RESEARCH ARTICLE

Effect of Nd-concentration in $Nd_{(2-x)}Fe_xO_3$ System on the Crystal Structure and Microwave Absorption Characteristics

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Effect of Nd-concentration in $Nd_{(2-x)}Fe_xO_3$ system on the structure and microwave absorption characteristics have been studied. $Nd_{(2-x)}Fe_xO_3$ system is one of perovskite based system which has a relative high permittivity. $Nd_{(2-x)}Fe_xO_3$ (x=0.5; 1.0 and 1.2) samples were synthesized by $Fe(NO_3)_3$ and $Nd(NO_3)_3$ in mole ratio using sol–gel method and then sintered at 800°C for 5 hours. All of the samples were characterized using XRD to identify the phase, SEM to observe the morphology and VNA was used to measure the microwave absorption. Phase identification of XRD data shows that single phase of $NdFeO_3$ have been formed for x = 1.0 composition (ABO_3). While multiphase have been formed which is indicated by the appearance of $NdFeO_3$ and Nd_2O_3 phase for x = 0.5, and then $NdFeO_3$ and Fe_2O_3 phase for x = 1.2. SEM image shows the samples of $Nd_{(2-x)}Fe_xO_3$ have homogenous morphology with particle size is approximately 200 nm. The results of microwave absorbing properties measured by using VNA (Vector Network Analyzer) shows the best ability of microwave absorption is x = 1.0 composition is around 96.27% at frequency of 10.46 GHz.

Introduction

The rare-earth ortho-ferrite, $REFeO_3$ (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 rare-earth (A) transition-metal (B) oxides belong to ABO_3 perovskite structure, B is usually a 3d or 4d transition metal surrounded by six oxygen atoms in octahedral coordination and A is normally a rare earth cation, 12-coordinate by oxygen atoms, have been extensively studied for many applications [**2-5**].

Specifically, perovskite oxide $NdFeO_3$ is semiconductor oxide material, they have high catalytic activities and high sensitivity so that can be used in several advanced technologies such as material for a gas sensor, solid oxide fuel cells, catalysts, chemical sensors, and electrode materials [**6-8**]. They have been the subject of intense research for variety of applications due to their unique dielectric, magnetic, magneto-electric, multiferroic and perovskites [**9**].

Based on the advantages of the properties of this material, so this research has investigated the ability of $NdFeO_3$ material to be used as a microwave absorber. Because one of the conditions that must be fulfilled as a microwave-absorbing material is that the material must have dielectric and magnetic loss. While both of these components have been owned by the perovskite oxide $NdFeO_3$ material.

$NdFeO_3$ has a significant magnetic property which has a relatively high magnetic order in Nd^{3+} at high temperature and also a clear spin reorientation in canted antiferromagnetic systems. In addition, Nd^{3+} can produce the ordered domain structure and is able to change the coupling state of electron, so as to ease polarization rotation and strong magnetic spin resonance, which in turn can increase dielectric and magnetic loss [**9**]. Some of the researchers have recently reported the ferroelectric nature of $NdFeO_3$ at room temperature. $NdFeO_3$ is known to be orthorhombically distorted perovskite structure with the *Pbnm* space group [**10,11**]. In $NdFeO_3$ there are three major magnetic interactions: Fe–Fe, Nd–Fe and Nd–Nd. These competing interactions determine their interesting structural and magnetic properties and lead to a number of applications [**12-14**]. Therefore, this material is suitable for use as a microwave absorber. Nowadays research on microwave absorbing material is very interesting to study because of its unique nature [**15-18**].

There are various methods that have been developed to prepare $NdFeO_3$ through chemical or physical route [**19**]. The synthesis of $NdFeO_3$ use sol-gel method

especially for the microwave absorber materials application are rarely reported until now. In the present study, we try to investigate the effects of Nd-ion concentration on structure and microwave absorption ability of $Nd_{(2-x)}Fe_xO_3$ system.

Experimental

The raw materials were $Nd(NO_3)_3.xH_2O$ (Sigma-Aldrich), $Fe(NO_3)_3.9H_2O$ (Sigma-Aldrich), Polyethylene glycol (Merck), NH_4OH and aquadest. The mixture between Nd $(NO_3)_3.xH_2O$ and $Fe(NO_3)_3.9H_2O$ was weighed based on mole ratio in accordance with the stoichiometry of $Nd_{(2-x)}Fe_xO_3$ (x = 0.5; 1.0; 1.2 in mol%) were dissolved in 20 ml of ethylene glycol at room temperature and the solution was heated at 80°C and then added with 1M NH_4OH solution (up to pH 7) to form a wet gel. After that the gel was dried at 120°C to form $Nd_{(2-x)}Fe_xO_3$ powder. The powder obtained was sintered at of 800°C for 5h [**20**]. The chemical reaction of $Nd_{(2-x)}Fe_xO_3$ is shown as follows:

$$(2\text{-}x)\ Nd(NO_3)_3 + xFe(NO_3)_3 + (CH_2OH)_n \longrightarrow Nd_{(2-x)}Fe_xO_3 \quad (1)$$

All of the $Nd_{(2-x)}Fe_xO_3$ samples (x = 0.5; 1.0; 1.2) were characterized by using XRD Pan Analytical to confirm the phase formation and refined by GSAS software and SEM (JEOL JSM-6510LA) to observe the particle morphology. Meanwhile VNA (Vector Network Analyzer) brand Advantest type R3770 300 kHz-20 GHz was used to measure the value of reflection loss (dB) of the samples with adapter wave guide X-band (WR95) and the measurement taken involved two-port configuration system.

Results and discussion

Diffraction patterns of all the $Nd_{(2-x)}Fe_xO_3$ samples (x = 0.5; 1.0 and 1.2) which have been synthesized by sol – gel methods is shown in **Fig. 1**. In the composition of x = 1.0 ($NdFeO_3$) has been formed a single phase of neodymium ortho-ferrite ($NdFeO_3$), which had an orthorhombic structure with lattice parameters = 0.5576 nm, b = 0.7756 nm, c = 0.5447 nm (space group *Pnma*). The XRD analysis shows only the pattern corresponding to perovskite type $NdFeO_3$ (JCPDS File no. 25-1149) which crystallizes in the orthorhombic system with a main diffraction peak at 2θ = 32.55° (121) plane.

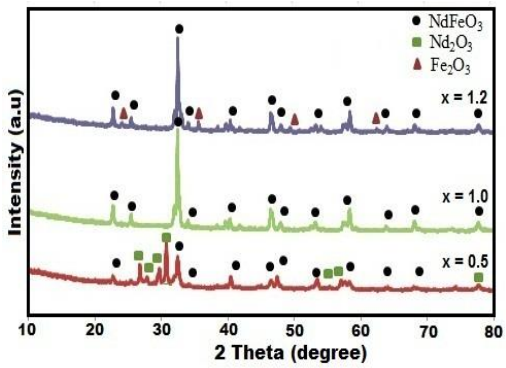
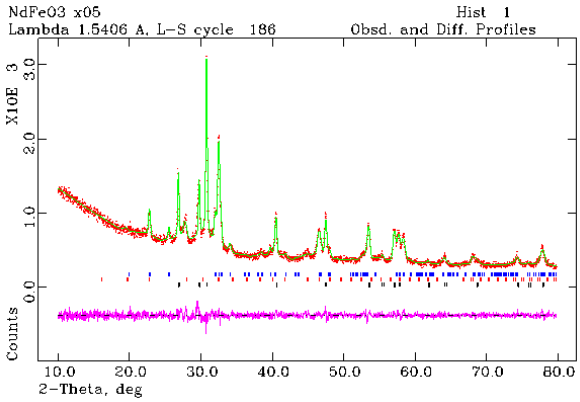
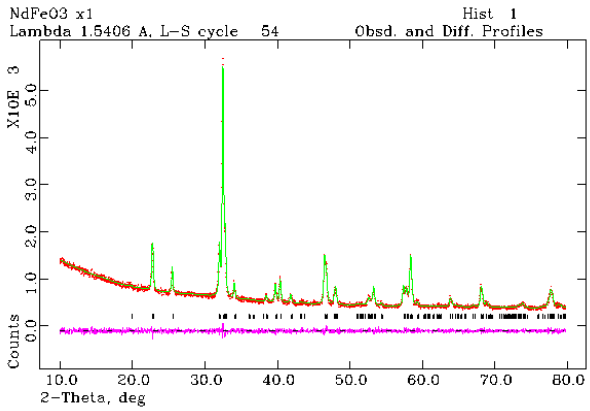


Fig. 1. X-ray diffraction pattern of the $Nd_{2-x}Fe_xO_3$ samples (x =0.5; 1.0 and 1.2).

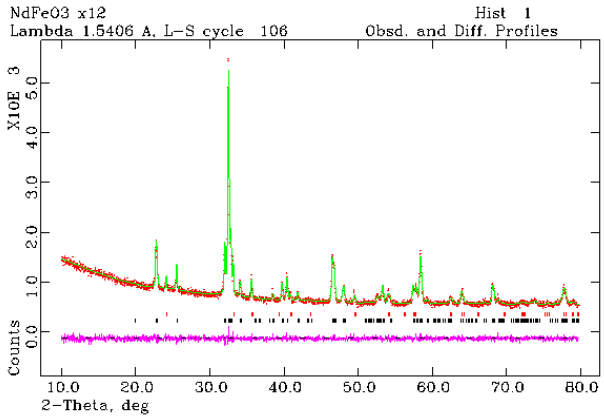
All refinement results were analyzed by using GSAS (General Structure Analysis System) which is based on the rietveld method for fitting all of the diffraction patterns of $Nd_{(2-x)}Fe_xO_3$ samples, as shown in **Fig. 2**. It was also supported by several diffraction peaks which also correspond to crystal plane of $NdFeO_3$ the peaks at 22.82° (101), 25.50° (111), 32.04° (200), 40.38° (022), 46.53° (202), 47.94° (230), 57.40° (321), 58.36° (042), 68.14° (242), and 77.69° (323). The phase identification of $NdFeO_3$ referred to Wang [**21**].



(a) x = 0.5



(b) x = 1.0



(c) x = 1.2

Fig. 2. Refinement of XRD pattern of the $Nd_{(2-x)}Fe_xO_3$ samples (x =0.5; 1.0 and 1.2).

The result of the phase identification for the composition of x = 0.5 and 1.2 indicate the presence of two main diffraction peaks. In the composition of x = 0.5 show that main diffraction peaks at 2θ = 30.77° and 32.55°, which corresponding to the $NdFeO_3$ (22.06%) and Nd_2O_3 (77.94%) phases. Nd_2O_3 phase has an orthorhombic structure with a main diffraction peak at 2θ = 30.77° that correspond to the (011) crystal plane.

While composition of x = 1.2 shows that main diffraction peak at 2θ = 32.55° and 36.36°, which corresponding to the $NdFeO_3$ (81.88%) and Fe_2O_3 (18.12%) phases. Fe_2O_3 phase has a trigonal structure with a main diffraction peak at 2θ = 36.36° that correspond to the (110) crystal plane.

Table 1. Structure parameters, criteria (R factor) and goodness of fit (S) of $Nd_{(2-x)}Fe_xO_3$ (x = 0.5; 1.0 and 1.2) samples.

Composition	x = 0.5		x = 1.0	x = 1.2	
Phase	$NdFeO_3$	Nd_2O_3	$NdFeO_3$	$NdFeO_3$	Fe_2O_3
Crystal structure	Ortho-rombic	Hexagonal	Ortho-rombic	Ortho-rombic	Hexagonal
Space group	Pbnm	P63/mmc	Pbnm	Pbnm	R-3c
Lattice parameter (Å)	a=5.5786 b=7.7538 c=5.4466 α=β=γ=90°	a=3.6579 b=7.7538 c=11.7992 α=β=90° γ=120°	a=5.5765 b=7.7539 c=5.4460 α=β=γ=90°	a=5.5763 b=7.7526 c=5.4451 α=β=γ=90°	a=5.0280 b=7.7538 c=13.7320 α=β=90° γ=120°
V ($Å^3$)	235.594	136.725	235.397	235.482	300.917
ρ ($gr.cm^{-3}$)	6.971	7.012	6.998	6.994	5.284
Fraction (wt%)	77.94	22.06	100	81.88	18.12
χ^2	1.218		1.152	1.242	
Rwp	0.0540		0.0412	0.0393	

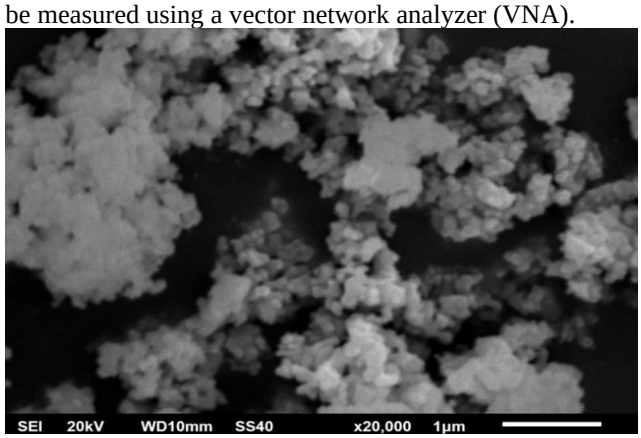
The XRD refinement results of the $Nd_{(2-x)}Fe_xO_3$ samples were analysed by using GSAS software (general structure analysis system) which is based on the Rietveld method for fitting all of diffraction patterns of the samples. As shown in **Table 1**, the refinement results have an excellent fitting quality with a very small R_{wp} factor. The R_{wp} factor is the criteria of fit and the S factor is the goodness of fit which is of very small value, and according to Izumi the value of S or χ^2 *(chi-squared)* is allowed to maximum 1.3 [**22**].

Based on **Fig. 3**, it can be seen that all of the samples had homogenous morphology with relatively uniform spherical. The particle size of the samples was about 200 nm. These powders are homogeny and nanoparticle size, and this was an advantage for the absorber materials. SEM investigated the morphology, structure and particle size of the $Nd_{(2-x)}Fe_xO_3$ samples with variations of molar ratio. **Fig. 3** shows the SEM image of the $Nd_{(2-x)}Fe_xO_3$ samples (x = 0.5; 1.0 and 1.2).

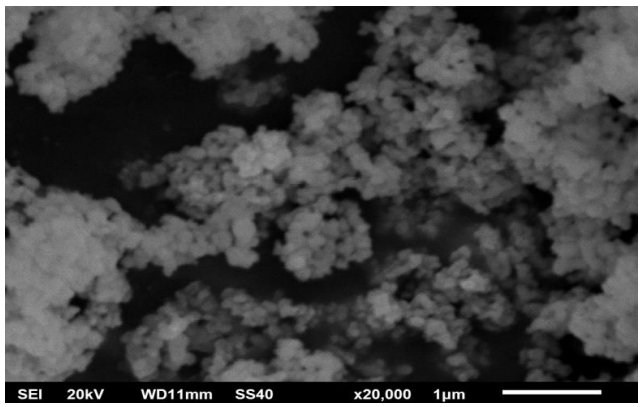
According to theory about the microwave absorption can be calculated by reflection loss of electromagnetic radiation of a single layer material as below equation [**23**];

$$RL\ (dB) = 20\ log\left|\frac{(Zin-Zo)}{(Zin+Zo)}\right|$$

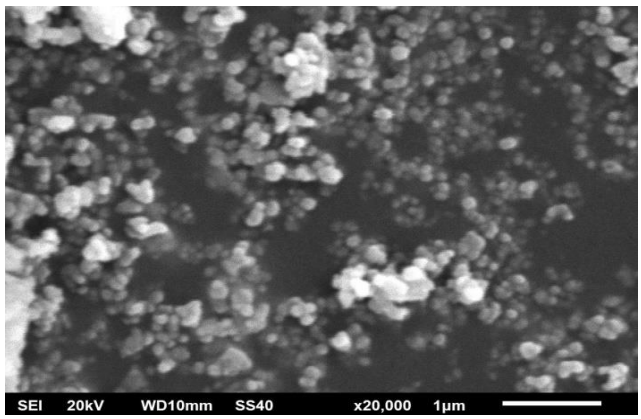
where Z_{in} is the material impedance, Z_o is the intrinsic impedance of vacuum. While experimentally the RL can be measured using a vector network analyzer (VNA).



(a) x = 0.5



(b) x = 1.0



(c) x = 1.2

Fig. 3. SEM image of the $Nd_{(2-x)}Fe_xO_3$ samples (x = 0.5; 1.0 and 1.2).

Fig. 4 shows the microwaves absorption of the sample $Nd_{(2-x)}Fe_xO_3$ synthesized by the sol-gel method were measured by VNA in the frequency range 9.0 to 12 GHz (X-band) in the form of reflection loss curves (RL). While the absorption parameters are shown in **Table 2**.

Reflection loss indicates resonance mechanism between spin magnetic of the electromagnetic wave with material causing microwave absorption. The depth of the reflection loss actually depends to some specific

frequency, the thickness of the material, permittivity and permeability value is very high, and microstructure of materials is homogeny of nanoparticle size [**24**].

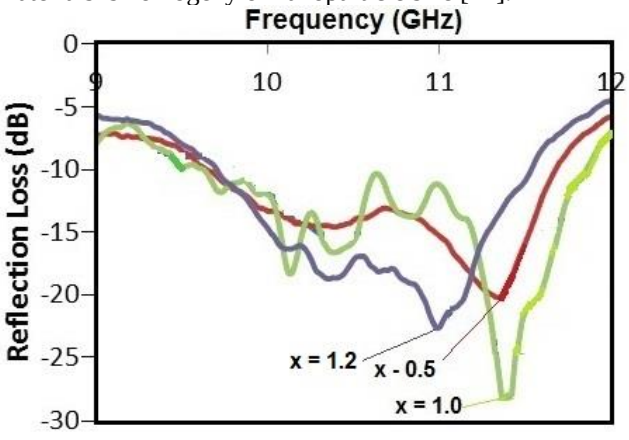


Fig. 4. Reflection loss curva of the $Nd_{(2-x)}Fe_xO_3$.

In addition, **Fig. 4** shows too that the $Nd_{(2-x)}Fe_xO_3$ samples with a composition of x = 0.5 and 1.2 has the lower of reflection loss value than x = 1, it is caused by mass fraction of the $NdFeO_3$ phase (Table 1) for both the samples (x = 0.5 and 1.2) decrease respective 77.94 and 81.88 wt%.

Table 2. The reflection loss value for all variation of the $Nd_{(2-x)}Fe_xO_3$ samples (x = 0.5; 1.0 and 1.2).

x values	Frequency (GHz)	RL (dB)	Microwave absorption (%)
0.5	11.2	-22.0	92.0
1.0	11.4	-28.1	96.07
1.2	11.0	-23.6	93.29

Conclusion

$Nd_{(2-x)}Fe_xO_3$ system with (x = 0.5; 1.0 and 1.2) have been synthesized by using sol-gel methods, and then characterized by using XRD pattern shows that single phase of $NdFeO_3$ has been formed at the composition of x = 1.0. Meanwhile multiphase has been formed at the composition of x = 0.5 which indicated by the appearance of $NdFeO_3$ and Fe_2O_3 phases, and then $NdFeO_3$ and Nd_2O_3 phase at the composition of x = 1.2. All of the samples have homogenous morphology with relatively uniform spherical with the particle size of the samples is about 200 nm. The measurement results of microwaves absorption show that the samples with the composition of x = 1.0 gives a maximum value up to -28 dB. It means that the sample with the composition of x = 1.0 able to absorb microwaves up to 96.27% at a frequency of 11.46 GHz. Thus, the composition of $Nd_{(2-x)}Fe_xO_3$ (x = 1.0) shows a prominent results to be applied as a main compound of absorbing materials.

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Conflicts of interest

The authors whose names are listed state that they have no conflicts to declare.

Keywords

$Nd_{(2-x)}Fe_xO_3$ system, perovskite system, sol-gel method, microwave absorption.

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