

# The Effect of Molar Ratio on Crystal Structure and Morphology of $\text{Nd}_{1+x}\text{FeO}_3$ ( $x=0.1, 0.2$ , and $0.3$ ) Oxide Alloy Material Synthesized by Solid State Reaction Method

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**Abstract.** Perovskite is an oxide alloy which has a structure of  $\text{ABO}_3$  ( $A = \text{La, Nd, Sm, Gd}$ ;  $B = \text{Fe, CO, Ni}$ ) and has an excellent catalytic activity and gas-sensitive properties.  $\text{NdFeO}_3$  and its derivatives are important candidates for gas sensors. In this study, the effect of molar ratio ( $x=0.1, 0.2$  and  $0.3$ ) on crystal structure and morphology of  $\text{Nd}_{1+x}\text{FeO}_3$  synthesized by solid state reaction method has been studied.  $\text{Nd}_{1+x}\text{FeO}_3$  samples were prepared using  $\text{Nd}_2\text{O}_3$  (99.99 %) and  $\text{Fe}_2\text{O}_3$  (99.99 %) as precursors. All of the samples were characterized using XRD to identify the phase and using SEM to identify the morphology. The synthesized  $\text{Nd}_{1+x}\text{FeO}_3$  samples showed that molar ratio strongly influences the intensity, FWHM, and crystalline size. The samples of  $\text{Nd}_{1+x}\text{FeO}_3$  have homogenous morphology and have three major phases, i.e.  $\text{NdFeO}_3$ ,  $\text{Nd}(\text{OH})_3$  and  $\text{Nd}_2\text{O}_3$  with crystalline sizes of  $\text{NdFeO}_3$  of  $137.0 \pm 0.1$  nm,  $152.2 \pm 0.1$  nm and  $137.0 \pm 0.1$  nm for  $\text{Nd}_{1.1}\text{FeO}_3$ ,  $\text{Nd}_{1.2}\text{FeO}_3$ , and  $\text{Nd}_{1.3}\text{FeO}_3$ , respectively. These results indicated that the sample of  $\text{Nd}_{1.2}\text{FeO}_3$  was a good candidate for a gas sensor material.

**Keywords:** Molar ratio; crystal structure; morphology;  $\text{NdFeO}_3$  oxide alloy; solid state method.

## 1. Introduction

The rare-earth orthoferrite,  $\text{ReFeO}_3$  (Re: rare-earth element), is a well-known crystalline in the orthorhombic structure derived from a perovskite structure belonging to Pbnm space group and has exhibited physical and chemical properties due to their ionic and electronic defects [1]. Further, it is known that nano-crystalline perovskite oxides,  $\text{ReBO}_3$  (Re = rare-earth elements, B = 3d transition metals and O = oxygen) on gas sensors have been studied [2]. Among these perovskite oxides,  $\text{NdFeO}_3$  was reported to have excellent gas-sensing properties [3]. The other result showed that  $\text{NdFeO}_3$  has high catalytic activities and high sensitivity with CO and HCs [4] comparing with other rare-earth elements.

There are various methods for the synthesis of  $\text{NdFeO}_3$  alloy oxide such as sol-gel method [5], gel combustion method [1], hydrothermal method [6], solid state reaction method [7], and so on. There are advantages of using solid state reaction because this method is cheap and easy to complete. Also, the product of the reaction has a high purity and excellent crystallinity. The expected results from using this approach are to obtain a larger size, better crystallinity, and a higher purity than other methods. However, in solid-state reaction method, there are many properties that influence the crystal structure



and morphology of  $\text{NdFeO}_3$  such as time and calcined temperature [1], and also milling process [8] but there is not a report that explains the effect of molar ratio on the synthesis of  $\text{NdFeO}_3$  by using this method employing  $\text{Nd}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  precursors.

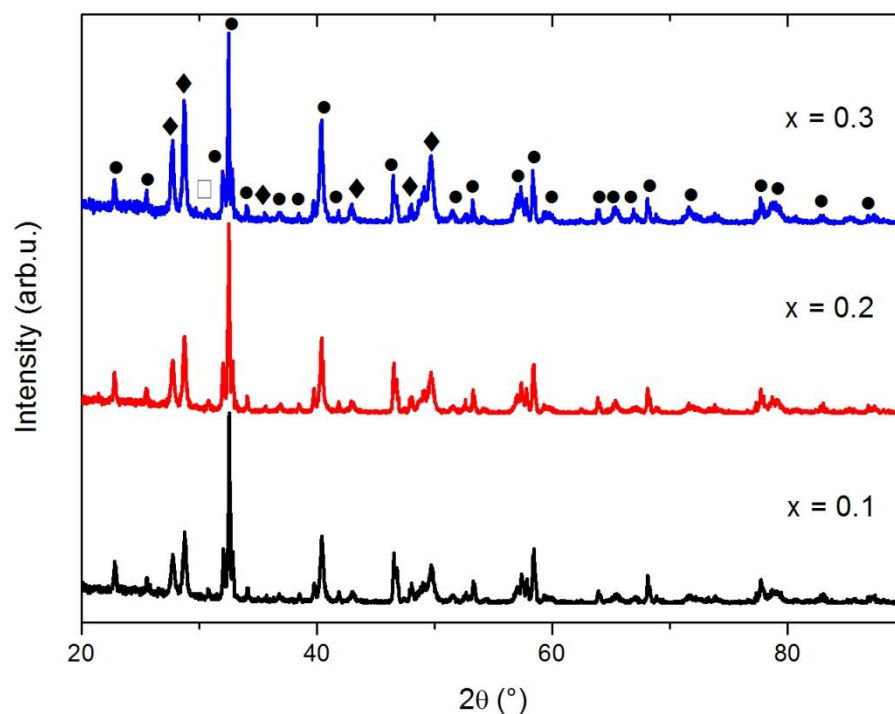
In this paper, we present the influence of molar ratio ( $x = 0.1, 0.2$  and  $0.3$ ) on crystal structure and morphology of  $\text{Nd}_{1+x}\text{FeO}_3$  which is synthesized by solid state reaction method from  $\text{Nd}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  precursors.

## 2. Experimental method

The raw materials of  $\text{Nd}_2\text{O}_3$  (Strem Chemicals, 99.99%) and  $\text{Fe}_2\text{O}_3$  (Sigma-Aldrich, 99.99%), were mixed based on the stoichiometric calculation to get an oxide alloy of  $\text{Nd}_{1.1}\text{FeO}_3$  and were ground using mortar for 3 hours to maximize the reaction and to increase the homogeneity. The mixed materials were then calcined using furnace at  $950^\circ\text{C}$  for 30 hours. After the calcination process was complete, the sample was then prepared into a pellet with 1.25 cm diameter under a 16-ton pressure. The pellet was then sintered at a temperature of  $950^\circ\text{C}$  for 20 hours and slowly cooled to a temperature of  $450^\circ\text{C}$  to be subsequently sintered again for 20 hours. The same procedure was repeated for the variation of the molar ratio at  $x = 0.2$  and  $x = 0.3$ . All of the pellets of  $\text{Nd}_{1+x}\text{FeO}_3$  ( $x = 0.1, 0.2$  and  $0.3$ ) were then characterized by XRD (Xpert Pro) using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) to obtain phase and by SEM (Inspect S50) to obtain the morphology contained in the pellets.

## 3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the  $\text{Nd}_{1+x}\text{FeO}_3$  samples as the variations of molar ratio were  $x = 0.1, 0.2$  and  $0.3$ , respectively.



**Figure 1.** XRD pattern of  $\text{Nd}_{1+x}\text{FeO}_3$  as variations of molar ratio of  $x = 0.1, 0.2$  and  $0.3$ , respectively (● =  $\text{NdFeO}_3$ , □ =  $\text{Nd}_2\text{O}_3$ , ◆ =  $\text{Nd}(\text{OH})_3$ ).

The phases analysis using *X'Pert High Score Plus* software revealed that there were three phases in each sample, i.e.  $\text{NdFeO}_3$  (PDF reference code 01-074-1473),  $\text{Nd(OH)}_3$  (PDF reference code 01-070-0215) and  $\text{Nd}_2\text{O}_3$  (PDF reference code 01-074-1147) with the highest intensity for  $\text{NdFeO}_3$ . It indicated that the samples were polycrystalline materials with a dominant phase of  $\text{NdFeO}_3$  with an orthorhombic structure. Lou Xiangdong et al has also done synthesis of  $\text{NdFeO}_3$  with a temperature of  $800^\circ\text{C}$  [9] and Yabin Wang et al. with a temperature of  $1000^\circ\text{C}$  [10], and they get similar results that the  $\text{NdFeO}_3$  phase existed at  $2\theta = 32.56^\circ$  with a hkl value of 121. Based on Figure 1, there were two minor  $\text{Nd(OH)}_3$  phases due to the absorption of hydrogen and oxygen by neodymium [8] and  $\text{Nd}_2\text{O}_3$  that existed due to the low temperature during the processes of calcination.

**Table 1.** Position ( $2\theta$ ), intensity and FWHM value of  $\text{NdFeO}_3$  phase as a variation of molar ratio

Molar ratio	$2\theta (^\circ)$	Intensity (counts)	FWHM ( $^\circ$ )
0.1	$32.5649 \pm 0.001$	$757.8600 \pm 0.001$	$0.1181 \pm 0.001$
0.2	$32.5352 \pm 0.001$	$795.8900 \pm 0.001$	$0.0984 \pm 0.001$
0.3	$32.5063 \pm 0.001$	$625.2100 \pm 0.001$	$0.1181 \pm 0.001$

Table 1 shows the influence of molar ratio on the position of  $2\theta$ , intensity, and the FWHM value on the phase of  $\text{NdFeO}_3$  for each sample. As illustrated, the increasing molar ratio of Nd content gradually shifted the XRD peaks towards a lower angle or higher  $d$  value due to larger ionic radii of Nd than Fe [11]. Peak position value  $2\theta = 32.5^\circ$  had the highest intensity compare with other peaks and this peak was related to the  $\text{NdFeO}_3$  phase with 121 hkl value based on the analysis using *Match!* software. Relating to the intensity, the molar ratio has influenced the intensity of the sample. Based on Table 1, it can be seen that the sample with a molar ratio of  $x = 0.2$  had the narrowest and highest intensity which indicated the growth of  $\text{NdFeO}_3$  crystallite and also gave information that the  $\text{Nd}_{1.2}\text{FeO}_3$  sample has an excellent crystallinity and conductivity. The sample with a molar ratio of  $x = 0.2$  has lowest FWHM value among others. This result indicates that the sample with a molar ratio of  $x = 0.2$  has a similar crystal structure [12,13]. The determination of the crystalline size can be calculated using *Debye-Scherrer* equation [2]:

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$  is the wavelength of X-ray (0.15406 nm),  $\beta$  is FWHM value at 121, and  $\theta$  is diffraction angle. Based on the calculation, the value of the crystalline size of  $\text{Nd}_{1+x}\text{FeO}_3$  which was synthesized with the variations of molar ratio of  $x = 0.1, 0.2$  and  $0.3$  were 137.0 nm, 152.2 nm, and 137.0 nm, respectively. Table 2 shows the lattice parameters of  $\text{Nd}_{1+x}\text{FeO}_3$  sample obtained by Rietveld refinement using *Rietica* software.

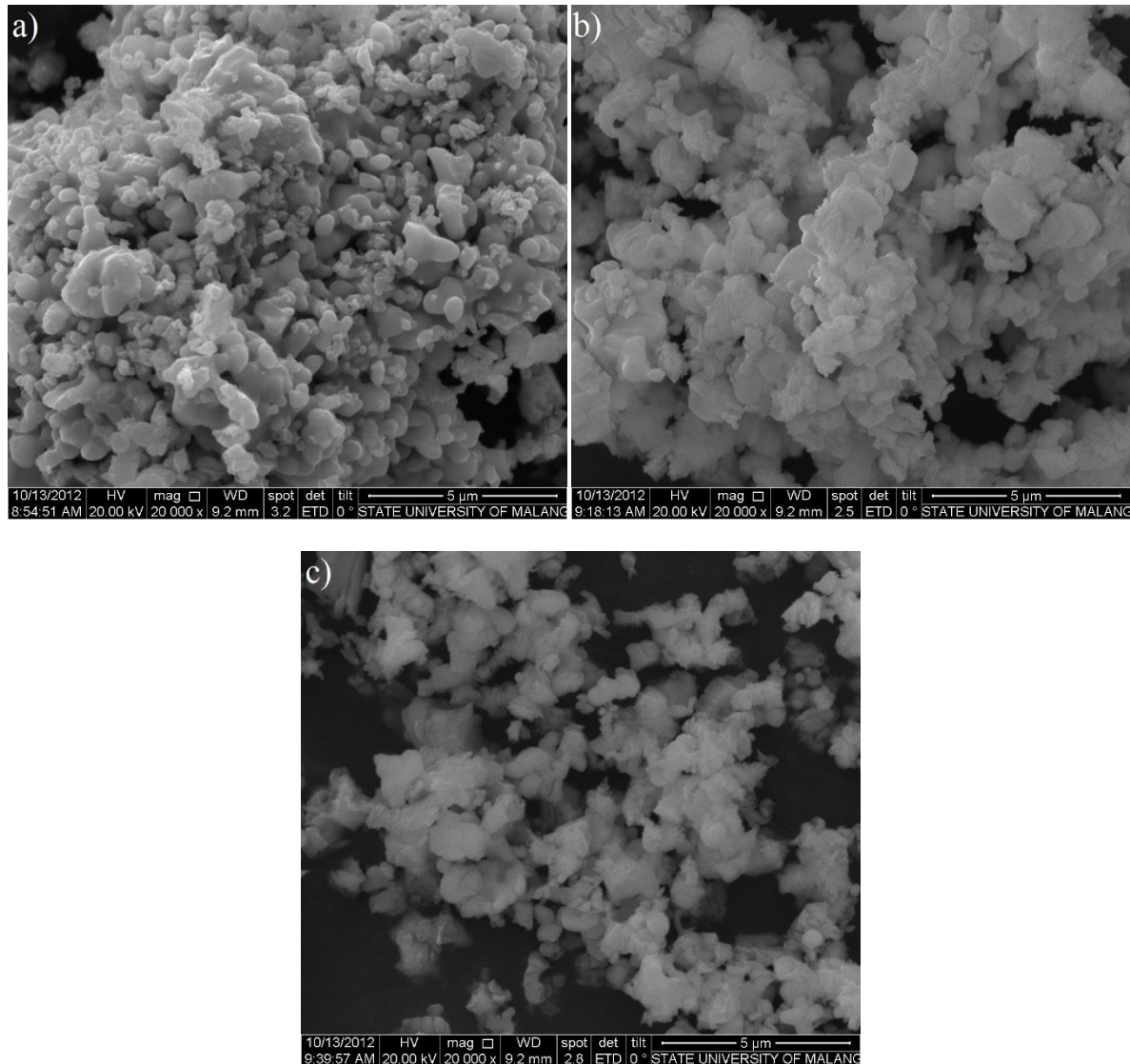
**Table 2.** Lattice parameters of  $\text{Nd}_{1+x}\text{FeO}_3$  obtained by Rietveld refinement

Sample	a (Å)	b (Å)	c (Å)	Rp	Rwp	Re	$\chi^2$
$\text{Nd}_{1.1}\text{FeO}_3$	$5.5837 \pm 0.0004$	$7.7620 \pm 0.0006$	$5.4519 \pm 0.0004$	19.58	26.06	15.83	2.71
$\text{Nd}_{1.2}\text{FeO}_3$	$5.5844 \pm 0.0005$	$7.7612 \pm 0.0006$	$5.4510 \pm 0.0004$	20.10	27.36	15.84	2.98
$\text{Nd}_{1.3}\text{FeO}_3$	$5.5852 \pm 0.0005$	$7.7623 \pm 0.0007$	$5.4520 \pm 0.0005$	20.63	27.56	15.55	3.14
A1	5.579100	7.763700	5.443000	-	-	-	-

It can be seen from Table 2 that the increasing molar ratio gradually increased the lattice parameter due to differences in ionic radii between Nd and Fe that caused the  $d$ -spacing became larger and

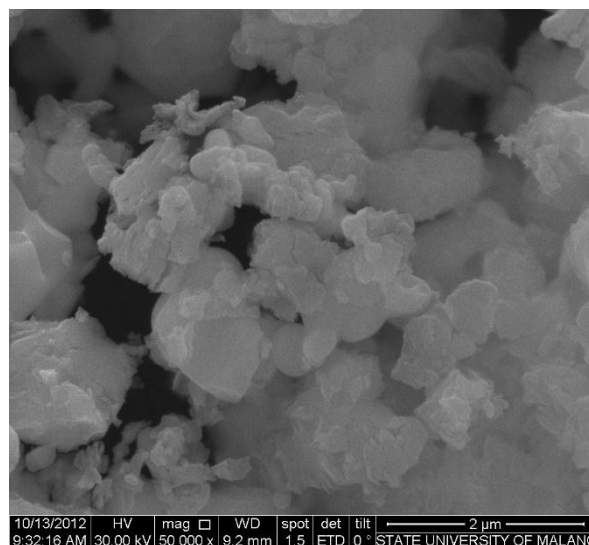
shifted the x-ray peaks to a lower degree. The A1 sample is a result of the  $\text{NdFeO}_3$  synthesis performed by Pedro et al. as a reference value [8].

SEM investigated the morphology, structure and particle size of the  $\text{Nd}_{1+x}\text{FeO}_3$  samples with variations of molar ratio. Figure 2 shows the SEM image of  $\text{Nd}_{1+x}\text{FeO}_3$  samples.



**Figure 2.**  $\text{Nd}_{1+x}\text{FeO}_3$  sample morphology with the variations of molar ratio of a) 0.1, b) 0.2 and c) 0.3, respectively.

Based on Figure 2, it can be seen that all of the samples had non-homogeneous morphology. There were still many agglomerates made due to the temperature and mechanical treatment. The particle size of the samples was about 1  $\mu\text{m}$ . These powders have high porosity, and this was an advantage for the gas sensor materials. A higher magnification of  $\text{Nd}_{1+x}\text{FeO}_3$  at  $x = 0.2$  can be seen in figure 3.



**Figure 3.** Morphology of Nd<sub>1.2</sub>FeO<sub>3</sub> sample at a higher magnification

A higher magnification for the Nd<sub>1.2</sub>FeO<sub>3</sub> sample showed that the grains were composed of fine particles with different shapes. The crystalline size of the Nd<sub>1+x</sub>FeO<sub>3</sub> sample was determined using Debye-Scherrer's equation from the highest peak of the x-ray pattern with the crystalline sizes varied from 137.0 nm to 152.2 nm. The similar results were obtained by Khorasani-Motlagh M. et al. that synthesized NdFeO<sub>3</sub> nanocrystals with a good porosity and with the crystalline size ranging from 28.82 nm to 200.71 nm [14].

#### 4. Conclusion

The Nd<sub>1+x</sub>FeO<sub>3</sub> powders with the variations of molar ratio ( $x = 0.1, 0.2$  and  $0.3$ ) were successfully synthesized using solid-state reaction method. The variation of molar ratio has a significant effect on the diffraction intensity, FWHM, and the crystalline size of the samples. Based on the calculation, it can be identified that the crystalline size of the samples was ranging from 137.0 – 152.2 nm.

All of the samples have non-homogeneous morphology with many different shapes and high porosity. The sample with the molar ratio of  $x = 0.2$  has the highest intensity, largest crystalline size, and highest porosity which indicated that the Nd<sub>1.2</sub>FeO<sub>3</sub> sample is a good candidate for a gas sensor material.

#### 5. References

- [1] Anhua W *et al* 2009 *Asia-Pac. J. Che. Eng.* **4** 518-521
- [2] Ho T G *et al* 2011 *Sensors and Actuators B.* **158** 246-251
- [3] Ru Z *et al* 2010 *Journal of Rare Earths.* **28** 591-595
- [4] Truong G H *et al* 2011 *Adv. Nat. Sci: Nanosci. Nantotechnol.* **2** 015012 4pp
- [5] Zhan-lei W *et al* 2010 *International Journal of Minerals, Metallurgy, and Materials.* **2** 141
- [6] You W *et al* 2014 *CrystEngComm.* **16** 858
- [7] Shujuan Y *et al* 2011 *Journal of Applied Physics.* **109** 07E141
- [8] Pedro V S *et al* 2016 *Materials Research.* **19(2)** 389-393
- [9] Lou X *et al* 2005 *Journal of Rare Earths.* **23** 328
- [10] Yabin W *et al* 2011 *Journal of Crystal Growth.* **318** 927-931
- [11] Prabeer B *et al* 2010 *Journal of Material Chemistry.* 1-8
- [12] Husain H *et al* 2015 *Jurnal Sainsmat.* **4(1)** 1-6
- [13] Wickenden A E *et al* 1994 *Journal of Applied Physics.* **75** 5367
- [14] Khorasani-Motlagh M *et al* 2013 *Int. J. Nanosci. Nanotechnol.* **9(1)** 7-14

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