The Effects of Calcination Temperatures on Crystal Structures and Morphologies of Nd$_{1.2}$FeO$_3$ Synthesized by Solid-State Reaction

E. H. Sujiono$^1$, M. Y. Dahlan$^1$, R. A. Imran$^1$, A.C. M. Said$^1$, and S. Samnur$^1$

$^1$Laboratory of Materials Physics Department of Physics, Universitas Negeri Makassar, Makassar 90224, Indonesia

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

Abstract. NdFeO$_3$ is one of the oxide alloys that can be used as a raw material for gas sensor. The NdFeO$_3$ have been synthesized using solid state reaction method by varying calcination temperatures of 750°C, 850°C, and 950°C for 6 h. All of the Nd$_{1.2}$FeO$_3$ samples were characterized using scanning electron microscope (SEM) and x-ray diffraction (XRD) to identify their morphologies and phases. The results show that all of the samples formed major phase is NdFeO$_3$ and minor phase of Nd$_2$O$_3$ and have homogenous morphology with estimating grain size is 0.2 μm for all samples. The value of FWHM and the crystal size of Nd$_{1.2}$FeO$_3$ was obtained for each sample is 0.22º and 372 nm. The orthorhombic phase with a dominant peak at hkl (121) is an indication that material has potential application as a gas sensor.

Keywords. Crystal structure, morphology, calcination, NdFeO$_3$, and solid state method.

1. Introduction

As increasing awareness of environmental issues and the development of industrial rapidly that affects pollutant gas emissions makes the demand for sensors increases. The active material in the gas sensor can be metal, metal oxide, composite polymer and conductive polymer but now also developed active material on gas sensor derived from oxide alloy material. In recent years, NdFeO$_3$ perovskite structure has been investigated its usefulness in a wide variety of applications such as in oxide fuel cells [1], gas sensors [2], the photocatalysis and catalytic converter [3]. NdFeO$_3$ has a perovskite-type orthorhombic structure [4]. The preparation of NdFeO$_3$ has been successfully investigated by many methods, such as combustion [5], hydrothermal [6], sol-gel citrate method [7], precipitation [8], sonication assisted precipitation [9], and solid state reaction [10] are used. Solid state reaction is the most widely used for the synthesis of inorganic materials because it is easy and inexpensive by involving the heating components at a high temperature for a relatively long period. We have experiences in fabrication of such an oxide material, e.g., YBa$_2$Cu$_3$O$_y$, NdBaCuO (off-stoichiometric), and NdFe$_x$Ba$_{2-x}$Cu$_3$O$_y$, the results have reported [11-13].

In this article, we reported our current results in the development of Nd$_{1.2}$FeO$_3$ oxide alloy material as one potential candidate for sensor application. Nd$_{1.2}$FeO$_3$ oxide have been synthesized using solid-state reaction method with two stages of heat treatment process and varying the calcination
temperature. Characterization of material has been done by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM).

2. Materials and methods

Nd$_{1.2}$FeO$_3$ oxide alloy has been synthesized using solid-state reaction method [14]. The raw material Nd$_2$O$_3$ 99.99 % (Strem Chemicals) and Fe$_2$O$_3$ 99.99 % (Sigma Aldrich) were mixed and grinded together for 3 h then calcined for 6 h at temperature 700 °C. The mixed powder then grinded for 5 h then sintered for 6 h at temperature 950 °C. The synthesis process and the heating are then repeated to obtain a better sample homogeneity [15]. The mixed powder was grinded for 3 h and calcined at temperature 750 °C, this process was repeated for temperature 850 °C and 950 °C. All of the powders were grinded for 5 h and sintered at temperature 950 °C for 6 h.

Nd$_{1.2}$FeO$_3$ powder characterized by X-ray diffractometer [Rigaku Mini Flex II, 2θ = 20° – 65° (CuKa, λ = 0.154 nm)] to determine the crystal structure which includes the value of FWHM (Full Width at Half Maximum) and peak height. The analysis of surface morphology and elemental of the powder were investigated using Scanning Electron Microscope and Energy Dispersive Spectroscopy (SEM-EDS) [Tescan Vega3SB] with a magnification of 5000 times.

3. Results and discussion

XRD diffraction patterns of oxide material Nd$_{1.2}$FeO$_3$ powder were synthesized by using the solid-state reaction method with variations of calcination temperatures of 750 °C, 850 °C and 950 °C are shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** XRD patterns of Nd$_{1.2}$FeO$_3$ as variation of calcination temperatures (*♦* = NdFeO$_3$, *•* = Nd$_2$O$_3$)

Figure 1 shows the peak of NdFeO$_3$ and Nd$_2$O$_3$ phase have been identified based on data adjustment using the Match! Software. This crystallographic curve shows that Nd$_2$O$_3$ and Fe$_2$O$_3$ raw materials have been formed of the new phase of NdFeO$_3$ which crystallizes in the orthorhombic system. The existence of minor phase formation of Nd$_2$O$_3$ is an indication that Nd$_{1.2}$FeO$_3$ raw material does not produce perfect phase. The reaction of imperfection is suspected due to the adjustment of calcination temperature and the heating time is less than optimal. On the other hand, Niu Xinshu et al.
also successfully synthesized NdFeO₃ with a temperature of 950 °C [16] and Yabin Wang et al. with a temperature of 1000 °C [17]. The results are similar to the current study with an indication of the dominant phase formation of NdFeO₃ located at 2θ = 32.56° corresponding to the hkl value (121). The dominant phase intensity hkl (121) increases when the heating temperature is increased [18].

The crystal size can be estimated by using Debye-Scherer equation as described in Equation 1:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda \) is the wavelength of the radiation Cu Kα (\( \lambda = 0.154 \) nm), \( \theta \) is the angle Bragg (°), and \( \beta = \) FWHM at the peak of hkl (121) is association 2θ of 32.56° [19]. The calculation results of crystal size and FWHM can be seen in Table 1.

| Samples | 2θ (°) | Intensity (Counts) | FWHM (°) | Crystal Size (nm) |
|---------|--------|--------------------|----------|------------------|
| YK 750  | 32.56  | 13063.33           | 0.22     | 372.17 ± 0.02    |
| YK 850  | 32.56  | 12686.67           | 0.22     | 372.22 ± 0.02    |
| YK 950  | 32.56  | 13050.00           | 0.22     | 372.17 ± 0.02    |

Based on Table 1, it can be seen that the FWHM values for each sample are same in order of 0.22°. Full-width at half maximum (FWHM) is still an effective method to confirm the quality of crystal structure [17]. FWHM value was influenced by the intensity of each crystal plane. The higher intensity is resulting in smaller FWHM value which indicating the good crystallinity of the samples.

**Figure 2.** The comparison of the relative peak intensity of Nd₁.₂FeO₃ samples with the variations of calcination temperature

Figure 2 shows the calculation result of relative intensities curve for each variation of calcination temperature. These results found that the variation of calcination temperature did not a significant change of crystal size of the sample. In fact, the existences of the atom due to the Nd₂O₃ phase will reduce the diffraction intensity of each sample. Sample with calcination temperature of 850 °C at peak hkl(121) is more dominant than other peaks. Thus, the Nd₁.₂FeO₃ oxide material with the parameters process as has explained above will be useful for the application as gas sensors as has been reported elsewhere [2, 9, 16].
The morphology, structure and particle size of samples Nd$_{1.2}$FeO$_3$ as a variation of calcination temperature were investigated by SEM. Figure 3 shows the SEM micrograph of the samples.

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**Figure 3.** Morphology of sample Nd$_{1.2}$FeO$_3$ as a variation of calcination temperature (a) YK750, (b) YK850 and (c) YK950, respectively

| Table 2. Data composition element of Nd$_{1.2}$FeO$_3$ samples using EDS |
|-------------------------|---------|---------|---------|---------|---------|---------|
| Element                | YK750   | YK850   | YK950   | YK750   | YK850   | YK950   |
| Sodium                 | 1.30    | 1.04    | 1.54    | 0.40    | 0.35    | 0.42    |
| Magnesium              | 0.61    | 0.31    | 0.76    | 0.22    | 0.16    | 0.24    |
| Aluminium              | 0.34    | 0.39    | 0.56    | 0.16    | 0.17    | 0.19    |
| Silicon                | 0.17    | 0.46    | -       | 0.12    | 0.16    | -       |
| Oxygen                 | 17.20   | 17.33   | 17.19   | 6.63    | 6.83    | 5.77    |
| Potassium              | 0.12    | 0.10    | 0.04    | 0.10    | 0.10    | 0.09    |
| Titanium               | 0.17    | 0.21    | 0.14    | 0.11    | 0.12    | 0.11    |
| Iron                   | 20.38   | 20.16   | 20.09   | 1.74    | 1.75    | 1.49    |
| Copper                 | 0.35    | 0.15    | 0.74    | 0.17    | 0.13    | 0.22    |
In Figure 3, it can be observed that all samples have high homogeneity indicated by the morphology of the sample forming small uniform granules, while the estimated grain size of each sample is 0.2 μm. This powder has high porosity, and this is one of the benefits to improve the characteristics of the NdFeO₃ oxide alloy material as a gas sensor application, as disclosed by Ho et al. [2].

The EDS results showed that Nd₁₂FeO₃ samples of YK750, YK850, and YK950 has contained Fe (20.38 wt%), Fe (20.16 wt%), Fe (20.09 wt%) and Nd (59.36 wt%), Nd (59.83 wt%), Nd (59.94 wt%), respectively and also contains a minor phase as shown in Table 2. It can be seen; there is no significant effect on the constituent elements of each sample. That existing of minor phase as indication due to the sample holder preparation process.

4. Conclusions
The Nd₁₂FeO₃ powders as a variation of calcination temperature of 750 °C, 850 °C, and 950 °C have been successfully synthesized using solid state reaction method. The results of X-ray diffraction analysis showed NdFeO₃ and Nd₂O₃ phase, in which the crystal structure of the phase NdFe₁₂O₃ is orthorhombic to the space group Pnma. Variation of calcination temperature higher than 700 °C did not the significant influence of diffraction intensity, FWHM, and crystallite size.

All of the samples have homogeneous morphology and high porosity with an estimated grain size of 0.2 μm. This study has been obtained compound NdFe₁₂O₃ oxide alloy with the dominant peak of hkl (121) which indicated that the sample is a good candidate for a gas sensor material as has been reported elsewhere.

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