



SYNTHESIS OF STRONTIUM COPPER OXIDE WITH SUBSTITUTION OF RARE EARTH ELEMENTS

Physics

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ABSTRACT

In this research have successfully synthesized $Sr_{1-x}Eu_xCuO_z$ superconductors with x are 0, 0.05, 0.10, 0.15 and 0.20. The synthesis process of $Sr_{1-x}Eu_xCuO_z$ superconductors uses $SrCO_3$ (99.9%), Eu_2O_3 (99.9%) and CuO (99.9%) materials. The sample synthesis process uses a wet-mixing method, wherein the starting material is added strongly HNO_3 acid, then stirred and heated to a crust. The calcination process was carried out at $600^\circ C$ for 3 hours and sintered at $950^\circ C$ for 3 hours. To know the success of sample synthesis, the first is X-ray diffraction (XRD) characterization to know the phases formed in the sample, lattice parameter values and unit cell volume. Second, the characterization of Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) to know particle size and precision of particle composition that have been made. Third, the characterization of Fourier Transform Infrared Spectroscopy (FTIR) is done to find out the frequency of vibration that occurs in the sample. The XRD characterization results show a sharp and separate spectrum with each other indicating that there has been a very good crystal formation. The addition of the Eu has resulted decreasing of lattice parameter of a-axis from 3.5828 to 3.5724 Å, lattice parameter of b-axis from 16.3308 to 16.3142 Å and lattice parameter of c-axis from 3.9135 to 3.9083 Å. That is caused ion radius of Eu is smaller than ion radius of Sr. The addition of doping of rare earth elements leads to the growth of new crystals containing rare earth elements with an increasing percentage in accordance with the addition of these elements, that is $Sr_{1-x}Eu_xCuO_z$ compound at an angle 32.5° , in line with a decreasing peak intensity of $SrCuO_z$ compound at an angle 31.8° . The result of crystal size of the sample is obtained about 185-213 nm. The addition of the Eu element to the $Sr_{1-x}Eu_xCuO_z$ superconductor causes the particle size to grow smaller. Fourier Transform Infrared Spectroscopy (FTIR) characterization results for all samples are shown in Figure 4.15. In general, the results show absorption waves at wave numbers 428.20, 858.32, 1188.15, 1460.11, 1714.72, 2210.42, 2499.75, 2735.06, 3005.10, 3290.56 cm^{-1} .

KEYWORDS

Strontium Copper Oxide, Rare Earth, wet-mixing method

1. Introduction

$SrCuO_2$ superconductors are of concern to current researchers because they have a high critical temperature of about 135 K. The $SrCuO_2$ compounds composed of CuO_2 layers are only separated by Sr. alkaline earth ions called infinite-layer compounds [M.G. Smith 1991]. The research of $SrCuO_2$ superconductor continues to be carried out, either by elemental substitution, doping treatment or attempting a new synthesis method, to produce $SrCuO_2$ superconductors with single phase, homogeneity, critical temperature, critical current density and high critical magnetic fields.

Research with the substitution of La elements and high pressure has been done by Jung and his friends [C.U. Jung 2001], substitutions with Ru and Gd elements in ruthenium copper oxides with an annealing treatment of O_2 have been reported by Awana, Takagiwa and colleagues [V.P.S. Awana 2002; H. Takagiwa 2001]. In addition to elemental substitution variations, the study also focused on variations in the use of synthesis methods. Several methods of synthesis have been done by previous researchers such as solid state reaction method and melting method. The method of solid state reacts with melting method has been done by Awana and his friends [V.P.S. Awana 2003] to synthesize magneto-superconducting compounds at a temperature of $1200^\circ C$ and a pressure treatment of about 6 GPa. While the growth of $La_{1-x}Ce_xCuO_4$ crystals has been observed using the method of Traveling Solvent Floating Zone (TSFZ) by Kunihiko and colleagues [Kunihiko Oka 2003]. The synthesis process using these methods of course requires high costs and special equipment to produce samples of good quality.

In this research the synthesis process is done by wet-mixing method to decrease the temperature of calcination and sintering, and substitution of rare earth element (Eu) to form the $Sr_{1-x}Eu_xCuO_z$ superconductor in powder form. All synthesis process is done by wet-mixing method and nitric acid (HNO_3) as a digest agent. The purpose of this research is to know the change of $Sr_{1-x}Eu_xCuO_z$ superconductor crystal structure without going through melting process and high pressure. Besides, to know and know the effect of substitution of rare earth element on $Sr_{1-x}Eu_xCuO_z$ superconductor crystal structure. The use of wet mixing method has been done to synthesize various superconductors. The synthesis of REBaCuO superconductors with the addition of HNO_3 as

digest agent has been done by Suharta and collegous [WG Suharta 2013] and synthesis of superconductor (NdLa) BaCuO with the addition of B_2O_3 flux using wet mixing method has also been done by Suharta and collegous [WG Suharta 2016].

2. Experiment

The materials used in this study were Sr_2CO_3 (99.9%), Eu_2O_3 (99.9%), Gd_2O_3 (99.9%) and CuO (99.9%). The synthesis process uses a wet-mixing method with nitric acid (HNO_3) as a digest agent.

The steps of the synthesis process of $Sr_{1-x}Eu_xCuO_z$ superconductors, starting from material weighing, wet mixing method, calcination and sintering is shown in the figure 1.

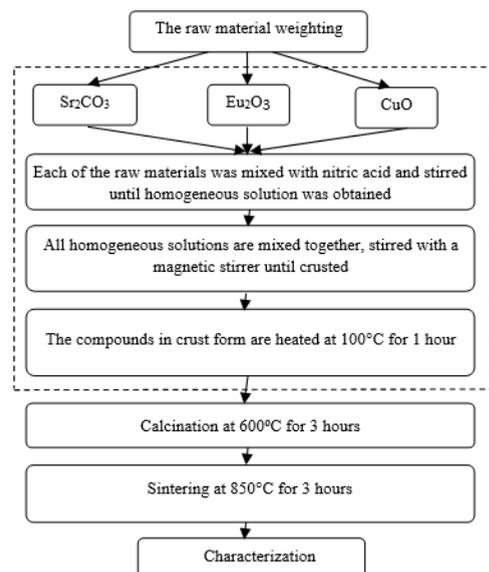


Figure 1. Process flow diagram of $Sr_{1-x}Eu_xCuO_z$ superconductor synthesis

Samples that have been successfully synthesized are characterized using:

- a. X-ray diffraction (XRD) to know the phases formed in the sample. Then to know the weight fraction of the $Sr_{1-x}Eu_xCuO_z$ compound and to know the phase of impurities that formed.
- b. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) to determine the morphology and particle size formed.
- c. Fourier Transform Infrared Spectroscopy (FTIR) is performed to determine the frequency of vibration that occurs in the sample.

The XRD characterization results of all samples are then matched (search match) using Match program. While refinement pattern diffraction (refinement) is done by Rietveld analysis using Rietica program. The Rietveld analysis is a non-linear matching method of numerical diffraction pattern curves (models) with observed diffraction patterns based on crystalline structure data using the least squares method.

3. Results and Discussions

The result of the characterization of $Sr_{1-x}Eu_xCuO_z$ sample with Eu element substitution (0.05-0.20) treated with calcination at 600°C for 3 hours and sintering at 850°C for 3 hours is shown in Figure 1. In general, all samples have shown sharp peaks that indicate the sample has been crystallized well.

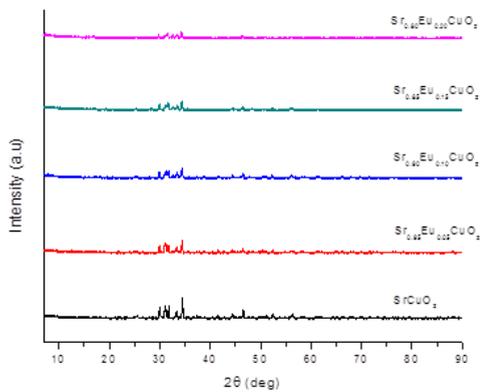


Figure 1. The result of XRD characterizations of $Sr_{1-x}Eu_xCuO_z$ superconductors

The substitution of the Eu on the $Sr_{1-x}Eu_xCuO_z$ superconductors resulted in a small 2 theta shift for all phases present in the sample. To clarify the occurrence of small angle shifts, the diffraction results focus on several short angles. The result of a small angle for the $Sr_{1-x}Eu_xCuO_z$ samples treated with calcination at 600°C for 3 hours and sintering at 850°C for 3 hours at a small angle of 25 to 40° were shown in Figure 2. In general the pattern of the formed spectrum has almost the same pattern for all samples and there is a decrease in the intensity of the count with the addition of the Eu element, for all samples. In some corners 2θ also shows the peak of each overlap. The addition of doping of rare earth elements leads to the growth of new crystals containing rare earth elements with an increasing percentage in accordance with the addition of these elements, that is $Sr_{1-x}Eu_xCuO_z$ compound at an angle 32.5°, in line with a decreasing peak intensity of SrCuO₂

compound at an angle 31.8°.

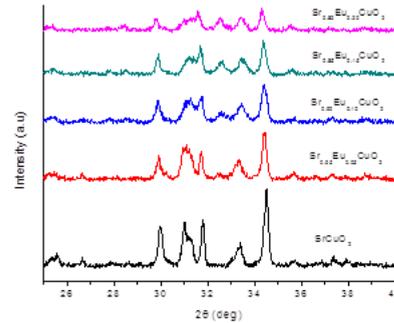


Figure 2. Focus angle shift and decrease in phase intensity of $Sr_{1-x}Eu_xCuO_z$ sample at angle 2θ from 25-40°

The XRD characterization results of $Sr_{1-x}Eu_xCuO_z$ samples treated with calcination at 600°C for 3 hours and sintering at 850°C for 3 hours generally showed peaks dominated by peak $Sr_{1-x}Eu_xCuO_z$. Further analysis was performed matching the diffraction peaks to determine the compounds formed in the sample, both $Sr_{1-x}Eu_xCuO_z$ compounds and impurities compounds. Matching is done by using Match program. Analysis using Match program also to know the percentage of $Sr_{1-x}Eu_xCuO_z$ compound formation and impurities compound. The diffraction peak match takes a long time because it must try various references to obtain accurate results.

The search match results show the phase $Sr_{1-x}Eu_xCuO_z$ phase with a fairly high percentage referring to the SrCuO₂ phase (PDF number 96-153-4696), with p63/mmc space group (194), hexagonal structure, lattice parameters a and c respectively 9.4900 and 33.5550 Å [Schreyer M, 2004]. In some angles also shows the impurities of Sr₂CuH₆O₆ (PDF number 96-200-2259), with the p121/n1 chamber group (14), the monoclinic crystal structure, lattice parameters a, b and c are respectively 5.7924, 6.1663 and 8.0748 Å [Sutovic S, 2009]. In addition, the imprint of Sr₂B₂CuO₆ (PDF number 96-151-0652), with pnma chamber group (62), orthorhombic crystal structure, lattice parameters a, b and c are 7.6120, 10.8540 and 13.5030 Å [Keszler, 1989]. Compounds Sr₂CuH₆O₆ and Sr₂B₂CuO₆ are impurities.

After knowing the phases formed in the sample, then Rietveld analysis is performed refinement diffraction pattern (refinement) with Rietica program [8]. The purpose of Rietveld's analysis is to determine the reliability and lattice parameter of $Sr_{1-x}Eu_xCuO_z$ crystal. Rietveld analysis is a method of matching between the calculated and observed diffraction patterns using the least squares method, which is expressed by R_{wp} (weighted profile factor), R_p (profile factor), R_c (expected weighted profile factor), S (goodness-of-fit), R_B (Bragg factor).

The results of refinement samples were obtained the value of lattice parameters (a, b, c), reliability, volume and density as shown in Table 1. The addition of the Eu to $Sr_{1-x}Eu_xCuO_z$ compound causes the values of lattice parameters both toward the-a-axis, b-axis and c-axis Decline. The lattice parameter toward the a-axis decreases from 3.5828 to 3.5724 Å, the lattice parameter toward the b-axis decreases from 16.3308 to 16.3142 Å, while the lattice parameter toward the c-axis also decreases from 3.9135 to 3.9083. Decreasing the lattice parameter values causes a decrease in the volume of the unit cell, instead increasing the atomic density in the unit cell.

Sample	Lattice parameter			Reliability				Volume (Å ³)	density (g cm ⁻³)
	a (Å)	b (Å)	c (Å)	R _p	R _{wp}	R _c	GoF		
SrCuO ₂	3.5828(7)	16.3308(9)	3.9135(7)	16.14	22.83	13.07	3.05	228.979	5.316
Sr _{0.95} Eu _{0.05} CuO _z	3.5811(1)	16.3201(3)	3.9124(7)	17.35	24.02	13.84	3.01	228.656	5.321
Sr _{0.90} Eu _{0.10} CuO _z	3.5794(5)	16.3188(8)	3.9116(9)	16.51	22.27	14.08	2.50	228.482	5.327
Sr _{0.85} Eu _{0.15} CuO _z	3.5780(8)	16.3167(7)	3.9097(4)	16.68	22.22	14.81	2.25	228.253	5.330
Sr _{0.80} Eu _{0.20} CuO _z	3.5724(5)	16.3142(6)	3.9083(6)	17.46	22.69	15.65	2.10	227.779	5.339

The Fourier Transform Infrared Spectroscopy (FTIR) characterization results for all samples are shown in Figure 3. In general, the results show absorption at wave numbers 428.20, 858.32, 1188.15, 1460.11, 1714.72, 2210.42, 2499.75, 2735.06, 3005.10, 3290.56 cm⁻¹.

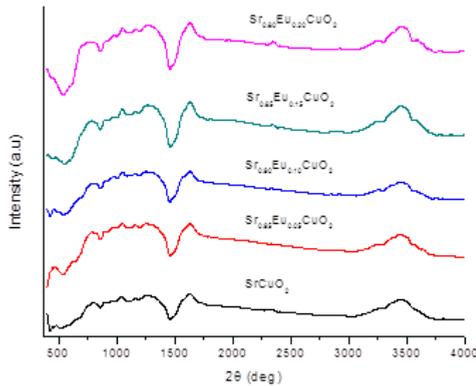


Figure 3. The result of the FTIR characterization of Sr_{1-x}Eu_xCuO₂ superconductor

The scanning electron microscope (SEM) characterization results for samples Sr_{0.80}Eu_{0.20}CuO₂ and Sr_{0.95}Eu_{0.05}CuO₂ are shown in Figures 4a and 4b. The images show 18,000 and 25,000 times magnification with size scale 1μm image. SEM characterization was performed to determine the morphology and size of the particles formed. Agglomeration has already begun, so the particle size becomes big. Most of the particles are in the form of bars.

The result of calculation of particle size using Scherrer equation is shown in figure 5. The curve shows a decrease in particle size values with the addition of Eu element to an Sr_{1-x}Eu_xCuO₂ superconductors.

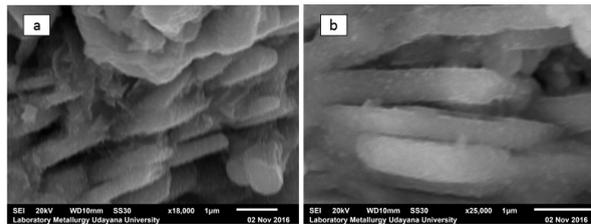


Figure 4. The result of the SEM characterization of a) Sr_{0.80}Eu_{0.20}CuO₂ and b) Sr_{0.95}Eu_{0.05}CuO₂ superconductors

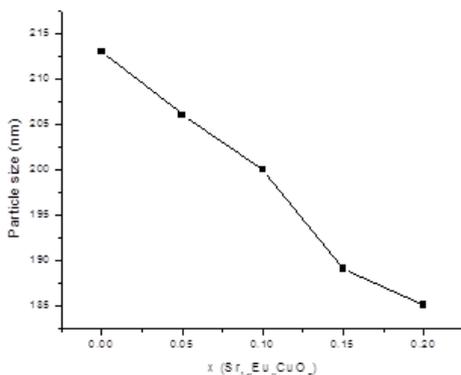


Figure 5. Changes in particle size by adding x to superconductor Sr_{1-x}Eu_xCuO₂

Figure 5 showed the addition of the Eu element to the Sr_{1-x}Eu_xCuO₂ superconductor causes the particle size to grow smaller. That is caused the ionic radii of Eu element smaller than Sr [RD Shannon 1976].

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 result of EDS characterization of Sr_{1-x}Eu_xCuO₂ samples is shown in Figures 6a and 6b.

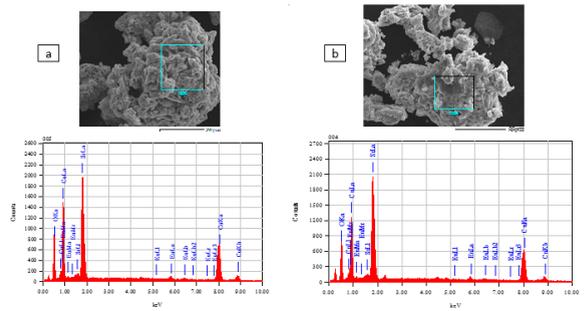


Figure 6. The spectra of the Sr_{1-x}Eu_xCuO₂ sample observed using EDS

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

No	Element	Sr _{1-x} Eu _x CuO ₂				
		x=0	x=0.05	x=0.10	x=0.15	x=0.20
		Atom (%)	Atom (%)	Atom (%)	Atom (%)	Atom (%)
1	O (K)	49.99	60.89	50.87	52.89	55.43
2	Cu (K)	26.19	20.07	25.79	24.52	23.21
3	Sr (L)	23.31	18.19	22.46	21.67	19.45
4	Eu (L)	0.51	0.85	0.88	0.92	1.91

Table 2 shows the percentages of each superconductor constituent for all samples. It appears that the resulting percentage is inconsistent with the addition of the Eu elements. This indicates that the sample is not homogeneous yet, so it needs to be repelled. In addition, to obtain high homogeneity, also need to increase the time of mixing in the synthesis process.

4. Conclusion

Based on the results of XRD, FTIR, SEM and EDS characterizations that obtained in this study, it can be concluded:

- The wet-mixing method has succeeded in growing the Sr_{1-x}Eu_xCuO₂ crystals represented by the emergence of sharp and separate spectra with each other.
- The addition of the Eu has resulted decreasing of lattice parameter of a-axis from 3.5828 to 3.5724 Å, lattice parameter of b-axis from 16.3308 to 16.3142 Å and lattice parameter of c-axis from 3.9135 to 3.9083 Å.
- The addition of Eu element resulted decreasing of the unit cell volume and increasing density value.
- The addition of the Eu element to the Sr_{1-x}Eu_xCuO₂ superconductor causes the particle size to grow smaller.

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