Effect of Molar Ratio on Crystal Structure and Surface Morphology of Nd$_1$(Fe)$_x$Ba$_{2-x}$Cu$_3$O$_7$ Oxide Alloy by Solid-State Reaction Method

N. A. Humairah$^1$, D. Sartika$^1$, Muris$^2$ and E. H. Sujiono$^2$

$^1$Department of Physics, Universitas Sulawesi Barat, Majene 91413, Indonesia
$^2$Laboratory of Materials Physics, Department of Physics, Universitas Negeri Makassar, Makassar 90224, Indonesia

E-mail: e.h.sujiono@unm.ac.id

Abstract. Processing of materials Nd$_1$(Fe)$_x$Ba$_{2-x}$Cu$_3$O$_7$ oxide alloy by varying the molar ratio of Fe doping, which $x$ varied from $+0.1$ to $+0.3$ has been developed by solid-state reaction method. This research has shown that the hkl plane of the sample has c-axis oriented, i.e., (005), (006), (007), (008) and (009), respectively. All of the samples have the most dominant peak of (006) with the crystal structure is tetragonal. The molar ratio of the samples having a composition of Nd:Ba:Fe:Cu = 1:(2 – $x$):$x$:3.1. Other results, by SEM characterization, indicate that variation of Fe doping influence of the grain size and grain orientation of the various samples. The result of XRD and SEM characterization analysis indicates that Fe doping has an effect on the crystal structure, composition, and surface morphology of Nd(Fe)BCO oxide alloy.

Keywords. Crystal structure, molar ratio, morphology, NdBaCuO, SEM, solid state reaction, and XRD

1. Introduction

Material science and engineering are fundamental to the development of modern technology, both for structural applications, electronics, thermal, electrochemical, environmental and biomedical. One of the oldest applied sciences has defined as process metallurgy. Its history can be traced back to 6000 BC. Currently, there are 86 known metals, and only 24 species were found during the 19th century. Each era is characterized by the discovery of new materials. The mechanical properties of the material are mainly influenced by the process of synthesis and material composition [1, 2, 3].

The highest technology application of superconductor materials not only at very low temperatures but also can be applied to high-temperature superconductors. It will require energy, i.e., an HTS (High-Temperature Superconductor) second-order sigma-delta modulator, and a pulse stretcher. It used as an interface between the modulator and the first semiconducting amplifier stage. Moreover, based on HTS (High-Temperature Superconductor) technology are very attractive since they can operate under the considerably relaxed cooling effort, which is one of the main problems with LTS (Low-Temperature Superconductor) circuits [4, 5].

With advantages of understanding physical properties of high-$T_c$ superconductors, development of practical materials of bulks, tapes, and thin films are now in rapid progress. The present concern is
now focused on YBa$_2$Cu$_3$O$_{7-x}$ while Rba$_2$Cu$_3$O$_{7-x}$ (R = light rare earth such as Nd, Sm, Eu, Gd) [5, 6, 7] is also promising especially for high field applications. The reason is that, e.g., NdBa$_2$Cu$_3$O$_{7-x}$ has higher $T_c$ (~96 K) and possible higher irreversible field, $H_{irr}$ (>10 T at 77 K) compared with those of YBaCuO [1, 7]. One of the properties of metal oxide alloys is superconducting at critical temperatures, for example, YBCO oxide alloys having 87 K and 87.4 K, deposited at 680 ºC and 700 ºC [8] and are magnetic at room temperature [9].

In addition, the development of NdBCO material has higher chemical stability than the YBCO system. The NdBCO system has the same structure as the YBCO system [8, 9, 10], but NdBCO is known to be higher and has stronger pinning flux. Thus it is possible to hold impedance doping variation [9]. The solid-state reaction method is a method for the preparation of polycrystalline solids from a mixture of solid starting materials [5]. Other oxide material processing techniques are making sol-gel [10], hydrothermal [11], Chemical Vapor Deposition (CVD) [8] and etc. There are advantages of preparing using solid state reaction because this method is cheap and easy to complete. Another thing that the product of the reaction has high purity and excellent crystallinity [2].

In this paper, we present the influence of the molar ratio of Fe doping on NdBCO with $x = (0.1, 0.2$ and $0.3)$ on crystal structure and surface morphology. The effects of doping determine by analyzing the data results using XRD and SEM characterization. The results describe the crystal quality presenting the value of FWHM, the lattice constant, and crystal orientation, also the surface morphology indicating at grain size, and grain orientation.

2. Materials and methods
Nd$_{(1-x)}$(Fe)$_x$Ba$_2$Cu$_3$O$_7$ alloys have been synthesized by solid reaction method. The sintering process has been done with the mixing stage of the Nd$_2$O$_3$ 99.99 %; CuO 99.99 %; BaCO$_3$ 99.99 % and Fe$_2$O$_3$ 99.9 % powder by grinding for 3 h until the precursor's powder has homogeneous. Then the precursor's powder was calcined for 20 h at a temperature of 950 ºC, then continuing with the pelletization process which was 0.5 cm in diameter and 0.25 cm. Samples bulk form had sintered for 10 h at a temperature of 950 ºC and followed by annealing process for 20 h at a temperature of 450 ºC, as shown in Figure 1.

The same procedure was used for all sample has a variation of $x=0.1$ to $x = 0.3$, respectively. Characterization process was conducted to identify the phases using X-ray diffraction with $\lambda = 1.54439$ Å [12, 13], and analyzed the surface morphology using SEM (Scanning Electron Microscope) [14].

![Figure 1](image-url)  
**Figure 1.** Scheme process of sintering and annealing temperature as a function of the time processing.
3. Results dan Discussion

XRD diffraction patterns of oxide material Nd(Fe)BCO powder were synthesized by using the solid-state reaction method with variations of the molar ratio at \( x = 0.1 \), \( x = 0.2 \) and \( x = 0.3 \) are shown in Figure 2.

In Figure 2 shows the \( hkl \) plane of the sample indicate of all peaks oriented to the \( c \)-axis orientation, i.e., peak I (005); peak II (006), peak III (007), peak IV (008), and peak V (009), where the most dominant peak is the peak II (006) for all sample with variation of \( x \) is 0.1, 0.2 and 0.3, respectively.

![Figure 2. XRD pattern of sample Nd(Fe)BCO for variation of \( x \) to 0.1, 0.2, and 0.3, respectively.](image)

Table 1. Position (2\( \theta \)) and Intensity of Nd(Fe)BCO phase as a variation of molar ratio

| Molar Ratio | 2\( \theta \) (°) | Intensity (counts) | FWHM (°) |
|-------------|-----------------|--------------------|----------|
| \( x = 0.1 \) | 32.40 ± 0.12 | 900 ± 2.5 | 0.12 |
| \( x = 0.2 \) | 32.38 ± 0.04 | 900 ± 2.5 | 0.04 |
| \( x = 0.3 \) | 32.50 ± 0.03 | 1195 ± 1.0 | 0.03 |

Table 1 shows the influence of molar ratio on the position of 2\( \theta \), intensity, and the value of FWHM (Full Width at Half Maximum) of Nd(Fe)BCO samples. As illustrated, the increasing molar ratio of Nd content gradually shifted the XRD peaks towards a lower angle or higher \( d \) value due [2, 3] to larger ionic radii of Nd than Fe [15]. Peak position value of 2\( \theta \) at 32.50° had the highest intensity compare with other peaks, and this peak was related to the \( hkl \) (006). Relating to the intensity, the molar ratio has influenced the intensity of the sample [1]. It can be seen in Table 1, that the sample with a molar ratio of \( x = 0.3 \) had the narrowest and highest intensity which indicated the growth of Nd(Fe)BCO crystallite sample has excellent crystallinity and conductivity. This result is in accordance with that most orderly arrangement and homogeneous of crystals in the correlation of the smaller of the FWHM value and tip width of the peak as has reported E. H. Sujiono et al [2]. The sample with a molar ratio of \( x = 0.3 \) has lowest FWHM value among others and has a similar crystal structure; this also affects the electrical properties of the sample [16]. Samples having an FWHM value lower than
0.5 will select a good crystal quality level, these results are similar with has reported Wickenden et al [17].

To determine the lattice parameter has used a formula derived from Bragg law as described in Equation 1 [18].

\[ 2 \sin \theta = \lambda \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \]  

with \( \lambda \) is the wavelength of the x-rays, \( a, b, \) and \( c \) are lattice constants of the crystal structure, and \( \theta \) is the diffraction angle.

Based on Table 2, the characterization results, it was found that the Nd(Fe)BCO sample in this study has a tetragonal crystal structure with the lattice parameters obtained for all peaks ranging from (11.2828 to 11.7518) Å. It can be assumed that variation of molar ratio \( x = 0.1 \) to \( x = 0.3 \) has a lattice constant value similar as was reported elsewhere [2, 4, 6]. These results indicate that oxide material produced in this study have excellent quality as superconducting material properties. The crystalline properties as has been describing, i.e., \( c \)-axis oriented with shaped the structure of crystals and small value FWHM as an indication of high crystal quality [8, 10]. The difference in height intensity and width of the peak as representing at the value of FWHM indicating of the effect variation of molar ratio \( x \). The highest intensity and smallest of FWHM means that \( hkl \) plane in which orientation has a form more dominant. These phenomena are similar as has reported elsewhere [1, 8].

**Table 2.** The lattice parameters for each variation of molar ratio

| Peaks \( (hkl) \) | Samples          | Lattice parameter (Å) |
|------------------|------------------|-----------------------|
| (006)            | Nd\(_1\)(Fe)\(_{0.1}\)Ba\(_{1.9}\)Cu\(_3\)O\(_7\) | 11.7518               |
|                  | Nd\(_1\)(Fe)\(_{0.2}\)Ba\(_{1.8}\)Cu\(_3\)O\(_7\) | 11.7518               |
|                  | Nd\(_1\)(Fe)\(_{0.3}\)Ba\(_{1.7}\)Cu\(_3\)O\(_7\) | 11.7518               |
|                  | Nd\(_1\)(Fe)\(_{0.1}\)Ba\(_{1.9}\)Cu\(_3\)O\(_7\) | 11.2614               |
| (005)            | Nd\(_1\)(Fe)\(_{0.2}\)Ba\(_{1.8}\)Cu\(_3\)O\(_7\) | 11.2708               |
|                  | Nd\(_1\)(Fe)\(_{0.3}\)Ba\(_{1.7}\)Cu\(_3\)O\(_7\) | 11.2828               |

Figure 3 shows the characterization result of SEM image of molar ratio variation \( (a) x = 0.1, (b) x = 0.2, \) and \( (b) x = 0.3 \), it can be seen that increasing of Fe ratio on NBCO oxide alloy reducing the number of grain boundaries. The surface morphology image is appearing of many variations of grain size as shown in Figure 3.a, the number grain size is reduced at molar ratio Fe of 0.2 and almost disappears at ratio Fe of 0.3. The analysis of samples showing the effect of Fe doping on of Nd(Fe)BCO alloy caused granular changes of the elongated rectangular pattern, into a short rectangular pattern [4]. In case of Fe doping of +0.3, it appears that a short rectangular granular group is identified as Fe\(_2\)O\(_3\) formation as shown in Figure 3. The substitution of Fe\(_2\)O\(_3\) which magnetic properties may lead to changes the surface morphology of NBCO compound as explained. Nd(Fe)BCO as a new alloy can improve the magnetism properties of NBCO at room temperature and as the center of pinning at superconducting state [9]. The developed of oxide alloy not only produce new superconducting material but also found in magnetic material that is very useful in the application of spintronics devices. The surface morphology results indicate that variation of Fe molar ratio changed the grain size and reduced the grain boundaries of the alloys caused improving the crystal quality.
Figure 3. The SEM micrograph of Nd(Fe)BCO oxide alloy as variation molar ratio Fe of (a) x = 0.1 (b) x = 0.2 dan (c) x = 0.3, respectively.

4. Conclusions
The Nd(Fe)BCO alloy with the variations of molar ratio x of 0.1, 0.2 and 0.3 have been successfully synthesized using solid-state reaction method. The variation of molar ratio has a significant effect on the intensity, FWHM, and the crystallite size of the samples. It was found that the Nd(Fe)BCO sample in this study has a tetragonal crystal structure with the lattice parameters obtained for all peaks ranging from (11.2828 to 11.7518) Å. The surface morphology also changes with the variation of Fe doping indicating with reduced of grain boundaries and caused granular changes of the elongated rectangular pattern.

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