JURNAL SAINS MATERI INDONESIA (JUSAMI)
ISSN: 1411-1098 (print), 2614-087X (online)
VOL. 24, ISSUE 1, October 2022
DOI: https://doi.org/10.17146/jsmi.2022.24.1.6674

ORIGINAL ARTICLE

The Effect of Conventional and Sonochemical Synthesis Methods on Gd_2O_3 Nanoparticles Properties

Muflikhah*[1], W Z Lubis[1], M Azizah[2], R P Caesariyanti[2] and Mujamilah[1]

[1]Research Center for Radiation Detection and Nuclear Analysis Technology-Research Organization of Nuclear Power, National Research and Innovation Agency (BRIN), Tangerang Selatan, Indonesia
[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, The Islamic University of Indonesia, Yogyakarta, Indonesia

ABSTRACT – Precipitation is the most common method to obtain nanoparticle including Gd_2O_3 that has potential as a contrast agent in bioimaging such as Magnetic Resonance Imaging (MRI). In this study, the characteristics of Gd_2O_3 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 Gd_2O_3 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 Gd_2O_3 nanoparticles obtained in both methods have a cubic phase. The saturation magnetization (Ms) 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 Gd_2O_3 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 Ms value comply with a request of contrast agent.

ARTICLE HISTORY
Received: 31 August 2022
Revised: 21 Sept 2022
Accepted: 14 Oct 2022

KEYWORDS
Gd_2O_3
Sonochemical
Paramagnetic
MRI

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 (Gd_2O_3) 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 Gd_2O_3 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 Gd_2O_3 nanoparticles via mixing technique has been done by Sakai et. al 2015 with particle diameter under 100 nm, by adjusting calcination temperature from 500 ^oC-1000 ^oC 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 Gd_2O_3 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 Gd_2O_3 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 Gd_2O_3 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 Gd_2O_3 nanoparticles using a user-friendly high-energy sonochemical method this at effective in time with the absence of surfactant. In this study, the Gd_2O_3 nanoparticles will be synthesized in the conventional (stirring) method and sonochemical method to understand the effect from both techniques. The

*CORRESPONDING AUTHOR | Muflikhah | ✉ mufl001@brin.go.id

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 Gd_2O_3 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^{o}C for an hour in air atmosphere.

Synthesis of Gd2O3 by sonochemical

Gadolinium oxide (Gd_2O_3) 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.

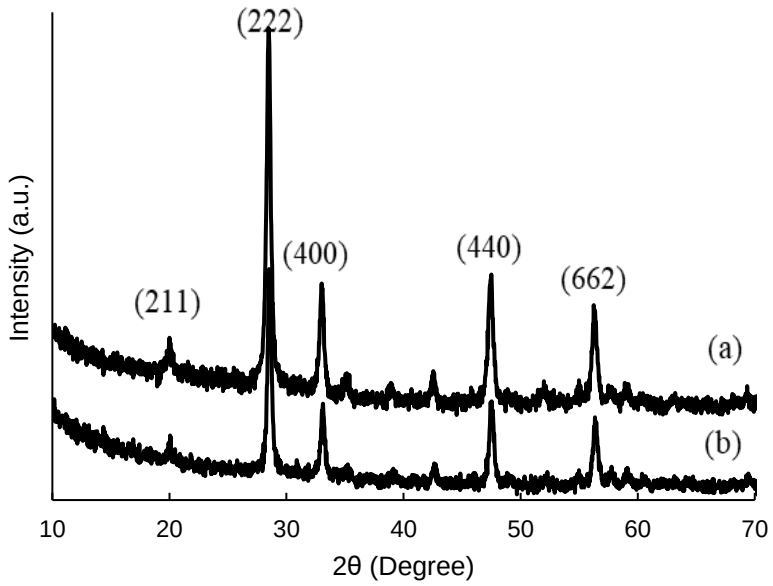


Figure 1. X-Ray powder diffraction pattern of Gd_2O_3 synthesized with (a) conventional method (b) sonochemical method

RESULT AND DISCUSSION

Figure 1 shows the diffraction pattern of Gd_2O_3 prepared with (a) conventional/stirrer method (Gd_2O_3 (S)) (b) sonochemical method (Gd_2O_3 (US)) after annealed at 750^{o}C. The XRD pattern shows main characteristic crystal planes of Gd_2O_3 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 Gd_2O_3 research [4][5]. It was found from calculation that Gd_2O_3 (S) has higher crystallinity (59.39 %) than US synthesized Gd_2O_3 (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 occured [12].

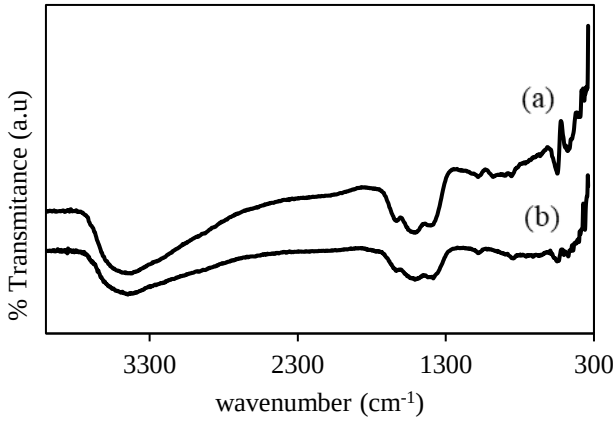


Figure 2. IR spectra of Gd_2O_3 synthesized with (a) conventional method (b) sonochemical method

The FTIR spectra of Gd_2O_3 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 Gd_2O_3 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 remanesence [15]. The magnetization values (Ms) of the both samples are not much different, 1.63 emu/g and 1.44 emu/g for Gd_2O_3 (S) and Gd_2O_3 (US) respectively. However, the higher Ms value of Gd_2O_3 (S) related to their higher degree of crystallinity compare to Gd_2O_3 (US) [16].

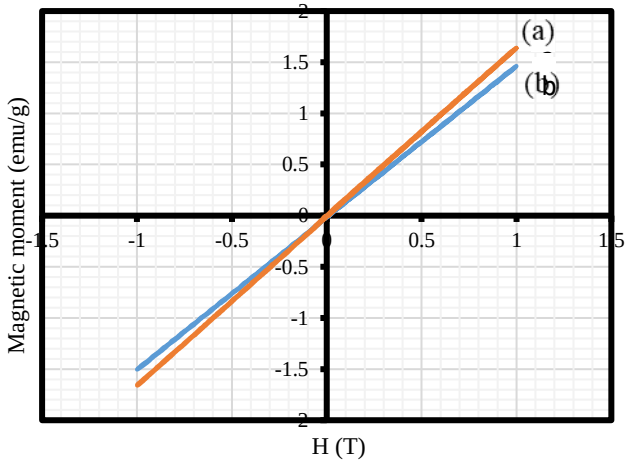


Figure 3. Magnetization curve of Gd_2O_3 synthesized with (a) conventional method (b) sonochemical method

Table 1. Magnetization value of Gd_2O_3 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 Gd_2O_3 nanoparticles have been investigated using dynamic light scattering technique as shown at Figure 4. Both Gd_2O_3 samples were dispersed in aqueous medium by sonication for 5 minutes before analyzed by DLS technique. The Gd_2O_3 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.

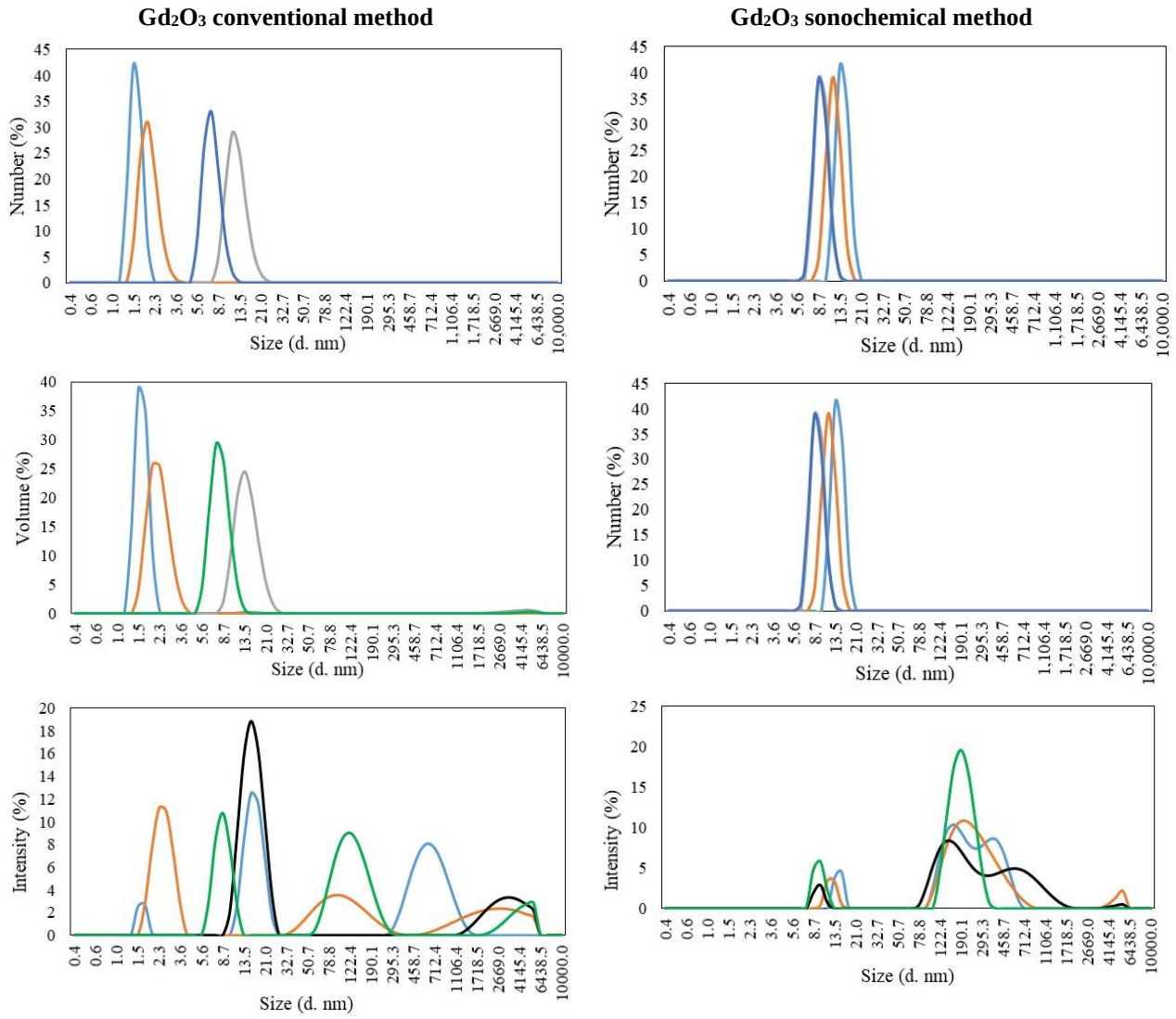


Figure 4. The particle size distribution of Gd_2O_3 nanoparticles synthesized with conventional and sonochemical method

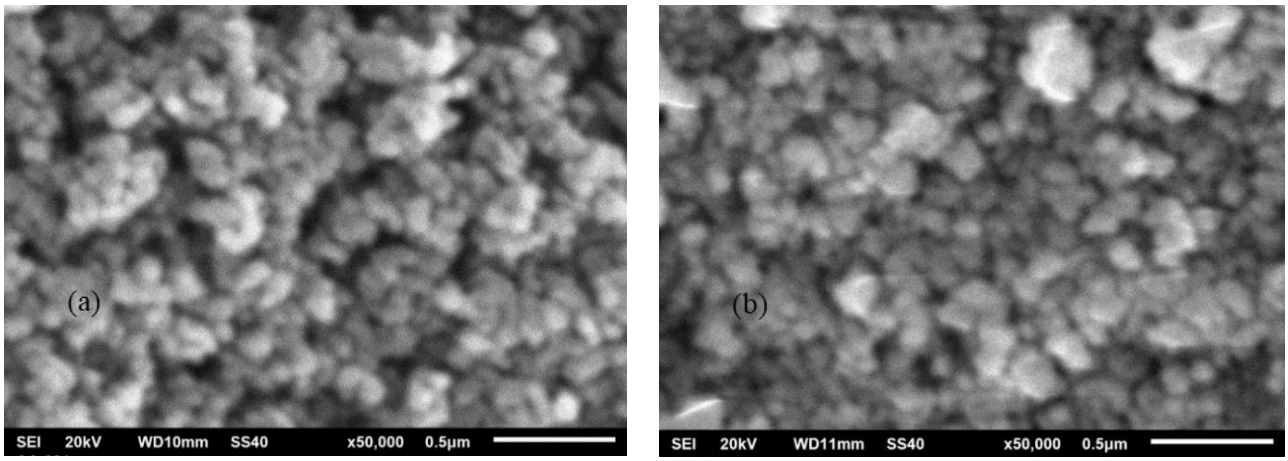
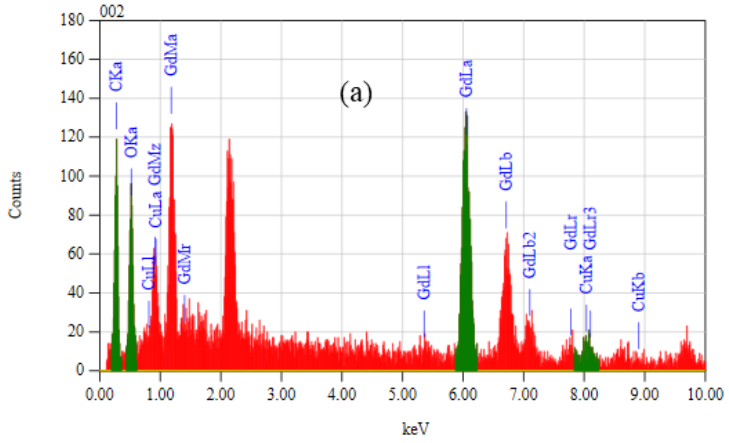


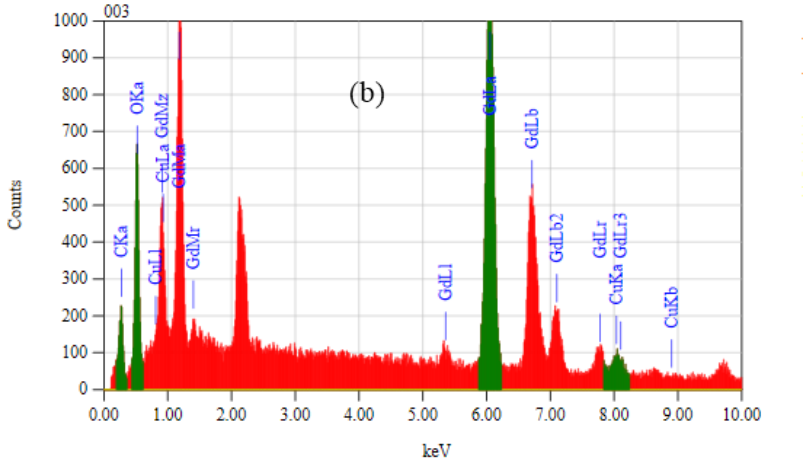
Figure 5. SEM micrograph of Gd_2O_3 nanoparticles synthesized with (a) conventional method (b) sonochemical method

The morphology of the Gd_2O_3 nanoparticles were determined using SEM as shown in figure 5. The micrograph images of Gd_2O_3 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 Gd_2O_3 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 Gd_2O_3 samples.



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.6289

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	21.52	0.16	55.86				8.8544
O K	0.525	15.62	0.38	30.44				15.2145
Cu K	8.040	4.22	1.11	2.07				5.5690
Gd L	6.053	58.64	1.26	11.63				70.3620
Total		100.00		100.00				



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.5110

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	4.48	0.13	21.45				1.5115
O K	0.525	13.01	0.24	46.79				13.5729
Cu K	8.040	2.91	0.89	2.64				3.2644
Gd L	6.053	79.60	1.01	29.12				81.6511
Total		100.00		100.00				

Figure 6. EDS spectra of Gd_2O_3 nanoparticles synthesized with (a) conventional method (b) sonochemical method

The data characterization of Gd_2O_3 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

Gd_2O_3 nanoparticles have been successfully prepared via conventional (stirring) sonochemical method (ultrasonication in short time) without surfactant, at room temperature. Diffraction pattern of the Gd_2O_3 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 Gd_2O_3 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 Gd_2O_3 that could be applied in many application fields.

ACKNOWLEDGEMENT

The author thanks to the Center for Science and Advanced Material Technology-National Nuclear Energy Agency for the funding and infrastructure to support this work. We are grateful for the help of XRD, PSA, and VSM staffs that support the sample characterization.

REFERENCES

[1] S. Kumar, V. K. Meena, P. P. Hazari, S. K. Sharma, and R. K. Sharma. “Rose Bengal Attached and Dextran Coated Gadolinium Oxide Nanoparticles for Potential Diagnostic Imaging Applications,” *Eur. J. Pharm. Sci.*, 2017.

[2] Z. Hu, M. Ahren, L. Selegard, C. Skoglund, F. Sçderlind, M. Engstrçm, X. Zhang, and K. Uvdal. ”Highly Water-Dispersible Surface-Modified Gd2O3 Nanoparticles for Potential Dual-Modal Bioimaging," *Chem. Eur. J.*, vol. 19, no. 38, pp. 12658-12667, 2013.

[3] M. Aghazadeh "Preparation of Gd_2O_3 Ultrafine Nanoparticles by Pulse Electrodeposition Followed by Heat-treatment Method,*" J Ultrafine Grained Nanostruct Mater*, 49, no. 2, pp. 80-86, 2016.

[4] N. Sakai, L. Zhu, A. Kurokawa, H. Takeuchi, S. Yano, T. Yanoh, N. Wada, S. Taira, Y. Hosokai, A. Usui, Y. Machida, H. Saito and Y. Ichiyanagi. "Synthesis of Gd2O3 Nanoparticles for MRI Contrast Agents," *J. Phys.: Conf. Ser.*, vol. 352, no. 1, p. 012008, Mar. 2012.

[5] M. S. Almeida, M. A. B. Santosa, R. F. Gonçalves, M. R. C. Santosa, A. P. A. Marques, E Longo , F. A. Portad, I. M. Pinattie, M. D. P. Silvae, and M. J. Godinhoa. "Novel $Gd(OH)_3$, GdOOH and Gd2O3 Nanorods: Microwave-Assisted Hydrothermal Synthesis and Optical Properties," *Materials Research*, vol. 19, no. 5, 2016.

[6] M. Z. A. M. Jamil, F. Mohamed, N. R. A. Rosli, and I A. Rahman. "Synthesis of Cubic Phase Gd_2O_3 Nanoparticles Using Hydrothermal Method," *J. App. Phys.*, vol. 9, no. 5, 2017.

[7] T. Q. Bui, H. Thi, M. Ngo, and H. T. Tran. “Surface-protective assistance of ultrasound in synthesis of superparamagnetic magnetite nanoparticles and in preparation ofmono-core magnetite-silica nanocomposites,” J. Sci. Adv. Mater. Devices, vol. 3, no. 3, pp. 323–330, 2018.

[8] H Khajuria, J. Ladol, R. Singh, S. Khajuria, and H. N. Sheikh. "Surfactant Assisted Sonochemical Synthesis and Characterization of Gadolinium Doped Zinc Oxide Nanoparticles," *Acta Chim. Slov.*, vol. 62, no. 4, pp. 849-858, 2015.

[9] I. Muneer, M.A. Farrukh, S. Javaid, M. Shahid, and M. Khaleeq-ur-Rahman "Synthesis of Gd_2O_3/Sm_2O_3 Nanocomposite via Sonication and Hydrothermal Methods and Its Optical Properties,” *Superlattices and Microstructures*, vol. 77, pp. 256-266, 2014.

[10] M. A. Dheyab, A. A. Aziz, M. S. Jameel, P. M. Khaniabadi, and A. A. Oglat, “Rapid Sonochemically-Assisted Synthesis of Highly Stable Gold Nanoparticles as Computed Tomography Contrast Agents,” *Applied Sciences*, vol. 10, no. 20, p. 7020, 2020.

[11] G. Boopathi 1, S. G. Raj, G. R.h Kumar, and R. Mohan. "Co–precipitation Synthesis, Sstructural and Luminescent Behavior of Erbium Doped Gadolinium Oxide (Er^{3+}: Gd_2O_3) Nanorod,” *Procedia Materials Science*, vol. 6, pp. 1436-1443, 2014.

[12] D. V. Pinjari and A. B. Pandit. "Room Temperature Synthesis of Crystalline CeO_2 Nanopowder: Advantage of Sonochemical Method Over Conventional Method," *Ultrason. Sonochemistry*, vol. 18, no. 5, pp. 1118-1123, 2011.

[13] F. Whba, F. Mohamed, N. Ratasha, A. Rosli, and I. Abdul. “The Crystalline Structure of Gadolinium Oxide Nanoparticles (Gd_2O_3-NPs) Synthesized at Different Temperatures via X-ray diffraction (XRD) Technique,” *Radiat. Phys. Chem.*, vol. 179, p. 109212, 2021.

[14] T. Selvalakshmi and A. C. Bose, “Optical Study on Gadolinium Oxide Nanoparticles Synthesized by Hydrothermal Method,” *Adv. Mat. Res.*, vol. 585, pp. 105-109, 2012.

[15] S. R. Alam, S. Haghgoob, E. Gorjib, N. R. Alam, and S. Haghgoo. “Size Reproducibility of Gadolinium Oxide Based Nanomagnetic Particles for Cellular Magnetic Resonance Imaging: Effects of Functionalization, Chemisorption and Reaction Conditions,” *Iran. J. Pharm. Res.*, vol. 14, no. 1. pp. 3, 2015.

[16] C.H. Chia, S. Zakaria, M. Yusoff, S.C. Goh, C.Y. Haw, Sh. Ahmadi, N.M. Huang, and H.N. Lim. "Size and Crystallinity-Dependent Magnetic Properties of $CoFe_2O_4$ Nanocrystals," *Ceramics International*, vol. 36, no. 2, pp. 605-609, 2010.

[17] A. Dougherty, E. L. Y. Nasution, F. Iskandar, and G. Dougherty, “Journal of Science : Advanced Materials and Devices Facile Solvothermal Synthesis and Functionalization of Polyethylene Glycol-Coated Paramagnetic $Gd_2(CO_3)_3$ Particles and Corresponding Gd_2O_3 Nanoparticles for Use as MRI Contrast Agents,” *J. Sci. Adv. Mater. Devices*, vol. 4, no. 1, pp. 72-79, 2019.