SYNTHESIS OF STRONTIUM COPPER OXIDE WITH SUBSTITUTION OF RARE EARTH ELEMENTS

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ABSTRACT
In this research have successfully synthesized Sr_{1-x}Eu_{x}Cu_{2}O_{3} superconductors with x are 0, 0.05, 0.10, 0.15 and 0.20. The synthesis process of Sr_{1-x}Eu_{x}Cu_{2}O_{3} superconductors uses SrCO_{3} (99.9%), Eu_{2}O_{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°C for 3 hours and sintered at 950°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 16.3142 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_{x}Cu_{2}O_{3} compound at an angle 32.5°, in line with a decreasing peak intensity of SrCuO_{2} 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_{x}Cu_{2}O_{3} superconductor causes the particle size to grow smaller. Fourier Transform Infrared Spectroscopy (FTIR) characterization results for all samples are shown in Figure 4. 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{sup-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 Awan, 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 react with melting method has been done by Awan and his friends [V.P.S. Awana 2003] to synthesize magneto-superconducting compounds at a temperature of 1200°C and a pressure treatment of about 6 GPa. While the growth of L_{a} Ce CuO_{2} 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_{x}Cu_{2}O_{3} 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_{x}Cu_{2}O_{3} 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_{x}Cu_{2}O_{3} 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_{2}O_{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_{2}Co_{3} (99.9%), Eu_{2}O_{3} (99.9%), Gd_{2}O_{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_{x}Cu_{2}O_{3}, 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_{x}Cu_{2}O_{3} superconductor synthesis](image-url)
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$_{0.95}$Eu$_{0.05}$CuO$_3$ 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$_x$CuO$_2$ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter</th>
<th>Reliability</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCuO</td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>Sr$<em>{0.95}$Eu$</em>{0.05}$CuO$_3$</td>
<td>3.5828(7)</td>
<td>16.3308(9)</td>
</tr>
<tr>
<td>Sr$<em>{0.95}$Eu$</em>{0.05}$CuO$_3$</td>
<td>3.581(1)</td>
<td>16.3201(3)</td>
</tr>
<tr>
<td>Sr$<em>{0.95}$Eu$</em>{0.05}$CuO$_3$</td>
<td>3.5794(5)</td>
<td>16.3188(8)</td>
</tr>
<tr>
<td>Sr$<em>{0.95}$Eu$</em>{0.05}$CuO$_3$</td>
<td>3.5780(8)</td>
<td>16.3167(7)</td>
</tr>
<tr>
<td>Sr$<em>{0.95}$Eu$</em>{0.05}$CuO$_3$</td>
<td>3.5724(5)</td>
<td>16.3142(6)</td>
</tr>
</tbody>
</table>

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$_x$CuO$_3$ 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$_p$ (weighted profile factor), R$_w$ (profile factor), R$_e$ (expected weighted profile factor), S (goodness-of-fit), R$_d$ (Bragg factor).

The search match results show the phase Sr$_{1-x}$Eu$_x$CuO$_3$ phase with a fairly high percentage referring to the SrCuO$_3$ 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 Sr$_2$Cu$_2$O$_4$ 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 Sr$_2$B$_4$CuO$_6$ (PDF number 96-200-2259), with the p121/n1 chamber group (14), the monoclinic crystal structure, lattice parameters a, b and c are respectively 7.6120, 10.8540 and 13.5030 Å [Keszler, 1989]. Compounds Sr$_2$Cu$_2$O$_4$ and Sr$_2$B$_4$CuO$_6$ are impurities.

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$_x$CuO$_3$ 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 3.9135 to 3.9083 Å, while the lattice parameter toward the c-axis also decreases from 16.3308 to 16.3142 Å, while the lattice parameter toward the c-axis also decreases from 3.9135 to 3.9083 Å. Decreasing the lattice parameter values causes a decrease in the volume of the unit cell, instead increasing the atomic density in the unit cell.

The refinement pattern curves (models) with observed diffraction (refinement) is done by Rietveld analysis using Rietica program [8]. The purpose of Rietveld's analysis is to determine the reliability and lattice parameter of Sr$_{1-x}$Eu$_x$CuO$_3$ 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$_p$ (weighted profile factor), R$_w$ (profile factor), R$_e$ (expected weighted profile factor), S (goodness-of-fit), R$_d$ (Bragg factor).

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![Figure 1. The result of XRD characterizations of Sr$_{1-x}$Eu$_x$CuO$_3$ superconductors](image1)

![Figure 2. Focus angle shift and decrease in phase intensity of Sr$_{1-x}$Eu$_x$CuO$_3$ sample at angle 20 from 25-40°](image2)
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.

The scanning electron microscope (SEM) characterization results for samples Sr₄Eu₅CuO₁₁ and Sr₄Eu₅CuO₁₀ 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 Sr₂Eu₄CuO₆ superconductor.

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

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.

Based on the results of XRD, FTIR, SEM and EDS characterizations, it can be concluded:

- The wet-mixing method has succeeded in growing the Sr₂Eu₄CuO₆ crystals represented by the emergence of sharp and separate spectra with each other.
- The addition of the Eu has resulted in decreasing of lattice parameter 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 in decreasing of the unit cell volume and increasing density value.
- The addition of the Eu element to the Sr₂Eu₄CuO₆ superconductor causes the particle size to grow smaller.

**Reference**