

## Synthesis and characterization of nano-structured perovskite type neodymium orthoferrite NdFeO<sub>3</sub>

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### ABSTRACT

In this investigation, neodymium orthoferrite (NdFeO<sub>3</sub>) nanoparticles has been synthesized through ultrasonic method in the presence of octanoic acid as surfactant. This method comparing to the other methods is very fast and it does not need high temperatures during the reaction. The spherical NdFeO<sub>3</sub> nanoparticles with an average particles size of about 40 nm can be obtained at a relatively high calcination temperature of 800 °C for 4 h. Also, product obtained by this method are uniform in both morphology and particles size. The phase composition, morphology, lattice parameters and size of particles in these product are characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX). The XRD analysis reveals only the pattern corresponding to perovskite type NdFeO<sub>3</sub> which crystallizes in the orthorhombic structure. Energy dispersive X-ray analysis confirms the elemental compositions of the synthesized material.

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## 1. Introduction

In the last two decades, the preparation and characterization of nanoparticles and nano-structured materials of various chemical compositions, structures, and morphologies has become a topic area in inorganic materials research.<sup>1</sup> These issues have emerged in the context of the development of nanotechnologies for manufacturing nanopowders, nanocomposites, and other nanomaterials for structural and functional applications.<sup>2</sup> The rare-earth orthoferrites, having perovskite structure of general formula RFeO<sub>3</sub> (where R is a rare-earth ion) have attracted much interest due to their novel magnetic<sup>3</sup> and magneto-optic<sup>4</sup> properties and are still the subject of much research aimed at a better understanding of properties of the magnetic subsystems and how interactions between them depend on external parameters, such as temperature, field, pressure, etc..<sup>3,4</sup> Among them, NdFeO<sub>3</sub> is known to be orthorhombically distorted perovskite structure.<sup>5</sup> These oxides have potential for various applications such as catalysts,<sup>6</sup> gas separators, solid oxide fuel cells (SOFCs)<sup>7</sup> sensor and magneto-optic materials.<sup>8</sup> The preparation of NdFeO<sub>3</sub> and related compounds has been achieved by many methods, including a

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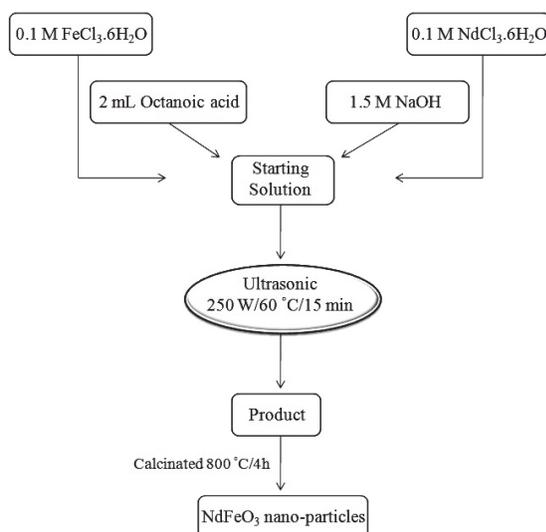
high temperature ceramic method, hydrothermal synthesis,<sup>9</sup> combustion synthesis,<sup>10</sup> sol-gel,<sup>2</sup> and precipitation.<sup>11</sup>

Nano-structured materials have been prepared by a variety of synthetic methods, including gas phase techniques, liquid phase methods, and mixed phase approaches. Among a variety of approaches, the utilization of ultrasound has been extensively examined over many years.<sup>12</sup> Sonochemical method can lead to homogeneous nucleation and a substantial reduction in crystallization time compared with conventional oven heating when nano-materials are prepared.<sup>13</sup> Many researchers have investigated the effect of ultrasound on chemical reactions, and most theories imply that the physical or chemical effects of ultrasound originate from acoustic cavitation within collapsing bubbles, which generates extremely localized hot spots having pressures of about 1000 bar, temperature of roughly 5000 K, and heating and cooling rates of about  $10^{10}$  Ks<sup>-1</sup>. Between the microbubble and the bulk solution, the interfacial region around the bubble has very large gradients of pressure, temperature, and the rapid motion of molecules leading to the production of excited states, bond breakage, the formation of free radicals, mechanical shocks, and high shear gradients.<sup>14</sup> These extreme conditions permit access to a range of chemical reaction space normally not accessible, which allows for the synthesis of nano-structured materials.<sup>15-18</sup>

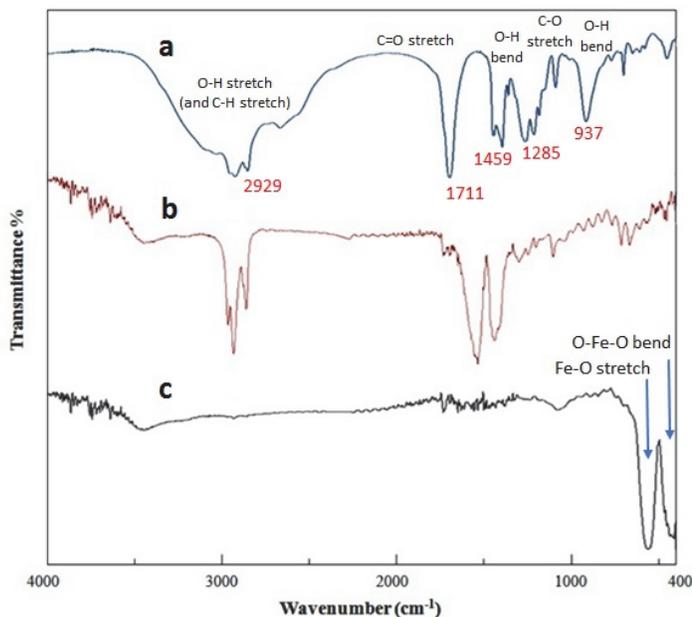
In this work, a simple and rapid method was developed for preparation of NdFeO<sub>3</sub> nanoparticles by ultrasound method in the presence of octanoic acid as organic surfactant. The crystalline phase with perovskite structure can be obtained by calcining the precursor at 800 °C. This method comparing to the other methods which have been used for preparing the NdFeO<sub>3</sub> is very fast and it does not need high temperatures during the reactions, and the other advantage of using ultrasound radiation is that it yields smaller particles.

## 2- Results and Discussion

Scheme 1 gives an overview of the method used for the preparation of nano-structured perovskite type orthoferrite neodymium. The FT-IR spectra of organic surfactant, the product before and after calcination in the frequency range from 4000 to 400 cm<sup>-1</sup>, are compared in Fig. 1.



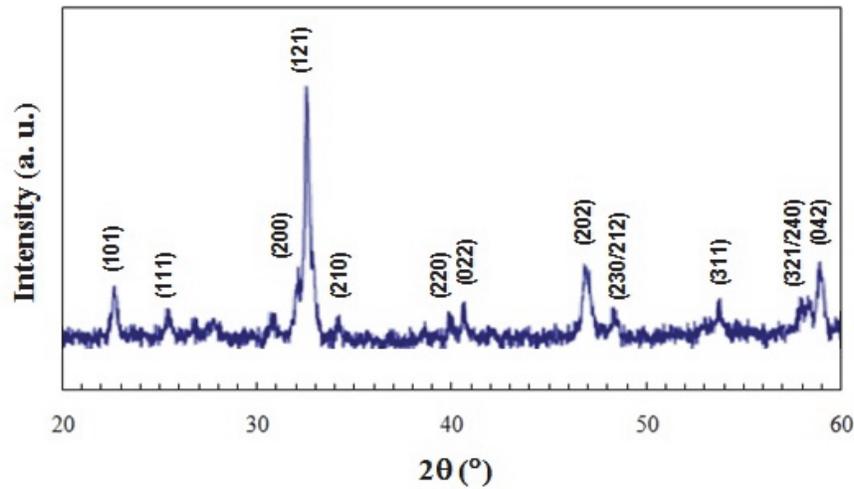
**Scheme 1.** The preparation of nano-structured perovskite type, NdFeO<sub>3</sub>.



**Fig. 1.** FT-IR spectra of (a) octanoic acid, (b) product before and (c) after calcination.

In FT-IR spectrum of pure organic surfactant, octanoic acid, the very broad feature from 3500 to 2500  $\text{cm}^{-1}$  is due to a very broad O–H stretch of the carboxylic acid.<sup>19</sup> The sharp bands at 2929 and 2857  $\text{cm}^{-1}$  are assigned to the asymmetric and symmetric  $\text{CH}_2$  stretch, respectively. The intense carbonyl stretch at 1711  $\text{cm}^{-1}$  is derived from the C=O of octanoic acid carbonyl. The stretch at 1285  $\text{cm}^{-1}$  is assigned to a C–O stretch. The O–H in-plane and out-of-plane bands appear at 1459 and 937  $\text{cm}^{-1}$ , respectively.<sup>19</sup> In the FT-IR spectrum of product before calcination, the characteristic bands of surfactant are shown to be shifted to a lower frequency region relative to free surfactant. The O–H in-plane appears at 1450  $\text{cm}^{-1}$ . The intense carbonyl stretch in free surfactant becomes weak in the product and shifted slightly to a lower frequency. In addition, the broad band in the range of 3600–3200  $\text{cm}^{-1}$  is due to  $\nu(\text{OH})$  of lattice water molecules. The results of FT-IR measurements indicate that there is an interaction between octanoic acid chain and the particles and the surface of the particles was partially covered with the organic ligands.<sup>20</sup> As can be seen from **Figure 1c**, all above bands were disappeared when the product was calcinated. We can see after calcination, the characteristic bands of OH groups disappeared and only strong bands due to the perovskite oxide appeared. In the FT-IR spectrum of the product after calcination, there are two strong absorption bands at about 572 and 424  $\text{cm}^{-1}$  which correspond to Fe–O stretching vibration and O–Fe–O bending vibration of perovskite  $\text{NdFeO}_3$ , respectively.<sup>21</sup> This finding proves the formation of the perovskite  $\text{NdFeO}_3$  and is in accordance with the XRD data.

X-ray diffraction pattern of the synthesized powder  $\text{NdFeO}_3$  were shown in **Figure 2** and confirms the formation of  $\text{NdFeO}_3$  nanoparticles. The XRD analysis shows only the pattern corresponding to perovskite type  $\text{NdFeO}_3$  (JCPDS File no. 25-1149) which crystallizes in the orthorhombic system with a main diffraction peak at  $d = 2.750 \text{ \AA}$  ((1 2 1) plane). The Miller indices are indexed at each diffraction peaks. No peaks attributable to  $\text{Nd}_2\text{O}_3$  and/or  $\text{Fe}_2\text{O}_3$  were observed and the compound was completely decomposed to single-phase  $\text{NdFeO}_3$ . The sharpening of the peaks is due to the improved crystallinity of the nanoparticles and no characteristic peaks of impurities are detected in the XRD pattern. The broadening of the peaks indicates that the particles were of nanometer scale.



**Fig. 2.** XRD pattern of NdFeO<sub>3</sub> nanoparticles

The lattice parameters and cell volume were calculated by Eq. (1) and Eq. (2) respectively.<sup>22</sup>

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

$$V = a.b.c \quad (2)$$

where  $d$  is the distance between crystalline planes with Miller indices  $(h k l)$ ,  $a$ ,  $b$ , and  $c$  are the lattice parameters, and  $V$  is cell volume.

The lattice parameters and cell volume for sample were reported in **Table 1**, which is in good agreement with the literature value.<sup>23</sup>

**Table 1.** Lattice parameters, size and atomic percentage of nano perovskite–type oxide NdFeO<sub>3</sub> synthesized using ultrasonic method.

Lattice constant (Å)			Cell volume V (Å <sup>3</sup> )	Average size (nm)		Atomic (%)	
a	b	c		XRD	SEM	Nd	Fe
5.56	7.76	5.46	235.57	42±1	44±1	52.45	47.55

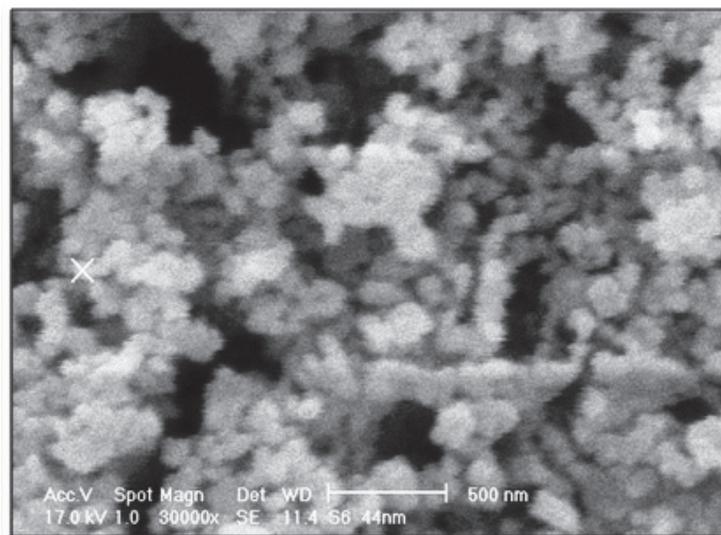
Also, from the XRD data, the crystallite size ( $D_c$ ) of NdFeO<sub>3</sub> nanoparticles was calculated using Scherrer equation:<sup>24</sup>

$$D_c = \frac{K\lambda}{\beta \cos \theta}, \quad (3)$$

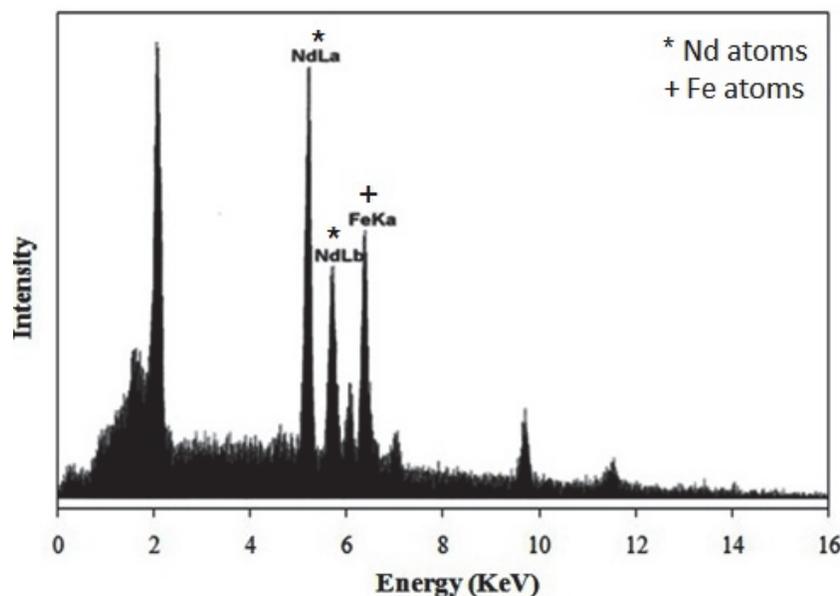
where  $K$  is the so-called shape factor, which usually takes a value about 0.9,  $\lambda$  is the wavelength of the X-ray source used in XRD,  $\beta$  is the breadth of the observed diffraction line at its half-intensity maximum in radian and  $\theta$  is the Bragg peak angle.

The average crystallite size of NdFeO<sub>3</sub> nanoparticles was reported in **Table 1**. The morphology, structure and size of the NdFeO<sub>3</sub> nanoparticles was characterized by scanning electron microscopy (SEM) and shows that it is composed of particles with size of about 44 nm. **Figure 3** shows the SEM image of the NdFeO<sub>3</sub> nanoparticles. As it can be seen, there are uniform nanometer scale particles with good size distribution and also, spherical shaped morphology has been observed for the nanoparticles.

Elemental analysis were tested by EDX, energy dispersive X-ray analysis showed that produced  $\text{NdFeO}_3$  nanoparticles is pure as shown in **Figure 4**. The atomic percentage of two elements neodymium and iron is listed in **Table 1**.



**Fig. 3.** SEM photograph of  $\text{NdFeO}_3$  nanoparticles



**Fig. 4.** EDX pattern of  $\text{NdFeO}_3$  nano-structured powders

**Table 2** presents a brief comparison of some representative textural of nano perovskite-type oxide  $\text{NdFeO}_3$  obtained in this study with those reported in the open literature, prepared using different preparation techniques and calcinated at different temperatures. In comparison with other synthetic methods, the formation time is decreased considerably by ultrasonic method. Also, the results show that a better mixing and a good distribution of cations in the solutions were achieved by ultrasonic method, which assures a better chemical and compositional homogeneity in the powder precursor compared to other methods.

**Table 2.** Comparison of some representative textural of nano perovskite-type oxide NdFeO<sub>3</sub> prepared using different methods and calcinated at different temperatures

Method of preparation	Temperature of calcination, °C	DXRD* (nm)
Combustion	600	20 <sup>25</sup>
Sol-gel	750	100 <sup>26</sup>
Thermal decomposition	600	- <sup>27</sup>
Sol-gel	700	13 <sup>2</sup>
Ultrasonic	800	42 <sup>**</sup>

\*DXRD: crystallite size calculated based on XRD line broadening; \*\*This study

### 3. Conclusions

In summary, the NdFeO<sub>3</sub> nanoparticles were successfully synthesized by ultrasonic irradiation in the presence of octanoic acid as surfactant. The X-ray diffraction pattern at room temperature shows the orthorhombic *Pnma* phase of the perovskite type with lattice parameters  $a=5.56 \text{ \AA}$ ,  $b=7.76 \text{ \AA}$ ,  $c=5.46 \text{ \AA}$ . Morphology of the sample made of nano-sized crystallites has been observed in the SEM image. The pure perovskite NdFeO<sub>3</sub> products were formed by heat treatment at 800 °C for 4 h. The size of the nanoparticles was measured both by XRD and SEM and the results were in very good agreement with each other. The importance of this method of synthesis is that it not only produce good yield but also it does not require high temperatures or high pressures, also this method, are rapid, environmental friendly and low-cost method.

### 4. Experimental

#### 4.1. Materials and physical techniques

All of the chemical reagents were of analytical grade and were used without further purification. Double distilled, deionized water was used as a solvent. Manipulations and reactions were carried out in air without the protection of nitrogen or inert gas. A multiwave ultrasonic generator (UP400S, Hielscher) equipped with a converter/transducer and titanium oscillator (horn) 12.5 mm in diameter, operating at 24 kHz with 8% power output of 400 W, was used for ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. FT-IR spectra were recorded using JASCO FT/IR-460 PLUS spectrophotometer in the range 400–4000 cm<sup>-1</sup> using the KBr disk technique. X-ray powder diffraction (XRD) analysis was performed on a Philips analytical PC-APD X-ray diffractometer with graphite monochromatic Cu K<sub>α</sub> ( $\lambda= 1.54056 \text{ \AA}$ ) radiation at room temperature in the  $2\theta$  range of 20–60°. Scanning electron microscopy (SEM) photographs were taken on a Philips XL-30 equipped with an energy dispersive X-ray (EDX) microanalysis.

#### 4.2. Preparation of NdFeO<sub>3</sub> nanoparticles by the ultrasonic method

In a typically synthesis, a 0.1 M (10 ml) solution of iron chloride (FeCl<sub>3</sub>.6H<sub>2</sub>O) and a 0.1 M (10 ml) solution of neodymium chloride (NdCl<sub>3</sub>.6H<sub>2</sub>O) were prepared separately and mixed together in 1:1 molar ratio. 2 ml of octanoic acid was added to the solution as a surfactant and coating material. Then, NaOH solution (1.5 M) was slowly added into the solution until the pH of the mixture was 7–8. After complete precipitation, the liquid precipitate was irradiated with ultrasonic waves. After cooling at room temperature, the resulting product were centrifuged for 15 min at 3000 rpm, washed with distilled water and ethanol several times to remove the excess surfactant from the solution. Then, precipitation was dried in an oven at 100 °C for 3 h. The resulting lightweight powder was calcinated at 800 °C for 4 h to remove any organic residue. The sonication time was found effective in the formation of the crystalline phase of nanoparticles. In our experimental condition, 15 min/60°C (400 W, 24 kHz) sonication resulted in the most pure NdFeO<sub>3</sub> phase.

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