theta$ for $Y_{0.9}La_{0.1}Ba_4Cu_7O_{15+\delta}$ bulk polycrystalline Slope presented to strain value of Williamson-Hall method

3.3. The Size-strain plot (SSP) method

The SSP method also provides better isotropic expansion performance, as it places more emphasis on low-angle reflections, where the resolution for low-angle reflections is greater than at higher angles. This is because the X-RAY data at lower angles are usually strongly overlapping peaks. Therefore, the measurement of SSP is performed using formula [23-25]. It is possible to draw a graph between $d B_{hkl} \cos\theta$ versus $d^2 \cos\theta$ of the $Y_{0.9}La_{0.1}Ba_4Cu_7O_{15+\delta}$ compound, where the X axis represents $d^2 \cos\theta$ and the Y axis represents by $d B_{hkl} \cos\theta$ as shown in Figure 4. This drawing gives the slope of the straight line crystal size value of the Size – stain method which is 33.832 nm when $x=.01$ and 29.762 and 182.6294 nm when $x=0.2$ and 0.3 respectively, their values are indicated in the table.

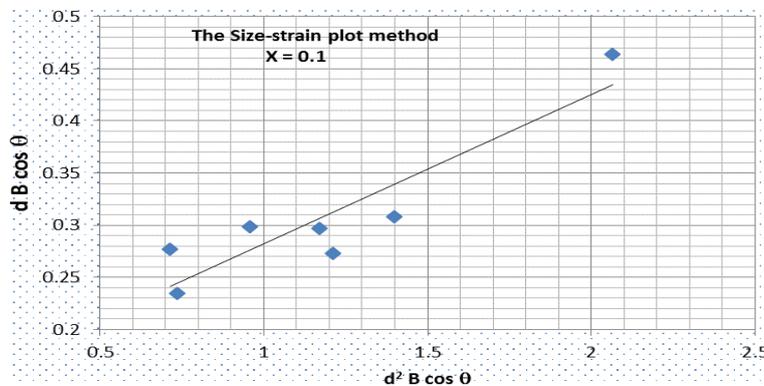


Fig. 4. $d B_{hkl} \cos\theta$ versus $d^2 \cos\theta$ for $Y_{0.9}La_{0.1}Ba_4Cu_7O_{15+\delta}$ bulk polycrystalline Slope presented to line crystal size value of the Size – stain method.

3.4. Crystallinity

The degree of crystallinity can be assessed using x-rays for many glass-ceramic materials and some polymers through which it is possible to identify and distinguish a mixture of crystalline

and amorphous regions, such as where crystallinity is generally observed as a percentage of the size of the crystalline material. Crystallinity can be measured using X-ray crystallography, applying the following equation [24, 25]:

$$\text{Crystallinity} = \frac{\text{Area of Crystalline peaks}}{\text{Area of all peaks (Crystalline+Amorphous)}} \times 100 \quad (1)$$

After applying the above equation, the results listed in the table were obtained. Figure 5 is drawn, which represents the relationship between the degrees of crystallinity as a function of the concentration of lanthanum. It should be noted that there was a change in the crystallization values with an increase in the concentration of lanthanum.

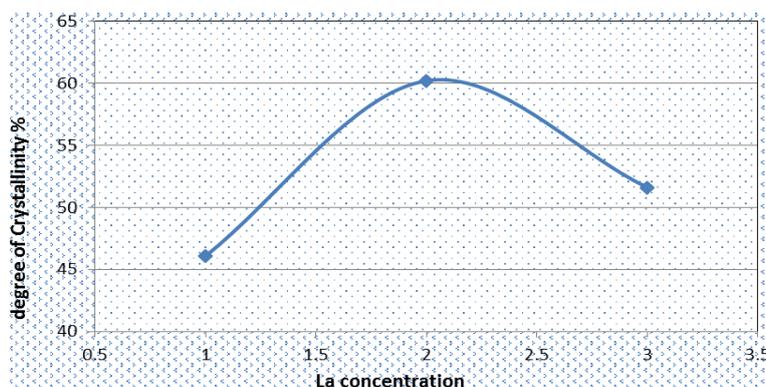


Fig. 5. Degree of Crystallinity as a function of La concentration for $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ bulk polycrystalline samples where $x=0.1, 0.2$ and 0.3 .

Table 1. Geometrical parameters of $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ compound using different Methods.

Crystallinity (%)	Scherrer plot method	Williamson- Hall method		The Size – stain method	
	Crystal size (nm)	Crystal size (nm)	strain	Crystal size (nm)	strain
46.0706	52.043	50.056	0.00236	33.832	0.1432
60.2045	261.3091	45.514	0.0017	29.762	0.252
51.6072	281.3589	258.9426	0.00209	182.6294	0.00304

4. Conclusions

In this manuscript the Perovskite $Y_{1-x}La_xBa_4Cu_7O_{15+\delta}$ bulk polycrystalline samples where $x=0.1, 0.2$ and 0.3 was successfully prepared by the solid-state reaction method. The three samples were examined with an X-ray diffraction XRD analysis. It was found all samples have orthorhombic structure and change of structure with increasing lanthanum concentration. XRD analysis using to calculate crystal size, strain and degree of crystallinity. The crystal size was calculated by different methods, namely the Shearer method, Williamson-Hall, and the Size-strain plot method, and the results were different for the three methods, because these methods depend on the type of material and the method of preparation. Shearer's method considers the effect of crystal size only, while Williamson-Hall and Size-strain plot mention addition to crystal volume accounting for induced strain. The results shown that the change lanthanum concentrations of all our samples produce a change in the crystal size, strain, degree of crystallinity and lattice parameters.

References

- [1] Durrell J H, Dennis A R, Jaroszynski J, Ainslie M D, Palmer K G B, Shi Y H, Campbell A M, Hull J, Strasik M, Hellstrom E E and Cardwell D A, A trapped field of 17.6T in melt-processed, bulk Gd-Ba-Cu-O reinforced with shrink-fit steel, *Supercond. Sci. Technol.* 27, (2014); <https://doi.org/10.1088/0953-2048/27/8/082001>
- [2] Zhai W, Shi Y H, Durrell J H, Dennis A R and Cardwell D A, The Influence of Y-211 Content on the Growth Rate and Y-211 Distribution in Y-Ba-Cu-O Single Grains Fabricated by Top Seeded Melt Growth Crystal, *Growth & Design*, 14, (2014) : 6367-75; <https://doi.org/10.1021/cg501135q>
- [3] Campbell A M and Cardwell D A, Bulk high temperature superconductors for magnet applications, *Cryogenics*, 37, (1997) : 567-75; [https://doi.org/10.1016/S0011-2275\(97\)00068-4](https://doi.org/10.1016/S0011-2275(97)00068-4)
- [4] Werfel F N, Floegel-Delor U, Rothfeld R, Riedel T, Goebel B, Wippich D and Schirrmeister P, Superconductor bearings, flywheels and transportation *Supercond. Sci. Technol.* 25, (2012); <https://doi.org/10.1088/0953-2048/25/1/014007>
- [5] Li B Z, Zhou D F, Xu K, Hara S, Tsuzuki K, Miki M, Felder B, Deng Z G and Izumi M, Materials process and applications of single grain (RE)-Ba-Cu-O bulk high-temperature superconductors, *Physica C*, 482, (2012) : 50-7; <https://doi.org/10.1016/j.physc.2012.04.026>
- [6] Nishio T, Itoh Y, Ogasawara F, Suganuma M, Yamada Y and Mizutani U, Superconducting And Mechanical-Properties Of YBCO-Ag Composite Superconductors, *Journal of Materials Science*, 24(32), (1989) : 28-34; <https://doi.org/10.1007/BF01139045>
- [7] Iida K, Babu N H, Shi Y H, Miyazaki T, Sakai N, Murakami M and Cardwell D A, 8th European Conference on Applied Superconductivity, ed S Hoste and M Ausloos (Bristol: Iop Publishing Ltd), (2008).
- [8] Haider M. J. Haider, Kassim M. Wadi, Hind A. Mahdi, Kareem A. Jasim, Auday H. Shaban, 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 Conf. Proc.* 1968, (2019) : 020033; <https://doi.org/10.1063/1.5116960>
- [9] Kassim M. Wadi, Aqeel N. Abdulateef, Auday H. Shaban, Kareem A. Jasim, Improvement of superconducting properties of $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ Ceramic by prepared under different pressures, *Energy Procedia*, 157, (2019) : 222-227; <https://doi.org/10.1016/j.egypro.2018.11.184>
- [10] K. A. Jassim, Tariq J. Alwan, J., The Effect of Simultaneous Substitution of Strontium at the Barium site of $\text{Tl}_0.6\text{Pb}_0.4\text{Ba}_{2-x}\text{Sr}_x\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}$ Superconductors, *Supercond. Nov. Magn.*, 22(8), (2009) : 861; <https://doi.org/10.1007/s10948-009-0512-7>
- [11] Kareem. A. Jasim, Tariq J. Alwan, H. K. Al-Lamy H. L. Mansour, Improvements of Superconducting Properties of $\text{Hg}_{0.6}\text{Pb}_{0.25}\text{Sb}_{0.15}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ Ceramic by controlling the sintering Time, *Journal of superconductivity and novel magnetism*, 24: 1963-1966, (2011); <https://doi.org/10.1007/s10948-011-1153-1>
- [12] Kareem. A. Jasim, The Effect of Simultaneous Substitution of Strontium at the Barium site of $\text{Tl}_{0.6}\text{Pb}_{0.4}\text{Ba}_{2-x}\text{Sr}_x\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}$ Superconductors, *Journal of superconductivity and novel magnetism*, 25(6), (2012) : 1713-1717.
- [13] Diko P, Krabbes G and Wende C 2001 Influence of Ag addition on crystallization and microstructure of melt-grown single-grain $\text{YBa}_2\text{Cu}_3\text{O}_7$ bulk superconductors, *Supercond. Sci. Technol.* 14(7), (2001) : 486; <https://doi.org/10.1088/0953-2048/14/7/311>
- [14] Nakamura Y, Tachibana K and Fujimoto H, Dispersion of silver in the melt grown $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ crystal, *Physica C: Superconductivity*, 306(3-4), (1998) : 259-270; [https://doi.org/10.1016/S0921-4534\(98\)00368-2](https://doi.org/10.1016/S0921-4534(98)00368-2)
- [15] Azambuja P d, Rodrigues JÃ°nior P, Jurelo A R, Serbena F C, Foerster C E n, Costa R n M, Souza G B d, Lepiensi C M c and Chinelatto A L, Effects of Ag addition on some physical properties of granular $\text{YBa}_2\text{Cu}_3\text{O}_7$ -' superconductor, *Brazilian Journal of Physics*, 39(6), (2009) : 38-44; <https://doi.org/10.1590/S0103-97332009000600005>
- [16] Mendoza E, Puig T, Varesi E, Carrillo A E, Plain J and Obradors X, Critical current

enhancement in YBCO-Ag melt-textured composites: influence of microcrack density, *Physica C: Superconductivity*, 334, (2000) : 7-14; [https://doi.org/10.1016/S0921-4534\(00\)00098-8](https://doi.org/10.1016/S0921-4534(00)00098-8)

[17] Matsui M, Sakai N and Murakami M, Effect of Ag₂O addition on the trapped fields and mechanical properties of Nd-Ba-Cu-O bulk superconductors, *Superconductor Science and Technology*, 15, (2002) : 1092; <https://doi.org/10.1088/0953-2048/15/7/320>

[18] Dimos D, Chaudhari P, Mannhart J and Legoues F K, Orientation Dependence Of Grainboundary Critical Currents In YBa₂Cu₃O_{7-d} Bicrystals, *Physical Review Letters*, 61(2), (1988) :19-22; <https://doi.org/10.1103/PhysRevLett.61.219>

[19] Durrell J H, Hogg M J, Kahlmann F, Barber Z H, Blamire M G and Evetts J E, Critical current of YBa₂Cu₃O_{7-d} low-angle grain boundaries, *Physical Review Letters*, 90, (2003) : 247006; <https://doi.org/10.1103/PhysRevLett.90.247006>

[20] Sawano K, Morita M, Tanaka M, Sasaki T, Kimura K, Takebayashi S, Kimura M and Miyamoto K, High Magnetic-Flux Trapping By Melt-Grown Ybacuo Superconductors, *Japanese Journal of Applied Physics Part 2-Letters*, 30, (1991) : L1157; <https://doi.org/10.1143/JJAP.30.L1157>

[21] Kareem A. Jasim Mohammed A.N. Thejeel Raghad Subhi Al-Khafaji, The Effect of Doping by Sr on the Structural, Mechanical and Electrical Characterization of La₁Ba_{1-x}Sr_xCa₂Cu₄O_{8.5+δ}, *Ibn Al-Haitham Jour. for Pure & Appl. Sci*, 27(1), (2014) : 213-219.

[22] Nakamura Y, Tachibana K, Kato S, Ban T, Yoo S. I. and Fujimoto H, Phase relation in Y₂11-Y₁₂₃-Ag system and morphology of silver in Y₁₂₃ crystal, *Physica C: Superconductivity and its Applications*, 294(3-4), (1998) : 302-315; [https://doi.org/10.1016/S0921-4534\(97\)01737-1](https://doi.org/10.1016/S0921-4534(97)01737-1)

[23] Kareem A. Jasim, Rihab Nassr Fadhil, Auday H. Shaban, Harith I. Jaafar, Bushra K.H. Maiyaly, Suad H. Aleabi, Ebtisam M-T. Salman, the effects of copper additives on the glass transition temperature and hardness for epoxy resin, *PIE, Progress in Industrial Ecology - An International Journal*, 13(2): 163-172, (2019); <https://doi.org/10.1504/PIE.2019.099357>

[24] Mustafa K. Kamil and Kareem A. Jasim, Calculating of crystalline size, strain and Degree of crystallinity of the compound (HgBa₂Ca₂Cu₃O_{8+σ}) by different method, *IOP Conf. Ser.: Mater. Sci. Eng.* 928, (2020) : 072109; <https://doi.org/10.1088/1757-899X/928/7/072109>

[25] Kassim Mahdi Wadi, Kareem A. Jasim, Auday H. Shaban, Mustafa K. Kamil, Firas Kadhim Nsaif, *Journal of Green Engineering (JGE)*, 10(9), September 2020.

[26] Abbas K.Saadon, Mustafa Mohammed Ali , Kareem A.Jasim & Duraid H.Younis, Study the Physical and Dielectric Properties of Ferrite - Sic Composite, *Ibn Al-Haitham Jour. for Pure & Appl. Sci*, 86, (2014) : 91-96.