Barium Hydroxide Octahydrate (Ba(OH)$_2$$\cdot$8H$_2$O) as a Substitute Alternative for Barium Carbonate (BaCO$_3$) in Synthesis Superconductor of Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ Phase

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Abstract

One of the basic ingredients in conventional preparation of cuprates-based superconducting materials such as the Nd-Ba-Cu-O superconducting system, especially the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase is Barium Carbonate (BaCO$_3$). It has the potential to produce the carbon dioxide (CO$_2$) air pollutant. Therefore it is necessary to look for other materials as the source of Ba atom which does not produce CO$_2$ gas. In this research has been successfully made the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase with the Barium Hydroxide Octahydrate (Ba(OH)$_2$$\cdot$8H$_2$O) as a source of Ba atom. The results of the characterization XRD has been shown the main peaks of the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase. Refinement of the XRD data by using Rietica software, obtained the value of GofF (Goodness of Fit) = 1.7023 and lattice parameter $a \approx b < c/3$ with a value of $c/3 = 3.9275$ Å.

Keywords

Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ Phase, Ba Atom, Barium Carbonate, Barium Hydroxide Octahydrate, GofF

1. Introduction

One of the high Tc superconducting cupric materials is the superconductor of Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase, it is Tc exceeds to the boiling point of liquid nitrogen (77 K) [1] [2]. It is widely studied because of it is high Tc and simple crystal lattice structures, and also it can operate with high Jc in a fairly high magnetic field at 77 K [3] [4] [5]. Therefore it can be one of the candidates of superconductor materials that can be applied in the field of industry.

There are two standard methods used to create high Tc superconductors,
namely solid-state reaction method and coprecipitation method [6]. The first method usually uses Barium Carbonate (BaCO₃) while the second method uses Ba(NO₃)₃ as a source of Ba atom. Similarly, in the preparation of the NdₓBaₙCu₃Oₓ₋δ phase typically uses a solid reaction method with Nd₂O₃, BaCO₃ and CuO powders as the starting material [3] [4] [7]. With these starting materials it potentially produces air pollutant compounds in the form of CO₂ gas, as indicated by the chemical reaction in Equation (1).

$$\text{Nd}_2\text{O}_3 + 4\text{BaCO}_3 + 6\text{CuO} \rightarrow 2\text{Nd}_2\text{Ba}_3\text{Cu}_3\text{O}_{6.5} + 4\text{CO}_2$$  \hspace{1cm} (1)

It is necessary to think about how to make superconducting material by the simple methods, non-toxic and does not produce air pollutants. In this research, the superconducting materials have been made by using Barium Hydroxide Octahydrate (Ba(OH)₂·8H₂O) as a source of Ba, as indicated by the chemical reaction in Equation (2).

$$\text{Nd}_2\text{O}_3 + 4\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} + 6\text{CuO} \rightarrow 2\text{Nd}_2\text{Ba}_3\text{Cu}_3\text{O}_{6.5} + 36\text{H}_2\text{O}$$  \hspace{1cm} (2)

It appears that it does not produce CO₂ gas, but it produces water vapor.

In this work the author describes the use of Ba(OH)₂·8H₂O as a substitute of BaCO₃ in synthesizing the NdₓBaₙCu₃Oₓ₋δ phase. The synthesis results are characterized by XRD. From XRD the existence of the NdₓBaₙCu₃Oₓ₋δ phase is established with Match-3.6.1 software, and the lattice parameter of the NdₓBaₙCu₃Oₓ₋δ is determined by using Rietica software.

2. Research Methods

In this study NdₓBaₙCu₃Oy samples were prepared by using solid-state reaction method with starting material in powder form. The first sample is made with the reagent grade chemicals of high purity (Aldrich 99.99%) Nd₂O₃, CuO and Ba(OH)₂·8H₂O powders were used as the raw materials, while the second sample is made with the starting material BaCO₃ as a comparison sample. In this research the wet mixing method is used to increase sample mixture homogeneity as conducted in a reference [8]. The starting materials of powder and alcohol are mixed with a magnetic stirrer for 4 hours, then it is heated at temperature of 200°C until a crust shaped sample is obtained. The crust shaped sample was cooled to room temperature, and after it being crushed in the mortar then it was calcinated at 900°C for 12 hours. The calcination product is then made in form a pellet, and finally sintered at a temperature of 910°C for 15 hours in an air environment within the furnace.

The phase analysis of the sample was performed with an X-ray Diffraction (XRD). The XRD characterization results were analyzed by Rietica software. The model of the cell unit structure is conducted by using the Diamon 4.1 software.

3. Result and Discussion

3.1. Refinement Result

Figure 1 shows the XRD pattern of the sample that is prepared with BaCO₃
Figure 1. The XRD patterns of: (A) the sample was synthesized with BaCO$_3$ and (B) the sample was synthesized with Ba(OH)$_2$·8H$_2$O. * = the impurities.

(marked by A) and Ba(OH)$_2$·8H$_2$O (marked by B) respectively. At intervals of 20˚ - 60˚, it appears that both spectra show the same pattern of diffraction spectra. Figure 1 has been shown the major peaks of the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase, i.e. the peaks of the diffraction plane (013) and (103) are occurred at an angle of 2θ between 32˚ - 32.8˚, the diffraction of planes (020) and (200) are occurred at an angle of 2θ between 46˚ - 47.3˚, and the diffraction of planes (123) and (213) are occurred at an angle of 2θ between 57.5˚ - 58.5˚ [3] [4] [9]. Search-match by using Match 3.6.1 software with entry number 96-154-0949 (formula Nd$_1$Ba$_2$Cu$_3$O$_{6.57}$) the volume fraction that of both sample are almost the same, i.e. 84% obtained. However, the diffraction peaks of sample B appear sharper and their intensity is higher than the same peaks in sample A. For example, peak of 103 at 2θ = 32.36, sample B have FWHM = 0.10 and intensity = 1926 counts, meanwhile same peak from sample A have FWHM = 0.16 and intensity = 1854 counts.

It has been conducted refinement to XRD data with Rietveld analysis method using Rietica software with ICSD Collection Code 78453 as a reference, and was obtained data as shown in Table 1 and Table 2. From value of Goodness of Fit (GofF) as formulated in [10] and from Table 1 was obtained the GofF i.e. 1.8891 and 1.7023 respectively for sample A and sample B. The refinement result is said to be good if GofF < 2 [10] therefore, sample A and B have a good match between the experiment and the expected results. It appears to that sample B has a smaller GofF than sample A. Table 2 shows that the lattice parameter values of $a$, $b$ and $c$ for sample B are slightly larger than of sample A. It also appears that the equivalent to particle size of the sample B is greater than of the sample A. It is indicates that the crystallization in the sample B is better than in the sample A.
Table 1. The profile factor refinement results.

| Sample | $R_p$ | $R_{wp}$ | $R_{exp}$ |
|--------|-------|----------|-----------|
| A      | 14.97 | 19.42    | 10.28     |
| B      | 14.95 | 18.81    | 11.05     |

Table 2. The value of the lattice parameter of refinement results.

| Sample | $a$ (Å) | $b$ (Å) | $c$ (Å) | Cell Volume ($\text{Å}^3$) | Equivalent to particle size (nm) |
|--------|---------|---------|---------|-----------------------------|----------------------------------|
| A      | 3.8952 ± 0.0014 | 3.9012 ± 0.0005 | 11.7617 ± 0.0006 | 178.7263 ± 0.0416 | 83.52 ± 2.23                     |
| B      | 3.9061 ± 0.0005 | 3.9076 ± 0.0005 | 11.7724 ± 0.0008 | 179.8382 ± 0.0349 | 115.02 ± 2.73                    |

Figure 2 shows the grouping of the peaks of the diffraction pattern based on the diffraction planes. The diffraction planes of (013) and (103), (006), (020) and (200), (123) and (213) are located at the $2\theta$ angle intervals of 32.0° - 32.8°, 45.7° - 47.0°, and 57.0° - 58.5° respectively. The peaks of diffraction patterns on each diffraction plane are separated by the very small $2\theta$ angle. These indirectly imply that the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase formed on the samples A and B their structure are tends to in tetragonal symmetry [11] [12].

Figure 2 also shows there is the plane splitting and the $2\theta$ angular shift toward a smaller $2\theta$ angle on the XRD peaks pattern of sample B, these indicate there to the difference of the lattice parameter value of Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase on the both samples as shown in Table 2. In this case the $c$-lattice parameter of sample B is greater than that of A. As it is well known that the structure of the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase can be in tetragonal or orthorhombic symmetry, it depends on the oxygen content. In the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ lattice parameter $c$ depends on the oxygen content $y = 7 - \delta$ with $0 \leq \delta \leq 1$ [4] [7]. The linear relationship between the lattice parameters $c$ and the oxygen content for the Nd$_1$Ba$_2$Cu$_3$O$_y$ phase as in [13],

$$c = (12.614 - 0.132y) \text{Å}$$

(3)

It can be seen that the $c$-lattice parameter value is increase with the decreasing of oxygen content $y$. If the oxygen content is calculated by using equation (3) and from the lattice parameter $c$ in Table 2 was obtained the oxygen content of the samples A and B are $y = 6.46$ and $y = 6.38$ respectively. It was found that the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase formed on samples A and B has different oxygen content with oxygen-deficient $\delta = 0.54$ and $\delta = 0.62$ respectively. The lattice parameters of $a$, $b$ and $c$ with $a \approx b < c/3$ as shown in Table 2, and the $c/3$ value of samples A and B are 3.9206 Å and 3.9275 Å respectively. These conditions indicate that both samples are in the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase formed on samples A and B has tetragonal symmetry [3] [14].

The orthorhombic splitting (OS) unit cell as in [9], i.e.

$$OS = \frac{b-a}{a+b}$$

(4)
Figure 2. The main diffractions that showing the changes of the Nd$_2$Ba$_2$Cu$_3$O$_{7-\delta}$ cell lattice parameters: (013) and (103), (006), (020) and (200), (123) and (213).
From Table 2, were obtained the value of $OS = 7.7 \times 10^{-4}$ and $1.9 \times 10^{-4}$ for samples A and sample B respectively. It was found the value of OS is very small, that gives a hint that the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase formed on sample A and B have a small that orthorhombicity.

Therefore, the symmetry of the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase on both the sample are tends to be tetragonal. This corresponds to the amount of which oxygen content in the cell unit less than to 6.55, oxygen-deficient $\delta > 0.45$ [2] [7].

3.2. Lattice Structure Model

It has been made a model of the lattice structure (cell unit) for both samples by using Diamon 4.4.0 software and the refinement result, it is shown in Figure 3. The legend of the Figure 3 corresponds to the legend of the figure that has made as in [14]. It was found that the structure of the Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase that formed on the sample A and B are similar.

The structure of Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ that has been produced in this study are agree to the structure of Y$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ [15] [16]. The crystal structure is characterized by the arrangement of copper-oxygen planes and copper-oxygen chains: CuO layer where in the $a$-$c$ plane, Cu(1) copper is surrounded by four oxygen ions (CuO$_4$) and it forms a chain along the $b$-axis. Two layers of CuO$_2$ where the Cu(2) is surrounded by five oxygen ions, it forms a polyhedron. Both layers of CuO$_2$ are separated by an Nd atom.

Figure 3 shows that Ba atom was positioned above and below of the cell unit, while the position of an Nd atom is at it’s a center. Nd and Ba atom are piled along the $c$-axis in the sequence of Ba-Nd-Ba. The position of Nd atom is lies between of the two CuO$_2$ plane and the Ba atom lies between CuO$_2$ planes and

![Figure 3. The Cell Unit Model of: (A) Sample A; (B) Sample B.](image)
CuO₄ chains. In the layered structure, the stacking sequence of layers along the c-axis of the cell unit as follows BaO-CuO-BaO-CuO₂-Nd-CuO₂-BaO-CuO-BaO [17].

4. Summary

The superconductors of the NdₓBa₂Cu₃O₇₋δ phase can be well synthesized by using Ba(OH)₂·8H₂O as a source of Ba atom, it is indicated by the GoF value of 1.7023. The difference of the lattice parameters a and b is very small so that the orthorhombicity is very small, therefore the unit cell of the NdₓBa₂Cu₃O₇₋δ tends to be in tetragonal symmetry. The calculation of oxygen content yields 6.38. Thus it can be concluded that the NdₓBa₂Cu₃O₇₋δ phase formed tends to be tetragonal phase. Therefore, it is suggested that for synthesizing of the NdₓBa₂Cu₃O₇₋δ phase by using Ba(OH)₂·8H₂O as a source of Ba atom is carried out in the oxygen atmosphere.

Acknowledgements

This research was supported by the Fundamental Research scheme of the RISTEKDIKTI. The authors are thankful to RISTEKDIKTI and LPPM of Udayana University.

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