Hydrothermal synthesis, structure and scintillation characterization of nanocrystalline Eu\textsuperscript{3+}-doped Gd\textsubscript{2}O\textsubscript{3} materials and its X-ray imaging applications

Bo Kyung Cha\textsuperscript{a,}\textsuperscript{*}, P. Muralidharan\textsuperscript{b}, Seung Jun Lee\textsuperscript{b}, Do Kyung Kim\textsuperscript{b}, Gyuseong Cho\textsuperscript{c}, Sungchae Jeon\textsuperscript{a}, Young Huh\textsuperscript{a}

\textsuperscript{a} Advanced Medical Device Research Center, Korea Electrotechnology Research Institute, Gyeonggi-do, Republic of Korea
\textsuperscript{b} Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea
\textsuperscript{c} Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

\textbf{A R T I C L E  I N F O}

Available online 4 February 2011

Keywords:
Hydrothermal synthesis
Nanocrystalline Gd\textsubscript{2}O\textsubscript{3}:Eu scintillator
X-ray imaging detector

\textbf{A B S T R A C T}

Nanocrystalline Gd\textsubscript{2}O\textsubscript{3}:Eu scintillators were successfully synthesized using a hydrothermal method and subsequent calcination treatment in the electrical furnace as an X-ray to visible light conversion material for an indirect X-ray image sensor. In this work, various Gd\textsubscript{2}O\textsubscript{3}:Eu scintillators were prepared in accordance with different synthesis conditions such as doped-Eu concentration, different calcination temperatures of 600–1400 °C and calcination time of 1–10 h. The transition of morphology from nanorods to particles was observed as the calcination temperature of Gd\textsubscript{2}O\textsubscript{3}:Eu scintillator increased. And the phase transformation of the sample from cubic to monoclinic structure was discovered at 1300 °C calcination temperature. In addition, scintillation properties such as luminescent spectra and light intensity under 266 nm UV illumination were measured as a function of calcination condition of as-synthesized Gd\textsubscript{2}O\textsubscript{3}:Eu powder. The nanocrystalline Gd\textsubscript{2}O\textsubscript{3}:Eu scintillator with a strong red light emission at near 611 nm wavelength under photo- and X-ray excitation will be employed for its potential X-ray image sensor applications in the future.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Digital X-ray imaging systems instead of analog X-ray imaging systems with conventional X-ray film-screen have been mostly used for general radiography applications. Indirect-detection with an X-ray converter (or a scintillation screen) and 2D imaging sensor is more widely used in medical diagnoses and industrial fields because of its high stability and high imaging performance. Scintillation screens such as terbium-doped gadolinium oxysulfide (Gd\textsubscript{2}O\textsubscript{2}S:Tb), Europium-doped gadolinium oxide (Gd\textsubscript{2}O\textsubscript{3}:Eu) and thallium-doped cesium iodide (CsI:Tl) with columnar structure are commonly used due to their high X-ray absorption efficiency, luminescence efficiency and appropriate emission wavelength (visible light region) [1–3]. In this work, nanocrystalline Gd\textsubscript{2}O\textsubscript{3}(Eu) scintillation powders were synthesized through a hydrothermal process and subsequent calcination in the electric furnace using different 600–1400 °C temperatures, calcination times and 3–10 mol\% Eu doping concentrations. The synthesized samples with different sized-nanorod and particle morphology at a variety of calcination temperatures and times were prepared and observed. The characterization, such as the crystal structures and morphology, of the synthesized nanocrystalline Gd\textsubscript{2}O\textsubscript{3}(Eu) scintillators were investigated. In addition, the scintillation properties of luminescent wavelength and intensity by photo- and X-ray excitation were measured.

2. Materials and methods

A simple hydrothermal process was carried out to prepare 5 mol\% Eu-doped nanocrystalline Gd\textsubscript{2}O\textsubscript{3} powders. 4.287 g of Gd(NO\textsubscript{3})\textsubscript{3} was added to 20 ml of distilled water and 0.2140 g of Eu(NO\textsubscript{3})\textsubscript{3} was added to the solution. The solution was made up to 50 ml by addition of water. 40 ml of 1 M NaOH solution was then added and followed by the addition of 10 ml water. The precipitate solution was mixed well by continuous stirring for 15 min. 80 ml of the final solution was poured into a Teflon jar and placed in an autoclave. The reaction was carried out at 180 °C for 24 h. The white precipitate was rinsed with distilled water and ethanol 3 times and dried at 90 °C for 12 h. The sample was
subsequently calcined at various temperatures of 600–1400 °C and times of 1–10 h in an electrical furnace [4,5].

The microstructures such as particle sizes, morphology and the existing phase of the synthesized Gd₂O₃:Eu scintillators using various calcination temperatures and times were observed by FE-SEM (JEM-2100F HR) and high resolution X-ray diffraction (Ultima IV, RIGAKU) with an analysis range 2θ of 20–90° respectively. The particle sizes of the prepared Gd₂O₃:Eu samples were also measured by the Deybye–Scherrer equation using the diffraction peak full-width at half-maximum (FWHM). Photoluminescence (PL) was measured by means of a Czerny–Turner spectrometer and intensified charge coupled device camera using a Nd:YAG laser with 266 nm excitation source. The relative light intensity was acquired by measuring an averaged pixel value over region of interest (ROI) in the X-ray images under the same X-ray exposure conditions [6].

3. Results and discussions

The morphology and particle size of the hydrothermally synthesized precursor and Gd₂O₃(Eu) scintillators with different calcination temperatures ranging from 700 to 1400 °C at a constant 5 mol% Eu and 5 h times are shown in Fig. 1. A nanorod shape of Gd₂O₃(Eu) scintillator with 30–80 nm size was observed until 1000 °C. The transition from nanorod to particle shape was observed at 1100 °C calcination temperature. As the calcination temperature increases, the average diameter of the powders increased from 20 nm to 1 µm. The morphology and size of Gd₂O₃(Eu) scintillators with different Eu doping concentration at constant 800 and 1000 °C temperatures, respectively, and 5 h calcination time changed little as shown in Fig. 2. As calcination time increases from 1 to 10 h, the shape and size of Gd₂O₃(Eu) scintillators at a constant 800, 1000 and 1100 °C temperature increased a little as shown in Fig. 3.

The XRD peak patterns of the synthesized Gd₂O₃(Eu) scintillator powders at various calcination temperatures ranging from 600 to 1400 °C at a constant 5 mol% Eu concentration and 5 h calcination time are displayed in Fig. 4. The synthesized powder shows an XRD peak pattern of the Gd(OH)₃ structure. X-ray peaks of the powders of Gd₂O₃(Eu) calcinated at 600–1200 °C has (2 1 1), (2 2 2), (4 0 0), (4 4 0), and (6 2 2) peaks and are in agreement with cubic crystal structures of Gd₂O₃ [4]. The phase transformation from the cubic to monoclinic structure was observed at 1300–1400 °C and their peaks correspond to the monoclinic phase. As calcination temperature increases from 600 to 1200 °C, the diffraction peak width was reduced and showed sharper pattern peaks. Even when the Eu doping concentration at a constant 1000 °C temperature and 5 h time increases, the cubic phase of Gd₂O₃(Eu) was not changed as shown in Fig. 5. The cubic phase of Gd₂O₃ was also not changed although calcination time from 1 to 10 h at constant temperature increases. As calcination time increases, the diffraction peak width also decreased and showed sharper pattern peaks. The PL intensities and emission spectra as a function of calcination temperatures are displayed in Fig. 6. The PL intensities of samples increased rapidly as the temperature.
Fig. 3. SEM images of Gd₂O₃: Eu powders with different calcination times at 800°C, 1000°C and 1100°C calcination temperature.

Fig. 4. XRD of Gd₂O₃: Eu powders with different calcination temperature.

Fig. 5. XRD of Gd₂O₃: Eu powders with different Eu doping concentration at 1000°C temperature.

Fig. 6. Emission spectra of Gd₂O₃: Eu powders with different calcination temperature.

Fig. 7. Light output of Gd₂O₃: Eu powders as a function of calcination temperature.
temperature increased until $1200^\circ C$ with a cubic crystal structure. However, the intensities then decreased above $1300^\circ C$ with monoclinic phase. Moreover, the main emission peak of the $\text{Gd}_2\text{O}_3:\text{Eu}$ scintillator with cubic structure was observed at $611$ nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), which corresponds to a typical red emission from the Eu$^{3+}$. The photoluminescence of the powders with the monoclinic phase calcinated at $1300$–$1400^\circ C$ showed a strong emission peak at $623$ nm wavelength. The light intensities of the $\text{Gd}_2\text{O}_3:\text{Eu}$ scintillator with various calcination temperatures and times at constant Eu concentration were measured by luminescence under X-ray source exposure at $80$ kVp and $30$ mA beam current. The highest light intensity by X-ray excitation was observed at $1200^\circ C$ as shown in Fig. 7. The $5$ mol$\%$ Eu-doped $\text{Gd}_2\text{O}_3$ scintillator calcinated at $1100^\circ C$ temperature and 5 h time showed the highest light output as shown in Fig. 8 [5,6].

### 4. Conclusion

Eu-doped nanocrystalline $\text{Gd}_2\text{O}_3:\text{Eu}$ scintillators were synthesized using a simple precipitation and subsequent calcination process for indirect X-ray imaging detector applications. In this work, the scintillators with average $20$ nm to $1$ $\mu$m particle size were prepared according to different heat-treatment conditions ranging from $600$ to $1400^\circ C$ calcination temperature. The morphology, particle sizes and crystal structure of the synthesized $\text{Gd}_2\text{O}_3:\text{Eu}$ powders were observed by SEM and XRD analysis. The phase transformation from cubic to monoclinic structure was discovered at $1300^\circ C$ calcination temperature. When the $\text{Gd}_2\text{O}_3:\text{Eu}$ was excited by UV illumination of $266$ nm, dominant emission peak of samples having cubic structure was seen at $611$ nm. The main peak of samples having a monoclinic structure was observed at $623$ nm. The highest light intensity by photo- and X-ray luminescence was seen at $1200$ and $1100^\circ C$ temperatures with $5$ h calcination time, respectively. In the near future, we will try the nanocrystalline $\text{Gd}_2\text{O}_3:\text{Eu}$ scintillator as a converter screen for indirect X-ray imaging detectors.

### Acknowledgment

This research was supported by the Cooperative R&D program (B551179-08-04-00) funded by the Korea Research Council for Industrial Science & Technology.

### References