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Refinement Analysis using the Rietveld Method of $Nd_{1.2}Fe_1O_3$ Oxide Material Synthesized by Solid-State Reaction

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Neodymium Ferrite Oxide ($Nd_{1.2}FeO_3$) has been successfully synthesized using solid state reaction by varying annealing time. Structural crystallographic characteristics were obtained by X-ray diffraction. The results of X-ray diffraction analysis showed the samples had been identified composed of $NdFeO_3$ and Nd_2O_3 phase, with peak dominant correspond to *hkl* (121), FWHM value of 0.22° and estimated crystal size of 393 nm. Analysis using Rietveld methods obtained $Nd_{1.2}FeO_3$ oxide material has a crystal structure is orthorhombic with space-group of PNMA. The results are comparable as was reported elsewhere that the oxide material is useful for gas sensor application.

Keywords: Annealing time, The Lattice constant, Solid-state reaction, The Rietveld method.

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1. INTRODUCTION

$NdFeO_3$ material has long attracted attention as a material that can be used as raw material gas sensor[1][2], fuel cells[3], the catalyst material gas sensor[4], and magnetic materials[5][6]. $NdFeO_3$ as a raw material gas sensor sensitive to some kind of gas. As research conducted by Niu Xinshu et al. (2003) showed that the nanocrystals $NdFeO_3$ could be used as H_2S gas sensor, which between selectivity and sensitivity of the sensor by H_2S concentrations have quite an interesting relation[1]. Additionally, the research carried out by Chen Tongyung et al. (2012) showed that $NdFeO_3$ could be to anode material S/O_2 and SO_2/O_2-SOFCs[3]. While the research conducted by Truong Giang Ho et al. (2010) showed that the catalyst of the gas sensor $NdFeO_3$ material has good stability and sensitivity to CO gas [4].

Has been known a variety of ways to synthesize oxide materials, one of the most conventional ways that are easy to use is a solid state reaction method. This method was done by mixing different metal oxide alloys at high temperatures[7, 8].

Rietveld analysis was advanced analysis to find out the physical properties of a material quantitatively based on the XRD data. Rietveld analysis was a method that matches the theoretical curve with the experimental curve until both curves appropriate [9]. Both of curve was an order by using the least squares method was performed repeatedly (iteration), so there's a match between two curves then that data can be observed by the data calculation [10].

In this study, $Nd_{1.2}FeO_3$ materials have been synthesized using solid state reaction by varying the annealing time for 1, 2 and 3 hours at 450 °C, respectively. Satyendra Singh (2012), presented that the optimal temperature for annealing $Nd_{1.2}FeO_3$material is at 450 °C because it would make the sample more responsive [11]. This annealing temperature is also has reported elsewhere for varied of oxide material which is YBaCuO and NdFeO[12 13, 14]. The sample obtained and then characterized by X-ray diffraction to identify the phase has formed. The lattice constant value will be performed with refinement analysis using Rietveld methods based on the results of X-ray diffraction characterization.

2. EXPERIMENTAL

$NdFeO_3$ material synthesized by using solid-state reaction method. Synthesis process begins by mixing of raw material Nd_2O_3 99.99 % (*Strem Chemicals*) and Fe_2O_3 99.99 % (*Sigma-Aldrich*) in accordance with stoichiometry calculations. In the first stage, the mixture of Nd_2O_3 and Fe_2O_3 grinded for ± 3 hours, then calcined at 700 °C for 6 hours. The material then grinded back for ± 5 hours and then sintered at 950 °C for 6 hours.

In the second stage, the sample was re-grinded for ± 3 hours, then calcined at 950 °C for 6 hours. Then grinded the sample back for ± 5 hours, then sintering at 950 °C, by varying the annealing time for 1, 2 and 3 hours respectively.

The obtained $Nd_{1.2}FeO_3$ oxide material has been synthesized and then characterized using x-ray diffraction (Rigaku Mini Flex II CuKα, $\lambda = 0.154$ nm) to find out phase formed. The results of x-ray diffraction characterization were then analyzed using the Rietveld method.

Refinement analysis begins by creating a sample database with regard phase and the atoms that make up phase, as well as the radiation source, used to characterize the sample. In addition, the space group determinate in accordance with the sample into one of the parameters that must be observed. In this research space group in accordance with the sample was PNMA. Calculation of refinement analysis using Rietveld method began by matching the background between the theoretical curve and the experimental curve. Then continued with match the peak of the curve by adjusting the scale phase and the lattice parameter of the sample in Phases menu. Then on the menu Histogram,

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which must be considered is the value of the parameter zero which is a 2θ correction instrument. Sample displacement which is the amount of inaccuracy in the measurement of the vertical position of the sample as well as the parameters of B^{-1}, B^0, B^1, and B^2 affecting the high peaks of the sample. Then the shape of the curve will be refined on the Sample menu. In this section, the shape and width of the peak will be refined through a U-Gaussian parameter, the Lorentzian parameter (size) and asymmetry. While the peak tail influenced by Lorentzian parameters (size). Refinement results can be seen at Information tab in the menu Output.

3. RESULTS AND DISCUSSION

3.1 Analysis of X-Ray Diffraction

The results of x-ray diffraction characterization of $Nd_{1.2}FeO_3$ the sintering at a temperature of 950 °C is shown in Figure 1.

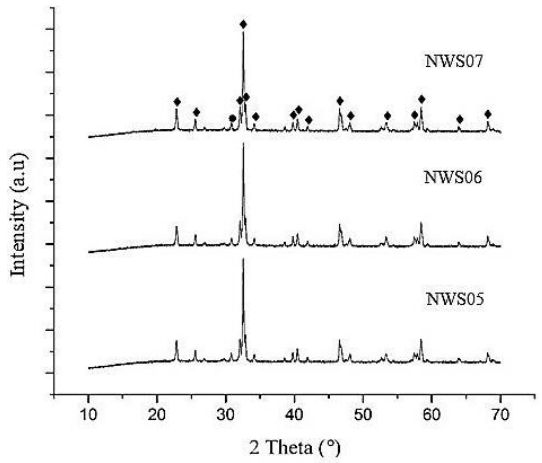


Fig. 1 – XRD pattern of $Nd_{1.2}Fe_1O_3$ powder in the variation of annealing time 1 hour, 2 hours and 3 hours, respectively (● = Nd_2O_3 ♦ = $NdFeO_3$)

In Figure 1 shows that in this study, there are two phases, the dominant phase $NdFeO_3$ (diamond) and phase Nd_2O_3 (circle). The $NdFeO_3$ material has formed a crystalline phase with the highest peak being on the plane (121). This was according to Yabin Wang et al. research (2010), which is known that the peak (121) was the most sensitive of peak to certain gases [12]. Results found equally to the research conducted by NiuXinshu et al. (2003) who found the peak (121) at $2\theta = 32.5°$[1].This pattern also indicated that the $NdFeO_3$material has a crystalline structure orthorhombic perovskite type. As has reported by previous researchers that the material crystal structure orthorhombic perovskite-type was a material that can be used as raw material gas sensor [1, 4, 11].

The results of X-ray diffraction analysis of the material $Nd_{1.2}Fe_1O_3$ can be seen from Table 1.

Table 1 shown the $NdFeO_3$ phase has formed at a 2θ angle of 32.5° with the peak intensity reached 13200 counts. In accordance with research Niu Xinshu, peaks at an angle 2θ of 32.5° were identified as *hkl* (121), which is the most sensitive peak to some specific types of gas [1]. FWHM value is an indication of the crystalline quality of the oxide material. The smaller FWHM value of the crystal means that the material quality more better [12-14]. Furthermore, FWHM values also indicate the level of homogeneity of materials. We found that in this study the FWHM value is similar; indicate that the variation annealing time does not affect the level crystal quality and the homogeneity of $Nd_{1.2}FeO_3$ oxide material.

Table 1 – XRD analysis results of $Nd_{1.2}FeO_3$ oxide material

Annealing time (hours)	2θ (°)	Peak Int. (cps)	FWHM (°)	Crystal size (nm)
1	32.56	13286.67	0.22	| 393.08±0.02 |
2	32.58	13233.33	0.22	| 393.10±0.02 |
3	32.58	12873.33	0.22	| 393.10±0.02 |

The crystal size can be estimated using Debye Scherrer equation (3.1):

$$D = \frac{0.89\lambda}{B}\cos\theta \qquad (3.1)$$

Where λ was the wavelength of the X-ray (1.54056 Å), θ was the Brag angle and B was FWHM. By applying of Debye Scherrer formula obtained crystal size for all samples is 393 nm, an indication that the oxide material has been studied is in categories of micro-material [16].

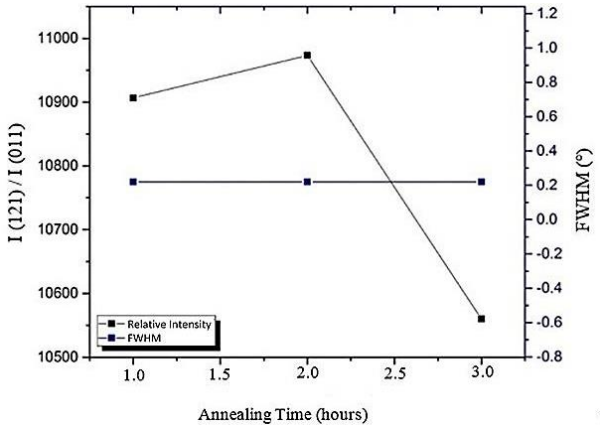


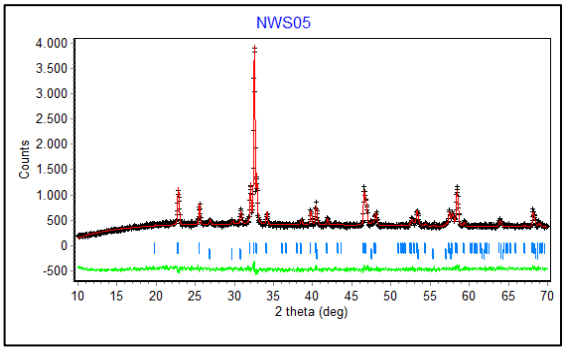
Fig. 2 – Comparison curve between the relative intensity and FWHM values for each variation of annealing time

Figure 2 shows the relative intensity, FWHM as a function of variation of annealing time. Relative intensity, in this case, was the ratio between the highest intensity for both the phase obtained, which is phase $NdFeO_3$ and phase Nd_2O_3. The highest peak phase $NdFeO_3$ is corresponding to *hkl* (121). Meanwhile, the highest peak on the phase of Nd_2O_3 is related to (011). In this study appearing of the Nd_2O_3 peak due to lack of grinding process before calcination treatment. It is can be caused the Nd_2O_3 less reacted with Fe_2O_3 phase to obtain formation of $NdFeO_3$ phase [2]. In contrast, decreasing peak of (011) will be correlated with increasing the intensity of the peak (121) and this data as an indication that the crystal quality of oxide material is improving. These results indicate that the variation of annealing time has a

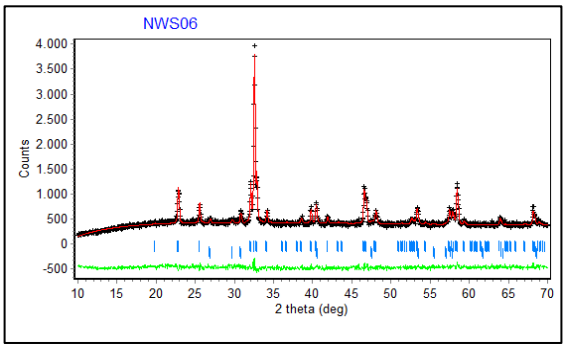
significant change of relative intensity of peaks (121) and (011), while the value of FWHM and crystal size has been obtained is similar.

3.2 Rietveld Analysis

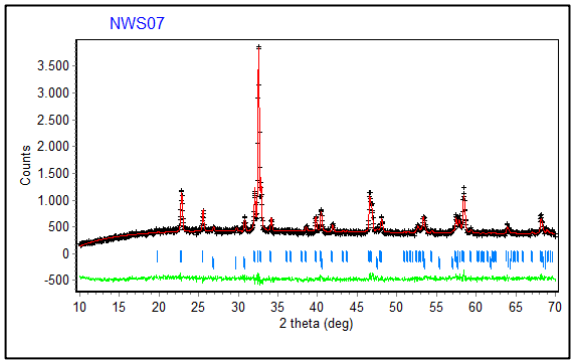
Advanced analysis of data from X-ray diffraction characterization was to use Rietveld method. In this study used Rietica software for smoothing data from X-ray diffraction characterization.



(a)



(b)



(c)

Fig. 3 – Refinement results of $NdFeO_3$ oxide material using the Rietveld method: (a) NWS05; (b) NWS06; and (c) NWS07, respectively

Refinement analysis results showed that the samples of $Nd_{1.2}FeO_3$ have an orthorhombic crystal structure with space group PNMA. This is according to research conducted by Sadhan Chanda et al. [17].

The observed data are indicated by pluses (+) and the calculated data by the solid line overlying them.

The lower curve shows the difference between the observed and calculated diffraction patterns (red). The success of refinement a sample was not only seen of a match between the theoretical curve and the experimental curve, that could only be observed visually, as shown in figure 3. But also seen from the GoF resulting from the refinement. If the value of GoFwas below 4 then refinement considered successful [18]. The Data of Rietveld refinement results can be seen in Table 2.

Table 2 – The Data of Rietveld refinement results using software Rietica based on XRD analysis

Annealing Time (hours)	Rp (%)	Rwp (%)	Rexp (%)	GoF (%)
1	4.50	6.06	6.43	0.8899
2	4.73	6.15	6.38	0.9303
3	4.67	6.06	6.37	0.9053
*)$NdFeO_3$ (Jada Shanker)	8.6	6.1	10.9	1.6

The data in Table 2 shows the GoF parameter obtained from the refinement results has been studied in this research and with the comparison, refinement is performed by Jada Shanker et al. [19].

Several results of the analysis can be read directly from the output data Rietveld analysis is the lattice parameter, the percentage of samples molar and sample displacement. The lattice parameters obtained that can be used to describe the location of atoms in the crystal structure of materials. Table 3 shows the molar percentage of the $Nd_{1.2}Fe_1O_3$ phase of each sample, ranging from 99 %. The value tend continues to increase with the heating time given. Molar percentage obtained show more accurate results than the traditional way. While the sample displacement indicates the value inaccuracy in the measurement sample vertical position, meaning the value close to 0 is the inaccuracies tend to be smaller.

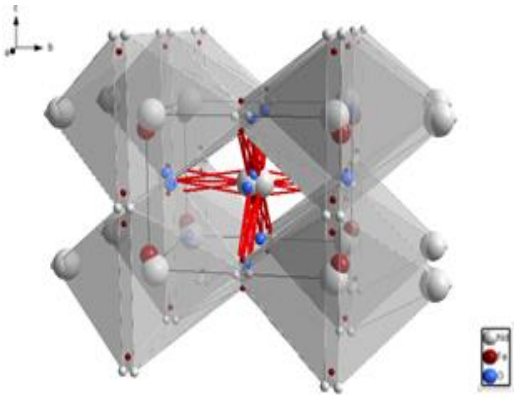


Fig. 4 – The visualization results of the crystal structure of $Nd_{1.2}Fe_1O_3$ based on data from refinement using Rietveld method (with a = 5.580412 Å, b = 7.758973 Å, c = 5.449359 Å)

Lattice parameters obtained from the refinement can be used to describe the location of atoms in the crystal structure $NdFeO_3$ which can be seen in Figure 4. Figure 4 shows the orthorhombic crystal structure of $NdFeO_3$ oxide material, where Nd atoms indicate gray color, Fe atom indicates red color, and O atom indicates blue color. While the bonds between the atoms are identified as a covalent bond.

Table 3 – The refinement result using software Rietica to analyze molar percentage of $Nd_{1.2}Fe_1O_3$ phase, the lattice parameter, and sample displacement

Annealing Time	Molar Percentage	Lattice Parameter			Sample Displacement
		A (Å)	B (Å)	C (Å)	
1 h	99.87 %	|5.581260±0.000682|	|7.759268±0.000888|	|5.448154±0.000616|	– 0.067404
2 h	99.93 %	|5.580412±0.000704|	|7.758973±0.000919|	|5.449359±0.000634|	– 0.100198
3 h	99.93 %	|5.580855±0.000712|	|7.760073±0.000924|	|5.448353±0.000644|	– 0.100198

4. CONCLUSION

$NdFeO_3$ synthesis using solid state reaction method has been successfully studied. The X-ray diffraction analysis obtained of two dominant phase which is $Nd_{1.2}Fe_1O_3$ oxide material and Nd_2O_3. The results also found that the highest peak is corresponding to *hkl* (121) which is known that peak as a sensitive to various gases. The FWHM value is 0.22° with an estimated crystals size of 393 . The refinement analysis using Rietveld method obtained the crystal structure of the material $NdFeO_3$ was orthorhombic with space group PNMA. Therefore, $NdFeO_3$ oxide material obtained in this study can be used as raw material for a gas sensor.

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