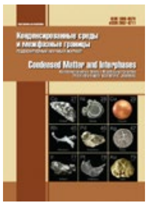

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Optical and magnetic properties of orthoferrite $NdFeO_3$ nanomaterials synthesized by simple co-precipitation method

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Abstract

In this work, orthoferrite $NdFeO_3$ nanomaterials with particle sizes 20-40 nm have been successfully synthesized via a simple co-precipitation method through the hydrolysis of Nd (III) and Fe (III) cations in hot water with 5% NaOH as a precipitating agent. Single-phase $NdFeO_3$ was generated after calcination of the as-prepared powder at 700, 800, and 900 °C for 1 hour. The UV-Vis spectra at room temperature presented strong absorption in the UV-Vis regions (λ = 200–400 nm and 400–600 nm) with small band gap energy (E_g = 2.2÷2.5 eV). The obtained $NdFeO_3$ nanomaterials exhibited a hard ferromagnetic behavior with high coercivity (H_c = 600–1600 Oe).

Keywords: $NdFeO_3$, Nanomaterial, Co-precipitation, Optical and Magnetic properties

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1. Introduction

The characteristic structure and properties of nanomaterials in general, and $RFeO_3$ rare-earth orthoferrite nanomaterials in particular, depend on several different factors such as particle size and morphology, crystal size, the distribution of the cations in the crystal lattice, the content of doping elements and also the preparation method [1–5]. Nano-sized rare earth orthoferrites $RFeO_3$ (R = La, Y, Nd, Pr, Ho, ...) have been studied and applied in many fields such as photocatalysis for the decomposition of toxic organic waste [6–7], electrodes for solid oxide fuel cells [8], gas sensor materials [9], photomagnetic and electromagnetic devices [10–11], etc. The rare earth orthoferrites $NdFeO_3$ is amongst the materials of interest to research. The structural and optical properties, magnetic properties or electrical properties of orthoferrite neodymium were previously studies [12–15], showing promising for application in As (V) adsorption [16].

$NdFeO_3$ nanomaterials have been synthesized by various methods such as high-temperature mechanosynthesis [14–15], sol-gel or gel-combustion [16, 17–18], hydrothermal or co-precipitation with surfactants [12–13]. In our previous report [19], based on the thermal behavior of the hydroxides of Fe (III), Nd (III) and their mixture (molar ratio Fe^{3+}/Nd^{3+} = 1/1), the appropriate annealing temperature for the formation of single phase perovskite was determined and $NdFeO_3$ nano particles of < 50 nm were synthesized by co-precipitation method (without any surfactant). By this simple co-precipitation method, our group has successfully prepared a series of rare earth orthoferrite such as $PrFeO_3$ [20], $HoFeO_3$ [21–22], [$LaFeO_3$ [23] or [$YFeO_3$ [24–25] and studied their structural and optical, magnetic properties. However, in [19], the optical and magnetic properties of $NdFeO_3$ nano materials have yet to be reported.

Follow-up to the work in [19], the aim of this paper is to study the characteristic optical and magnetic properties of $NdFeO_3$ orthoferrite nanomaterial synthesized by simple co-precipitation method without any surfactants.

2. Experimental and methods

$NdFeO_3$ orthoferrite nano powder was prepared by co-precipitation method according to [19]. 50 mL aqueous solution of the mixture of two salts $Nd(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ (molar ratio of 1/1) was added dropwise to 400 mL boiling water on a stirring hot plate (t° > 95 °C), resulting in a reddish-brown sol. Slowly adding the solution of Fe (III) and Nd (III) salts into water at high temperature helped speed up the hydrolysis of metal cations and restrict the particle size of resulting $NdFeO_3$ particles, as proven previously for the synthesis of $HoFeO_3$ and $YFeO_3$ nano orthoferrite [22, 24]. Next, NaOH 5% solution was added dropwise to the system until all the cations Nd^{3+} and Fe^{3+} were completely precipitated (phenolphthalein paper turned pink). The obtained mixture was kept stirring for another 60 minutes, settled for 20 minutes, then vacuum filtered and washed with water until pH ~ 7.0. After drying at room temperature (for 5–7 days), the precipitate was ground with porcelain mortar and pestle into a yellowish-brown fine powder (precursor for $NdFeO_3$). The precursor was then annealed at 700, 800 or 900 °C for 1h to study the formation of single phase orthorhombic $NdFeO_3$.

Powder X-ray diffraction analysis (PXRD) of the $NdFeO_3$ samples was carried out using a D8-ADVANCE X-ray diffractometer (Bruker, Bremen, Germany) with CuK_α radiation, λ = 0.154184 nm, angle range of 2θ = 10–80°, and scan rate of 0.02 °/s. Average crystal size (D_{XRD}, nm) of the $Nd_{1-x}Sr_xFeO_3$ samples was calculated by Debye-Scherrer formula, lattice parameters (a, b, c, V) were calculated according to [13]. The morphology of the samples was determined by transmission electron microscopy (TEM) using a Joel JEM-1400 microscope (Jeol Ldt., Tokyo, Japan).

The UV-Vis absorption spectra of the $NdFeO_3$ nanomaterials were studied on a UV-Visible spectrophotometer (UV-Vis, JASCO V-550, Japan). The optical energy gap (E_g, eV) of the samples was calculated according to [22]. Magnetic characteristics of nanopowders, including the coercive force (H_c, Oe), remanent magnetization (M_r, emu·g^{-1}) and saturation magnetization (M_s, emu·g^{-1}), were investigated at room temperature using a vibrating magnetometer (VSM, MICROSENE EV 11, Japan) with a maximum magnetic field of ± 20 kOe.

3. Results and discussion

Fig. 1 shows the PXRD patterns of the precursor for $NdFeO_3$ nano orthoferrite after annealed at 700, 800 or 900 °C for 1 hour. All three samples exhibited single phase $NdFeO_3$ orthoferrite with orthorhombic structure, Pbnm (62) space group.

The observable peaks match well with the standard pattern of $NdFeO_3$ (JCPDS: 01-074-1473). When the annealing temperature increased, the degree of crystallinity (I, a.u), lattice cell volume (V, Å^3) and average $NdFeO_3$ crystal size according to Debye–Scherrer formula also increased (Table 1).

The morphology of the material $NdFeO_3$ after annealing at 800 °C for 1h was studied by transmission electron microscopy (Fig. 2), showing particles with the size varying from 20-40 nm and clear boundaries. However, the aggregation was significant because the attraction between those magnetic particles inhibited the scattering of the samples for TEM study.

The UV-Vis spectra at room temperature of the $NdFeO_3$ materials annealed at different temperatures (700, 800 or 900 °C for 1h) show strong absorption in the UV (~ 200-400 nm) and visible regions (~ 400-600 nm) (Fig. 3a). In the UV range, the absorption of the materials tends to decrease when rising the annealing temperature (increment of crystal size). However, there were no remarkable variations in the absorption in

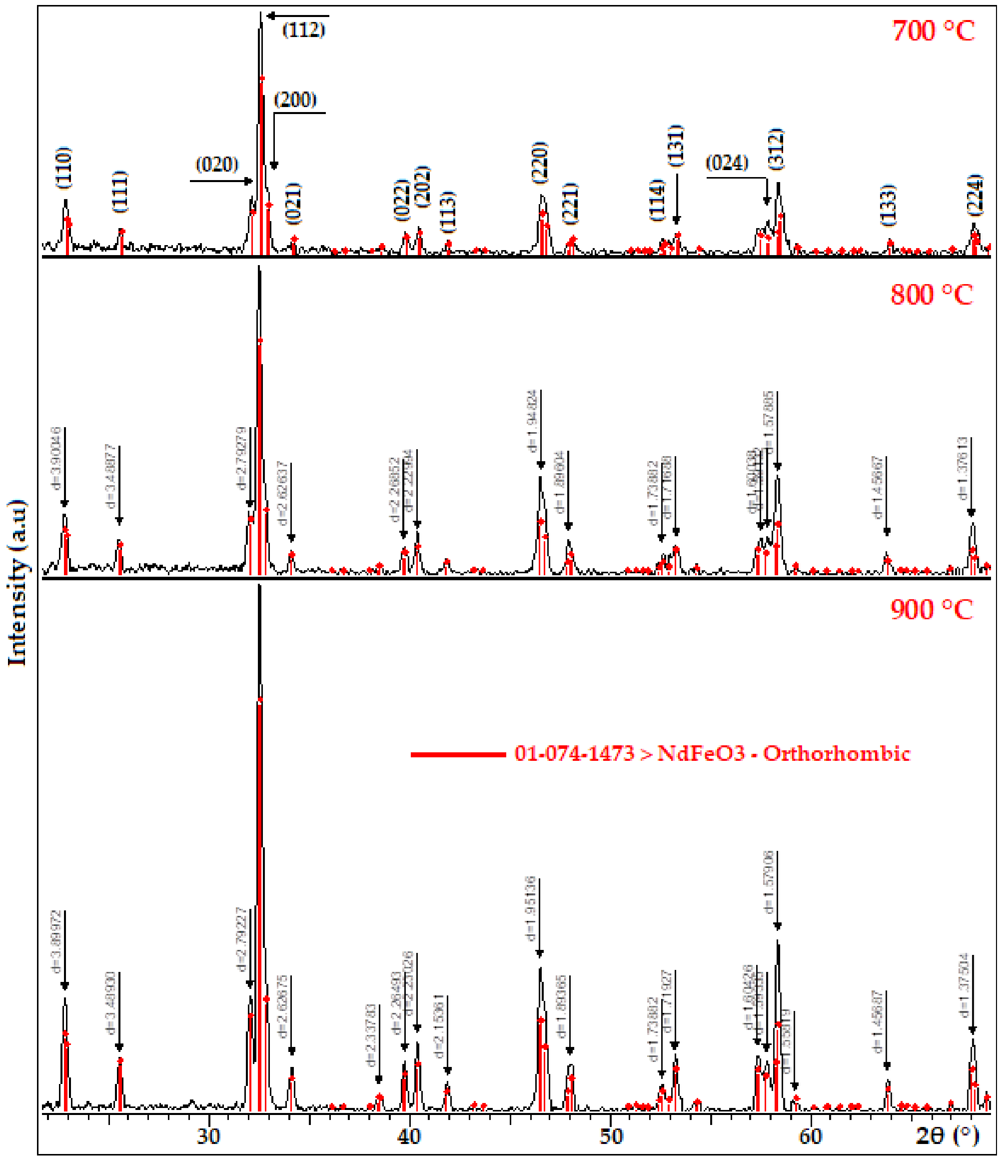

Fig. 1. XRD patterns of $NdFeO_3$ formed at 700, 800 and 900 °C for 1h

Table 1. Structural characteristics of crystalline $NdFeO_3$ nanoparticles annealed at 700, 800 and 900 °C for 1 h

$NdFeO_3$	I, (a.u.)	d, (Å)	*D*, (nm)	Lattice constants, (Å)			V, Å³
				a	*b*	c	
700 °C	120.29	2.75320	24.41	5.4417	5.6747	7.7727	240.02
800 °C	157.82	2.75322	25.37	5.4522	5.6827	7.7967	241.57
900 °C	269.33	2.75210	29.13	5.4573	5.6963	7.8154	242.95

the visible region for $NdFeO_3$ nanomaterials with different annealing temperature, thus showing the stability of the absorption of the materials at the wave length of λ ~ 750 nm. This can be originated from the minor amount of $NdFeO_3$ hexagonal phase (h-$NdFeO_3$) which has very indistinguishable PXRD peaks from those of orthorhombic phase (o-$NdFeO_3$). The increase in the absorption of the hexagonal phase in the visible region was also reported previously for the materials containing the o-$YbFeO_3$/h-$YbFeO_3$ mixture [26]. The existence of o-$NdFeO_3$ and h-$NdFeO_3$ in the samples is in good consistence with the band gap values (E_g, eV) showing in Fig. 3b. The band gap of $NdFeO_3$ nanomaterials varied from 2.2 eV to 2.5 eV (Table 2), remarkably lower than that of $NdFeO_3$ orthoferrite in earlier work [26] with E_g = 4.3 eV and $HoFeO_3$ with E_g = 3.39 eV) [11] prepared by solid-state reaction method. The E_g value of $NdFeO_3$ nanomaterials in this work is comparable with $HoFeO_3$ orthoferrite (E_g = 2.1–2.6 eV) in our previous study [22]. This low band gap of $NdFeO_3$ nanomaterials is favorable for the application as photocatalysts to decompose toxic organic substances for environmental remediation [6–7, 21, 27].

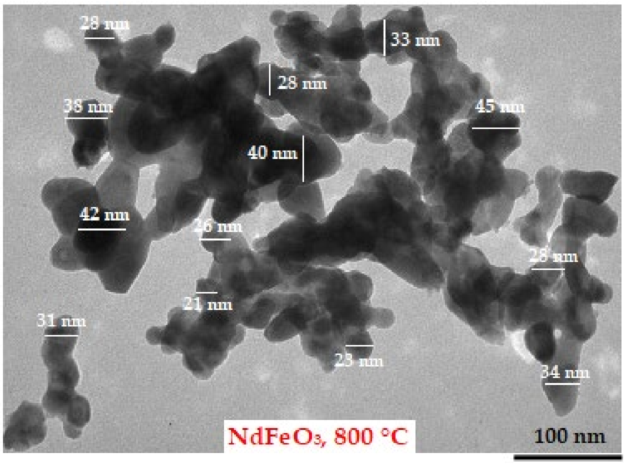

Fig. 2. TEM image of the $NdFeO_3$ nanoparticles annealed at 800 °C for 1 h

From the *M-H* curves at room temperature (300 K) of the $YFeO_3$ samples annealed at 700, 800 and 900 °C, saturation magnetization

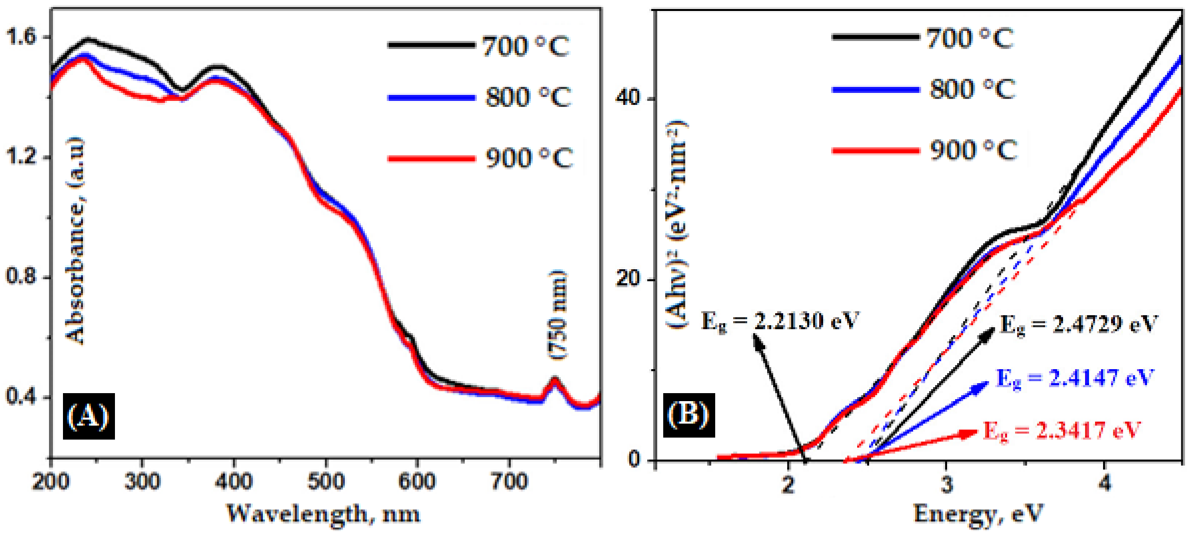

Fig. 3. (A) Room-temperature optical absorbance spectrum of the $NdFeO_3$ samples; (B) Tauc plot of $(Ah\nu)^2$ as a function of photon energy for $NdFeO_3$ nanoparticles annealed at 700, 800 and 900 °C for 1 h

Table 2. Optical and magnetic characteristics of $NdFeO_3$ nanoparticles annealed at 700, 800 and 900 °C for 1 h

Samples	E_g, (eV)	H_c, (Oe)	M_r, emu·g^{-1}	M_s, emu·g^{-1}
$NdFeO_3$, 700 °C	2.2130–2.4729	1620.66	$7.7 \cdot 10^{-2}$	0.81
$NdFeO_3$, 800 °C	2.2130–2.4147	1453.30	$7.5 \cdot 10^{-2}$	1.01
$NdFeO_3$, 900 °C	2.2130–2.3417	590.17	$4.9 \cdot 10^{-2}$	1.47

(M_s) continued increasing in the magnetic field H = ± 20000 Oe (the saturation was not reached). When the annealing temperature increased, the coercivity (H_c, Oe) and remanent magnetization (M_r, emu·g^{-1}) decreased, while he saturation magnetization (M_s, emu·g^{-1}) increased (Table 2). As the annealing temperature rose, the crystallinity of the materials also increased, the crystals became more stable, and thus the crystal anisotropy decrease, resulting in a drop in the value of M_r and H_c and an increment in M_s [28–29]. With a high coercivity (H_c >> 100 Oe), the obtained $NdFeO_3$ orthoferrite nanomaterials can be classified as hard magnetic materials that can be applied for the manufacture of permanent magnet or magnetic tape.

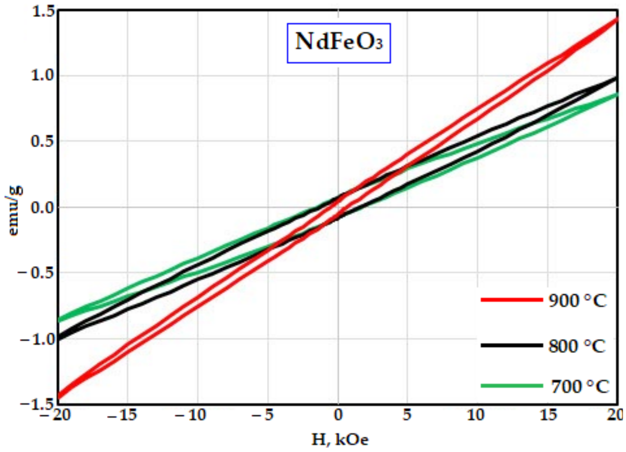

Fig. 4. Room-temperature magnetic hysteresis loops of as-prepared $NdFeO_3$ nanoparticles annealed at 700, 800 and 900 °C for 1h

4. Conclusions

$NdFeO_3$ orthoferrite nanomaterials were successfully synthesized by simple co-precipitation method via the hydrolysis of neodymium (III) and iron (III) cations in boiling water. Single-phase $NdFeO_3$ can be obtained after annealing the precursor at 700, 800 or 900 °C for 1h, having the crystal size of 25–30 nm, particle size of 20–40 nm and lattice cell volume of 240–243 Å^3. The synthesized $NdFeO_3$ nanomaterials exhibited low band gap value (2.2–2.5 eV), and hard magnetic properties with high coercivity (H_c ≫ 100 Oe), thus have great potential in photocatalysis for the decomposition of toxic organic waste and can be recovered easily by rare-earth magnetics.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors maintain that they have no conflict of interest to be described in this communication.

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