

Synthesis and Characteristic Properties of Perovskite-type NdMnO₃ Nanocrystal materials via a Co-Precipitation Method

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ABSTRACT

The synthesis of well-dispersed NdMnO₃ nanocrystals is developed in the presence of octanoic acid as surfactant by using Co-Precipitation method. By using this method can produce fine, high-purity, stoichiometric particles of single and multicomponent metal oxides. The prepared sample is characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and energy dispersive X-ray spectrometer (EDX). The XRD analysis shows only the pattern corresponding to perovskite-type NdMnO₃ which crystallizes in the single phasic orthorhombic system. The spherical NdMnO₃ nanocrystals with an average particle size of about 69 nm can be obtained at a relatively high calcining temperature of 850°C. By using SEM it shows sphere-like NdMnO₃ nanocrystals obtained by this method are uniform in both morphology and particle size. The results indicate that the amount of surfactant, pH and rate of stirring have an important role in the homogeneity and size of product. The preparation process can be also applied to synthesize other metal oxides.

KEYWORDS: Octanoic acid, Co-precipitation, Perovskite-type, Nanocrystals

INTRODUCTION

The size less than 100 nm in metal particle considered as a nanoparticles. It is interesting in chemical, Electronic, magnetic and optical properties[1]. The majority of catalysts used in modern chemical industry are based on mixed metal oxides including perovskite-type oxides ABO₃, where A is a rare-earth element, and B is 3d transition metal[2]. The perovskite-type oxides crystals can have most of the applications in advanced technologies such as solid oxide fuel cells, catalysts and chemical sensors, magnetic materials, electrode materials, etc [3-5]. NdMnO₃ prefer to be orthorhombic ally distorted perovskite-type structure [6]. In NdMnO₃, there are three major magnetic interactions: Mn-Mn, Nd-Mn and Nd-Nd [7]. These interactions determine their structure and magnetic properties and also shows number of applications. One application of NdMnO₃ nanopowders is in efficient gas sensors for H₂S [8] and C₂H₅OH [9] detection. The preparation of rare earth orthomagnetites have been prepared by many methods, including hydrothermal, combustion, sol-gel, precipitation methods and sonication assisted precipitation[10]. A simple co-precipitation procedure to prepare orthomagnetite neodymium nanocrystals(NdMnO₃) in aqueous solution at relatively high temperature. The perovskite-type structure can be obtained by Calcining the precursor at 850 °C. The Co-precipitation can produce fine, high-purity, stoichiometric particles of single and multicomponent metal oxides. If the conditions of this process, such as solution pH, reaction temperature, stirring rate, metal salts concentration and surfactant concentration are Controlled, oxide particles of the desired shape and sizes can be produce

EXPERIMENTAL

Material and characterization

For the preparation process double distilled, deionized water was used as a solvent. The reactions were carried out in air without the protection of nitrogen or inert gas. The Crystal structure identification was done by X-ray diffraction (XRD) using a Philips analytical PCAPDX-ray diffractometer with Cu K α ($\lambda = 1.54056\text{\AA}$) radiation, Fourier transform infrared (FT-IR)spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer using KBr pellets, Scanning electron microscopy (SEM) images were taken on a Philips XL-30ESEM equipped with an energy dispersive X-ray (EDX) spectroscopy.

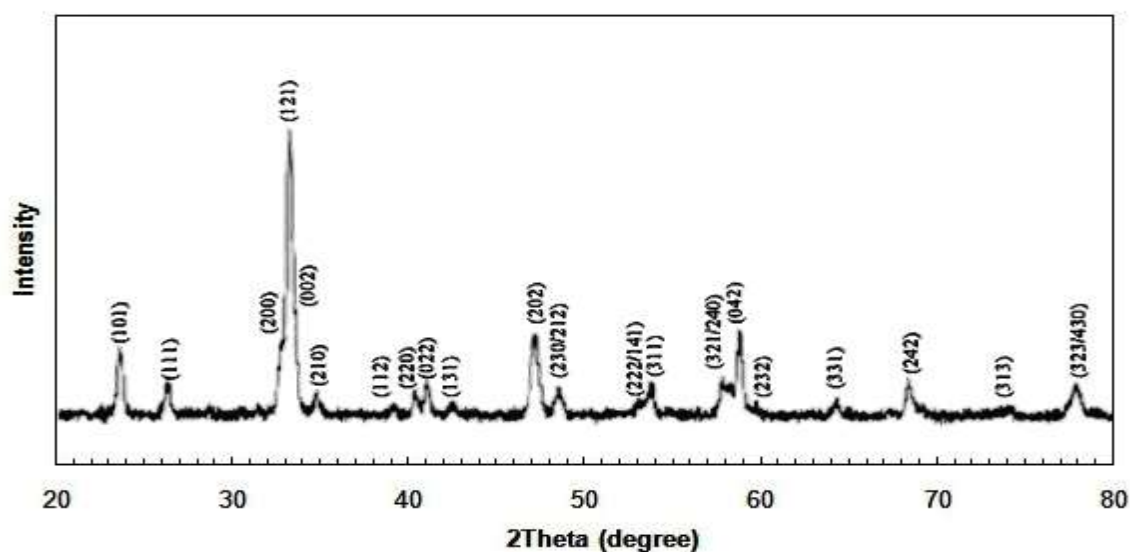


Figure 2: XRD pattern of the NdMnO₃ nanocrystals

Table-1: The particles size of NdMnO₃ nanocrystals using of XRD pattern.

[2 θ]	Angle	(hkl)	d-Value [\AA]	Size of particle (nm)
23.06		(101)	3.75	200.71
25.94		(111)	3.40	28.82
32.37		(200)	2.50	51.17
32.86		(121)	2.65	40.98
34.45		(210)	2.55	102.88
39.99		(220)	2.20	83.62
40.73		(022)	2.15	29.96
46.92		(202)	1.75	61.22
48.32		(230/212)	1.59	43.04
53.63		(311)	1.66	36.71
57.72		(321/240)	1.49	56.08
58.76		(042)	1.50	32.23
68.45		(242)	1.35	39.60
78.12		(323/430)	1.20	126.61

Table.2: Lattice parameter and size of nano-perovskite-type oxide NdMnO₃ synthesized using Co-precipitation method.

Lattice parameters (Å ⁰)			Cell volume	average size (nm)	
a	b	c	V(Å ³)	XRD	SEM
5.53	7.70	5.38	229.08	67	58

Synthesis of NdMnO₃ nanocrystals

A typical synthesis, a 0.1 M (10 ml) solution of neodymium chloride (NdCl₃.6H₂O) and a 0.1 M (10 ml) solution of Manganese chloride (MnCl₃.6H₂O) were mixed in double distilled deionized water. Deionized distilled water was used as the solvent in order to avoid the production of impurities in the final product. A specified amount of octanoic acid was added to the solution as a surfactant and coating material. The pH of the solution was constantly monitored as the NaOH solution was added. A 1.50 M (30 ml) solution of sodium hydroxide (NaOH) was prepared and slowly added to the salt solution dropwise. The reactants were constantly stirred using a magnetic stirrer until a pH level of 7.0–8.5 was reached. The liquid precipitate was then brought to a reaction temperature of 75°C and stirred for 1.5 h. The product was then cooled to room temperature. To get particles free from sodium and chlorine compounds, the precipitate was washed twice with distilled water and then with ethanol to remove the excess surfactant from the solution. To isolate the supernatant liquid, the beaker contents were then centrifuged for 20 min at 3500 rpm. The supernatant liquid was then decanted, and then centrifuged until only thick brown precipitate remained. The obtained products were dried at 110°C for 2 h. The acquired substance was then ground into a fine powder. At this stage the product (NdMnO₃) contains some associated water (up to 10 wt %), which was then removed by heating at 850°C for 4 h. The final samples were then confirmed by different techniques, such as XRD, FTIR, SEM, EDX, etc.

RESULTS AND DISCUSSION

The sample are prepared by Co-precipitation method. The XRD analysis shows only the pattern corresponding to perovskite-type NdMnO₃ (JCPDS File no. 25-1149), which crystallizes in the orthorhombic system with a main diffraction peak at $d = 2.723 \text{ \AA}$ ((1 2 1) plane). No peaks attributable to Nd₂O₃ and/or Mn₂O₃ were observed and the compound was completely decomposed to single-phase NdMnO₃. 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. All the characteristic peaks of NdMnO₃ are present and can be seen in Table 1. The lattice parameters and cell volume were calculated by the following equation (1) and (2), respectively[11].

$$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \dots\dots\dots (1)$$

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

Where d is the distance between crystalline planes with Miller indices ($h k l$), a , b , and c are

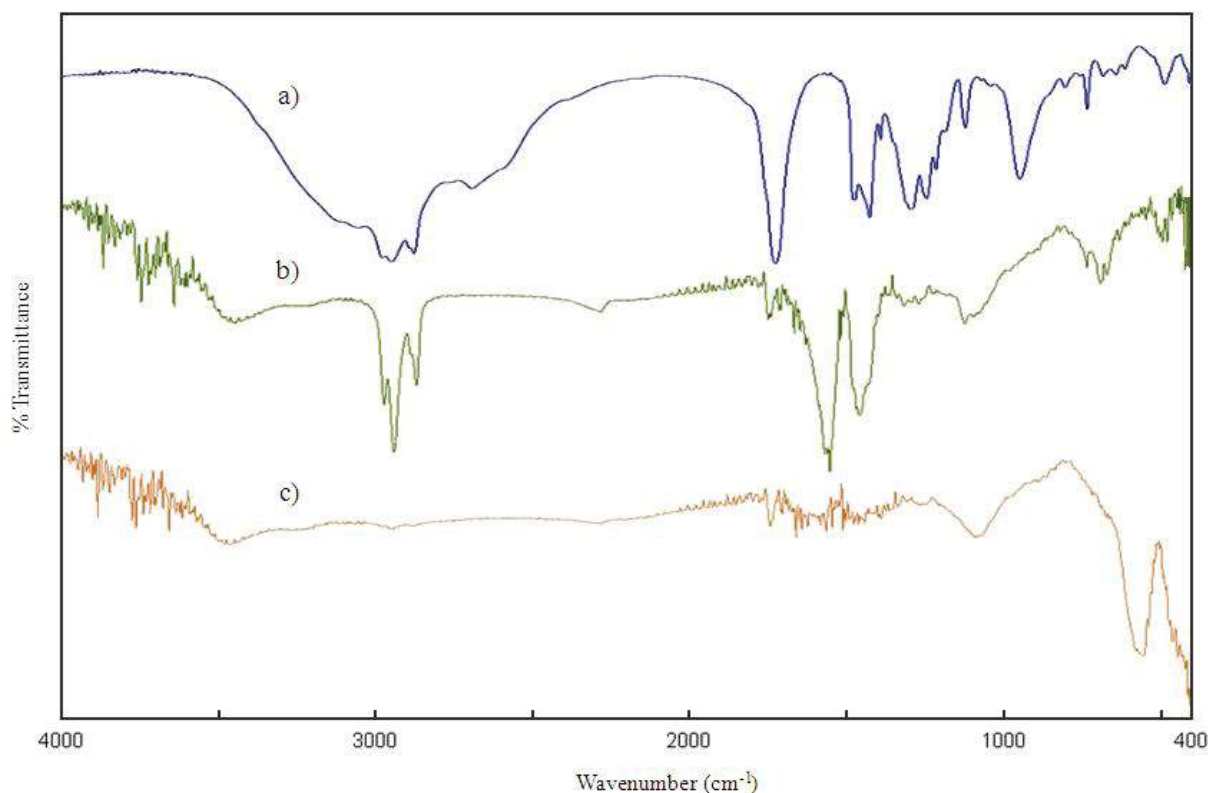


Figure 3: FT-IR spectra of (a) octanoic acid, (b) sample before furnace, (c) sample after furnace.

the lattice parameters, and V is cell volume. The lattice parameters and cell volume for sample were reported in Table 2, which is in good agreement with the literature values [12]. Also, the average size of the NdMnO_3 crystallites (D) was evaluated from XRD line broadening using the Debye-Scherrer equation [13]:

$$D = \frac{0.89\lambda}{B \cos\theta} \dots \dots \dots (3)$$

where λ is the wavelength of the X-ray radiation (1.54056 \AA), θ is the Bragg angle and B is the width of the observed diffraction line at its half maximum intensity. The average crystallite size of the NdMnO_3 nanoparticles is demonstrated in Table 1.

The FT-IR spectra of octanoic acid (a), perovskite NdMnO_3 before furnace (b), and perovskite NdMnO_3 after furnace (c), in the frequency range from 4000 to 400 cm^{-1} , are shown in Figure 3. The spectrum of the NdMnO_3 before furnace showed absorption band around 3000 cm^{-1} which is attributed to acid's -OH group that will be disappeared in spectrum after furnace. Also, the broad band in the range of $3400\text{-}3600 \text{ cm}^{-1}$ is attributed to $\nu(\text{OH})$ of the lattice water molecules. In the FT-IR spectrum of the final product, there are two strong absorptive bands at about 560 and 420 cm^{-1} which correspond to metal oxide Mn-O stretching vibration and O-Mn-O bending vibration of perovskite NdMnO_3 , respectively. This finding proves the formation of the perovskite NdMnO_3 and is in correlate with the XRD data. The morphology, structure and particle size of the as-prepared sample were investigated by SEM. Figure 4 shows the SEM micrographs of the product. Lower magnification reveals that the product consists of loosely aggregated grains about $1 \mu\text{m}$ in size (Figure 4a). Higher magnification confirms that the grains are composed of extremely fine particles and are essentially

secondary agglomerates of primary particles (Figure 4b). One can observe that nano-sized particles started to become evident within the grains and agglomerates. As it can be seen, sphere like NdMnO_3 nanostructures obtained by this method are uniform in both morphology and particle size. For further demonstration, EDX was performed on NdMnO_3 nanocrystals. The EDX spectrum given in Figure 5 shows the presence of neodymium and manganese as the elementary components.

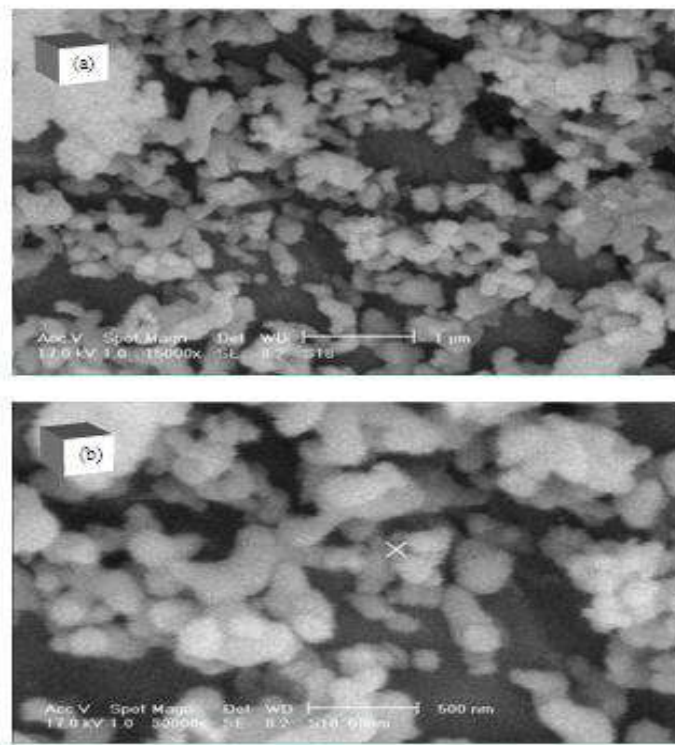


Figure 4: SEM micrographs of NdMnO_3 in two different magnifications.

It is necessary to point out that the adding manner of NaOH solution has an important influence on the shape of the NdMnO_3 nanocrystals. It is assumed that when the NaOH solution was added dropwise into the mixture solution, some small NdMnO_3 crystal nuclei was formed at the initial stage of the reaction. With the increase of the NaOH solution, the slowly produced NdMnO_3 crystallites grew along one growth direction on the basis of the initially formed NdMnO_3 crystal nuclei. The epitaxial growth of crystallites, the slow nucleation, and the growth rates result in the formation of nanoparticles. On the contrary, if NaOH solution was quickly added into the mixture solution, the solute was consumed rapidly and the growth of crystallites was effectively inhibited. Meanwhile, the quick addition of NaOH solution can provide a quick rate to the crystal growth. The faster growth rate results in the crystal growth being considerably less selective in directions and hence spherical NdMnO_3 nanocrystals are produced.

The shape and size of NdMnO_3 nanocrystals can be further tuned by adding small amounts of surfactants. The result demonstrates that the presence of small amounts of octanoic acid leads to the shape change of NdMnO_3 products. Also, the presence of octanoic acid led the particles to be well dispersed with no agglomeration, while much larger particles flocculating together were synthesized in the absent of octanoic acid. The use of a surfactant to control the morphological evolution of nanocrystals has been extensively explored. It is generally accepted that the surfactant kinetically controls the growth rates of various faces of nanocrystals by selective adsorption and desorption on these surfaces [14,15]. The octanoic acid may adsorb into the fastest growth face of NdMnO_3

nanocrystals. Hence, the epitaxial growth of nanocrystals is effectively inhibited and spherical NdMnO₃ nanocrystals are produced.

CONCLUSIONS

The Co-precipitation method is suitable for the control of nanoparticle sizes with variation of reaction condition. The pure phase NdMnO₃ nanoparticle powder were synthesized by co-precipitation method shows single phase an orthorhombic structure in presence of octanoic acid as surfactant. The product perovskite NdMnO₃ were formed by heat treatment at 850^oc for 4 hr. The size of the nanocrystals was measured both by XRD and SEM and the results were in good agreement with each other. The morphology of the neodymium nanoparticle (NdMnO₃) was sphere-like nanoparticles in this method.

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