Study synthesis of (La$_{1-x}$Gd$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ superconductors at low temperature

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Abstract. This study has been conducted on synthesis of (La$_{1-x}$Gd$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ superconductors with the substitution of Gadolinium (Gd) (x = 0.25, 0.5, 0.75, 1) and sintering temperature (700-960°C) variation using a wet-mixing method. Characterization is done by XRD, RAMAN and SEM. XRD characterization results of all samples have shown sharp peaks which indicate that the sample had crystallized well. Search match results showed an impurity phase such as BaCO$_3$, CuO and BaCuO$_2$. Rietveld analyses for all samples gave decreasing lattice parameters (a-axis from 3.9069 to 3.8936 Å, b-axis from 3.9231 to 3.9055 Å and c-axis from 11.8489 to 11.6597 Å) with the addition of Gd contents (from 0.25 to 1.00). Such addition also caused a decrease of lattice parameters (a-axis from 4.901 to 3.9875 Å, b-axis from 3.9658 to 3.8986 Å and c-axis from 11.7254 to 11.6758 Å) with the addition of sintering temperature (from 700 to 960°C). Characterization of FTIR seen the bending vibration absorption by CO$_3^{2-}$, absorbs mode apical oxygen of La (Gd) -O-Cu(2) and Cu(1)-O(1)-Cu(2). The addition of sintering temperatures also increases the intensity of the superconducting phase, reduce the intensity of an impurity phase (based on search results match) and increase the particle size (based on SEM characterization and Scherrer calculation).

1. Introduction

Researchers interested in conducting research of GdBa$_2$Cu$_3$O$_{7}$ superconductor materials (Gd-123), due to application of the material can penetrated in various aspects of life. Some of these applications are superconducting quantum interference device (SQUID) and manufacture of fast trains by using magnetic levitation.

The discovery of ceramic superconductor on LBCO systems by Bednorz and Muller [1] with a critical temperature of about 30 K has inspired researchers to conduct further research. Wu, et.al. [2] has reported YBCO superconductor with a critical temperature of about 90 K. Then replacing the block Y to block RE has increased the critical temperature to 93 K. The rare earth element (RE) is a rare earth element such as Nd, Eu, Gd, Dy, Sm and others. These elements are magnetic materials with the element RE on the position (1/2, 1/2, 1/2) in Tri-perovskite structure.

In the synthesis process of GdBa$_{2-x}$Cu$_x$O$_{7-\delta}$ superconductor, some researchers have reported a variety of methods, like more flux variations, variations of doping, variations of temperature and sintering time. The addition of Zr doping has reported by Caixuan Xu, et. al. [3] on GdBa$_{2-x}$Cu$_x$O$_{7-\delta}$ superconductor using the method of melting at a temperature of 1030°C modified by the top-seed and the annealing process using oxygen and argon gas.
Additional Zr doping has produced the critical current of 105 A/cm²² at a temperature of 77 K. E Ban, et.al. provided dope of ZnO and ZrO₂ on (Nd₀.₁₃Eu₀.₃₃Gd₀.₂₈)Ba₂Cu₃Oₓ superconductor to improve the critical current density [4], while T Goto, et.al. synthesized the same material with added 0.1% Zr and the addition of 0.1% and 0.1% oxygen with an argon gas solution spinning method [5]. Giving dope of Ag on GdBa₂₋ₓCu₃O₇₋₄ superconductor to fill the porosity, grain boundary, the normal state resistivity and weak-link effects have been reported by N Sakai [6]. While the infiltration methods by giving doping Ag was used by N Mori, et.al. for crystal growth YBa₂₋ₓCu₃O₇₋₄ [7].

S. Nariki, et.al. has conducted research to get a large grain size of GdBa₂₋ₓCu₃O₇₋₄ superconductor with added BaCeO₃, 20 % Ag₂O and 0.5 % Pt and drained 1 % oxygen. That has produced samples with a grain size of 25 to 33 mm [8]. Research to get large particle size is also done by Y Kimura, et.al. [9] with added a mixture of compounds Bi-Sn-Cd.

In this study observed the effect of Gd substitution on LBCO to form La₁₋ₓGdₓBa₂Cu₃O₇₋₄ superconductors. The synthesis process using wet-mixing method and sintering at low temperatures, to get homogeneity of grains and to know evolve the growth that superconductor. The contribution of this paper is to give knowledge about the effect of Gd element on LBCO superconductors to the crystal structure. Besides, it aims to produce an effective method of generating homogeneous grain size.

2. Experiment

Samples (La₁₋ₓGdₓ)Ba₂Cu₃O₇₋₄ synthesized using a wet-mixing method with variation of gadolinium (Gd) (x = 0.25, 0.5, 0.75, 1) and sintering temperature (700-960°C). The raw material using Gd₂O₃ powder compound (99.9%), La₂O₃ (99.9%), BaCO₃ (99.9%) and CuO (99.9%). The raw materials are weighed according to the nominal composition, then each material dissolved with HNO₃ solution accompanied by stirring for 30 minutes to get homogeneous solutions. All solution mixed and stirred with added sintering temperature slowly (with a temperature of less than 100°C) until crusted. Then, the precipitate heated at 100°C for 1 hour [10, 11]. The results calcined at 650°C for 3 hours and sintering at 700-900°C respectively for 1 hour. The samples were characterized using X-ray diffraction (XRD), fourier transform infrared (FTIR) and scanning electron microscopy (SEM).

3. Results and Discussion

The XRD characterization results of the (La₁₋ₓGdₓ)Ba₂Cu₃O₇₋₄ samples with the variation of x (0.25, 0.5, 0.75, 1) and sintering at a temperature of 800°C for 1 an hour are shown in figure 1. While the sample (La₀.₅Gd₀.₅)Ba₂Cu₃O₇₋₄ with sintering temperature variations (700, 800, 900, 960°C), respectively for 1an hour are shown in figure 2. In general, the spectrum shows sharp peaks indicating that crystallization had occurred to the good and perfect. But in some peaks still indicated the existence of peaks that overlap or have not been properly separated. This is due to the sintering temperature is still too low compared ideally sintering temperature (970°C), so that the thermal energy required for the formation of a single phase is not enough. Besides, it takes longer to acquire the heating to growth superconductor phase at a higher intensity.
The matching of the XRD diffraction peak of the samples has done using Match program. The results of matching were identified impurity phases such as BaCO$_3$, CuO and BaCuO$_2$ especially at angle 2θ of 22 to 35° shows that figure 3 (for x variations) and figure 4 (for sintering temperature variations). Emerge an impurity phase with high intensity, caused by give of sintering temperature is still low, so the energy that is available has not been able to foster a phase (La$_{0.5}$Gd$_{0.5}$)Ba$_2$Cu$_3$O$_{7-\delta}$ omit.
BaCO₃ and CuO compounds capable decomposes rapidly, probably caused by wet-mixing synthesis method, in which happen the ionic bond. Decomposition of BaCO₃ and CuO impurity followed by the growth of BaCuO₂ phase.

Table 1. The volume fraction of (La₁₋ₓGdₓ)Ba₂Cu₃O₇₋δ samples with variations of x

| x    | LGBCO (%) | BaCO₃ (%) | BaCuO₂ (%) | CuO (%) | Other impurity (%) |
|------|-----------|-----------|------------|---------|--------------------|
| 0.25 | 55.3      | 20.3      | 3.5        | 14.8    | 6.1                |
| 0.50 | 56.4      | 19.6      | 3.8        | 15.4    | 4.8                |
| 0.75 | 56.1      | 19.4      | 3.6        | 15.8    | 5.1                |
| 1.00 | 55.8      | 20.1      | 3.2        | 14.7    | 6.2                |

Table 2. The volume fraction of (La₀.₅Gd₀.₅)Ba₂Cu₃O₇₋δ samples with variations of sintering temperature (700, 800, 900, 960°C)

| T (°C) | LGBCO (%) | BaCO₃ (%) | BaCuO₂ (%) | CuO (%) | Other impurity (%) |
|--------|-----------|-----------|------------|---------|--------------------|
| 700    | 53.1      | 21.2      | 3.1        | 17.2    | 5.4                |
| 800    |           |           |            |         |                    |
| 900    |           |           |            |         |                    |
| 960    |           |           |            |         |                    |
Rietveld refinements were performed using Rietica [12] by employing Newton-Raphson strategy-Voight peak shape function. The refinement results showed that the addition of Gd content from 0.25 to 1 resulted in a decrease of the lattice parameter ($a$-axis from 3.9069 to 3.8936 Å, $b$-axis from 3.9231 to 3.9055 Å and $c$-axis from 11.8489 to 11.6597 Å) as shown in figure 5. The decline in values of lattice parameter is caused by the difference of ionic radii Gd and La, where ionic radii of La (117.2 pm) larger than Gd (107.8 pm) [13].

The addition of sintering temperature from 700 to 960°C resulted in a decrease of lattice parameter ($a$-axis from 4.901 to 3.8975 Å, $b$-axis from 3.9658 to 3.8986 Å and $c$-axis from 11.7254 to 11.6758 Å) as shown in figure 6. The decline in values of lattice parameter is caused by loss of oxygen, hydrogen and nitrogen. The reduces of oxygen, hydrogen and nitrogen resulted in the distance between the superconducting blocks closer. This indicates that the superconductivity is better.

![Figure 5](image)

**Figure 5.** The curve as relationship of the lattice parameter values and $x$

![Figure 6](image)

**Figure 6.** The curve as the relationship of the lattice parameter values and the sintering temperature variations

The results of the FTIR characterization of ($\text{La}_{0.5}\text{Gd}_{0.5}$)$\text{Ba}_2\text{Cu}_3\text{O}_7-\delta$ samples with sintering temperature variations (700, 800, 900°C) were shown in figure 7. The results of search match supported by the results of FTIR measurements.

The absorption peaks at 3374.23 and 1611.97 cm$^{-1}$ attributed to stretching vibration of the O-H bond and the bending vibration of the H-O-H respectively [14, 15], from water molecules on the external surface of the samples during handling to record the spectra. Also, the stretching C=O vibration at about 1750 cm$^{-1}$ confirm form the sample indicating ordinate of the carbonyl group to the metal [16, 17]. The peak shown at about 580 cm$^{-1}$ in the spectrum is attributed to the stretching frequency at 3422 cm$^{-1}$ and a weak asymmetric band at 1627 cm$^{-1}$ support the presence of the OH-group due to the absorption of water by nanoparticle during sample preparation. The presence of two M-O stretching and bending frequencies at about 690 cm$^{-1}$, 854 cm$^{-1}$ respectively.

Classification of modes associated with displacements of atoms at specific sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, there is a total of 39 vibrational modes : 15 of which are Raman active with symmetries of $5\text{Ag} + 5\text{Big} + 4\text{B}2\text{g} + \text{B}3\text{g}$. The 21 infrared active modes are 7($\text{B}1\text{u} + \text{B}2\text{u} + \text{B}3\text{u}$) and there are three acoustic modes. The most interesting result is that the motion of Cu(1) and O(1) do not contribute to Raman
active modes, but they are infrared active. The O(4) motion in the “flat” part of the Cu(1) ribbons may contribute to a Raman active mode however [18].

Figure 7. The results of FTIR characterization sample of (La_{0.5}Gd_{0.5})Ba_2Cu_3O_{7-δ} with sintering temperature variations (700, 800, 900°C)

The Raman characterization results showed in figure 8 (for x variation) and figure 9 (for sintering temperature variation). Six Raman peaks observed : at 210, 248, 338, 451, 505 and 610 cm^{-1} appearing. These lines correspond to A_g modes [19].

Figure 8. Results of Raman characterization of (Gd_{1-x}La_x)Ba_2Cu_3O_{7-δ} samples with a variation of x (0.25, 0.5, 0.75, 1.0)

Figure 9. Results of Raman characterization of Gd_{0.5}La_{0.5}Ba_2Cu_3O_{7-δ} samples with sintering temperature variations (700, 800, 900, 960°C)
The morphological characterization results of Gd$_{0.5}$La$_{0.5}$Ba$_2$Cu$_3$O$_{7-\delta}$ samples by using SEM with sintering temperature variations (700, 800, 900°C) showed in figure 10. The sample of Gd$_{0.5}$La$_{0.5}$Ba$_2$Cu$_3$O$_{7-\delta}$ with sintering temperature of 700°C (figure 10a) shows homogeneous particle size and distributed in the sample with the form of rods, which describes the characteristic of the orthorhombic-shaped, with the lattice parameter values in the direction of the $a$-axis and $b$-axis are almost the same, while the value of the $c$-axis is almost three times the value of $a$ and $b$. Additional sintering temperature of 700, 800 and 900°C resulted in agglomerations, so that granules with a grain of another one already began to coalesce to form a molecular bond (figure 10b and 10c). The calculation result using Scherrer equation obtained the particle size values of 168, 215 and 275 nm respectively at the sintering temperature of 700, 800 and 900°C.

4. Conclusion

The synthesis of (La$_{1-x}$Gd$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ (for variation of $x$ and sintering temperature) samples by using wet-mixing methods has been successfully performed with the highest volume fraction is 66.7%. Additional Gd content resulted decrease of the lattice parameter. Additional sintering temperature resulted decrease of lattice parameter, increasing the volume fraction of superconductor phase, decreasing volume fraction of impurity phase and increasing the particle size. The synthesis using a wet-mixing method is quite effective and efficient to get homogeneous grain size.
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