The Effect of Rare Earth Dopants in Crystal Structure of Bi-2212 Superconductor

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Abstract. Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ samples have been successfully synthesized by doping rare earth (RE) variations using wet-mixing method. Samples calcined at 600°C for 3 hours and sintered at 850°C for 10 hours. The purpose of research is to determine the effect of the RE dopant on the microscopic structure of BSCRECO superconductors. Therefore, the research was conducted characterization by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). Measurements with XRD could be carried out and crystal system of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ with rare earth (RE) dopants could be determined clearly. Generally, crystallization has occurred very well demonstrated by the diffraction peaks are sharp, which is dominated by the emergence of Bi-2212 phase. Search match results of XRD spectrum showed Bi$_2$Sr$_2$CuO$_x$ (2201) and Ca$_2$CuO$_3$ (21) as an impurity phase with small intensity. Also, that is showing volume fraction from 85 to 92% and orthorombic value for all samples from 5 to 7%. The effect of RE dopants resulted a shift angle $2\theta$ and changes in the volume of the unit cells of each sample. The value of the unit cell volume of the largest to smallest is BS(CN)CO, BS(CNG)CO, BS(CNEG)CO, BS(CNE)CO, BS(CG)CO, BS(CEG)CO and BS(CE)CO. Measurement with FTIR showed the bending vibration absorption by CO$_3^{2-}$ in the wavelength range between 1500 and 1520 cm$^{-1}$, vibration of M-O between 420 and 650 cm$^{-1}$, the complex formation of BSCCO in the wavelength range between 1690 and 1700 cm$^{-1}$. Measurement with SEM showed rod shape with particle size in hundreds nanometer.

Keywords : superconductor, wet-mixing, wavelength

1. Introduction

Superconductor of the Bismuth system (BSCCO) is one of the high-temperature superconductors as candidate in applications. Superconductivity symptoms of BSCCO system occur at Cu-O layer. While Sr-O and Bi-O layers, each are an insulator and semiconductor. Superconductor of BSCCO system have the general formula Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4}$ and has three phases associated with n = 1, 2, 3, namely: Bi-2201, Bi-2212 and Bi-2223. Phase Bi-2201 with a critical temperature of 30 K has one layer of Cu-O, phase Bi-2212 with a critical temperature of 80 K has two layers of Cu-O and phase Bi-2223 with a critical temperature of 110 K has three layers of Cu-O [1].

Provision of doping for growth of superconductor crystals have been affecting the properties of the superconductor material. The addition of Ag doping on Bi-2212 phases have been capable of producing the critical current density of 2750 A/mm$^2$ at a temperature of 4.2 K and zero field Tesla [2]. While the addition of Ag doping on Bi-2223 superconductor resulted in the critical current density (Jc) 3x10$^4$ A/cm$^2$ at 77 K [3]. The addition of Mn on Bi-2212 superconductor produces a small pure...
crystal and the sample does not melt [4]. The substitution of Nb on Bi/Pb-2223 superconductor has been studied by Marek Pekala et al [5], while the addition of Mo, Cd and Y have been also reported by Beables [6].

In this paper, we report the effect of RE dopants with one, two and three combinations on the crystal structure of Bi$_2$Sr$_2$(RE$_x$Ca$_{1-x}$)Cu$_3$O$_{8+\delta}$ superconductors. The contribution of this paper is the knowledge about the influence of RE dopant on the shift 2θ angle of XRD spectrum, changes of lattice parameter, volume fraction and unit cell volume of Bi$_2$Sr$_2$(RE$_x$Ca$_{1-x}$)Cu$_3$O$_{8+\delta}$ superconductors. We also report the infrared absorption and showed shape and particle size of the samples.

2. Experiment

Samples Bi$_2$Sr$_2$(RE$_x$Ca$_{1-x}$)Cu$_3$O$_{8+\delta}$ synthesized using a wet-mixing method [7] with one, two and three of RE combinations. The raw material using Bi$_2$O$_3$ powder compound (99.9%), SrCO$_3$ (99.9%), Nd$_2$O$_3$ (99.9%), Gd$_2$O$_3$ (99.9%), Eu$_2$O$_3$ (99.9%), CaCO$_3$ (99.9%) and CuO (99.9%). The each raw materials are dissolved with HNO$_3$ and stirred about 1 hour to obtain a clear solution. Then all solutions mixed into one and stirred to obtain a homogeneous solution. That solution heated at 100°C until crust. The crust calcinated at 600°C for 3 hours and sintered at 850°C for 10 hours. Steps of synthesis process is also done by W.G. Suharta et.al [8]. In this research has been conducted characterization using XRD, FTIR and SEM.

3. Results and Discussion

Samples Bi$_2$Sr$_2$(RE$_x$Ca$_{1-x}$)Cu$_3$O$_{8+\delta}$ has been successfully synthesized by using wet-mixing methods and variations of RE, and then calcinated at 600°C for three hours and sintered at 850°C for ten hours. Samples that have been synthesized are Bi$_2$Sr$_2$(Ca$_{0.5}$RE)$_x$Cu$_3$O$_{8+\delta}$ with one, two and three combinations of RE. Sample Bi$_2$Sr$_2$(Ca$_{0.5}$Nd$_{0.3}$)Cu$_3$O$_{8+\delta}$ with symbol BS(CN)CO, sample Bi$_2$Sr$_2$(Ca$_{0.5}$Eu$_{0.5}$)Cu$_3$O$_{8+\delta}$ with symbol BS(CG)CO, sample Bi$_2$Sr$_2$(Ca$_{0.5}$Gd$_{0.5}$)Cu$_3$O$_{8+\delta}$ with symbol BS(CNE)CO, sample Bi$_2$Sr$_2$(Ca$_{0.5}$Nd$_{0.25}$Gd$_{0.25}$)Cu$_3$O$_{8+\delta}$ with symbol BS(CNEG)CO.

The results of the XRD characterization of Bi$_2$Sr$_2$(Ca$_{0.5}$RE)$_x$Cu$_3$O$_{8+\delta}$ samples that was calcinated at 600°C for 3 hours and sintered at 850°C for 10 hours is shown in Fig. 1. In general, all of the samples have shown the occurrence of crystallization very well, which is characterized by a sharp spectrum. All samples showed the same pattern spectrum. On some peak also shows that there are still overlapped peaks. This happens because the sintering time was too short, so we need the addition of sintering time, so that the overlaps peaks can be separated as well.
The results of search match of BS(CRE)CO at $2\theta$ from 5$^\circ$ to 30$^\circ$ are shown in Fig. 2. While the results of search match of BS(CRE)CO at $2\theta$ from 30$^\circ$ to 60$^\circ$ are shown in Fig. 3.

In general, the appearance of the diffraction peaks dominated by the phase BS(CRE)CO, but in some peaks showed an impurity phase with a very small intensity. That impurity is 2201 phases ($\text{Bi}_2\text{Sr}_2\text{CuO}_x$) and 21 phases ($\text{Ca}_2\text{CuO}_3$).

**Figure 1.** Spectrum of BS(CRE)CO samples with a variation of RE that was calcinated at 600$^\circ$C for 3 hours and sintered at 850$^\circ$C for 10 hours

**Figure 2.** The results of search match of BS(CRE)CO samples at $2\theta$ from 10$^\circ$ to 35$^\circ$. Symbol o (Bi-2212 phase), ∆ (Bi-2201 phase), ● (Bi-21 phase)

**Figure 3.** The results of search match of BS(CRE)CO samples at $2\theta$ from 30$^\circ$ to 60$^\circ$. Symbol o (Bi-2212 phase), ∆ (Bi-2201 phase), ● (Bi-21 phase)
The addition of the element RE (rare earth) on the superconductor BSCCO (Bi-Sr-Ca-Cu-O) resulted the angle shift of X-ray diffraction peak. The angle shift of X-ray diffraction peaks at an angle $2\theta$ between 20 and 26° are shown in Fig. 4. While the angle shift at 2θ from 26 to 30° are shown in Fig. 5. The shift is caused by differences in ionic radii of Ca and RE. The angle shift of samples from the largest angle to smallest angle is BS(CN)CO, BS(CNG)CO, BS(CNEG)CO, BS(CNE)CO, BS(CNE)CO, BS(CEG)CO and BS(CE)CO.

Rietveld analysis is a method of refinement or matching of the diffraction pattern of models with the observed diffraction pattern using the least squares method. The degree of match between the diffraction pattern calculation results and observations were expressed by $R_{WP}$ (weighted profile factor), $R_p$ (profile factor), $R_e$ (expected weighted profile factor), S (goodness-of-fit), $R_B$ (Bragg factor).

The value of lattice parameter, reliability and fraction volume of BS(CRE)CO samples are shown in Table 1. Refinement results was showed changes on lattice parameters and unit cell volume changes at each sample. The value of the lattice parameters (a, b, c) and the volume of the unit cell from the largest to smallest is BS(CN)CO, BS(CNG)CO, BS(CNEG)CO, BS(CNE)CO, BS(CG)CO, BS(CEG)CO and BS(CE)CO.

| Sample     | Lattice Parameter | Reliability | FV   |
|------------|-------------------|-------------|------|
|            | a (Å)            | b (Å)       | c (Å) | $R_p$ | $R_{wp}$ | $R_e$ | GoF (%) |
| BS(CN)CO   | 5.4318(2)        | 5.4601(3)   | 30.6070(1) | 17.90 | 23.05    | 17.20 | 1.79   | 87     |
| BS(CNG)CO  | 5.4385(4)        | 5.4463(1)   | 30.5835(2) | 17.90 | 23.37    | 17.25 | 1.80   | 85     |
| BS(CNEG)CO | 5.4377(1)        | 5.4398(4)   | 30.5585(2) | 18.03 | 23.45    | 16.27 | 2.08   | 89     |
| BS(CNE)CO  | 5.4348(6)        | 5.4408(8)   | 30.5502(5) | 18.48 | 24.08    | 16.79 | 2.06   | 88     |
| BS(CG)CO   | 5.4433(2)        | 5.4382(1)   | 30.5102(3) | 18.19 | 23.89    | 16.66 | 2.06   | 92     |
| BS(CEG)CO  | 5.4345(3)        | 5.4403(3)   | 30.5425(7) | 17.94 | 23.40    | 16.56 | 1.99   | 90     |
| BS(CE)CO   | 5.4341(7)        | 5.4422(4)   | 30.5144(2) | 17.80 | 23.53    | 16.10 | 2.14   | 89     |
Figure 6. The value of the volume of unit cell BS(CRE)CO samples

Figure 7. The value of the orthorombicity of BS(CRE)CO samples

Figure 8. The results of FTIR characterizations of BS(CRE)CO samples

Figure 8 shows the presence of a broad absorption peak at around 4000-450 cm\(^{-1}\) from the FTIR spectrum. Peak around 3012.81-3055.24 cm\(^{-1}\), 2872.01-2883.58 cm\(^{-1}\), 1695.43-1701.22 cm\(^{-1}\) and 1500.62-1514.12 cm\(^{-1}\) are corresponding to the stretching vibrations of carbon-hydrogen (C-H). The bending vibrations of carbon-hydrogen (C-H) is detected at 1413.82-1416.21 cm\(^{-1}\). Peak around 1691.57-1701.22 cm\(^{-1}\), 1514.12 cm\(^{-1}\), and 1344.38 cm\(^{-1}\) are corresponding to the stretching vibrations of carbon-oxygen (C-O), while the absorption of CO\(_3^{2-}\) is presented around 1500.62-1514.12 cm\(^{-1}\). Peak around 503.42-522.71 cm\(^{-1}\) and 426.27-439.77 cm\(^{-1}\) are corresponding to the stretching vibrations of metal-oxide (M-O) [9, 10, 11]. The absorption band of SrCO\(_3\) is detected at 929.69-952.84 cm\(^{-1}\), while peak around 3734.19-3747.69 cm\(^{-1}\) is corresponding to the stretching vibrations O-H. The value of the absorption bands in the FTIR spectra of BS(REC)CO sample is shown in Table 2.
Table 2. The value of the absorption bands in the FTIR spectra of BS(REC)CO samples

| Assignment (ions) | EG     | NEG    | NE     | NG     | N      | G      | E      |
|------------------|--------|--------|--------|--------|--------|--------|--------|
| M-O              | 432.05 | 431.98 | -      | 428.20 | 426.27 | 428.43 | 439.77 |
| M-O              | 509.21 | 506.32 | 511.14 | -      | 503.42 | 520.78 | 522.71 |
| M-O              | 648.08 | 636.51 | 644.22 | 646.15 | 640.37 | 632.65 | 626.87 |
| C-H (stretching) | 1697.36| 1695.43| 1691.57| 1697.36| 1691.57| 1701.22| 1697.36|
| C-H (stretching) | 2881.65| 2872.01| 2881.32| 2877.79| 2883.58| 2881.25| 2881.65|
| C-H (stretching) | 3051.39| 3055.24| 3030.17| 3026.31| 3012.81| 3037.89|        |
| C-H (bending)    | 1413.82| 1416.21| -      | -      | -      | 1414.65| -      |
| SrCO₃            | 950.91 | 952.84 | 947.05 | 929.69 | 927.76 | 932.12 | 943.19 |
| C-O/-COO-        | 1697.36| 1695.43| 1691.57| 1697.36| 1691.57| 1701.22| 1697.36|
| C-O/-COO-        | 1288.45| 1287.34| 1296.16| 1328.95| 1319.31| 1319.31| 1344.38|
| CO₃²⁻            | 1500.62| 1510.26| 1514.12| 1506.41| 1514.12| 1506.41| 1514.12|
| O-H              | 3739.97| 3737.90| 3734.19| 3734.19| 3739.97| 3747.69| 3736.12|

The morphological characterization results of BS(REC)CO samples by using SEM was shown in Fig. 9, 10, 11 and 12. These pictures show the rod-shaped particles and plate-shaped particles. Rod-shaped particles in accordance with the orthorhombic of BSCCO crystal structure. While a plate-shaped particles indicates that agglomeration process is already happening. This happens in all samples. The crystal size calculation was done using two ways, first by Scherrer calculation and the second using ImageJ program. The result of the calculation both ways are shown in Table 3. There are differences in the results of calculations for crystal size. Scherrer calculations utilizing the characterization results of XRD involving the whole sample information, while the calculation with ImageJ uses the results of SEM or TEM characterization involving information on the material surface.

Value crystal size between 92.81 and 202.85 nm is obtained from Scherrer calculation, while the value of crystal size of between 63.99 and 182.48 nm is obtained by utilizing the ImageJ program. Crystal size calculation results for all samples using both methods are shown in Table 3.
Figure 11. SEM image of BS(CEG)CO samples

Figure 12. SEM image of BS(CNEG)CO samples

Table 3. The value of particle size of BS(CRE)CO samples

| Sample         | Particle size (nm) | Scherrer equation | ImageJ |
|----------------|--------------------|-------------------|--------|
| BS(CN)CO       | 192.81             | 118.19            |
| BS(CNG)CO      | 153.94             | 93.99             |
| BS(CNEG)CO     | 196.01             | 124.03            |
| BS(CG)CO       | 202.52             | 182.42            |
| BS(CNE)CO      | 192.47             | 85.88             |
| BS(CEG)CO      | 172.21             | 89.19             |
| BS(CE)CO       | 183.54             | 93.75             |

Conclusions

XRD characterization results showed that the addition of RE doping on the superconducting BSCCO result shift of angle that caused by differences in ionic radii RE with Ca. Also, RE dopants resulting in a change in the unit cell volume. The volume of the unit cell from the largest to smallest is BS(CN)CO, BS(CNG)CO, BS(CNEG)CO, BS(CNE)CO, BS(CG)CO, BS(CEG)CO and BS(CE)CO. FTIR characterization results showed the characteristic vibrations of M-O, C-H (stretching), C-H (bending), C-O/-COO- and O-H. Crystal size was obtained in this study between 90-200 nm.

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