Study of The Synthesis Process and Microscopic Structure of Y-124, Y-259, and Y-358 Superconductors

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Abstract. The superconductor of Y-124, Y-259, and Y-358 phases has been successfully synthesized using the wet-mixing method. The compounds of Yttrium Oxide, Barium Carbonate, Cuprum Oxide, and Nitric Acid as a digesting agent have been used. The sample was prepared by calcination at 600 °C for 3 hours and subsequently sintering at 850 °C for 5 hours. The synthesis of Y-124, Y-259, and Y-358 phases were processed using a wet-mixing method. The phases were assumed to have the same initial temperature of crystalline growth around 800 °C. The a and b-axis lattice parameters decreased by the increase in Y atoms. On the other hand, the c-axis lattice parameter increased by adding Cu atoms. The volume of unit cells increased with the addition of Ba and Cu atoms. It was also found that LIBS was very effective in detecting the atoms contained in the sample and predicted in the percentage of the atoms in the sample.

Keywords: Synthesis, microscopic structure, superconductor, Y-124, Y-259, Y-358.

1. Introduction
The Y-123 superconductor which has a critical temperature of 90 K was developed into a Y-124 superconductor with a critical temperature of 70 K [1] and Y-358 superconductor with a critical temperature of 100 K [2,3,4]. Besides that, Y-247 superconductors have a critical temperature between 30 and 80 K [5] which is affected by the oxygen content. Furthermore, the development is related to the number of CuO₂ layers contained in unit cells. To date, it is believed that the number of CuO₂ layers affects the critical temperature value of superconductors. The Y-123 has 3 layers of CuO₂, while Y-358 has 5 layers of CuO₂. In the development of the Yttrium system superconductor, the researcher assumes that the number of Ba and Y atoms is equal to Cu atoms. However, there are also those who try to ignore these assumptions, such as at Y-124. When compared to the Y-123 superconductors, Y-124 has the excess Cu atoms.

Development is not only carried out with a molar variety of compounds but also the variations of synthesis methods. The synthesis method that is often performed in the synthesis of superconductors is a solid-state reaction method. The synthesis with the solid-state reaction method is generally followed by a long time calcination and sintering process. Therefore, in this study, a synthesis was executed using the wet-mixing method. Especially for the wet-mixing method used in this study, it has also been used to grow BSCCO and YLBCO superconductors [6,7,8].
In this study, Y-358, Y-124, and Y-259 superconductors were synthesized using sintering mediated by the wet-mixing method. In the synthesis process, an HNO₃ solution was used as a digesting agent. The calcination temperature at 600 °C for 3 hours and the sintering temperature at 850 °C for 5 hours had been done. This study aimed to observe the effect of adding Y and Cu atoms to the changes in crystal structure. The samples were characterized using TGA, XRD, and SEM. We further analyzed the comparison of the molar composition of each constituent atom using LIBS.

2. Methods
The synthesis of Y-124, Y-259, and Y-358 samples was firstly conducted by a wet-mixing method. The raw materials with high purity of Y₂O₃-99.99%, BaCO₃-99.99%, and CuO-99.99% were used without any further treatment. Each raw material was dissolved using HNO₃ and stirred using magnetic stirrer, then heated below 100 °C until crust. The crust was calcined at 600 °C for 3 hours and subsequently sintered at 850 °C for 5 hours. All samples have been characterized using Thermal Gravimetry Analyzer (TGA), X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), and Laser-Induced Breakdown Spectroscopy (LIBS).

3. Results and Discussion
Thermal analysis has been carried out using a thermal gravimetry analyzer (TGA). TGA characterization results provided information on the changes in mass during the heating process. In this study, TGA characterization was undertaken after the calcination process at 600 °C for 3 hours. Therefore, the TGA curve does not show a weight loss below 600 °C as shown in Figure 1. The TGA curve for all samples shows a significant weight loss at temperatures between 600 and 800 °C. Above 800 °C, there was no weight loss, which was the starting temperature of the formation of Y-124, Y-259, and Y-358 phases. However, in this study, sintering was carried out at 850 °C so that crystal growth was more convincing.

![Figure 1. The thermogravimetric curve of Y-124, Y-259, and Y-358 after calcined at 600°C for 3 hours](image-url)
The XRD spectra of Y-124, Y-259, and Y-358 samples after calcined at 600 °C for 3 hours and sintered at 850 °C for 5 hours are shown in Figure 2. The phase identification of the XRD spectra was performed using Match software [9]. The XRD spectra showed a sharp peak dominated by Y-124, Y-259, and Y-358 with the presence of the intensity of Y-113 and Y-211. Some peaks also showed the existence of overlap peaks. The Y-358 and Y-259 samples refer to the results obtained by DA Landinez Tellez et al. [2]. The Y-124 sample refers to the results obtained by Schwer et al. [10]. Meanwhile, Y-113 as impurities refers to Schreiner [11] and Y-247 refers to Ono et al. [12].

The volume fraction of the superconductor and impurity phase is shown in Table 1. The volume fraction of the impurity phase was relatively high. The existence of this phase was due to the short sintering time, which was 5 hours. To increase the purity or to reduce the impurity phases could be by prolonging the sintering time. The feature of these phases was clearly different compared to other superconducting phases as La-214 [14,15] or Bi-based superconductors [16].

![XRD spectra of Y-124, Y-259, and Y-358 samples](image)

**Figure 2.** XRD patterns of Y-358, Y-124, and Y-259. The symbol of o, ●, x, ◊, and Δ are designated for superconducting, Y-211, Y-113, Y-247, and (Cu₄SO₄(OH)₆) phases respectively.

| Sample | Superconductor phase | Y-113 phase | Y-211 phase | Y-247 phase | Cu₄SO₄(OH)₆ phase |
|--------|---------------------|-------------|-------------|-------------|------------------|
| Y-124  | 59                  | 12          | 4           | 9           | 16               |
| Y-259  | 79                  | 7           | 5           | 6           | 3                |
| Y-358  | 67                  | 8           | 13          | 5           | 7                |

**Table 1.** The volume fraction of superconductor and impurity phase

It is found that all samples showed the superconducting phase. Several weak peaks were also found in minor phases of Y-211, Y-113, and Y-247. A relatively weak peak of (Cu₄SO₄(OH)₆) phase was also observed in Y-358 and Y-124 phases. It suggests that the wet mix route may produce a side phase. To find the lattice parameters, reliability, goodness-of-fit, and volume of each sample, Rietveld analysis by refinement using Rietica software [13] was carried out. The refinement results of Y-259 and Y-359 samples are shown in Figure 3 and 4. The refinement refers to the DA. Landinez et al. [2], Schwer et al.
[10] and Schreiner [11] using Newton-Raphson strategy, normal calculation method, and peak shape Voigt. The results of the refinement of each sample are shown in Table 2. In general, the lattice parameter values toward a-axis and b-axis decreased with the increase in Y atoms. On the other hand, the lattice parameter values toward c-axis increased with the increase in Cu atoms. From Table 2, the most significant difference was the lattice parameter value towards the c-axis between Y-124 samples with Y-259 and Y-358 samples. It was caused by the differences of the number of Cu atoms in each sample. It resulted in lattice parameter values towards the c-axis for Y-259 and Y-358 samples greater than Y-124 samples. The relationship between the number of Cu atoms and the lattice parameter values towards the c-axis is shown in Figure 5. The volume of unit cells increased with the addition of Ba and Cu atoms as shown in Table 2.

![Graph 1](image1.png)

**Figure 3.** The results of the refinement of Y-124 samples

![Graph 2](image2.png)

**Figure 4.** The results of the refinement of Y-259 samples
Figure 5. The results of the refinement of Y-358 samples

From Figure 3 to Figure 5, we may infer, that in general, the observed histograms are mostly fit with the model. During the fitting we did not exclude any impurities. Several weak peaks were not fit with the superconducting phases which are consistent with the phase identification results. The obtained lattice parameters are listed in table 2.

| Sample  | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | Volume (Å\(^3\)) | Orthorhombic strain (%) |
|---------|------------|------------|------------|-------------------|-------------------------|
| Y-124   | 3.832 (1)  | 3.888 (7)  | 26.034 (4) | 402.787           | 1.4467                  |
| Y-259   | 3.896 (6)  | 3.841 (9)  | 31.151 (0) | 465.163           | 1.4153                  |
| Y-358   | 3.888 (2)  | 3.826 (2)  | 31.089 (0) | 462.446           | 1.6173                  |

From the lattice parameters of Table 2, we could obtain the orthorhombic strains calculated using the formula \(\eta = \frac{2(b - a)}{(b + a)}\). The results of the calculation of orthorhombic strain are also shown in the last column of Table 2. The values of reliability and goodness-of-fit of the samples after calcined at 600 °C for 3 hours and sintered at 850 °C for 5 hours are shown in Table 3. The refinement was performed using Rietica [13]. Goodness-of-fit values obtained are varied, between 1.37 and 2.15.

| Sample  | \(R_p\) | \(R_{wp}\) | \(R_{exp}\) | GoF |
|---------|---------|------------|-------------|-----|
| Y-124   | 21.67   | 28.53      | 19.44       | 2.15|
| Y-259   | 18.40   | 24.36      | 20.79       | 1.37|
| Y-358   | 19.74   | 25.99      | 19.50       | 1.78|
Figure 6. The effect of the number of Cu atoms on the c lattice parameter

LIBS (Laser-Induced Breakdown Spectroscopy) is the development of the OES (Optical Emission Spectroscopy) to omit an atom. A laser beam fired on the surface of the material will produce plasma and emissions from the plasma captured by the detector, then analyzed qualitatively to find out the atoms contained in the plasma.

The cylindrical sample with a diameter of 1.5 cm and a thickness of 0.5 cm were placed in the sample holder in the LIBS. The LIBS with laser source Nd:YAG (λ = 1064 nm, the pulse width of 7 ns) focused on the surface of the sample. A laser with an energy of 100 mJ was fired on the surface of the sample and formed a plasma. The plasma emissions of radioactive atoms were captured by HR 2500+ spectrometers (200-980 nm with 7 channel spectra ranges) using 7 detectors, 14.336 linear silicon CCD array elements. The data were processed with OOLIBS software to display spectrum atomic emission intensity as a wavelength function and add LIBS to analyze spectrum.

Figure 7. LIBS spectra of Yttrium atoms in Y-124, Y-259, and Y-358
To clarify, the emission results of all samples are displayed according to the wavelength which only raised certain atoms. Figure 7 is typical LIBS spectra of Y atom contained on Y-124, Y-259, and Y-358 samples emission after calcined at 600 °C for 3 hours and sintered at 850 °C for 5 hours. From the picture, the intensity of the Y atoms was higher, started from Y-124, Y-259, and Y-358. The comparison of the intensity of the Y atoms from the results of LIBS was 1:2:3. The results were in accordance with the comparison of the Y molar composition of each sample. This indicated that the characterization using LIBS was very effective in detecting the atoms contained in the sample and predicting the percentage of the atoms in the sample.

Figure 7 is typical LIBS spectra of Ba atom contained on Y-124, Y-259, and Y-358 samples. From the picture, the intensity of the Ba atoms contained on Y-259 was as high as on Y-358 but higher than Y-124. The results were in accordance with the comparison of the Ba molar composition of each sample with a comparison of 5:5:2 each for Y-259:Y-358:Y-124.

![Figure 8. LIBS spectra of Barium atoms in Y-124, Y-259, and Y-358](image)

![Figure 9. LIBS spectra of Cu atoms in Y-124, Y-259, and Y-358.](image)
Figure 9 is typical LIBS spectra of Cu atoms contained on Y-124, Y-259, and Y-358 samples after calcined at 600 °C for 3 hours and sintered at 850 °C for 5 hours. From the picture, the intensity of the Cu atom from the smallest to the biggest was Y-124, Y-358, and Y-259. The results were in accordance with the comparison of the Cu molar composition of each sample with the comparison of 4:9:8 each for Y-124: Y-358: Y-259.

The morphologies of the samples of Y-124, Y-259, and Y-358 are shown in Figure 10, 11, and 12 respectively. The image is shown at a scale of 0.5 μm with an enlargement of 40,000 times. All samples showed granules in a rod shape and agglomeration had begun caused by a long sintering time. The results of calculations using the Scherrer equation obtained the particle size between 500-750 nm.

4. Conclusion

The synthesis of superconductors of Y-124, Y-259, and Y-358 using sintering and prepared by a wet-mixing method has been successfully performed under the calcination at 600 °C for 3 hours and sintering at 850 °C for 5 hours. The a and b-axis lattice parameter decreased by the increase in Y atoms. The c-axis lattice parameter increased by the addition of Cu atoms. The volume of the unit cells increased with the increase in Cu layers. The characterization using LIBS was very effective in detecting the atom contained in the sample and predicting the percentage of the atom in the sample. To increase the purity of the phases, we suggest prolonging the sintering time as well as their heating after wet mixing.

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