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Synthesis and Characterization of $Gd_2O_2SO_4$:Pr^{3+} Scintillation Material Produced by Sol–Gel Process for Digital Imaging System

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Scintillation materials are widely used in digital X-ray imaging applications, radiotherapy applications coupled with suitable photoreceptors. $Gd_2O_2SO_4$ (GOS) scintillator doped with trivalent praseodymium (Pr^{3+}) presented high X-ray absorption properties and good spectral compatibility which were utilized extensively for imaging system of X-ray microscopy, soft X-ray phosphor screen for water window. In this study, GOS:0.01Pr^{3+} scintillation material was synthesized by unique sol–gel process which was not previously applied and its characterization properties were investigated. Structure and luminescence properties of GOS:Pr^{3+} were optimized by utilizing X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and luminescence spectroscopy.

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1. Introduction

Thanks to the fact that phosphorescence materials have the physical and chemical properties, they are used as vital material in specific devices and electronics systems [1]. Because of the intensive requirements of phosphorescence materials, developments in these materials are continuously being updated [2]. GOS phosphorescence materials are used as scintillation material in imaging systems, because of the effective luminescence behavior, which transform X- and/or γ-rays to visible light [3]. Therefore, identifying the luminescence properties such as; crystal structure, particle shape, emission wavelength, light yield, lifetime and intensity parameters should be experimentally examined and further development must be sustained [4]. At this point, studies on synthesis and characterization of Eu^{3+} and/or Tb^{3+} rare earth elements activated GOS materials were performed. For instance $Gd_2O_2SO_4$:Tb^{3+} nanopieces were synthesized by a combined approach of electrospinning and calcination at 1000 °C in mixed gas of sulfur dioxide and air. The nanopieces excited by a 230 nm light showed excellent green luminescence with the strongest emission peak at 545 nm due to the $^5D_4$–$^7F_5$ transition of Tb^{3+} [5]. In addition to, $(Gd_{1-x},Eu_x)_2O_2SO_4$ nanophosphors were synthesized by a novel co-precipitation method from commercially available Gd_2O_3, Eu_2O_3, H_2SO_4 and NaOH starting materials. Photoluminescence (PL) spectroscopy reveals that the strongest emission peak is located at 617 nm under 271 nm light excitation, which corresponds to the $^5D_0$–$^7F_2$ transition of Eu^{3+} ions [6]. Furthermore, $Gd_2O_2SO_4$:Eu^{3+} nanoparticles have been synthesized in the presence of Gd^{3+} ions and sodium dodecyl sulphate by the simple complexation-thermal decomposition method [7]. In this study, GOS:Pr^{3+} nanoparticles, which had never previously been available in the literature, were synthesized by innovative sol–gel method and the resulting nanoparticles were characterized by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and PL spectra devices.

2. Experimental details

In order to prepare the solution, after weighing the starting chemicals composed of based Gd-, S-, urea, and Pr-alkoxides, pure water is used for the solution of precursors which are powder based. The amount of Pr dopant was 0.01% mol. The solution was stirred until it became transparent in an ultrasonic mixer at 80 °C. The sol–gel is a sophisticated method of producing various powder materials from liquid forms, which are widely used. Therefore, the starting point of the liquid form is carefully obtained in order for the targeted final structure to be successful by the sol–gel method. In this scope, various tests were applied for the characterization of the prepared solution. A blur test of the solution was performed using a standard VELP TB1 Model turbidity meter and the pH was measured. Turbidity and pH values were detected 10 ntu and 6.1, respectively. After the gel formation was complete, drying was performed at 200 °C. The production of the scintillator material was achieved at 950 °C. The detection of the current phase of the produced based GOS:Pr^{3+} material was analyzed by

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Thermo Scientific Cu K_α model XRD. Imaging of the microstructures of particles were carried out at 100k× magnification and 5 kV accelerating voltage using a FEI Nova NanoSEM 650. Elemental analysis was performed using the Thermo-Scientific Al K_α model XPS device. Steady-state PL measurements were recorded using a red sensitive photomultiplier tube equipped spectrofluorometer system (Edinburgh Instruments, UK). The instrument was equipped with a standard 15 W Xe lamp for steady-state measurements.

3. Results and discussion

The XRD pattern of produced GOS:Pr^{3+} particles at 950 °C is shown in Fig. 1. As a result of the analysis, well-defined diffraction peaks are revealed and the lattice parameters ($a = 4.04$ Å, $b = 4.17$ Å, $c = 12.97$ Å) belong to the orthorhombic phase matching with the standard (JCPDS no. 029-0613) values of GOS:Pr.

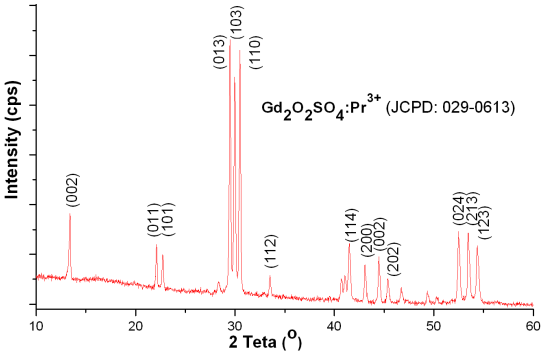

Fig. 1. XRD pattern of produced GOS particles at 950 °C.

Elemental analysis of GOS:Pr^{3+} powder can be observed in Fig. 2. According to the results, Gd, O, S, and also Pr are seen in the structure. Carbon has 285 eV binding energies that belong to the carboxyl group and it is thought to be an impurity in the structure. Gd 3*d* was detected at 1285 eV, which could be said that it belongs to the structure of GOS. O 1*s* was seen at 530 eV and it also is known to belong to metal oxide structure. Pr 3*d* was identified at 931 eV. It showed Pr^{3+} ions are a doped structure.

SEM microstructures in 50k× magnifications of GOS:Pr^{3+} nanoparticles are seen in Fig. 3. When the structure is analyzed, the SEM image clearly indicated that GOS:Pr^{3+} structure consisted of cactus needle-like nanoparticles assembled by orientation mechanism. Each needle grains were observed to be 200–400 nm in size. These results showed that the rod-like structure was more stable than the spherical structure. In the study by Manigandan et al., a similar microstructure was already obtained [8].

Figure 4a and b shows the excitation and emission spectra of GOS:Pr^{3+} nanoparticles. According to energy

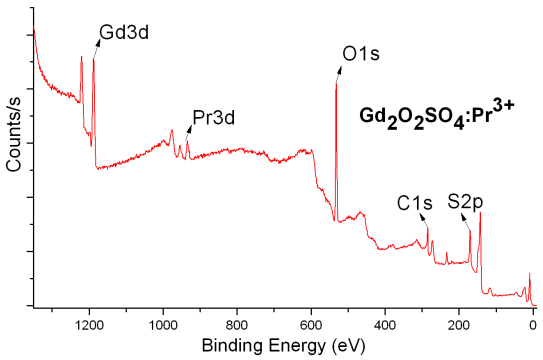

Fig. 2. XPS pattern of GOS:Pr^{3+} powder.

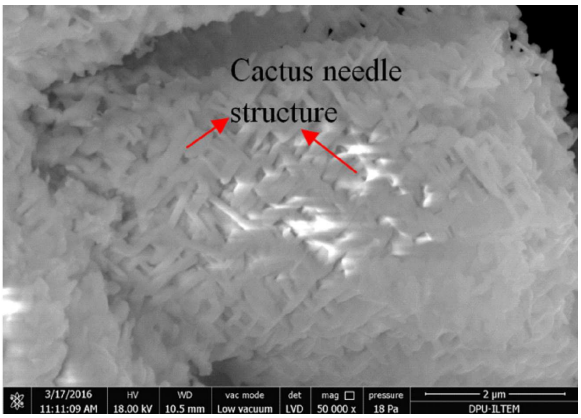

Fig. 3. SEM image of GOS:Pr^{3+} nanoparticles (50k×).

transition of praseodymium at 562 nm, when the excitation scan was made, it had the best spectrum at 374 nm (see Fig. 4a). Emissions under excitation at 374 nm of GOS:Pr^{3+} nanoparticles are indicated in Fig. 4b. GOS's host switching between 420 and 460 nm was observed. Due to Pr^{3+} dopant, respectively $^3P_0$–$^3H_4$ and $^3P_0$–$^3H_5$ energy transitions were observed at 504 and 562 nm.

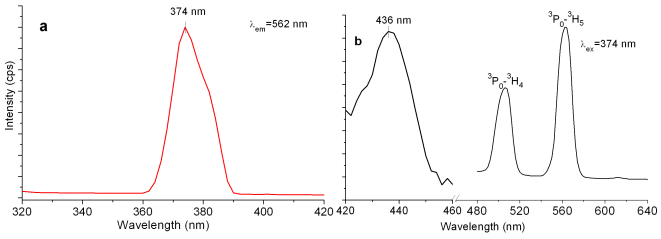

Fig. 4. Photoluminescence spectrum: (a) excitation spectra of the GOS:Pr^{3+}, (b) emission spectra of the GOS:Pr^{3+}.

4. Conclusion

The orthogonal is 300–500 nm in size and semispherical GOS:Pr^{3+} scintillator particles were simply and functionally produced by the sol–gel method. Particles were heat-treated at 950 °C and were characterized using

XRD, XPS, SEM, and PL spectra devices. The strongest emission peak was located at 562 nm under 374 nm UV light excitation appearing on the GOS:Pr^{3+} nanoparticles. Thus, sol–gel is a convenient and highly successful method to synthesise pure GOS:Pr^{3+} nanoparticles.

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References

[1] P. Lecoq, A. Annenkov, A. Gektin, M. Korzhik, C. Pedrini, *Inorganic Scintillators for Detector Systems: Physical Principles and Crystal Engineering*, Springer Science & Business Media, New York 2006.

[2] S. Yildirim, M. Yurddaskal, T. Dikici, I. Aritman, K. Ertekin, E. Celik, *Ceram. Int.* **42**, 10579 (2016).

[3] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer Science & Business Media, New York 2012.

[4] P. Lecoq, in: *Detectors for Particles and Radiation. Part 1: Principles and Methods*, Springer, Berlin 2011, p. 45.

[5] C. Feldmann, T. Jüstel, C.R. Ronda, P.J. Schmidt, *Adv. Funct. Mater. 13*, 511 (2003).

[6] L. Song, P. Du, Q. Jiang, H. Cao, J. Xiong, *J. Lumin.* **150**, 50 (2014).

[7] J. Lian, F. Liu, X. Wang, X. Sun, *Powder Technol.* **253**, 187 (2014).

[8] R. Manigandan, K. Giribabu, R. Suresh, S. Munusamy, S. Muthamizh, T. Dhanasekaran, V. Narayanan, *RSC Adv.* **5**, 7515 (2015).