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Influence of Annealing Time Variation on Crystal Structure and Morphology of Oxide Material Nd$_{1.2}$FeO$_3$ by Solid-State Reaction Method

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Abstract. NdFeO$_3$ is one of the oxide material can be detected various gases, like S/O$_2$, CO, H$_2$S, etc. In this research, Nd$_{1.2}$FeO$_3$ as oxide material have been synthesized by solid-state reaction with a variation of annealing time. Characterized by XRD shows that the samples have form crystal perovskite structure with dominant phase and peak intensity correspond to hkl (121). FWHM value for the dominant peak was 0.22°. The crystallite of the samples was determined using Debye Scherer formula were 393.08, 393.10, and 393.10 nm, respectively. While the SEM characterized showed the morphology of the samples was homogenous with grain size estimates of 0.2μm. These results indicate the variation of annealing time 1, 2, and 3 hours did not significantly affect the crystallinity and morphology of Nd$_{1.2}$FeO$_3$ oxide material.

Keywords. Annealing time, crystallinity, morphology, Nd$_{1.2}$FeO$_3$ oxide material, and solid-state reaction.

1. Introduction

Currently in the modern chemical industry mixed metal oxide including perovskite oxide structure with general structure ABO$_3$ where A was a rare-earth element and B was 3D transition metal had been used remain prominent [1]. Iron was metal in the first transition series that has an orthorhombic structure with perovskite-type that was a subject of extensive investigated [2–4]. A number of research shown their utility in a wide range of applications such as a catalytic gas sensor, magnetic material, pigment material, fuel cells, gas sensor, etc. [2–6]. As a gas sensor, NdFeO$_3$ was very efficient for H$_2$S, CO and LPG detection [6–8].

Material oxide could be synthesized in several ways, such as ceramic method, chemical precipitation process, float zone technique, sol-gel and solid-state reaction [3,8–12]. The solid-state reaction was one of the most conventional methods, which was an easy and inexpensive method to a synthesized oxide material. The method was mixed different metal oxide alloys at high temperatures [13]. In this research, Nd$_{1.2}$FeO$_3$ oxide material was synthesized by solid-state reaction. Characteristic of the crystalline structure of oxide material was studied using x-ray diffraction (XRD) and the morphology using Scanning Electron Microscopy (SEM). The full width at half maximum (FWHM) is one effective method to confirm the
crystal quality and the morphology of the material. The crystal quality has category higher due to the smaller of FWHM value and the crystal size in dimension to nanometer [14].

In this paper, presented influence of annealing time (t) as a variation of 1 h, 2 h, 3 h on crystal structure and morphology of Nd$_{1.2}$FeO$_3$ synthesized by solid-state reaction method. Variation of annealing time has an effective treatment for removing structural grain boundaries of ionic defects [15]. It is an indication that annealing process would increase the crystal quality of the material. The composition of Nd$_{1.2}$FeO$_3$ used has been reported elsewhere [16]. Therefore, this paper would be a focus on appearing results of variation annealing time on crystal quality and morphology.

2. Materials and methods

The Nd$_{1.2}$FeO$_3$ have been synthesized by solid stated reaction method with repeated heating treatment. The synthesized process was started by the mixed stoichiometric powder of Nd$_2$O$_3$ 99.99 % (Strem Chemicals) and Fe$_2$O$_3$ 99.99 % (Sigma-Aldrich) and grinded them for 3 h [16]. The samples were calcinates at 700 °C for 6 h. After that sample were grinded for 5 h and sintered at 950 °C for 6 h. This process was called the first heat treatment. Then, the sample was grinded for 3 h and calcined at 950 °C for 6 h. The last, the sample was grinded for 5 h and continued using in situ annealed at 450 °C for 1 h, 2 h, and 3 h, respectively. This process was called the second heat treatment.

The synthesized powder samples of Nd$_{1.2}$FeO$_3$ were characterized by using x-ray diffraction (Rigaku Miniflex II CuKα, λ = 0.154 mm) and Scanning Electron Microscopy (Tescam Vega-SB) for analyzed crystal structure and the morphology of the samples.

3. Results and discussion

In this research, the samples have characterized by X-ray diffraction (XRD). The intensity was observed over 2θ range 10° to 70°. The XRD pattern of the Nd$_{1.2}$FeO$_3$ oxide material is shown in Figure 1. The pattern has formed a crystal with the orthorhombic phase of perovskite-type (JCPDS File no 25 – 1149) with the highest peak at 2θ = 32.5° and correspond to hkl (121) plane. This result has similar as reported by Satyendra Singh et al., with annealing temperature at 450 °C for 2 h [17].

![Figure 1. XRD pattern of Nd$_{1.2}$FeO$_3$ as variation of annealing time a = 1 h, b = 2 h, and c = 3 h, respectively (●= NdFeO$_3$, ○= Nd$_2$O$_3$).](image-url)
In this research, we also found that the highest peak intensity is corresponding to $hkl$ (121). The peak was a very sensitive peak as a gas sensor, reported by Niu Xinshuet et al. The $hkl$ (121) has high sensitivity, excellent selectivity, and quick response and recovery behavior to H$_2$S [6]. The (121) peak also suitable for detecting the CO gas as reported by Truong Giang Ho [2]. Based on this result and references indicate that Nd$_{1.2}$FeO$_3$ was a good material as a gas sensor.

The Rietveld analysis using Rietica software had refinement results of the lattice parameters for each sample. Lattice parameters for samples with annealed time varied for 1 h, 2 h, and 3 h has value is $a = 5.58 \text{ Å}$, $b = 7.76 \text{ Å}$, $c = 5.45 \text{ Å}$, this similar as reported [10]. The average Goodness of Fit (GoF) for samples was 0.91%, profile (Rp) 4.63 %, Weighted Profile (Rwp) 6.09 %, and Expected (Rexp) 6.39 %, this data indicates a good agreement within the experiment result and database calculation as reported elsewhere [18].

Phase analysis using Match software obtaining two phases that contain each Nd$_{1.2}$FeO$_3$ oxide materials as a variation of annealing time. There is was observed in Figure 1, peak with attribute circle correspond to Nd$_2$O$_3$ and diamond to Nd$_{1.2}$FeO$_3$. The samples suspected were not completely reacted and did not form a single phase of NdFeO$_3$ oxide material. Increasing intensity of peak Nd$_{1.2}$FeO$_3$ (121) would be accompanied by the decreased intensity of peak Nd$_2$O$_3$ (011) as confirmed in Figure 2. It was mean that Nd$_2$O$_3$ as a raw material was not perfectly reacted Fe$_2$O$_3$ to form NdFeO$_3$ sintered at 950 °C and annealed time varied at 1 h, 2 h, and 3 h. The suggestion it was needed a higher temperature and longer time to heat treatment process to form perfect Nd$_{1.2}$FeO$_3$ phase. Figure 2 was shown sample was annealed time to 2 h has higher ratio intensity between Nd$_{1.2}$FeO$_3$ (121) and Nd$_2$O$_3$ (011).

Figure 2. Curve comparison relative intensity of Nd$_{1.2}$FeO$_3$ (121) and Nd$_2$O$_3$ (011) for each variation of annealing time

The crystallite size of oxide material was calculated by Debye Scherer’s formula, which is given as:

$$D = \frac{0.94 \lambda}{\beta_{hkl} \cos \theta}$$ (1)

where $D$ is the crystallite size, $\beta_{hkl}$ is the full width at half maximum (FWHM) intensity value, $\theta$ is the diffraction angle, and $\lambda$ represents the x-ray wavelength. The crystallite size of Nd$_{1.2}$FeO$_3$ was shown in...
Table 1. Based on the result as was described in Table 1, phase and crystallite size have similar than previous research [16].

| Annealing time (h) | 2θ (°)  | FWHM (°) | Crystallite Size (nm) |
|-------------------|---------|----------|----------------------|
| 1                 | 32.56   | 0.22     | \[393.08 \pm 0.02\] |
| 2                 | 32.58   | 0.22     | \[393.10 \pm 0.02\] |
| 3                 | 32.58   | 0.22     | \[393.10 \pm 0.02\] |

The surface morphology, structure and particle size of the samples were investigated by SEM. Figure 3 was shown the SEM micrograph of the samples at 5000 magnification. SEM micrograph showed that morphology of samples was homogeneous grain orientation and grain size with an estimated size was 0.2 μm. It can be seen, a variation of annealing time as a parameter process has obtained nanostructure with uniform in both morphology and particle size. This result confirms that annealing time at 2 h has more homogeneous morphology [17].

**Figure 3.** SEM micrograph of Nd$_{1.2}$FeO$_3$ as variation of annealing t of (a) 1 h, (b) 2 h, and (c) 3 h, respectively.

EDS analysis results are given in Table 2. The results showed the existence of iron and neodymium as a dominant element. In addition, it can be seen the percentage value the presence of another minor oxide in each sample due to the sample holder.
Table 2. EDS analysis of Nd$_{1.2}$FeO$_3$ oxide material as variation of annealing time

| Compound | Norm. | t = 1 h | t = 2 h | t = 3 h |
|----------|-------|--------|--------|--------|
| Nd       |       | 71.44  | 67.95  | 70.77  |
| Fe       |       | 26.86  | 26.36  | 26.90  |

Based on the XRD and SEM analysis has been describing above, the variation of annealing time did not significantly affect on crystalline quality and morphology of Nd$_{1.2}$FeO$_3$ oxide material. Annealing was not a process to form a new phase, but to maintain the oxygen ion of an oxide material. Therefore annealing treatment not affect significantly the crystal structure and sample morphology, but will affect the electrical properties of the material. This phenomenon was similar to the case of YBa$_2$Cu$_3$O$_{7-\delta}$ oxide material which is annealing did not affect the crystal structure and morphology of material. Annealing affects the conductivity of the sample as corresponding to oxygen composition [14, 19, 20]. This also occurred in case of TiO$_2$ material that annealing variation affects the resistivity of the material [21].

4. Conclusions
Nd$_{1.2}$FeO$_3$ oxide material has been synthesized by solid-state reaction method with a variation of annealing time. XRD result shown the oxide has a crystal structure with the orthorhombic phase of perovskite-type with the highest peak of hkl (121) at 2θ is 32.5º. There were Nd$_{1.2}$FeO$_3$ and Nd$_2$O$_3$ phases contain in each sample. The calculation using Debye Scherer’s formula given crystallite size is 393 nm with FWHM 0.22º. SEM micrograph of the samples shown morphology was uniform grain size around 0.2 μm. Based on XRD and SEM results, a sample with annealing time for 2 h has ratio intensity of hkl (121) more dominant as an indication of the best sample in this research.

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References
[1] Pena M A and Fierro J L G 2001 Chemical Structures and Performance of Perovskite Oxides Chemical Reviews 101 1981 – 2018
[2] Ho T G et al 2011 Nanosized perovskite oxide NdFeO$_3$ as material for a carbon-monoxide catalytic gas sensor Advanced in Natural Science: Nanoscience and Nanotechnology 2 15012 – 15015
[3] Taneja S et al 1993 Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms Nuclear Instruments and Methods in Physics Research 76 127 – 129
[4] Opuchovic O et al 2015 Sol-gel synthesis, characterization and application of selected sub-microsized lanthanide (Ce, Pr, Nd, Tb) ferrites Dyes and Pigment. 118 176 – 182
[5] Tongyun C et al 2012 NdFeO$_3$ as anode material for S/O$_2$ solid oxide fuel cells Journal of Rare Earths. 30 1138 – 1141
[6] Xinshu N et al 2003 Journal of Rare Earths. 21 550 – 553
[7] Ru Z et al 2010 Electrical and CO-sensing properties of NdFe$_{1-x}$Co$_x$O$_3$ perovskite system Journal of Rare Earths. 28 591 – 595
[8] Motlagh M et al 2013 Chemical Synthesis and Characterization of Perovskite NdFeO$_3$ Nanocrystals via a Co-Precipitation Method International Journal of Nanoscience and Nanotechnology. 9 7 – 14
[9] Song G et al 2015 Spin reorientation transition process in single crystal NdFeO$_3$ Solid State Communication. 211 47 – 51
[10] Chanda S, Saha S, and Sinha T 2013 Raman spectroscopy and dielectric properties of nanoceramic NdFeO$_3$ Material Research Bulletin. 48 1688 – 1693
[11] Pikula T et al 2014 Structure and hyperfine interactions in Bi$_{1-x}$Nd$_x$FeO$_3$ solid solutions prepared by solid-state sintering Journal of Alloys and Compounds. 606 1 – 6
[12] Belessi V C et al 1999 Structure and catalytic activity of La$_{1-x}$FeO$_3$ system ($x=0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.35$) for the NO+CO reaction Applied Catalysis A : General. 177 53 – 68
[13] Eko H S 2008 Paduan oksida logam Nd1(Fe)XBa2-XCu3OY dan metode pembuatannya I. D. Patent No. P00200800471 (in Indonesia)
[14] Eko H S et al 2001 Crystal Structure and Morphology Analysis of Nd$_{1+X}$Ba$_{2−X}$Cu$_3$O$_7$ Oxide Alloy Surface Developed by Solid State Reaction Method Physica Status Solidi (A) Applied Research. 187 471 – 479
[15] Bhagavannarayana G et al 2005 A study of the effect of annealing on Fe-doped LiNbO$_3$ by HRXRD, XRT and FT–IR Journal of Applied Crystallography. 38 768 – 771
[16] Zharvan V et al 2017 The Effect of Molar Ratio on Crystal Structure and Morphology of Nd$_{1+X}$FeO$_3$ (X=0.1, 0.2, and 0.3) Oxide Alloy Material Synthesized by Solid State Reaction Method IOP Conference: Materials Science and Engineering. 202 012072
[17] Singh S et al 2013 Fabrication of nanobeads structured perovskite type neodymium iron oxide film: Its structural, optical, electrical and LPG sensing investigations Sensors and Actuators B: Chemical. 177 730 – 739
[18] Tighineanu A et al 2010 Conductivity of TiO$_2$ nanotubes: Influence of annealing time and temperature Chemical Physics Letters. 494 260 – 263
[19] Eko H S 2007 Optimization of Surface Smoothness of Nd 1.12 Ba 1.88 Cu$_3$O$_{7−δ}$ Thin Films Indonesian Journal of Physics. 18 107 – 110
[20] Eko H S, Arifin P, and Barmawi M 2002 YBa$_2$Cu$_3$O$_{7−δ}$ thin films deposited by a vertical MOCVD reactor Materials Chemistry and Physics. 73 47 – 50
[21] Shanker J, Suresh M B, and Babu D S 2015 Synthesis, Characterization and Electrical Properties of NdXO$_3$(X=Cr, Fe) Nanoparticles Materials Today: Proceedings. 3 2091 – 2100