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Effects of Molar Ratios and Sintering Times on Crystal Structures and Surface Morphology of $Nd_{1+x}FeO_3$ Oxide Alloy Prepared by using Solid Reaction Method

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Abstract. The effects of molar ratios and sintering times on crystal structures and surface morphology on $NdFeO_3$ oxide alloy have been studied. $NdFeO_3$ oxide alloy formed by chemical preparation with solid reaction method using raw oxide Fe_2O_3 (99.9 %) and Nd_2O_3 (99.9 %) powders. In this article we reported the effects of molar ratios x = (–0.1, –0.2 and –0.3) and sintering times for 15 h and 20 h on crystal structures and surface morphology of $Nd_{1+x}FeO_3$ synthesized by solid-state reaction method. The results indicate that variation of molar ratio and sintering time has influenced the FWHM, crystalline size and grain size. The $Nd_{1+x}FeO_3$ have a major phase is $NdFeO_3$, and other minor phases are Fe_2O_3, Nd_2O_3 and $Nd(OH)_3$. The dominant intensity of *hkl* (121) with a value in FWHM, crystallite size, and grain size an indication the results will be applied as a gas sensor material as the focus of the further study.

Keywords. Crystal structure, $Nd_{1+x}FeO_3$, molar ratio, sintering time, surface morphology, and solid state reaction method.

1. Introduction

Metal particles smaller than 100 nm in primary particle diameter are generally considered as nanoparticles. Such metal nanoparticles often exhibit very interesting electronic, magnetic, optical, and chemical properties [1]. For example, their high surface-to-volume ratios have large fractions of metal atoms at surface available for catalysis [2, 3]. The phase majority of catalysts used in modern the chemical industry is based on mixed metal oxides including perovskite oxides ABO_3 [4]. The nano-perovskite oxides ABO_3 (*A*: La, Nd, Sm, and Gd; *B*: Fe, Co and Ni; and O: oxygen) have high catalytic activities and high sensitivity with CO and HCs. Their applications in gas sensors were studied especially for its properties in electrical and response for CO gas [5]. $NdFeO_3$ is a perovskite transition metal oxide with an orthorhombic structure and space group of Pbnm possesses insulator properties at room temperature [6].

One of $NdFeO_3$ synthesis method is solid reaction method [7]. Solid reaction method is the synthesis of solid materials by reacting with another solid at high temperatures [8]. Solid reaction method is having advantages such as the resulting crystals having good purity and crystallized.

However, the synthesis results obtained in this method produce particles of a large size and irregular morphology [9]. Based on the interesting phenomena developing of oxide materials using the solid-state method, the authors have the conduct of previous research for fabrication oxide material such as $YBa_2Cu_3O_y$, $NdBa_2Cu_3O_y$, $NdFe_xBa_{2-x}Cu_3O_y$ and $Nd_{1+x}FeO_3$, the results have been reported elsewhere [10–14].

In this study will be assessed the effect of molar ratio and sintering time on crystalline structure and surface morphology of $Nd_{1+x}FeO_3$ prepared by solid-state reaction method. Heating temperature, heating time and molar ratio are important because it can be adjusted to crystallinity, grain size, and homogeneity. Therefore, the development of $NdFeO_3$ oxide material needs to be realized to obtain the best crystal structure and surface morphology for gas sensor application.

2. Materials and methods

Preparation of $Nd_{1+x}FeO_3$ material was made 6 samples, 3 samples with a variation of molar ratio indicate with sample #1, #2 and #3, and 3 samples with a variation of sintering time indicate with sample #4, #5 and #6. In this study, $Nd_{1+x}FeO_3$ oxide Alloy Material were synthesized from Nd_2O_3 (99.9 %) and Fe_2O_3 (99.9 %) powder using solid state reaction method. Stoichiometric calculation of raw material mass used Proust law with molar ratio value are x = –0.1, x = –0.2 and x= –0.3 for sample #1, #2 and #3, respectively and x = 0 for sample #4, #5 and #6. The mixed was grinded by mortar and pastel for ± 3 hours to maximize the reaction and then were calcined using the furnace. The sample #1, #2 and #3 was calcined at 950 °C for 50 h, sample #6 at 600 °C for 40 h. Sample #4 and #5 without calcination process. After calcination process is complete, the sample then prepared into a pellet with 1.25 cm diameter under 16 t pressure. The pellet of sample #1, #2 and #3 then sintered at temperature 950 °C for 67 h, sample #4 and #6 at 400 °C for 20 h and sample 5 at 400 °C for 15. All of the samples were characterized using XRD to identify the crystalline phase and using SEM to identify the surface morphology.

3. Results and discussion

3.1. Variation of molar ratio

3.1.1. Chemical Composition

The spectrum showed that increased of peaks intensity and widened of peaks width when the value of the molar ratio is added. However, there are some irregularities where the intensity of the peak sample #2 (x = –0.2) higher than sample #1 (x = –0.1) at certain positions.

Figure 1 shows the addition of the molar ratio, the peak intensity continues to increase, and the peak width becomes wider. However, there are some deviations in which the intensity of the peak x = -0.2 is higher than x = –0.1 at certain positions, e.g., at 32.6° corresponding to the *hkl* (121). The XRD characterization result obtained that the sintering temperature influence of the FWHM. The FWHM is 0.11° for the sample #1, related to the intensity of 984.56 counts. The similar results have been reported on reference [2, 4, 11, 14] though with different research method.

The crystals size of $NdFeO_3$ was calculated on the basis of Scherrer's equation at the highest peak and obtained the crystals size from the smallest to the largest is associated with x = –0.2 (94.0 nm), x = –0.1 (109.7 nm) and x = –0.3 (131.6 nm). While XRD diffraction pattern obtained of FWHM value for molar ratio varied of x = –0,1, x = –0,2 and x = 0, at 32.6° corresponding to the *hkl* (121) are 0.11°, 0.13° and 0.12° and the intensity for each molar ratio is 834 counts, 979 counts and 474 counts, respectively.

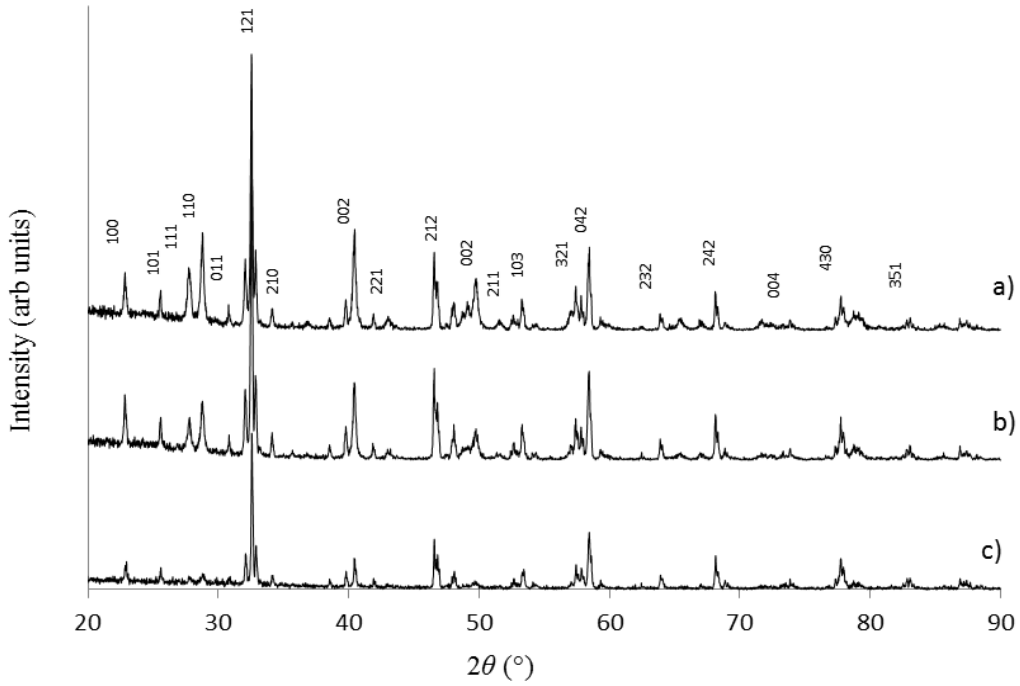

Figure 1. XRD spectra of a) sample #1 , b) sample #2 and c) sample #3, respectively.

3.1.2. Microstructure and Microanalysis

Figure 2 shown SEM image of the $Nd_{1+x}FeO_3$ alloy was prepared with different parameter process. As shown in the figure, it can be seen that the morphology in Figure 2.a and Figure 2.b is more homogeneous although there are still grain boundaries. This data indicated that the result from phase composition was obtained is confirmed. On the other hand, based on Figure 2.c shows that many of grain size shape were observed and this is caused by appearing of grain boundaries. Therefore, we confirmed that the sintering temperature also has influence formed of grain size and grain boundary [3, 9, 11]. Based on the SEM image of the samples above, the variation of the molar ratio has a clumpy surface morphology in which the grain boundary appears on the sample looks very thin and is almost invisible, and the crystalline grain appears much unified.

Crystalline phases analysis using the software *Match!* shows each sample contains four phases is $NdFeO_3$, $Nd(OH)_3$, Fe_2O_3 and Nd_2O_3. It can be seen in Table 1, increasing of molar ratio gradually increase the percentage of $NdFeO_3$ phase. Similar results have been reported in previous studied [13], and there is a minority phase of $Nd(OH)_3$ due to the absorption of hydrogen and oxygen by neodymium [15].

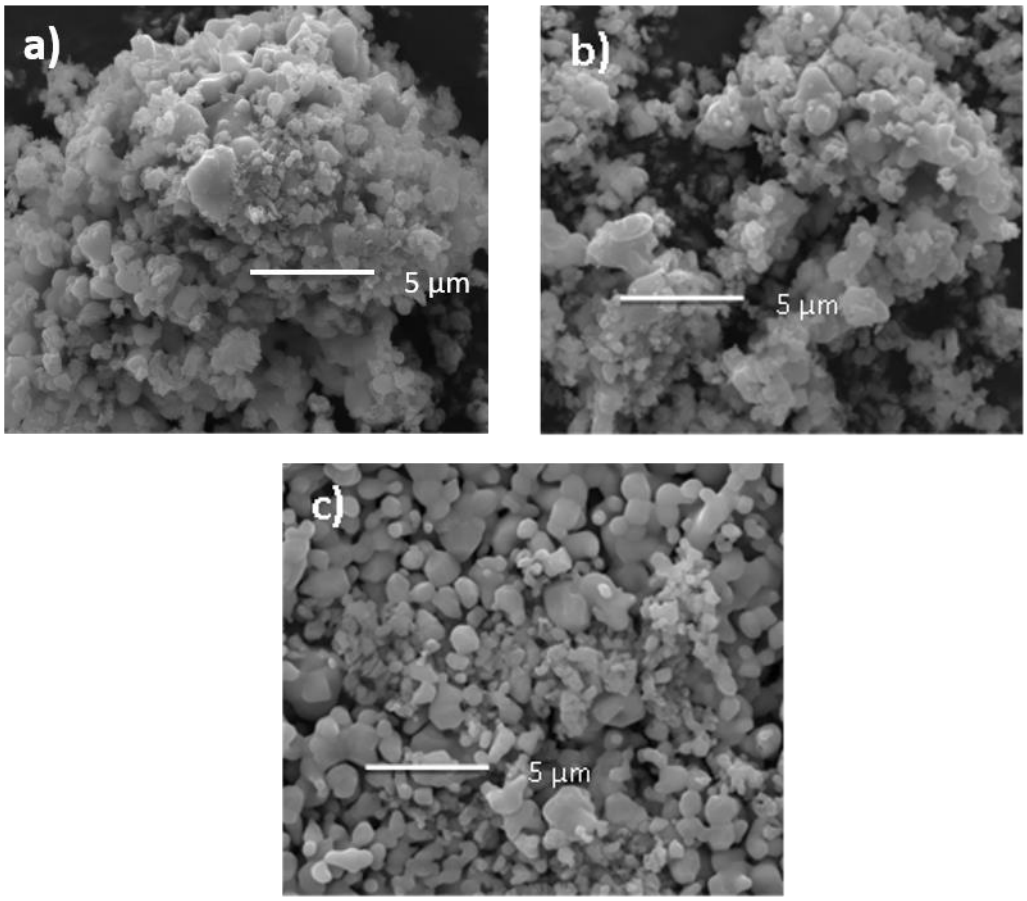

Figure 2. SEM images of a) sample #1, b) sample #2 and c) sample #3 with mag. of 20,000x.

Table 1. Phase analysis of the $Nd_{1+x}FeO_3$ samples.

Samples	$NdFeO_3$ (%)	Nd_2O_3 (%)	Fe_2O_3 (%)	$Nd(OH)_3$ (%)
#1	83	4	-	13
#2	83	4	5	8
#3	78	4	7	11

3.2. Variation of sintering times

3.2.1. Chemical Composition

The XRD graph shown in Figure 3, it is can be seen that if $Nd(OH)_3$ phase formed almost dominant, in contrast, that the oxide alloy material has not formed $NdFeO_3$ phase. It can be seen clearly that there are many peaks with a variation of intensity value as shown in Figure 3.a sample #4 and Figure 3.b sample #5. These results also confirmed that the synthesis process does not show the formation of $NdFeO_3$ phase. However, based on the results of sample #5 the oxide alloy material still forms the $Nd(OH)_3$ phase, although the sintering time is 5 h longer than sample #4 which is sintered for 15 h. This structure can also be seen that the most dominant peak as an indication of $NdFeO_3$ phase still does not observe as consequences of the sintering process at a low temperature of 400 °C and without calcination. In contrast Figure 3.c sample #6 show the formation of $NdFeO_3$ phase indicate the appearance of a peak at 32.6° corresponding to the *hkl* (121). In fact, this result confirmed of a strong indication that calcination process at 600 °C for 40 h following sintering process at a low temperature of 400 °C still produce oxide alloy with $NdFeO_3$ phase. It means the calcination process has the more dominant effect of the crystal structure if compare than the sintering time at low temperature.

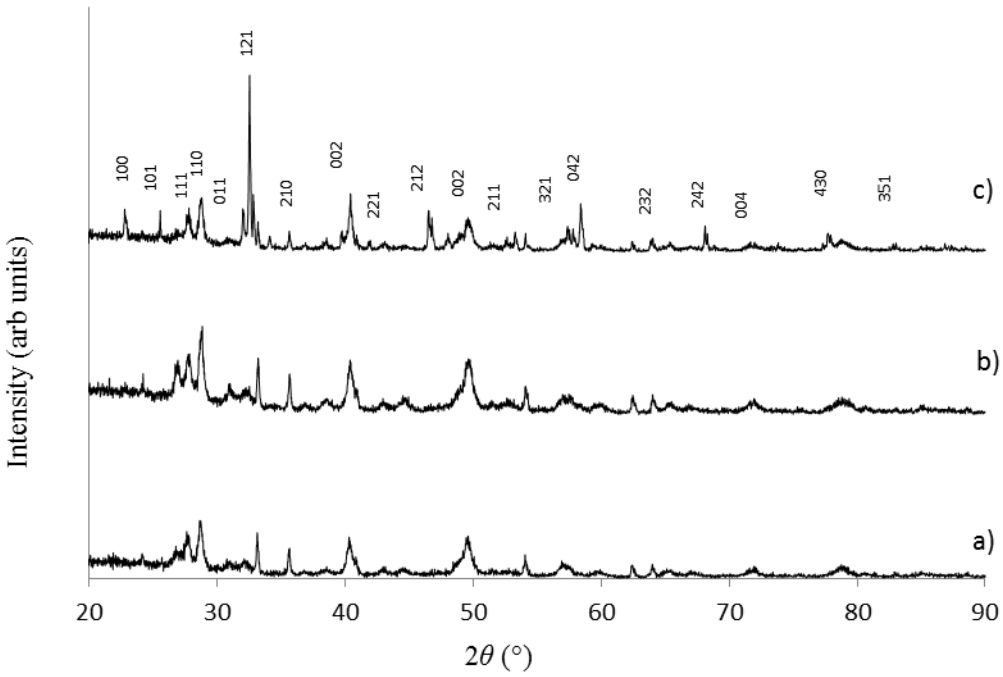

Figure 3. XRD spectra of a) sample #4, b) sample #5 and c) sample #6, respectively.

Calculation of grain size using Debye-Scherrer's equation on the highest intensity obtained crystalline size value are (163.97 ± 0.01) nm, (167.21 ± 0.01) nm and (255.47 ± 0.01) nm for the sample#4, sample #5, and sample #6, respectively. While based on XRD diffraction pattern obtained FWHM value at 2θ of 32.6° for sample #4, sample#5 and sample #6 are 0.19°, 0.19° and 0.12° and the intensity for each sample are 57 counts, 76 counts, and 1227 counts, respectively. This result is similar as has reported by Lou Xiangdong et al. with temperature 800 °C [8], Yabin Wang et al. with temperature 1000 °C [9] and they get similar results that phase $NdFeO_3$ exist at 2θ = 32.56˚ with *hkl* value is (121). V. Zharvan *et al.* [13] reported the crystalline size of samples ranging at 137.0 – 152.0 nm.

3.2.2. Microstructure and Microanalysis

The SEM image of $Nd_{1+x}FeO_3$ samples was shown in Figure 4. It can be seen that all of the samples have non-homogeneous morphology. There are still many agglomerates made due to temperature and mechanical treatment.

Figure 4.a sample #4 and Figure 4.b sample #5 shows an unfinished grain growth forming of $NdFeO_3$ oxide alloy. Correspond to the crystal structure as have been explained, the surface morphology of the sample #4 and sample #5 indicate with granular patterns that are very difficult to identify. Given the variation of sintering time in these two samples, it does not show any significant difference grain size. However, if we observe more closely at Figure 4.b sample #5, there are some parts that have formed a grain. In contrast, the surface morphology of the sample#6 as shown in Figure 4.c which was calcined for 40 h at a temperature of 400 °C then sintered for 20 h at a temperature of 600 °C indicates a better morphology than the two samples which is sample #4 and sample #5 without calcination process. The size of the grains is large and in some parts of the surface appear grain growth is not perfect due to the low sintering and calcination temperature. Similiar results were obtained by Khorasani-Motlagh M. *et al*. that synthesis nanocrystals NdFeO3 materials with has good porosity and the crystalline size influence of time and temperature heat treatment [16].

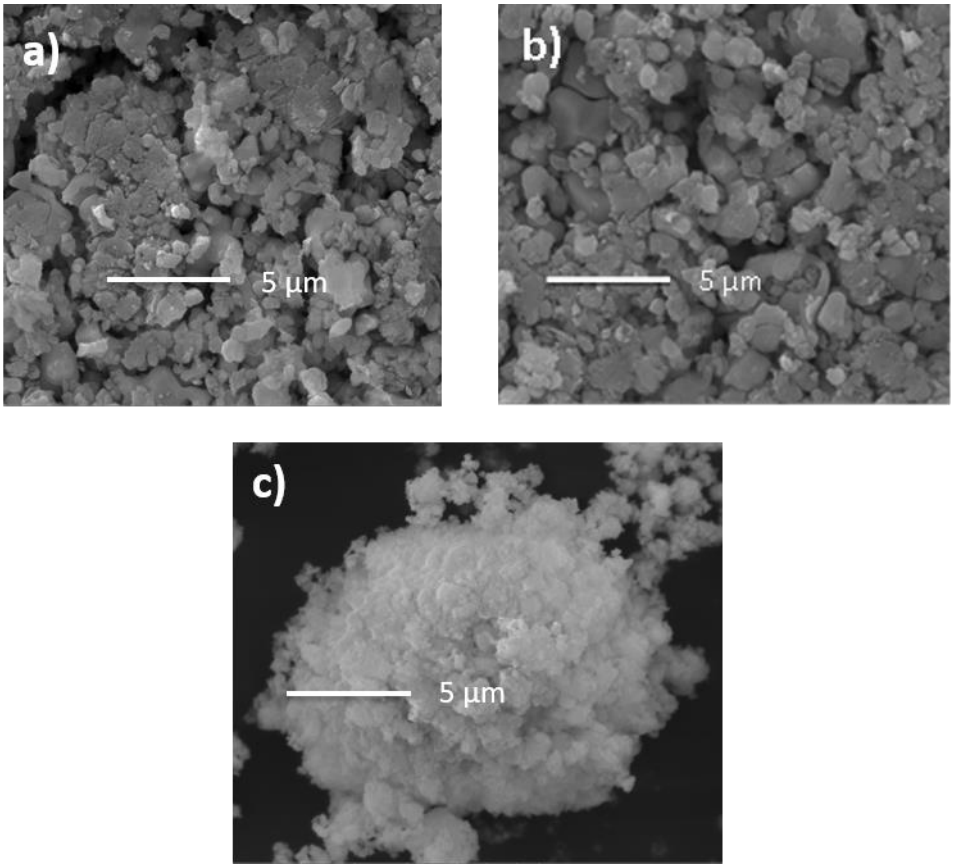

Figure 4. SEM image of a) sample #4, b) sample #5 and c) sample #6 with mag. of 20.000x.

Phases analysis using the software *Match!* show dominant phases of $NdFeO_3$ and contains phase in each sample are $Nd(OH)_3$, Fe_2O_3 and Nd_2O_3, respectively. The highest intensity corresponds to the $NdFeO_3$ phase with polycrystalline material and orthorhombic structure.

Table 2. Phase analysis of the $Nd_{1+x}FeO_3$ samples.

Samples	$NdFeO_3$ (%)	Nd_2O_3 (%)	Fe_2O_3 (%)	$Nd(OH)_3$ (%)
#4	55	8	20	17
#5	53	9	19	17
#6	74	2	14	10

It can be seen in Table 1 and Table 2, the percentage of $Nd(OH)_3$ are quite large due to the absorption of hydrogen and oxygen by neodymium [15]. Its means to produce high quality of $NdFeO_3$ oxide alloy the temperature of calcination and sintering process for synthesis should be higher than 950 °C or increasing the heating time that the reaction of the raw material occurs perfectly and containing lattice -OH has missing.

4. Conclusions

The molar ratio greatly affects the crystal structure of $Nd_{1+x}FeO_3$ oxide alloy, which is indicated intensity differences, FWHM value, and crystal size. The XRD analyzed was obtained FWHM value is 0.11, 0.13, 0.12, 0.19, 0.19 and 0.12, and crystalline size value of $NdFeO_3$ are (294.86 ± 0.01) nm, (248.30 ± 0.01) nm, (288.17 ± 0.01) nm, (163.97 ± 0.01) nm, (167.21 ± 0.01) nm and (255.47 ± 0.01) nm for sample #1, #2, #3, #4, #5 and #6, respectively. There are four phases that contain each sample:

$NdFeO_3$, $Nd(OH)_3$, Fe_2O_3 and Nd_2O_3. The highest intensity of $NdFeO_3$ giving information that samples are a polycrystalline material with dominant phase formed is orthorhombic correspond to *hkl* (121).

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