



EU DOPING EFFECT ON THE CRYSTAL STRUCTURE OF $Y_{3-x}Eu_xBa_2Cu_3O_{7-x}$ SUPERCONDUCTOR

Physics

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ABSTRACT

This study aims to determine the effect of the Eu doping on the crystal structure of $Y_3Ba_2Cu_3O_{7-x}$ superconductor. The synthesis process used the raw material of Y_2O_3 (99.9%), Eu_2O_3 (99.9%), $BaCO_3$ (99.9%), CuO (99.9%) and HNO_3 . The raw material was dissolved with HNO_3 and calcinated at $600^\circ C$ for 3 hours. That is followed by sinter at $930^\circ C$ for 3 hours. The characterization of this research is X-ray diffraction (XRD), Scanning electron microscope (SEM), energy dispersive X-ray spectrometry (EDS) and Fourier Transform Infrared Spectroscopy (FTIR). The XRD characterization results show that the samples are well crystallized which is marked by the sharp peak appearance. The addition of the Eu element to the $Y_3Ba_2Cu_3O_{7-x}$ sample resulted in the angle shift in each diffraction spectrum. The greater of the Eu element substitution, the higher of the lattice parameter values, the larger of the unit cell volume, while the atomic density in the unit cell is smaller. In this study, the range of lattice parameter values obtained was 3.823-3.825 Å for the a-axis, 3.890-3.896 Å for the b-axis, 11.665-11.689 Å for the c-axis. These results are supported by SEM characterization, where the particle size increases with the addition of the Eu elements. FTIR characterization results obtained by absorption at wavelengths of 445.56, 507.28, 597.93, 856.39, 952.84, 1224.80, 1438.90, 2387.87 cm^{-1}

KEYWORDS

superconductor, lattice parameter, angle shift

1. Introduction

Since the discovery of a high-temperature superconductor (La_2CuO_4) in 1986 by Berdnorz and Muller [J.G. Berdnorz, 1987] with a critical temperature of 30 K, the study of superconductor materials began to rise after nearly 60 years of vacuum. A year later in 1987, only by replacing La^{+3} with Y^{+3} , the critical temperature can be increased from 30 to 90 K. That is known as Y-123 or YBCO with stoichiometry of $YBa_2Cu_3O_{7-x}$. YBCO superconductors are highly potential in applications such as transportation and power transmission cables, because it has a high critical temperature (90 K) [L. Rostila, 2006, P. Tixador, 2010].

The Y-123 superconductor study was intensified, until the Y-358 superconductor was discovered by Aliabadi [Aliabadi, 2009] with stoichiometry of $Y_3Ba_2Cu_3O_{7-x}$ compound having a critical temperature of 100 K. Microscopically, the Y-358 superconductor had five CuO_2 layers in a single cell Unit [Tavana, 2010]. The researcher's problem is how to increase critical temperature, critical current density and critical magnetic field of the material to be applied.

In the case of doping and substitution variations, some researchers have synthesized of rare earth elements that are magnetic materials to increase the critical magnetic field of YBCO superconductors [Suharta W.G., 2013]. Suharta and colleagues have done research of adding B_2O_3 doping to see the change of NLBCO crystal structure [Suharta W.G., 2016]. In general, the method of synthesis process is done by using solid state reaction with sintering time above 24 hours [Alirez, 2009, Roaa, 2015].

In this research, $Y_3Ba_2Cu_3O_{7-x}$ superconductor was substituted with the Eu element variation to see the crystal structure change of Y-358. The synthesis process is done by using wet-mixing method by adding nitric acid (HNO_3) with short sintering time (three hours).

2. Experiment

The raw materials used for the formation of $Y_{3-x}Eu_xBa_2Cu_3O_{7-x}$ phase superconductors were Y_2O_3 (99.9%), Eu_2O_3 (99.9%), $BaCO_3$ (99.9%), CuO (99.9%) and HNO_3 . The Eu element is varied from 0.05, 0.10,

0.15, 0.20 and 0.25. Synthesis process is done by wet-mixing method with steps :

- The raw material is weighed according to the molar composition or the composition of the weight of the compound.
- The process of wet-mixing method includes : 1) mixing and stirring of each raw material using a magnetic stirrer until a homogeneous solution is obtained, 2) The homogeneous solution is stirred using a magnetic stirrer accompanied by a slow temperature increase (below $100^\circ C$) to the crust.
- The compound in crust form is calcined at $600^\circ C$ for 3 hours, followed by a sintering process at $930^\circ C$ for 3 hours.

The result of sample synthesis is in the form of powder. The sample was characterized using X-ray diffraction (XRD), Scanning electron microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR). Phase identification is done by match matching (search match) using Match program, while Rietveld Analysis is done by refinement using Rietica program.

3. Result and Discussion

The XRD characterization results for all samples are shown in Figure 1. The observation is done by enumeration starting from angle $2\theta = 7^\circ$ up to angle $2\theta = 90^\circ$. The $Y_{3-x}Eu_xBa_2Cu_3O_{7-x}$ samples are given the symbol ($Y_{2.95}Eu_{0.05}$)BCO for $x = 0.05$, ($Y_{2.90}Eu_{0.10}$)BCO for $x = 0.10$, ($Y_{2.85}Eu_{0.15}$)BCO for $x = 0.15$, ($Y_{2.80}Eu_{0.20}$)BCO for $x = 0.20$, ($Y_{2.75}Eu_{0.25}$)BCO for $x = 0.25$. In general, all samples exhibit the same spectral pattern with a sharp peak that illustrates well crystallization. At some angles show an overlap peak, that indicates there is more than one phase.

Eu doping on the $Y_{3-x}Eu_xBa_2Cu_3O_{7-x}$ superconductor resulted in a 2θ shift for all phases that appeared in the sample. To clarify the angular shift, the diffraction results are focused at a short angle. The angle shift of $Y_{3-x}Eu_xBa_2Cu_3O_{7-x}$ was treated with calcination at $600^\circ C$ for 3 hours and sintered at $930^\circ C$ for 3 hours at an angle of 30 to 35° , shown in Figure 2. While the angular shift of 2θ from $36-44^\circ$ are shown in Figure 3 respectively.

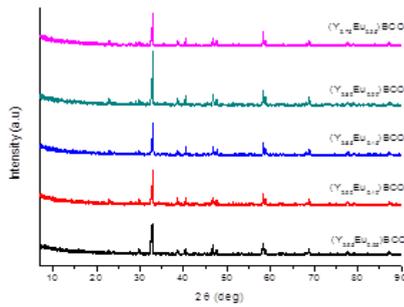


Figure 1. Result of XRD characterization of sample $Y_{3-x}Eu_xBa_2Cu_3O_{7-δ}$ ($x=0.05-0.25$) treated with calcination at temperature $600^\circ C$ for 3 hours and sintering at $930^\circ C$ for 3 hours

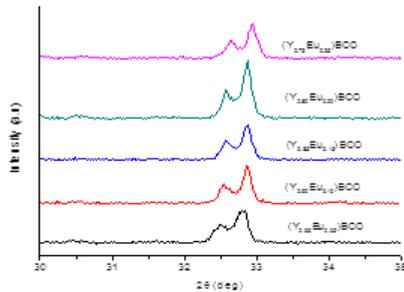


Figure 2. The angle shift of 2θ sample $Y_{3-x}Eu_xBa_2Cu_3O_{7-δ}$ ($x=0.05-0.25$) was treated with calcination at a temperature of $600^\circ C$ for 3 hours and sintered at $930^\circ C$ for 3 hours at an angle of 30 to 35°

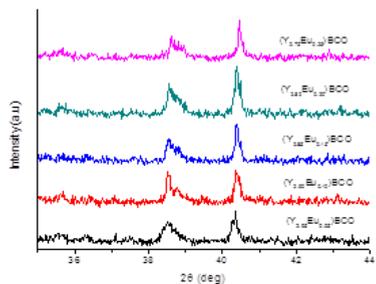


Figure 3. The angle shift of 2θ sample $Y_{3-x}Eu_xBa_2Cu_3O_{7-δ}$ ($x=0.05-0.25$) was treated with calcination at a temperature of $600^\circ C$ for 3 hours and sintered at $930^\circ C$ for 3 hours at an angle of 35 to 44°

The search match analysis is performed using the Match program. The diffraction peak matching results show the emergence of the high intensity $Y_{3-x}Eu_xBa_2Cu_3O_{7-δ}$ phase and the low-intensity Y_2BaCuO_5 , $BaCO_3$ and $BaCuO_2$ impurity phases. Phase Y_2BaCuO_5 refers to reference PDF number 100-1222. Phase $BaCO_3$ refers to PDF number 045-1471 [A. Kern, 1993] which has orthorhombic systems, Pnma space chamber 62 and lattice parameters a (6,433), b (5,315), c (8,904) and $BaCuO_2$ phases refer to PDF number 038-1402 [N. Wong, 1987] which has a cubic system, the Im3m space group (229) and the 18.2932 lattice parameter. The appearance of Y_2BaCuO_5 , $BaCO_3$ and $BaCuO_2$ impurities are also obtained in $Y_{1-x}Nd_xBa_2Cu_3O_{7-δ}$ as reported by W.G. Suharta et. al. [W.G. Suharta, 2013].

To determine the reliability and lattice parameters of the synthesized $Y_{3-x}Eu_xBa_2Cu_3O_{7-δ}$ crystals, Rietveld's analysis was performed by refinement using Rietica [B.A. Hunter, 1997]. Refinement process using Newton-Raphson strategy, 5th order polynomial, normal calculation method and peak shape Voigt. The reference used in the refinement process is a neodymium barium copper oxide with a code of ICSD 78453, space group of pmmm, orthorhombic crystal structure, which has a parameter of the lattice in the direction of the axis is 3.856 Å, the direction of the axis b is 3.912 Å and toward the c axis is 11,719 Å [Guillaume, 1994].

Results of refinement of sample $Y_{2.90}Eu_{0.10}Ba_2Cu_3O_{7-δ}$ are shown in Figures 4. Refinement results show the peak of reference diffraction (red color) compared with the sample data (black color) to obtain the difference peaks marked in green. While the values of lattice parameters, reliability, goodness of fit (GoF) and density are shown in Table 1. From the results of refinement in Table 1 and figure 5, it appears that Eu doping on YBCO superconductors results in changes in the lattice parameter values (a, b, c), where the lattice parameter values (a, b, c) increase in length with increasing Eu substitutions. This causes the unit cell volume to increase, while the unit cell density becomes smaller.

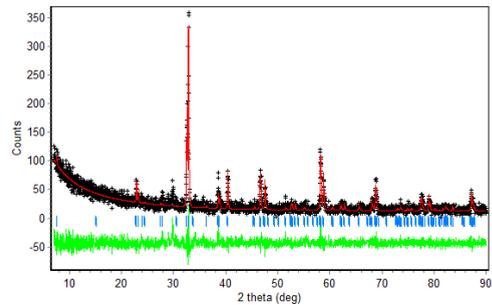


Figure 4. Result of refinement of $(Y_{2.90}Eu_{0.10})BCO$ samples which was treated with calcination at temperature of $600^\circ C$ for 3 hours and sintering at $930^\circ C$ for 3 hours

Table 1. Lattice parameter values (a, b, c), reliability, volume and unit cell density

Sample	Lattice Parameter			Reliability				Volume (Å ³)	density (g cm ⁻³)
	a (Å)	b (Å)	c (Å)	R _p	R _{wp}	R _c	GoF		
(Y _{2.75} Eu _{0.25}) BCO	3.8303(2)	3.8924(4)	11.6937(1)	17.43	23.27	20.07	1.34	174.342	7.022
(Y _{2.80} Eu _{0.20}) BCO	3.8298(0)	3.8921(2)	11.6902(1)	16.91	22.55	18.55	1.47	174.172	7.028
(Y _{2.85} Eu _{0.15}) BCO	3.8256(1)	3.8914(0)	11.6886(7)	16.65	21.92	19.49	1.27	174.007	7.038
(Y _{2.90} Eu _{0.10}) BCO	3.8248(8)	3.8900(9)	11.6740(2)	17.18	22.43	18.15	1.53	173.691	7.042
(Y _{2.95} Eu _{0.05}) BCO	3.8230(5)	3.8870(5)	11.6626(6)	17.29	22.44	18.35	1.49	173.306	7.048

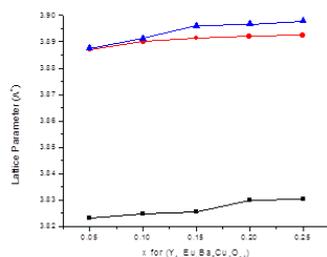


Figure 5. The curve changes the lattice parameters of the element substitution in $Y_{3-x}Eu_xBa_2Cu_3O_{7-δ}$ ($x=0.05-0.25$)

treated with calcination at $600^\circ C$ for 3 hours and sintering at $930^\circ C$ for 3 hours

The scanning electron microscope (SEM) characterization results for the $Y_{2.95}Eu_{0.05}Ba_2Cu_3O_{7-δ}$ and $Y_{2.85}Eu_{0.15}Ba_2Cu_3O_{7-δ}$ samples are shown in Fig. 6a and 6b respectively. The images show 55.000 times magnification with a $0.2 \mu m$ image size scale. SEM characterization is performed to determine the morphology and size of the particles formed. The SEM results show the particle in the form of a rod, which corresponds to the orthorhombic crystal structure with the price of the lattice parameter toward the a-axis almost equal to b, whereas the c-axis is 3 times the length of a and b. In the same magnification and scale, the sample stem $Y_{2.95}Eu_{0.05}Ba_2Cu_3O_{7-δ}$ looks shorter and thinner than the $Y_{2.85}Eu_{0.15}Ba_2Cu_3O_{7-δ}$ sample. This is in accordance with the

results of XRD characterization, where the addition of Eu resulted in the price of lattice parameters and cell volume of the satua getting longer and larger.

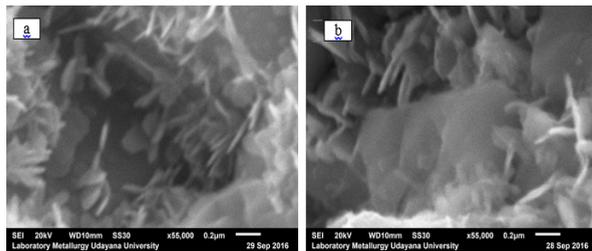


Figure 6. Result of SEM characterization : a) $Y_{2.95}Eu_{0.05}Ba_5Cu_8O_{18}$, b) $Y_{2.85}Eu_{0.15}Ba_5Cu_8O_{18}$. That samples were calcinated at 600°C for 3 hours and sintered at 930°C for 3 hours

The dispersive energy characterization of X-ray spectrometry (EDS) is performed to prove whether the constituent elements of the starting compound and the molar ratio composition of the synthesized compound are in accordance with the composition of the molar ratio of the starting compound. The EDS sample characterizations of $Y_{2.95}Eu_{0.05}Ba_5Cu_8O_{18}$ and $Y_{2.85}Eu_{0.15}Ba_5Cu_8O_{18}$ samples are shown in Figure 7a and 7b respectively, also the spectra of the constituent elements are shown in that Figure. The content of the elements, energy, percentage of the mass and percentage of atoms detected in the sample is shown in Table 2.

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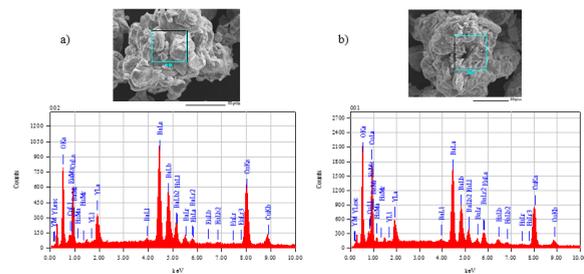


Figure 7. The sample particles of a) $Y_{2.95}Eu_{0.05}Ba_5Cu_8O_{18}$ and b) $Y_{2.85}Eu_{0.15}Ba_5Cu_8O_{18}$ were observed using EDS

Table 2. The content of the elements, energy, percentage of mass and percentage of atoms detected in the sample

No	Element	$(Y_{2.75}Eu_{0.25})$	$(Y_{2.80}Eu_{0.20})$	$(Y_{2.85}Eu_{0.15})$	$(Y_{2.90}Eu_{0.10})$	$(Y_{2.95}Eu_{0.05})$
		BCO	BCO	BCO	BCO	BCO
		Atom (%)				
1	O (K)	53.86	52.31	55.23	47.57	61.13
2	Cu (K)	24.57	25.11	25.02	30.52	19.18
3	Y (L)	6.12	5.62	6.27	4.11	4.22
4	Ba (L)	14.97	13.52	12.14	17.44	12.90
5	Eu (L)	0.48	0.44	0.34	0.35	2.57

Table 2 shows the constituent elements of $Y_{3-x}Eu_xBa_5Cu_8O_{18}$ superconductors, where all constituent elements have been detected from EDS characterization, that are Y, Ba, Cu, O and Eu elements. However, the percentage of the number of atoms is varied for each sample, indicating that the homogeneity of the sample is not evenly distributed. This can be overcome by the addition of mixing time to the synthesis process.

Fourier Transform Infrared Spectroscopy (FTIR) characterization results for all samples are shown in Figure 8. In general, the results show absorption waves at wave numbers 445.56, 507.28, 597.93, 856.39, 952.84, 1224.80, 1438.90, 2387.87 cm^{-1} . The resulting curve pattern of each sample is almost the same, only at the wave number of 500, 850 and 1300 cm^{-1} , which is OH and CO cluster, the intensity decreases with the addition of the Eu element.

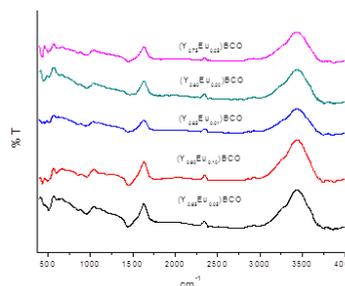


Figure 8. Result of FTIR characterization of $Y_{3-x}Eu_xBa_5Cu_8O_{18}$ sample

4. CONCLUSION

From the results of research that has been done, then it can be concluded that Eu doping on $Y_{3-x}Eu_xBa_5Cu_8O_{18}$ superconductor has resulted the angular shift due to the difference in radius of Eu and Y ions. The addition of substitution of the Eu element has resulted the greater the lattice parameter values (a, b and c), the larger unit cell volume and the smaller atomic density in the unit cell. The addition of the Eu element has resulted decreases of the absorption of OH and CO cluster.

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