Effect of yttria substitution on the light output of (Gd,Y)$_2$O$_3$:Eu ceramic scintillator

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Abstract

For the application of the computed tomography (CT) scanner, Gd$_{1.94}$Y$_{0.06}$O$_3$ ceramic scintillator was prepared. We investigated the effect of the relative contents of Y$_2$O$_3$ for Gd$_2$O$_3$ matrix on the light output properties by the measurements of the emitted light spectra, relative light output, and X-ray diffraction (XRD) patterns. From the measurement results, it was found that maintaining the crystalline structure as cubic phase after sintering process is important to achieve high light output properties on (Gd,Y)$_2$O$_3$ ceramic scintillators, and the scintillation conversion process is more dominant for high light output of cubic phase than the optical transparency.

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1. Introduction

Recent remarkable development of semiconductor materials and signal-processing electronics has opened the renaissance of digital X-ray imaging both on medicine and industry. Complicate image-information mechanism, getting a digital image on final user’s way from the incident X-ray quanta as the first image-information carriers in a digital X-ray imaging system, could be modeled as a serial cascade of many stages. It is noted that since information-carrying quanta are lost irrecoverably through successive transferring stage of the cascaded imaging chains, the first stage is largely responsible for the total performance of the system. Therefore, the optimum design of the first X-ray interacting element is essential for a digital X-ray imaging system.

As X-ray interacting element, the inorganic scintillator is most widely used in which luminescent ions are doped. Scintillation mechanism
might be simplified into two processes: first, energy absorption within a scintillator and, second, its conversion to energies of optical photons [1]. These generated optical photons with various energies or wavelengths can be practically utilized when they are successfully escaped from the scintillator.

Among many candidates of currently available inorganic scintillators, a polycrystalline ceramic scintillator is lately in the spotlight with definite advantages over other scintillators: flexible tailored-made in compositions according to the applications and co-doping process to reduce the afterglow [2]. A disadvantage of polycrystalline ceramic scintillator is low escape efficiency, that is, low optical transmittance by mainly pores and grain-boundaries in the microstructure. Few kinds of ceramics have been successful as transparent optical ceramic scintillator [3–8].

Eu-doped (Gd,Y)2O3 ceramic is one of the successful examples in transparent ceramic scintillator. Gd2O3 is added into well-known Y2O3:Eu phosphor to enhance the X-ray stopping power. The content of Gd2O3 in this ceramic scintillator was confined under 50 molar percent because of monoclinic phase at the Gd2O3-rich region [6,7]. It was known that monoclinic phase powder resulted in only optically opaque ceramic scintillator after the sintering. However, we have proved that transparent ceramic scintillator is possible in Gd2O3-rich region by using a specific ceramic processing [8].

For the purpose of use in the computed tomography (CT) scanner, we have prepared Eu-doped (Gd,Y)2O3 ceramic scintillators. The light output, that is a major parameter governing the performance of a scintillator, from Eu-doped (Gd,Y)2O3 ceramic scintillators when excited by the X-ray has been measured. The effect of Y2O3 concentration on the light output properties of (Gd,Y)2O3 ceramic scintillators is discussed in detail.

2. Experimental

The powder synthesis method used in this paper is glyline-nitrate combustion process [9]. An experimental composition was chosen as Gd1.94–xYxEu0.06O3 (x: 0.0, 0.2, 0.4, 0.6, 0.97 and 1.34). The stoichiometric molar ratio of glycine/nitrate was calculated by the method of Jain and Adiga [10]. As-synthesized powder was ball-milled for 24 h using zirconia balls in isopropanol as a liquid medium. After drying, heat-treatment was conducted for 8 h under vacuum (4 h) and air condition (4 h) at 400 °C. Prepared powder was sintered to transparent ceramic by hot-pressing process at 1400 °C for 2 h with a pressure of 30 MPa in Ar atmosphere. Post heat-treatment was conducted at 1150 °C for 2 h in air to remove the residual carbon that was originated from graphite environment of hot-pressing furnace. Crystalline structures of specimens were investigated with an X-ray diffraction (XRD) analysis by CuKα radiation.

The emitted optical photons distribution as a function of wavelength was measured by the spectrometer (USB2000, Ocean Optics Inc., Dunedin, FL) incorporating the silicon CCD as a photo-sensor. The relationship between the measured optical photon distribution emitted from the scintillator, SM(λ), and the generated optical photon distribution emitted within the scintillator, S0(λ) can be given by

\[
S_M(\lambda) = \int S_0(\lambda')\eta(\lambda,\lambda')d\lambda',
\]

(1)

where \( \lambda \) is a wavelength and the kernel \( \eta(\lambda,\lambda') \) is the response function or simply the quantum efficiency of the spectrometer. The light output was calculated by

\[
Y = \int S_M(\lambda)d\lambda.
\]

(2)

The correction for non-uniformity of the quantum efficiency of the spectrometer was not considered in this study. All investigated ceramic specimens have same thickness of 1 mm, which is much smaller than the lateral dimension, and the escaped light was collected by an optical fiber with a diameter of 1 mm. The emission spectrum of powder was measured with powder pellet that has a thickness of 0.35 mm. For the excitation of the scintillator, X-ray generator with a tungsten target was operated at 100 kVp.
3. Results and discussion

Figs. 1(a) and (b) show light spectra as a function of wavelength and the relative light output for various compositions of 3 mol% Eu-doped (Gd,Y)₂O₃ ceramic scintillator, respectively. The light spectrum was obtained by Eq. (1) and the light output was calculated by Eq. (2). More than 20 mol% of Y₂O₃-substituted ceramic scintillators exhibit the spectra with the main peak around 610 nm, as shown in Fig. 1(a), which means that the scintillation mechanism through \( ^5D_0 \rightarrow ^7F_2 \) is well operated at Eu\(^{3+} \) activator.

As shown in Fig. 1(b), the light output gradually increased as the concentration of Y₂O₃ decreased down to about 20%. Since the atomic number (\( Z \)) and physical density (\( \rho \)) of Gd are higher than those of Y, the figure of merit, \( \rho Z^4 \text{eff} \), describing the energy absorption efficiency within a scintillator becomes larger as the relative content of Y₂O₃ is smaller. Therefore, the first process in the scintillation mechanism as described in Section 1 works well up to the concentration of 20 mol% Y₂O₃. However, it is noted that below 20% of the concentration of Y₂O₃ the light output abruptly reduced. In addition, the main peak of the spectrum around 610 nm disappeared as depicted in Fig. 1(a). It is known that Eu-doped (Gd,Y)₂O₃ luminescent material with monoclinic phase shows a spectrum of 615 and 624 nm peaks rather than 610 nm peak of cubic phase. These 615 and 624 nm peaks are also originated from \( ^5D_0 \rightarrow ^7F_2 \) emission mechanism at Eu\(^{3+} \) ion. The spectrum difference is attributed to the variation in the Eu\(^{3+} \) site symmetry [11,12].

From the XRD patterns as shown in Fig. 2, in ranges less than 20 mol% of Y₂O₃, monoclinic structure was observed instead of cubic structure. Previous study reported that composition boundary of phase change is 50 mol% of Y₂O₃ in ceramic scintillator made by vacuum sintering at 1900 °C [6]. This discrepancy was attributed from the lowered ceramic processing temperature by using the different ceramic processing [8]. According to the phase diagram, as the content of Y₂O₃ increases the transition temperature of cubic–monoclinic raises. At the composition of 20 mol%
Y$_2$O$_3$, cubic phase is changed to cubic–monoclinic mixture at about 1500 °C, and then to monoclinic completely at about 1600 °C [13]. Ceramic processing temperature of this study, such as powder synthesis (~1300 °C) and sintering (1400 °C) temperature, are lower than these temperature, and the cubic phase is maintained through ceramic processing steps [8].

Crystalline phase affects not only on the shape of emission spectrum, commented above, but also sintering step and, therefore, sintered density and final optical transmittance. Sintered density, shown in Fig. 3, did not reach the theoretical density at the monoclinic phase region, and only the optically opaque state was obtained.

From these observations, two possible factors can be deduced to understand relatively lower light output from the samples with less than 20 mol% of Y$_2$O$_3$. First is the poor optical transmittance of monoclinic phase microstructure, in which appreciable optical photon scattering and high absorption probability is possible, thereby providing the reduced light output for detection by the spectrometer. Second is low scintillation conversion process from the absorbed energy into the optical photon energy.

In order to separate the effect of optical transparency we measured the light output of samples in the form of as-synthesized powders, which has optically opaque state. As presented in Fig. 4(b) the light output measurements give same tendency with the sintered ceramics except for the cases of 0 and 10 mol% of Y$_2$O$_3$ concentration. The higher light output at 10 mol% of Y$_2$O$_3$ concentration than at 0 mol% can be understood by the coexistence both of cubic and monoclinic phases at 10 mol% of Y$_2$O$_3$ concentration as viewed in Fig. 5. Fig. 4(a) supports the existence of cubic phase at 10 mol% of Y$_2$O$_3$ concentration by observation of the 610 nm-peak. At the composition of 10 mol% Y$_2$O$_3$, it is reported that the crystal phase is changed from cubic phase to the mixture of cubic and monoclinic at about 1300 °C and completely to the monoclinic phase at 1400 °C [13]. These temperature is well coincided with powder synthesis and sintering condition of this study, respectively. This result implied that the scintillation conversion process is more dominant for the
low light output of Eu-doped (Gd,Y)\textsubscript{2}O\textsubscript{3} ceramic scintillator with monoclinic phase than the poor optical transmittance.

4. Conclusions

For the application of the computed tomography (CT) scanner, various compositions of 3 mol\% Eu-doped (Gd,Y)\textsubscript{2}O\textsubscript{3} ceramic scintillator have been prepared, and their relative light output as a function of the concentration of Y\textsubscript{2}O\textsubscript{3} was measured. The measurements showed that the light output gradually increased as the concentration of Y\textsubscript{2}O\textsubscript{3} decreased down to about 20\%, while below 20\% of the concentration of Y\textsubscript{2}O\textsubscript{3}, the light output abruptly reduced. Results of as-synthesized powders imply that the reduced light output was due to the lower scintillation conversion efficiency rather than the poor optical transmittance. It can be concluded that maintaining the crystalline structure as cubic phase after sintering process is important to achieve high light output on (Gd,Y)\textsubscript{2}O\textsubscript{3} ceramic scintillators, because of higher scintillation conversion coefficient of cubic phase. In this study, 20 mol\% substitution of Y\textsubscript{2}O\textsubscript{3} to Gd\textsubscript{2}O\textsubscript{3} matrix is optimal composition with respect to the best light output in 3 mol\% Eu-doped (Gd,Y)\textsubscript{2}O\textsubscript{3} ceramic scintillators.

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References