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Synthesis of Cubic Phase Gd_2O_3 Nanoparticles Using Hydrothermal Method

Muhammad Zul Azri Muhammad Jamil[1], *Faizal Mohamed[1],
Nur Ratasha Alia Md. Rosli[1], Irman Abd Rahman[1]
[1] *School of Applied Physics, Faculty of Science and Technology, The National University of Malaysia (UKM), 43600 Bangi Selangor, Malaysia*
Corresponding Author: Faizal Mohamed

Abstract: *Synthesis of Gd_2O_3 nanorod powder using hydrothermal reaction had been conducted using $GdCl_3.6H_2O$ as the precursor. X-ray diffraction measurements, transmission electron microscopy, magnetometer and thermal analysis were used to characterize the phase evolution and morphology of the final product. A solid state displacement reaction $GdCl_3.6H_2O + NaOH + PEG \rightarrow Gd(OH)_3 + NaCl + PEG$ was induced during heating process at 140°C for 1 hour followed by 180°C for 4 hour. It is revealed that calcining of the $Gd(OH)_3$ at 500°C and 800°C led to formation of Gd_2O_3 with the size < 200 nm having a cubic structure. The room temperature magnetic field versus magnetization measurements confirmed the magnetic Gd_2O_3 nanoparticles is paramagnetic due to smallest coercivity (Hci) and magnetizarion (M_s) value.*

Keywords: *hydrothermal, Gd_2O_3 nanoparticles, cubic phase*

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I. Introduction

Studies on Gd_2O_3 nanoparticles have been carried out worldwide nowadays especially in the field of nanomaterials. Gadolinium is the one of lantanide element that have been mostly used in industrial and medical studies. Gadolinium oxide nanoparticles are used in electronic [1], catalyst [2, 3] and laser [4]. Moreover, gadolinium have high neutron cross section that have been used to detect the tumor using neutron therapy [5].

Gadolinium also has a potential application in biomedicine [6-8]. For example, it is used in magnetic resonance imaging [9-12] due to its paramagnetic properties [13]. There are have many method to synthesize the gadolinium nanoparticles such as microemulsion [14] sonochemical [15], hydrolysis [16] and solvent extraction [17-19].

One of the most widely employed techniques to prepare nanostructure materials involves the hydrothermal method. In this study, hydrotermal method was chosen to produce Gd_2O_3 nanoparticles due to its advantages: cost-effective, capable of providing high purity and high yield, does not use any catalyst and template.

Herein, we demonstrate production of Gd_2O_3 nanoparticles via user-friendly and cost effective hydrothermal approach, without using any sort of catalyst or template. Characteristic properties with respect to structural and magnetic responses of synthesized nanoparticles are discussed.

II. Experimental

2.1 Materials

The chemical used were analytical grade. Gadolinium chloride hexahydrate ($GdCl_3.6H_2O$) with 99.9% purity was purchased from Sigma-Aldrich, polyethelene glycol (PEG) Bioultra, 2000 was purchased from Sigma-Aldrich (λ: 260 nm, Amax: 0.03), sodium hydroxide pellets (NaOH) and methanol were purchased from Merck KGaA, Darmstadt, Germany. All of these chemical were used for preparation of Gd_2O_3 nanoparticles.

2.2 Methods

2.2.1 Synthesis of super paramagnetic Gd_2O_3 nanoparticles

$GdCl_3.6H_2O$ was dissolved in the poly ethelene glycol (PEG) as a precursor with ~0.2 mol/L cation concentration. The solution was vortexed at room temperature for 8 min. Then ~ 0.6 mol/L of NaOH was added in the precursor solution and the solution was vortexed at room temperature for 8 min to get a homogen mixture. To obtain nanoemulsion, the solution was sonicated for 30 min and votexed at room temperature for 8 min. The mixture solution was heated at 140°C for 1 hour, and then the temperature was raised to 180°C for

another 4 hour. A white product of $Gd(OH)_3$ was then collected by filtering the precursor using a Whatman filter. The product was washed several time using deionised water and then methanol to eliminate any unwanted impurities followed by oven drying at 90^{o}C for one night. Finally, the hydroxide powder was annealed at 500^{o}C and 800^{o}C for 2 hour to facilitate spontaneous decomposition of $Gd(OH)_3$ and consequently, dehydration to yield Gd_2O_3 nanopowder. The collected white Gd_2O_3 nanoparticles were dried in an oven at 60^{o}C for 24 hr.

2.2.2 Characterisation of Gd_2O_3 nanoparticles

X-ray diffraction measurent (XRD): X-ray diffraction (XRD) technique is an effective tool to identify cristal structure of Gd_2O_3 nanoparticles. Cu Kα1 radiation was used to investigate purity of Gd_2O_3 powder with wavelength 1.54060 cm^{-1}. The diffraction angle was varied in the range 5^o – 80^o and with a steps angle of 0.1^o. The XRD patterns were collected on a Bruker D8 Advance.

Thermo gravimetric analysis (TGA): The weight loss and the decomposition temperature in the sintering process were carried out determined using TGA (Shimadzu 50).

Transmission electron microscopy (TEM): The morphology, size distribution and the average particle diameter of $Gd(OH)_3$ and Gd_2O_3 nanoparticles were studied using a Philip/TEMCM12 electron microscope, operated at 120 kV.

Vibrating sample magnetometer (VSM): magnetic hysteresis measurement was carried out on a particular sample (prepared at 800^{o}C) at room temperature using Lakeshore 7404 series magnetometer. The samples were vibrated at a frequency of 85 Hz to shear the magnetic flux created and any signal generated from the samples was recorded by Gauss meter.

III. Result And Discussion

3.1 XRD and phase evolution

Figure 1 shows the XRD patterns of the precursor and powder calcined at different temperature. XRD pattern indicated that the nanocrystal consists of crystalline Gd_2O_3 nanoparticles. The wide-angle XRD pattern of the nanocrystal shows the characteristic peak of the hexagonal phase $Gd(OH)_3$ and cubic phase Gd_2O_3 nanoparticles.

Based on the pattern of diffraction, there are five major peak on the $Gd(OH)_3$ nanoparticles: peak 131 ($2\theta = 16.147^o$), peak 88 ($2\theta = 28.157^o$), peak124 ($2\theta \approx 29.452^o$), peak 84 ($2\theta \approx 41.175^o$) and peak 70.5 ($2\theta \approx 50.596^o$) with the [h,k,l] value are [1,0,0], [1,1,0], [1,0,1], [2,0,1] and [2,1,1] (JCPDS No. 01-083-2037) respectively. After the samples were annealed at 500^{o}C, the incomplete cubic phase of Gd_2O_3 was formed with the the [h,k,l] value were [2,2,2], [4,4,0], [6,2,2] and [8,0,0], which are well consistent with JCPDS no. 00-011-0608. Absence of $Gd(OH)_3$ peak on the heat treated samples confirmed the formation of Gd_2O_3 nanoparticles. Subsequently, a better cubic phase of Gd_2O_3 nanoparticles formed after the samples was annealed at 800^{o}C with the excellent peak fitting (JCPDS no. 00-012-0797).

The sintered time also dependent on the formation of cubic phase during anealling process. At 500^{o}C, the sample were sintered at 360^{o}C for 15 min and 45 min for 800^{o}C. A short time of sintered gave incomplete phase due to incomplete decomposition $Gd(OH)_3$ to Gd_2O_3 (fig. 2). The lattice parameter of the samples synthesized at 500^{o}C and 800^{o}C were estimated to be 10.79Å and 10.81Å. The percent of crystalinity of cubic phase Gd_2O_3 nanoparticles was 71.00%.

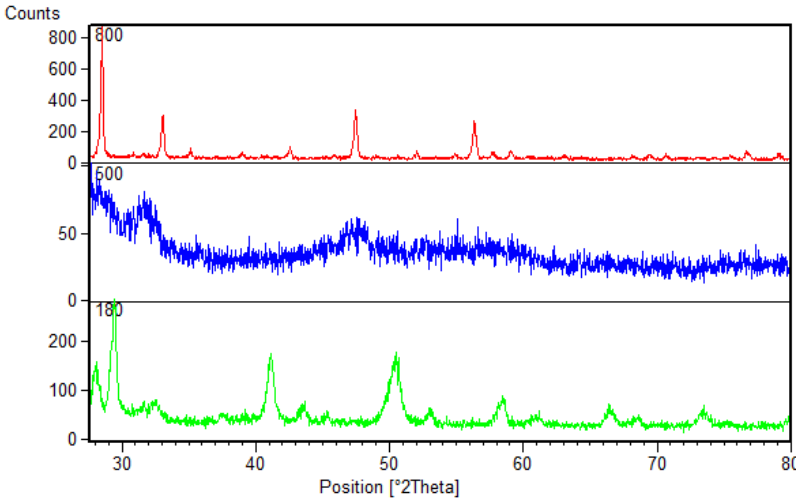

Figure 1. XRD patterns of Gadolinium (III) nanoparticles at various reaction temperatures

3.2 TGA analysis

Thermal analysis was performed to study the decomposition temperature for formation of Gd_2O_3 nanoparticles. Figure 2 shows the TGA curve for progressive weight loss of $Gd(OH)_3$ within a range of temperature (27-600^oC). The weight loss in the early stage of annealing can attributed to the removal of the water molecules into the atmosphere. Endothermic peak at 360^oC is assigned to the decomposition of the $Gd(OH)_3$ to Gd_2O_3 with the weight loss 10.47% (1.330 mg). Gd_2O_3 can be formed on annealing the samples above 360^oC which well supported by diffraction pattern of samples annealed at 360^oC more than 45 min.

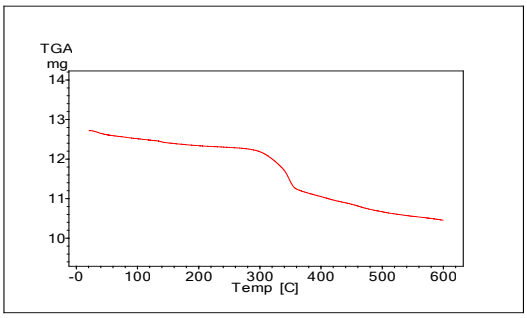

Figure 2. Thermogravimetric analysis of unsintered $Gd(OH)_3$ product

3.3 Morphology of the structure

From Figure 3, the morphologies and the size of the powders calcined at 180^oC, 500^oC and 800^oC synthesized have a little bit different. The particle sizes of these powders are about ~ 259 nm, ~ 192 nm and ~ 175 nm, respectively, as estimated from the TEM images. The size of Gd_2O_3 at 500^oC reduce 67 nm from $Gd(OH)_3$ due to dehydration process. Increasing the temperature showed that the size and shape of nanorods become smaller and shorter which are corresponding to the distribution of diffraction pattern peak on XRD.

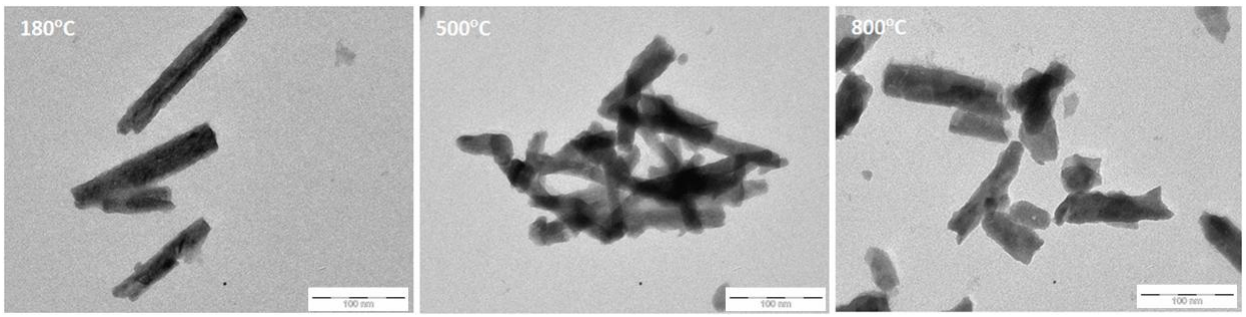

Figure 3. TEM images of $Gd(OH)_3$ (180^oC)and Gd_2O_3 (500^oC and 800^oC) nanoparticles prepared at various reaction temperatures with magnification 60,000X

3.4 Magnetometer of the samples

In order to study the magnetic property of the samples, the vibrating samples magnetometer were used. The magnetization of the obtained Gd_2O_3 nanoparticles is shown in Fig. 4. The saturation magnetization value (M_s) varies with the particle dimension that depends on the temperature of the precursor. Magnetization (M_s) against magnetic field (G) was measured at 300 K and the field was recorded at range -2 G to 12000 G. In this context, magnetic measurement was not performed on Gd_2O_3 at 500^oC due to the incomplete cubic phase that has been proved by the diffraction pattern. Thus, measurement on magnetic Gd_2O_3 nanoparticles at 800^oC was used in evaluating the magnetic properties.

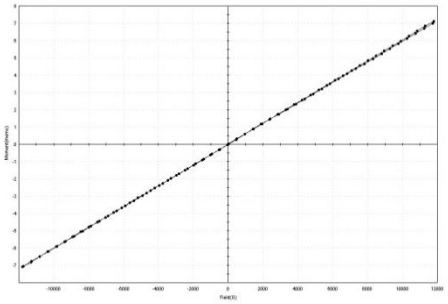

Figure 4. Magnetization curve obtained for Gd_2O_3 nanoparticles at 800^oC measured at 25^oC

Since there is no clear curve was observed, these samples may be paramagnetic due to its nature of seven unpaired electrons in *f*-orbital [20, 21]. Besides that, based on VSM analysis showed that the coercivity (Hci), magnetizarion (M_s) and retentivity (M_r) value were 19 610 G, 7.1175 x 10^{-3} emu and 12.530 x 10^{-6} emu, respectively. The reading of Hci and M_r on Gd_2O_3 nanoparticles is closed to 0, it can be speculated that the magnetic gadolinium may be superparamagnetic due to the size of sample was < 200 nm x 27 nm.

IV. Conclusion

We have developed a Gd_2O_3 nanostructure with different size of morphologies. After calcining the precursor, Gd_2O_3 powder was obtained. It was found to be strongly dependent on the hydrothermal temperature, with different time of sintered coming out of the formation of different morphology structures. This method could be also expected suitable to the synthesis of other kinds of rare earth oxide element for various purposes.

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