

RESEARCH PAPER

Synthesis and Characterization of $Gd_2O_2S:Tb^{3+}$ Phosphor Powder for X-ray Imaging Detectors

Maliheh Hassani^{1,*}, Parvin Sarabadani², Ali Hashemizadeh Aghda¹

¹ Department of Physics, Payame noor University (PNU), Tehran, Iran

² Nuclear Science and Technology Research Institute, Karaj, Iran

ARTICLE INFO

Article History:

Received 11 May 2019

Accepted 11 July 2019

Published 01 October 2019

Keywords:

Phosphor

Synthesis

Terbium Doped Gadolinium

Oxysulfide

X-ray Detector

ABSTRACT

Gadolinium oxysulfide phosphor doped with trivalent terbium have been synthesized using urea homogenous precipitation and followed by sulfurization at 800 °C under argon atmosphere. Structural and morphological of synthesized phosphor powder were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectrometry (FT-IR). Hexagonal structure of $Gd_2O_2S:Tb^{3+}$ phosphor was confirmed by XRD. Compositional analysis was carried out by energy dispersive x-ray (EDX) and particle induced x-ray emission (PIXE). Photoluminescence emission spectra was measured by the fluorescent spectrometer. A sedimentation technique is used to deposit the phosphor powder directly on the glass substrate using poly vinyl alcohol as a paste. A number of phosphor layers have been synthesized with the layer thickness ranging from 150 to 268 μm . Measurement results of x-ray conversion efficiency for layers were investigated using 300 kVp X-ray tube in which the maximum light output and contrast were observed for the layer with a thickness of 193 μm . Oxysulfide phosphor layer was analyzed by ion beam induced luminescence (IBIL). Emitting of green light from phosphor layer confirms its luminescence property.

How to cite this article

Hassani M, Sarabadani P, Hashemizadeh Aghda A. Synthesis and Characterization of $Gd_2O_2S:Tb^{3+}$ Phosphor Powder for X-ray Imaging Detectors. J Nanostruct, 2019; 9(4): 616-622. DOI: 10.22052/JNS.2019.04.003

INTRODUCTION

The rare earth oxysulfide phosphors have gained considerable attraction in recent years due to their advantages such as high luminescence efficiency [1]. These materials are widely used as luminescent host materials for X-ray application because of their high conversion efficiency (12–25%) of the exciting radiation [2-5]. Terbium activated gadolinium oxysulfide ($Gd_2O_2S:Tb$), one of the rare earth oxysulfide group of phosphors, is known to be an efficient phosphor and shows bright green luminescence and high efficiency under UV, cathode-ray and X-ray excitations [6].

Terbium activated gadolinium oxysulfide phosphors were prepared by different methods such as flux method [7], combustion [8] and

solvothermal [9]. However, in most of these methods to achieve the desired size, the particles must be milled, which causes defects in the surface and non-radiative recombination of electrons and holes with a drop in the luminescence efficiency. Among these methods, the homogeneous precipitation method [1] is more appropriate than others due to its simplicity, rapidity and economy.

Herein, gadolinium oxysulfide phosphor doped with trivalent terbium was prepared via urea homogenous precipitation and followed by sulfurization at 800 °C under argon atmosphere.

MATERIALS AND METHODS

Gadolinium oxide and terbium activated oxysulfide were prepared through homogenous

* Corresponding Author Email: maliheh.hasani@gmail.com

precipitation method [1].

For preparing of gadolinium oxide, typically, 0.54 g $Gd(NO_3)_3 \cdot 6H_2O$ was dissolved in 25 mL water (0.5 M), then diluted to 500 mL with deionized water and heated for 30 min at 90 °C. After that, urea solution (30 g urea dissolved in 120 mL water) was added to it and stirred for 30 min at 90°C. The mixture solution was aged for a period when visible bluish tint occurred. After aging, the precipitates generated were observed on the bottom of the beaker. The resulting precipitate was separated by centrifugation (4000 rpm), washed two times with deionized water and once with ethanol, then was dried at 100°C for 24 h. The dried precipitate was calcined at 800°C for 1 h to obtain the white Gd_2O_3 powder.

Terbium activated gadolinium oxysulfide were also prepared through homogenous precipitation method via two steps. In the first step, typically, 25 mL $Gd(NO_3)_3 \cdot 6H_2O$ (0.5 M) and the proper amount of $Tb(NO_3)_3 \cdot 5H_2O$ (0.01 M) stock solutions were weighed out, mixed, then diluted to 500 mL with deionized water and heated for 30 min at 90 °C. After that, urea solution (30 g dissolved in 120 mL water) was added to it and stirred for 30 min at 90 °C. The obtained solution was aged overnight. After that, urea solution (30 g urea dissolved in 120 mL water) was added to it and stirred for 30 min at 90 °C. The mixture solution was aged for a period when visible bluish tint occurred. After aging, the precipitate generated was observed on the bottom of the beaker. The resulting precipitate was separated by centrifugation (4000 rpm), washed two times with deionized water and once with ethanol, and was dried at 100°C for 24 h. The dried precipitate was calcined at 800°C for 1 h to obtain the yellowish $Gd_2O_3:Tb$ powder.

In the second step, the sulfurization of oxide was carried out by the solid-gas reaction. A mix of sulfur and the $Gd_2O_3:Tb^{3+}$ powders (ratio of S to $Gd_2O_3:Tb^{3+}$ was 1 to 1.5) was placed into a quartz tube and the sulfurization reaction was performed at 900°C under argon atmosphere. The heating temperature of the sulfur powder was 400°C, and the sulfur vapor flow was controlled by adjusting the intensity of argon gas flow. After the reaction was kept for 1 h, the sulfurization was stopped and only the argon gas flow was supplied until the sample was cooled to the room temperature. Finally, the white $Gd_2O_2S:Tb^{3+}$ powder was obtained.

Terbium activated gadolinium oxysulfide

phosphor layers were fabricated using by sedimentation method [10]. In this method, the coating solution was first prepared by dissolving 15 g polyvinyl alcohol (PVA) into 500 mL deionized water with proper agitation. After the PVA was fully dissolved, the solution poured into a, flat-bottomed Plexiglas vessel for mixing with phosphor particles. The solution in the vessel was stirred, then a small amount of the additives was introduced followed by gradual addition of weighted phosphor particles. The overall mixing process must be subject to agitation until the phosphor particles were able to fully disperse into the polymer matrix. Here, the rate of agitation played a critical role. It must yield enough centrifugal force to keep the phosphor particles suspended in solution for dispersion. Agitation was terminated when the particles were fully dispersed and then a homogeneous coating system was achieved. The scintillator layer thickness was varied by varying the amount of used $Gd_2O_2S:Tb^{3+}$ powder: 0.9, 1.9 and 2.9 g. The amount of used PVA as a binder was constant (15 g). After that, the glass substrates introduced to solutions and put settled for different times, as shown in Table. 1. When all of the particles settled down completely, the phosphor-coated substrates were removed and calcined at 60 °C in an oven for 1 hr. Fig. 1(a) and (b) show Plexiglas vessel containing PVA solution and phosphor coated layers, respectively.

The crystal structures were identified by a powder X-ray diffractometer (XRD, Inel model Equinox-3000) employing Cu $K\alpha$ radiation ($k=1.5418 \text{ \AA}$). The XRD Patterns of phosphors were confirmed by comparing with the JCPDS (Joint Committee on Powder Diffraction Standards) data. The morphology of the synthesized phosphors was imaged by scanning electron microscopy (SEM, Tescan model MIRA3 XMU). Chemical composition of the synthesized phosphors was determined by Energy dispersive x-ray spectroscopy (EDS, Samx)

Table 1. Used amounts of $Gd_2O_2S:Tb^{3+}$ and PVA powders at different settle times for preparation of phosphor layer

Samples	PVA (g)	$Gd_2O_2S:Tb^{3+}$ (g)	Settle time (h)
1	15	0.9	21
2	15	0.9	42
3	15	0.9	63
4	15	1.9	21
5	15	1.9	42
6	15	1.9	63
7	15	2.9	21
8	15	2.9	42

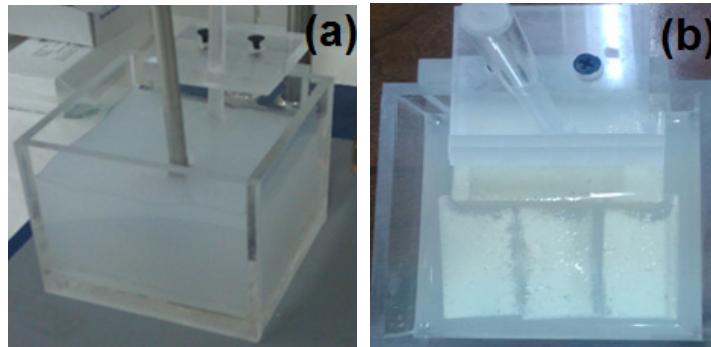
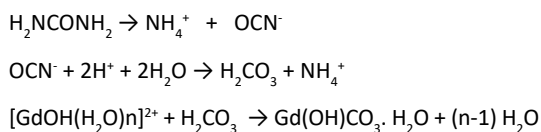


Fig. 1. (a) Plexiglas vessel containing PVA solution; (b) Phosphor coated layers

and particle induced x-ray emission (PIXE). The PIXE analysis was carried out using conventional RBS-PIXE reaction chamber at the facilities of Van de Graff Lab in Tehran [11]. A 2000 keV proton beam of about 1 mm diameter was applied for analysis. The X-ray spectra were collected by a Si(Li) X-ray detector placed at a scattering angle of 135°. FT-IR spectra (4000–400 cm⁻¹) in KBr were recorded using a Bruker-vertex 70 spectrometer. Emission spectra of Gd₂O₂S:Tb³⁺ were measured by a Varian Carry Eclipse fluorescent spectrometer at room temperature with a xenon flash lamp as excitation source. An X-ray tube model Baltospot Ceram35 was used for irradiation of prepared phosphor layers.

RESULTS AND DISCUSSION

Terbium activated gadolinium oxysulfide was synthesized through two steps. In the first step, spherical hydroxyl carbonate precursor powder was prepared using the urea homogeneous precipitation method at over 90°C [12]. The homogeneous precipitation technique is based on the slow hydrolysis of Gd³⁺ ion for the preparation of Gd(OH)CO₃. The whole process can be simplified as the release of CO₂ and NH₃ by urea decomposition, followed by the sequential addition of the ligands OH⁻¹ and CO₃²⁻ to the Gd³⁺ ion until the concentration of reactants reaches critical supersaturation and then precipitation occurs [13]. The chemical reactions to obtain precursors are given below:



In the second step, obtained precipitate was

converted to the gadolinium oxysulfide through sulfurization treatment under argon atmosphere.

The Fig. 2 shows the XRD patterns of different synthesized samples. It is obvious from the XRD patterns (curve (a)), the diffraction peaks at 2θ= 28.6, 33.1, 47.5, and 56.4° are for (222), (400), (440) and (622) of cubic Gd₂O₃ [14], in good agreement with reported data (JCPDS Card number 43-1014). The high intensity of the diffraction peaks in (curve (b)) indicates good crystallinity of the Gd₂O₃:Tb³⁺. This also means that the Tb³⁺ ions have been effectively built into the host lattice of Gd₂O₃ [15]. After the Gd₂O₃:Tb³⁺ powders were sulfurized

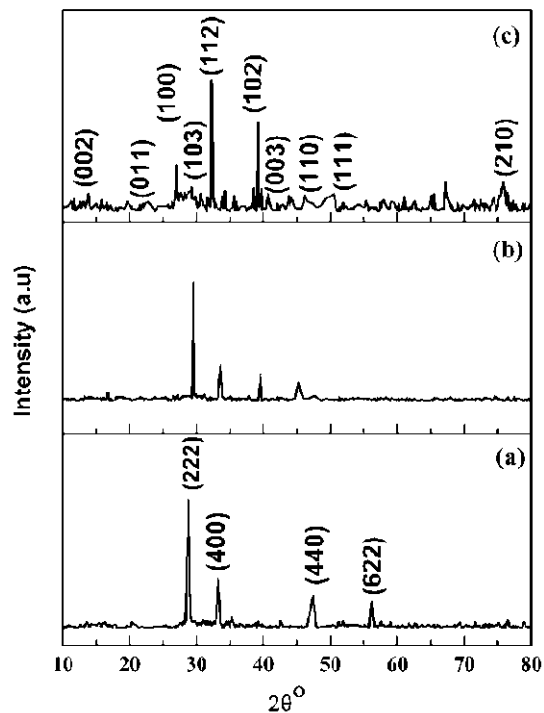


Fig. 2. XRD patterns of different samples: (a) Gd₂O₃; (b) Gd₂O₃:Tb³⁺; (c) Gd₂O₂S:Tb³⁺

at 800°C for 1 h under nitrogen atmosphere containing sulfur vapor (curve (c)), the XRD lines of sample are matched with the data of JCPDS Card No.26-1422, which shows pure hexagonal phase of Gd₂O₂S:Tb³⁺ powder.

Fig. 3 shows the FTIR spectra of the Gd₂O₃ (curve (a)), Gd₂O₃:Tb³⁺ (curve (b)) and Gd₂O₂S:Tb³⁺ (curve (c)). For the precursor, the broad absorption band around 3460 cm⁻¹ can

be assigned to O-H stretching vibration; the bands around 1460 and 1630 cm⁻¹ result from C-O asymmetrical stretching vibration; the peak that appears at 1042 cm⁻¹ can be assigned to C-O symmetric stretching vibration; the strong peak at 420-510 cm⁻¹ associated with the vibration of Gd-O and Gd-S [16] is observed, indicating the formation of Gd₂O₂S:Tb³⁺.

Spherical nano-particles formation of Gd₂O₂S:Tb³⁺ phosphor were confirmed by SEM images as shown in Fig. 4. According to it, the phosphor particles are well separated from each other and exhibit smooth surfaces with a spherical shape.

The chemical composition of gadolinium oxide, terbium doped gadolinium oxide and terbium doped gadolinium oxysulfide were analyzed by EDS and the results are shown in Fig. 5. The results of quantitative analysis confirm the presence of Gd and O in Gd₂O₃ (graph (a)), Gd, O and Tb

in Gd₂O₃: Tb³⁺ (graph (b)) and Gd, O, S and Tb in Gd₂O₂S: Tb³⁺ (graph (c)), which are compatible with the obtained result from particle induced X-ray emission (PIXE) for c sample (Fig. 6).

The Photoluminescence emission spectra of the Gd₂O₂S:Tb³⁺ particles excited at 254 nm respectively is shown in Fig. 7. The luminescence peaks in the figure arise from the transitions

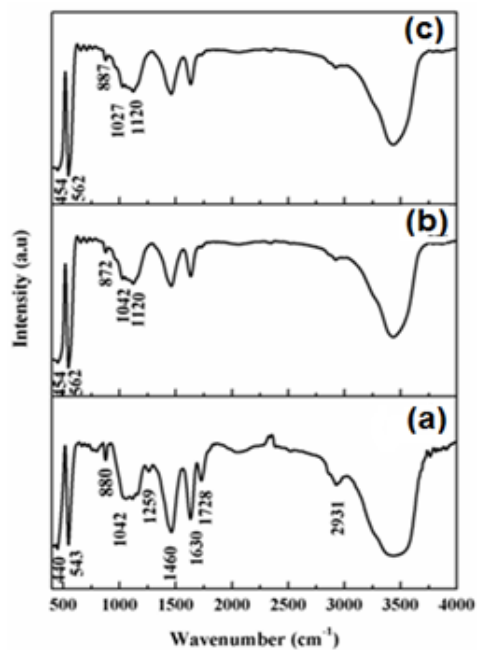


Fig. 3. FTIR spectra of the: (a) Gd₂O₃; (b) Gd₂O₃: Tb³⁺ and (c) Gd₂O₂S: Tb³⁺ powders

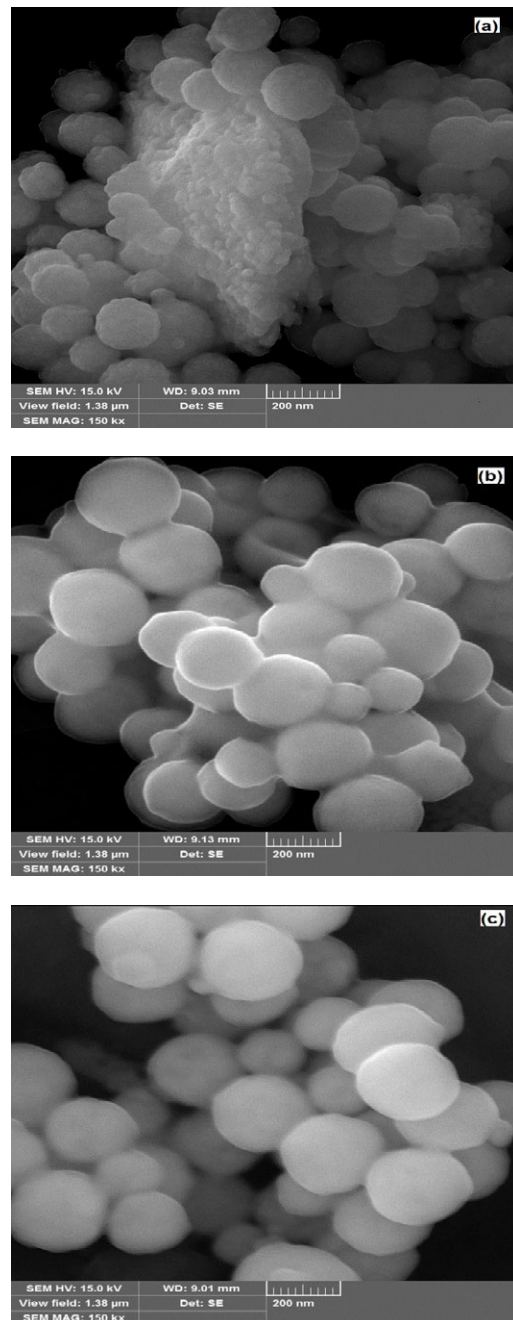


Fig. 4. Scanning electron micrograph of the: (a) Gd₂O₃; (b) Gd₂O₃: Tb³⁺ and (c) Gd₂O₂S: Tb³⁺ powders

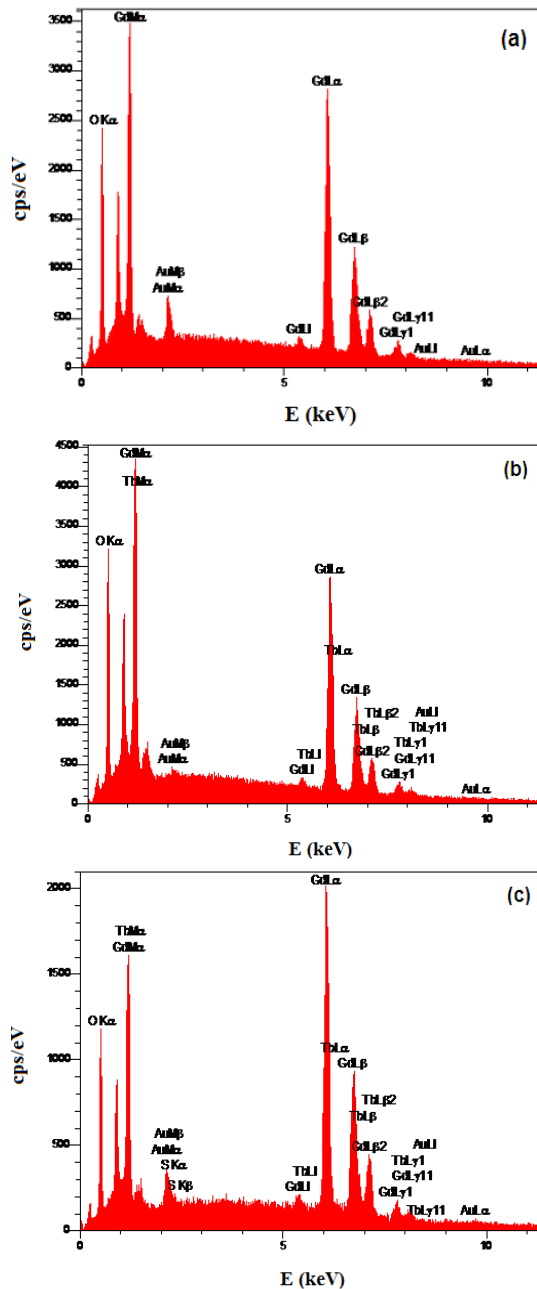


Fig. 5. EDX spectra of the: (a) Gd_2O_3 ; (b) $Gd_2O_3:Tb^{3+}$ and (c) $Gd_2O_3:S:Tb^{3+}$ powders

of 5D_3 and 5D_4 excited state levels to 7F_J ($J=0-6$) ground state levels, respectively, and belong to the characteristic emission of Tb^{3+} . The emission lines between the 370 and 450 nm correspond to the $^5D_3 \rightarrow ^7F_J$ ($J=0-6$) transitions, and the emission lines between the 480 and 600 nm correspond to the $^5D_4 \rightarrow ^7F_J$ ($J=3, 4, 5, 6$) transitions [17].

Moreover, the photoluminescence property of oxysulfide phosphor layer was investigated by ion

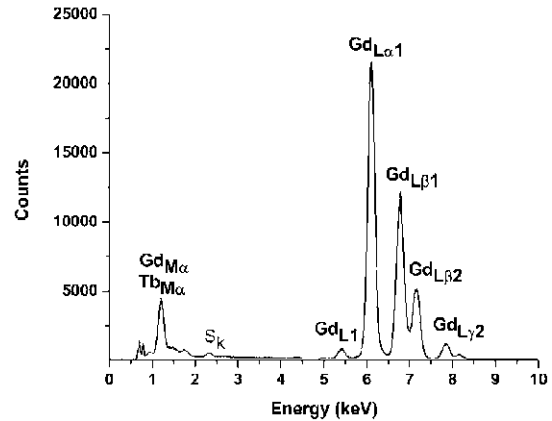


Fig. 6. PIXE spectra of $Gd_2O_3:S:Tb^{3+}$ powder

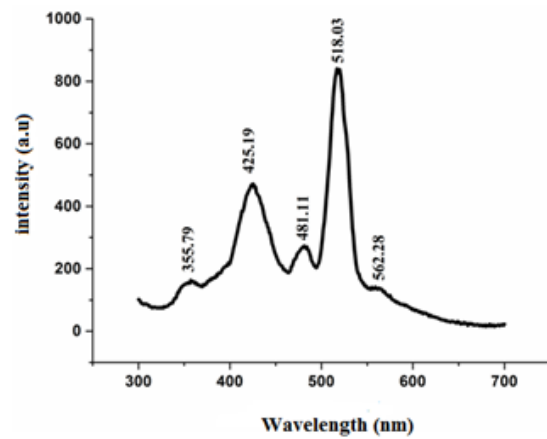


Fig. 7. Photoluminescence emission ($\lambda_{ex} = 254$ nm) at room temperature for $Gd_2O_3:S:Tb^{3+}$ powder



Fig. 8. Ion beam induced luminescence (IBIL) of $Gd_2O_3:S:Tb^{3+}$ layer

beam induced luminescence (IBIL). As is shown in Fig. 8, emitting of green light from phosphor layer confirm its luminescence property.

Eight of $Gd_2O_3:S:Tb^{3+}$ scintillator layers with

Table 2. The thickness of prepared layers

Samples No.	1	2	3	4	5	6	7	8
Thickness (μm)	181	189	268	196	193	150	150	162

Table 3. Contrast dependence on the thickness of phosphor layer

Samples No.	1	2	3	4	5	6	7	8
Thickness (μm)	181	189	268	196	193	150	151	162
Contrast	0.463	0.483	0.497	0.471	0.525	0.165	0.124	0.143

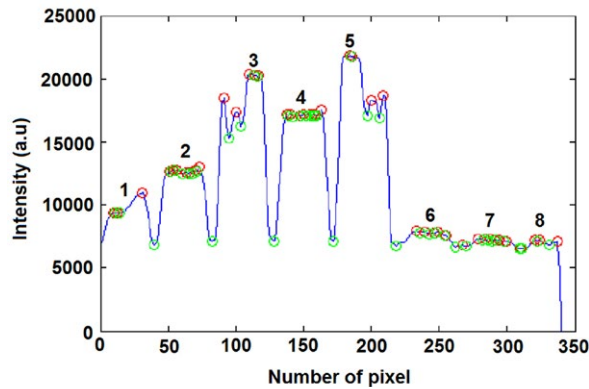


Fig. 9. The effect of thickness on light output

various thickness were prepared and optically coupled with a CCD image sensor for X-ray imaging performance measurement. Table. 2 shows the thickness of prepared layers.

The pixelated Gd₂O₂S: Tb³⁺ scintillator layers were tested by 300 kVp X-ray beam at 5 mA as beam current. The light outputs were measured in a dark box by a CCD camera. The relative light output of the layers with various thickness was estimated from the pixel values of the CCD images. Fig. 9 shows the light intensity in terms of a number of pixel for phosphor layers.

As seen in Fig. 9, maximum light output of the Gd₂O₂S: Tb³⁺ scintillator layer was obtained for sample no.5 with 193 μm thickness. The effect of different thickness on the contrast is also presented in Table. 3. The results listed in this table show that the contrast is increased by increasing the thickness of the phosphor layer, then is reduced. The reason may be that a thicker layer of phosphor can absorb more radiation, which increases the dispersion and so reduce the contrast.

CONCLUSION

In this study, green phosphor Gd₂O₂S:Tb³⁺ scintillator were obtained using urea homogeneous precipitation method. Hexagonal structure of Gd₂O₂S:Tb³⁺ phosphor powder was confirmed by

XRD. Obtained phosphor have spherical shape. The phosphor powders were deposited on the glass substrates using poly vinyl alcohol as a paste via sedimentation method. The effect of thickness layer on light output and contrast were investigated. The results show, the optimum thickness was 193 μm. Moreover, emitting of green light from phosphor layer confirm its luminescence property.

ACKNOWLEDGEMENTS

The authors wish to thank Nuclear Science & Technology Research Institute.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Tian Y, Cao W-H, Luo X-X, Fu Y. Preparation and luminescence property of Gd₂O₂S:Tb X-ray nano-phosphors using the complex precipitation method. *Journal of Alloys and Compounds*. 2007;433(1-2):313-7.
2. Issler SL, Torardi CC. Solid state chemistry and luminescence of X-ray phosphors. *Journal of Alloys and Compounds*. 1995;229(1):54-65.
3. Wickersheim KA, Alves RV, Buchanan RA. Rare Earth Oxysulfide X-Ray Phosphors. *IEEE Transactions on Nuclear Science*. 1970;17(1):57-60.

4. Shepherd JA, Gruner SM, Tate MW, Tecotzky M. Study of persistence in gadolinium oxysulfide x-ray phosphors. X-Ray and Ultraviolet Sensors and Applications; 1995/06/15: SPIE; 1995.
5. J.P. Creasey, G.C. Tyrrell, SPIE-The International Society for Optical Engineering. 3942 (2000) 114.
6. Giakoumakis GE, Nomicos CD, Sandilos PX. Absolute efficiency of $Gd_2O_2S:Tb$ screens under fluoroscopic conditions. Physics in Medicine and Biology. 1989;34(6):673-8.
7. Popovici E-J, Muresan L, Hristea-Simoc A, Indrea E, Vasilescu M, Nazarov M, et al. Synthesis and characterisation of rare earth oxysulfide phosphors. I. Studies on the preparation of $Gd_2O_2S:Tb$ phosphor by the flux method. Optical Materials. 2004;27(3):559-65.
8. Bang J, Abboudi M, Abrams B, Holloway PH. Combustion synthesis of Eu-, Tb- and Tm- doped Ln_2O_2S ($Ln=Y, La, Gd$) phosphors. Journal of Luminescence. 2004;106(3-4):177-85.
9. Young Park J, Chae Jung H, Seeta Rama Raju G, Kee Moon B, Jeong JH, Hwan Kim J. Solvothermal synthesis and luminescence properties of Tb^{3+} -doped gadolinium aluminum garnet. Journal of Luminescence. 2010;130(3):478-82.
10. Hu X, Han Z, Li G, Gu M. Microstructure and properties of Ti-Si-N nanocomposite films. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films. 2002;20(6):1921.
11. Kakuee OR, Fathollahi V, Lamehi-Rachti M, Oliyai P, Seyedi H, Safa S, et al. Ion Beam Analysis of Hydrogen-Treated Ti/TiN Protective Nanomultilayers. Acta Physica Polonica A. 2012;122(1):132-7.
12. Vecht A, Gibbons C, Davies D, Jing X, Marsh P, Ireland T, et al. Engineering phosphors for field emission displays. Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures. 1999;17(2):750.
13. Willard HH, Tang NK. A Study of the Precipitation of Aluminum Basic Sulfate by Urea. Journal of the American Chemical Society. 1937;59(7):1190-6.
14. Choi J, Tseng T-K, Davidson M, Holloway PH. Enhanced photoluminescence from $Gd_2O_3:Eu^{3+}$ nanocores with a Y_2O_3 thin shell. Journal of Materials Chemistry. 2011;21(9):3113.
15. Jia G, Yang M, Song Y, You H, Zhang H. General and Facile Method To Prepare Uniform $Y_2O_3:Eu$ Hollow Microspheres. Crystal Growth & Design. 2009;9(1):301-7.
16. Hirai T, Orikoshi T. Preparation of yttrium oxysulfide phosphor nanoparticles with infrared-to-green and -blue upconversion emission using an emulsion liquid membrane system. Journal of Colloid and Interface Science. 2004;273(2):470-7.
17. Kang S-S, Park J-K, Choi J-Y, Cha B-Y, Cho S-H, Nam S-H. Electrical characteristics of hybrid detector based $Gd_2O_2S:Tb$ -Selenium for digital radiation imaging. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment. 2005;546(1-2):242-6.