

ORIGINAL ARTICLE

The Effect of Conventional and Sonochemical Synthesis Methods on Gd₂O₃ Nanoparticles Properties

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ABSTRACT – Precipitation is the most common method to obtain nanoparticle including Gd₂O₃ that has potential as a contrast agent in bioimaging such as Magnetic Resonance Imaging (MRI). In this study, the characteristics of Gd₂O₃ nanoparticles that prepared using conventional and sonochemically precipitation methods have been investigated. Gadolinium nitrate was used as a precursor and ammonium hydroxide as precipitating agent. The synthesized Gd₂O₃ nanoparticles were characterized using X-Ray Diffractometer (XRD), Particle Size Analyzer (PSA), Scanning Electron Microscope (SEM), and Vibrating Sample Magnetometer (VSM). It was found that Gd₂O₃ nanoparticles obtained in both methods have a cubic phase. The saturation magnetization (M_s) values of conventional and sonochemical samples were 1.63 emu/g and 1.44 emu/g respectively. The morphology of both samples shows agglomerated spherical shape in the nanometer range. The nanoparticles size of Gd₂O₃ that was confirmed by the Dynamic Light Scattering technique show samples from the sonochemical method in short period has narrower size distribution (higher homogeneity) compare to samples from the conventional method. It was also found that the sonochemical synthesis technique is faster (time-saving), simple, convenient, and environmentally benign with size distribution and M_s value comply with a request of contrast agent.

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INTRODUCTION

Magnetic resonance imaging (MRI) is a crucial test in clinical diagnosis. To provide high resolution anatomical images in MRI, a contrast agent (CA) is added [1]. Gadolinium oxide is one of the rare earth oxide that has been proven to be promising candidate as positive contrast agent in magnetic resonance imaging (MRI) [2], [3]. Contrast agent that uses paramagnetic gadolinium oxide nanoparticles work as T1 which produces bright contrast in MR images by shortening the longitudinal relaxation time [1].

Recently research on gadolinium oxide (Gd₂O₃) nanoparticles attempts to provide strong paramagnetic material as contrast agent [3]. Besides that, the possibility to do multifunctionalization with other molecules such as drug, polymer, and silica, make them have more wide application (drug delivery, medical marker, hyperthermia agent) [4], [5]. Many methods has been applied to prepare Gd₂O₃ nanoparticles such as hydrothermal, sol-gel, chemical reduction, pulse electrodeposition, microemulsion, conventional stirring, and sonochemical [3], [6]. Each method usually has parameter control including pH, temperature, and concentration of reactant to achieve the desired product. Production of Gd₂O₃ nanoparticles via mixing technique has been done by Sakai et. al 2015 with particle diameter under 100 nm, by adjusting calcination temperature from 500 °C-1000 °C in air condition for 10 hours [4]. Nevertheless, conventional stirring gives lower energy that makes particles move slowly and tend to cluster resulting inhomogeneity [7]. The synthesis of Gd₂O₃ nanoparticles via sonochemical has been carried out by Khahureea et. al 2015 with the presence of a surfactant to control the morphology and size distribution of nanoparticles under a high-intensity ultrasound probe for 30 minutes [8]. The same method combined with the hydrothermal process has also been done by Muneer et.al 2015 to obtain Gd₂O₃ nanoparticles [9]. The advantages of the sonochemical method are the efficiency of cost and reaction time, with the fine powder product in uniform size distribution [9]. In sonochemical, the acoustic cavitation generates localized hot spots and creating bubbles that also considered as the storage of highly high potential-energy, which could be released to be shock waves. These waves could directly interact with particles and accelerates nucleation which inhibits growth, as the key factor for synthesizing nanometer particles in aqueous solutions with narrow size distribution [10]. Synthesis gold nanoparticles via sonication in short period (5 minutes) conducted by Dheyab et. al 2020 obtained nanoparticles with spherical shape [10]. Based on this evidence, the synthesis and characterization of Gd₂O₃ nanoparticles using ultrasonic with high energy in a short period without surfactant has not been revealed yet, that will be discussed in this paper.

In this research, we proposed to synthesize Gd₂O₃ nanoparticles using a user-friendly high-energy sonochemical method this at effective in time with the absence of surfactant. In this study, the Gd₂O₃ nanoparticles will be synthesized in the conventional (stirring) method and sonochemical method to understand the effect from both techniques. The

calcination process was referred to the experiment that has been done by Boopathi et. al 2014 and Sakai et. al 2012 [4], [9]. Characterization of the samples has been focused on crystalline phase, magnetic properties, morphology, and size distribution.

EXPERIMENTAL METHOD

Materials and Instruments

Gadolinium nitrate solution from SPEC was used as a precursor. Ammonium hydroxide 32 % from Sigma-Aldrich was used as precipitating agent. All of the chemicals were used without further treatment.

The main equipments used in this experiment were a magnetic stirrer-Fisher Scientific Hot Plate Stirrer11-100-49SH and an Ultrasonic horn (Sonic-Vibra Cell VCX 500 Sonicator, 20 kHz). Characterizations of the samples have been performed using X-ray powder diffraction (XRD-PANalytical) to analyze the crystallite phase. The particle size distribution has been done using DLS analysis (Malvern). Magnetization measurements were subjected to VSM (OXFORD 1.2H). The morphology and elemental contents of the samples were examined by scanning electron microscopy (SEM) (JEOL-JED 2300).

Synthesis Gd₂O₃ by conventional/stirrer (S) method

The conventional method of Gd₂O₃ nanoparticles synthesis has been prepared using 25 mL of gadolinium nitrate solution 0.029 M as a precursor. An amount of 5 mL ammonium hydroxide 32 % was used as precipitating agent. The gadolinium precursor solution was placed on the magnetic stirrer, then ammonium hydroxide was added drop-wise while the mixture was magnetically stirred. The stirring process has been conducted at 350 rpm for an hour at room temperature. The resulting white precipitate was washed with DI-water and then dried at room temperature for 24 hours. The dried product was then annealed at 750°C for an hour in air atmosphere.

Synthesis of Gd₂O₃ by sonochemical

Gadolinium oxide (Gd₂O₃) nanoparticles prepared using the sonochemical method have been done using the same reagent as in the conventional method. Gadolinium nitrate solution was placed under an Ultrasonic horn at 40% amplitude for 5 minutes (1 minute pulse 5 second relaxation cycle). In the early minute ammonium hydroxide was added rapidly while the solution being sonicated. The resulting white precipitates were treated the same as described in conventional method.

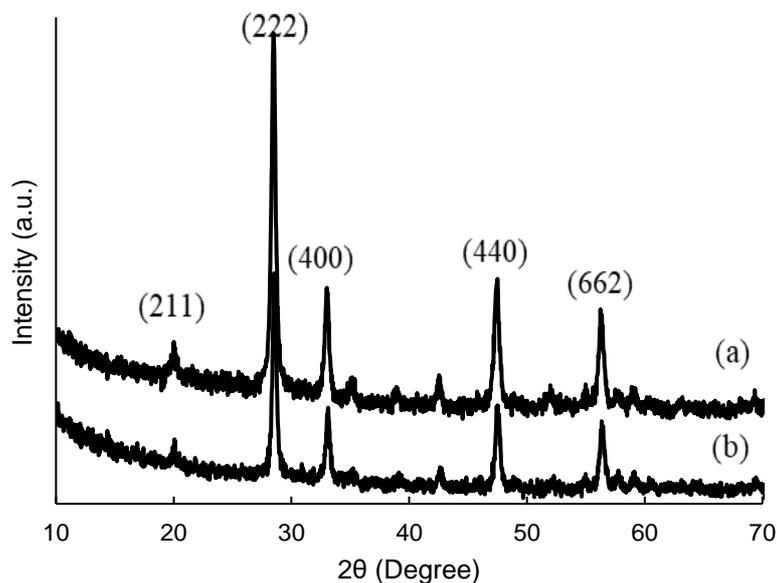


Figure 1. X-Ray powder diffraction pattern of Gd₂O₃ synthesized with (a) conventional method (b) sonochemical method

RESULT AND DISCUSSION

Figure 1 shows the diffraction pattern of Gd₂O₃ prepared with (a) conventional/stirrer method (Gd₂O₃ (S)) (b) sonochemical method (Gd₂O₃ (US)) after annealed at 750°C. The XRD pattern shows main characteristic crystal planes of Gd₂O₃ with cubic phase (211), (222), (400), and (440). The peaks in the diffractogram match exactly with the powder diffraction file (PDF) from Inorganic Crystal Structure Database (ICSD) Ref. no. 98-009-4892. These crystal planes are also match with other Gd₂O₃ research [4][5]. It was found from calculation that Gd₂O₃ (S) has higher crystallinity (59.39 %) than US synthesized Gd₂O₃ (45.57 %). The lower of crystallinity in US synthesized sample may because of the local

high energy dissipation rate due to cavitation phenomenon that led faster reaction which not allowing the nucleation and crystal growth fully occurred [12].

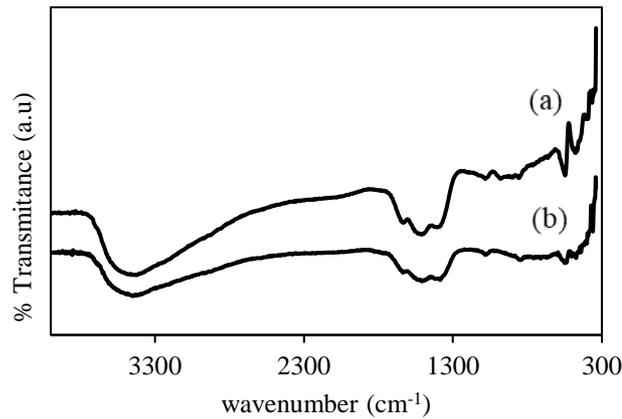


Figure 2. IR spectra of Gd₂O₃ synthesized with (a) conventional method (b) sonochemical method

The FTIR spectra of Gd₂O₃ synthesized with conventional method (b) sonochemical method are shown in figure 2. The broad peak at 3500 cm⁻¹ representing the hydroxyl group from adsorbed water molecules from air [3, 11]. The O-H stretching and bending vibration of water molecule are also detected at 1630 cm⁻¹ and 1380 cm⁻¹ [3], [14]. The both spectra show peaks at 545 cm⁻¹ and 466 cm⁻¹ that assigned to the Gd-O vibration [3, 11]. The FTIR peaks that correspond to Gd-OH vibration at 668 cm⁻¹ have diminished that indicate all Gd(OH)₃ have completely decomposed [13]. It confirms that Gd₂O₃ has already formed by calcined the prepared samples at 700 °C which in agreement with XRD result.

The results of magnetization measurement using vibrating sample magnetometer are shown in figure 3. The hysteresis loops show linier relationship between magnetization (M) and applied field (H) with positive slope that indicate paramagnetic phenomenon of the samples. It happened when by removing the applied magnetic field didn't lead to coercivity and remanence [15]. The magnetization values (Ms) of the both samples are not much different, 1.63 emu/g and 1.44 emu/g for Gd₂O₃ (S) and Gd₂O₃ (US) respectively. However, the higher Ms value of Gd₂O₃ (S) related to their higher degree of crystallinity compare to Gd₂O₃ (US) [16].

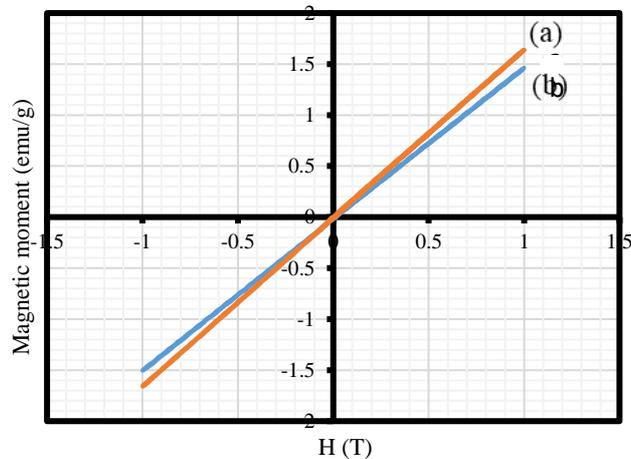


Figure 3. Magnetization curve of Gd₂O₃ synthesized with (a) conventional method (b) sonochemical method

Table 1. Magnetization value of Gd₂O₃ nanoparticles comparison in some methods

| No. | Method | Surfactant | Ms (emu/g) | Size (nm) | Ref. |
|-----|--|------------|------------|-------------------------|---------------|
| 1. | Conventional (stirrer 1 hour) | - | 1.63 | ~100 (less homogeneous) | This research |
| 2. | Sonochemical (ultrasonic horn for 5 minutes) | - | 1.44 | ~100 (homogeneous) | This research |
| 3. | Pulsed Electron Beam Evaporation | PEG | 1.28 | 175-200 | [6] |
| 4. | Sonochemical | PVP/CTAB | - | 50-80 nm | [8] |
| 5. | Solvothermal | PEG | 1.12 | 80 nm | [17] |

The particle size distributions of the synthesized Gd₂O₃ nanoparticles have been investigated using dynamic light scattering technique as shown at Figure 4. Both Gd₂O₃ samples were dispersed in aqueous medium by sonication for 5 minutes before analyzed by DLS technique. The Gd₂O₃ nanoparticles from both methods are polydisperse. The size

distributions of Gd_2O_3 (S) are in the range from 1.5 nm to 200 nm with polydispersity index (PDI) 0.548. While Gd_2O_3 (US) has narrower size distribution (more uniform size) with diameter around 5 nm to 200 nm and PDI value 0.425. However, unmodified Gd_2O_3 nanoparticles in water medium are agglomerate easily which presented in size distribution by intensity curve.

The magnetization value and particles size distribution of Gd_2O_3 in this research compare to other methods is presented in Table 1. It shows that sonochemical method using ultrasonic horn in 5 minutes without surfactant obtained Gd_2O_3 homogeneous nanoparticles with Ms value in the range for contrast agent application.

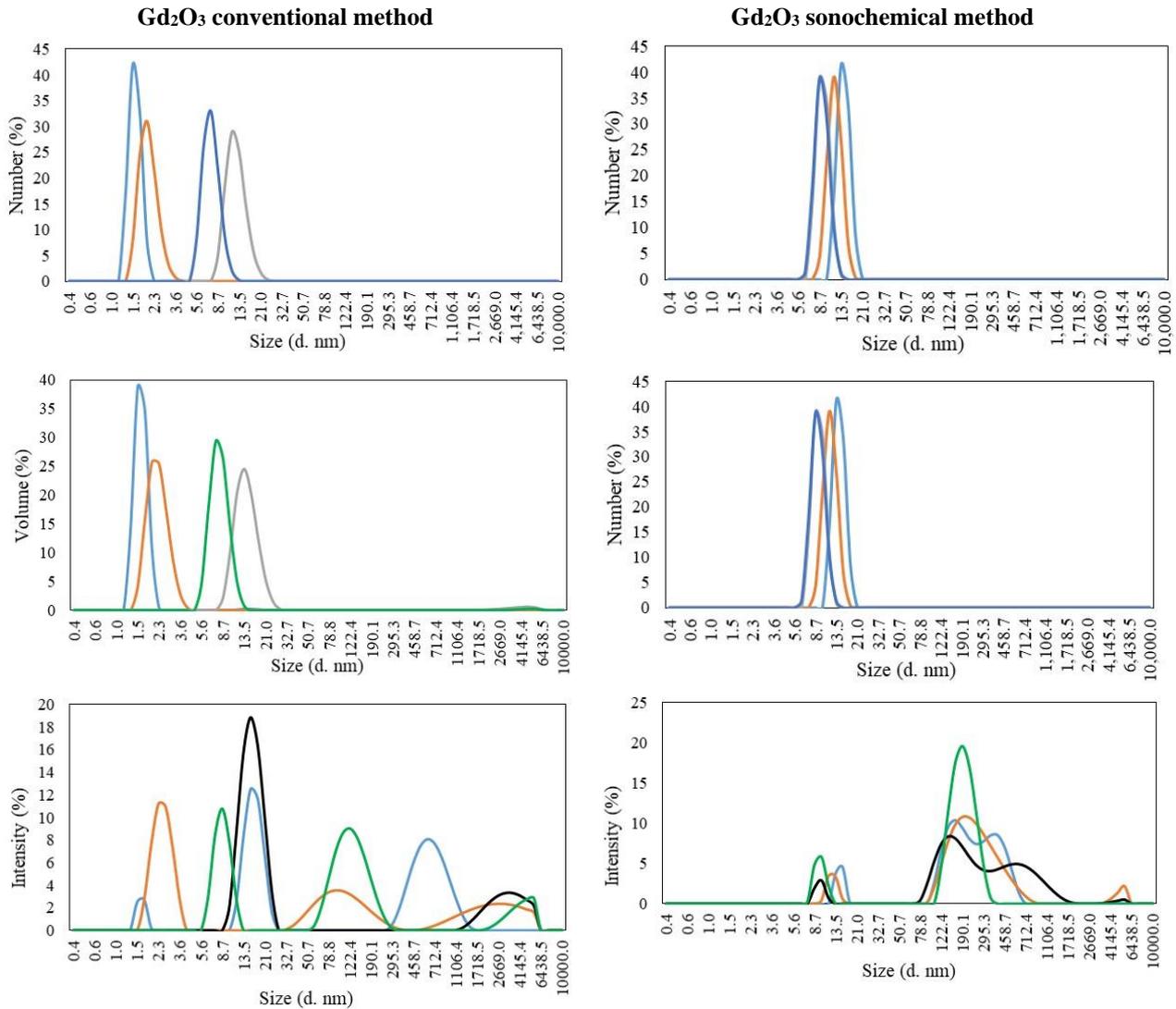


Figure 4. The particle size distribution of Gd_2O_3 nanoparticles synthesized with conventional and sonochemical method

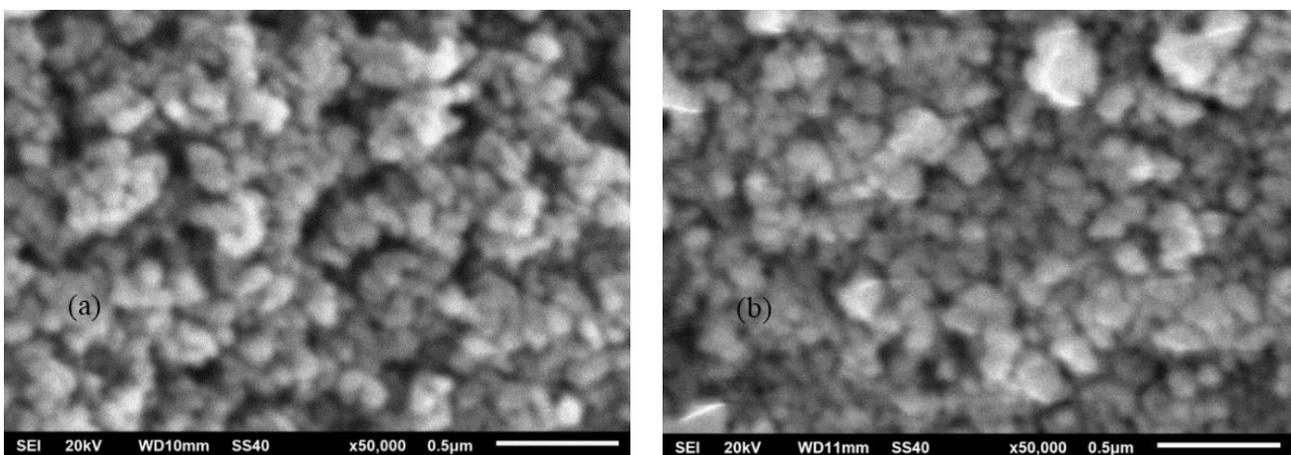


Figure 5. SEM micrograph of Gd_2O_3 nanoparticles synthesized with (a) conventional method (b) sonochemical method

The morphology of the Gd₂O₃ nanoparticles were determined using SEM as shown in figure 5. The micrograph images of Gd₂O₃ from both synthesis methods show the particles agglomeration in spherical shape with diameter size about 40-50 nm. The nanoparticles with spherical shape are suitable for biomedical applications (drug delivery), due to the easiness to uptake by cell. Beside that spherical shape also easy to do some modification [17]. The EDS spectra (Figure 6) show the composition of Gd₂O₃ from both methods, the characteristic peaks of Gd and O are observed. It means that Gd element exist in the sample and no other metal elements are detected, which indicates there is no impurity in the Gd₂O₃ samples.

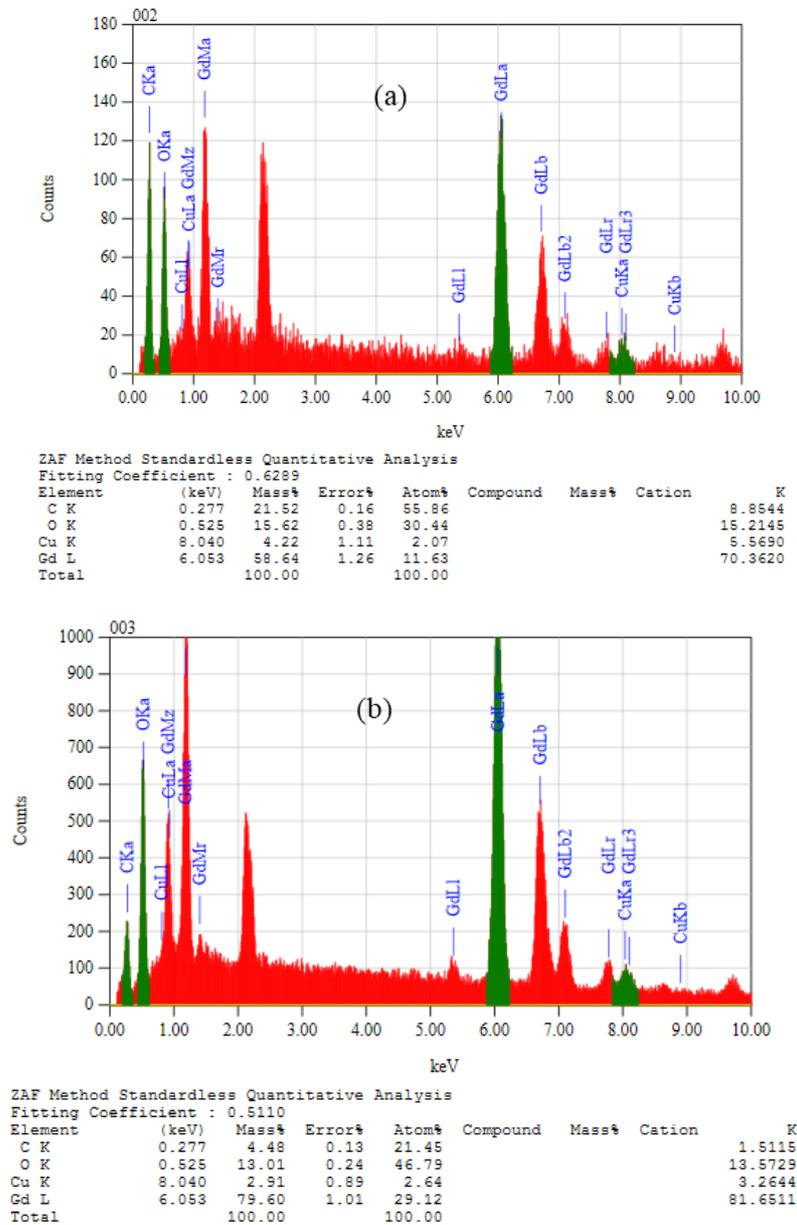


Figure 6. EDS spectra of Gd₂O₃ nanoparticles synthesized with (a) conventional method (b) sonochemical method

The data characterization of Gd₂O₃ nanoparticles from conventional and sonochemical process show that the physical properties of both samples (phase, shape, magnetic) are not much different. However, the sonochemical process give narrower size distribution, and shorter synthesis time.

CONCLUSION

Gd₂O₃ nanoparticles have been successfully prepared via conventional (stirring) sonochemical method (ultrasonication in short time) without surfactant, at room temperature. Diffraction pattern of the Gd₂O₃ nanoparticles were well matched with the cubic structure. The magnetic analysis showed paramagnetic properties of the samples. Both synthesis method obtained particles with nano-sized that revealed by DLS technique. The short time ultrasonic process without surfactant for Gd₂O₃ nanoparticles synthesis in this research has advantages due to its time saving and less energy, also the product has narrower size distribution compare to other methods. Therefore, we believe that the US technique will suit for getting nanoparticle Gd₂O₃ that could be applied in many application fields.

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