Crystal Growth and Luminescence Properties of Yb-doped Gd₃Al₂Ga₃O₁₂ Infra-red Scintillator

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Abstract

1-mol%-Yb-doped Gd₃Al₂Ga₃O₁₂ infra-red scintillator crystal has been studied as a novel implantable radiation monitor in radiation therapy. Powder X-ray diffraction measurement and chemical analysis with a field emission scanning microscope and wavelength dispersive spectrometer determined its garnet structure and average chemical composition of Yb_{0.03 ± 0.01}Gd_{2.99 ± 0.07}Al_{2.21 ± 0.08}Ga_{2.64 ± 0.09}O_{12.10 ± 0.09}. Transmittance measurements reached high values of approximately 70% in the human body transparency region between 650 to 1200 nm. Photoluminescence peaks were detected around 970 and 1030 nm under the 940 nm excitation with a Xe lamp. Infra-red scintillation emissions were clearly observed around 970 and 1030 nm due to Yb³⁺ 4f – 4f transitions under X-ray excitation. Therefore, these results suggest that Yb-doped Gd₃Al₂Ga₃O₁₂ might be used as an infra-red scintillator material.

Keywords: Infra-red scintillator, Radiation therapy, Yb:GAGG, Bulk crystal

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1. Introduction

Radiation therapy which is a novel method to treat a human cancer has been widely used in a number of medical institutions. However, serious medical accidents such related to over- or under-exposure occur frequently during the therapy [1]. The mentioned difficulties result from the absence of real-time dose monitoring system. In order to avoid such accidents, the development of an implantable real-time dose monitoring system has become an urgent matter.

According to recent photo-biologic studies, it was discovered that human tissues are transparent around near-infra-red region between 650 to 1200 nm, which is often called as “optical window” [2]. This significant feature of human tissues indicates that a novel real-time dosimeter system could be developed employing scintillators emitting in the infra-red region. This system consists of an X-ray generator, implanted scintillator (dosimeter crystal) and CCD camera (Fig. 1). Near-infra-red scintillation photons could penetrate through human body and can be further detected from outside, which allows to obtain real-time dose information from the measured scintillation intensity and prevent serious radiation accidents. Previous studies included a preliminary dosimeter experiment using a prototype monitoring system and pork tissue as an alternative of the human one. These experiments successfully demonstrated that the implantable dosimeter system can be realized with infra-red scintillators [3]. Therefore, optimization of the infra-red scintillators for the above described application is required.

Recently, $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (GAGG) crystal was studied as a visible-emitting scintillator. The Ce-doped GAGG crystal has various advantages such as [4]: (i) large density (6.68 g/cm^3) and high stopping power, (ii) non-hygroscopic nature, (iii) non-intrinsic background due to radio-active isotopes and (iv) higher light output of more than 40,000

photon/MeV (662 keV gamma rays). Thus, this scintillator crystal has found its application in gamma-ray detection.

For the described application, the infra-red scintillators are required to have non-hygroscopic nature and high stopping power due to their small size required for implantation. Therefore, GAGG is one of the host-material candidates for infra-red scintillators.

In this research, we have studied Yb-doped $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ crystal for infra-red scintillator. Ytterbium-doped crystals are widely used as near-infra-red laser materials, and Yb: $\text{Y}_3\text{Al}_5\text{O}_{12}$ (Yb:YAG) has an emission wavelength of around 1030 nm[5][6]. In this paper, we reported the optical properties and infra-red scintillation performance of Yb:GAGG for the first time.

2. Materials and Methods

Yb-doped $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (Yb:GAGG) crystal was grown by a micro-pulling down method (μ -PD [7]) under nitrogen atmosphere. The chemical composition of the starting material was equivalent to $(\text{Yb}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_2\text{Ga}_3\text{O}_{12}$, and it consisted of 99.99% purity Yb_2O_3 , Gd_2O_3 , $\alpha\text{-Al}_2\text{O}_3$ and $\beta\text{-Ga}_2\text{O}_3$ powders. The mixture was set in an iridium crucible of the μ -PD apparatus and heated by the induction heating system up to melting temperature. The growth rate was kept constant at the value of 0.05 mm/min for the whole growth process. After the growth, the as-grown crystal was cut and mirror-polished. The sample size was $3 \times 2 \times 1 \text{ mm}^3$.

Powder X-ray diffraction measurement was performed on the as-grown crystal with a diffractometer (RIGAKU: RINT-2000, X-ray Source Target: Cu), and its crystal structure was determined by the comparison between the obtained XRD pattern and the

data of JCPDS cards. In addition, actual chemical composition of the as-grown crystal was investigated by a field-emission scanning electron microscope with a wavelength-dispersive spectrometer (Nihon Denshi: JXA-8621MX).

In order to evaluate its optical properties, transmittance spectra of the sample were obtained with spectrophotometers (JASCO: V-530 and Shimadzu: UV-3100PC) within ultraviolet to near infra-red (NIR) regions. The infra-red photoluminescence spectrum of this sample was also measured with a photoluminescence measurement system (Hamamatsu: C9920-03G). The excitation light was generated by a Xe lamp (Hamamatsu: L9799-02), whose emission wavelength was approximately 940 nm.

X-ray excited radio-luminescence in NIR optical window region was measured with our VUV-VIS-IR spectrometer (NIR-1600-X) consisting of a vacuum monochromator (Princeton Instruments: Acton VM-504) and an InGaAs Infra-red detector (Hamamatsu: G6126). The X-ray was generated using an X-ray tube (Amptek: Mini-X, X-ray Source: Ag) and its constant output power was approximately 3.4 W (38 kV, 90 uA).

3. Results and discussions

The bulk crystal of Yb:GAGG was obtained as shown in Fig. 2. Powder X-ray diffraction pattern of this sample is depicted in Fig. 3. All the diffraction peaks approximately corresponded with the data of $\text{Gd}_3\text{Al}_3\text{Ga}_2\text{O}_{12}$ Garnet (JCPDS No. 46-0448). The small shift to smaller 2 theta values compared to the JCPDS data was observed, and it is related to the expansion of the lattice due to the decrease of the Al/Ga ratio. It was confirmed that the crystal structure of the as-grown crystal corresponded with the typical garnet structure (Cubic, Space group: $Ia\bar{3}d$). In addition, chemical analysis by the FE-SEM-WDS determined that the average composition of the as-grown

Yb:GAGG crystal was equivalent to $\text{Yb}_{0.03 \pm 0.01} \text{Gd}_{2.99 \pm 0.07} \text{Al}_{2.21 \pm 0.08} \text{Ga}_{2.64 \pm 0.09} \text{O}_{12.10 \pm 0.09}$. The composition distribution along its crystal-growth direction is shown in Fig. 4, indicating that all the elements are homogeneously distributed in the whole crystal. Therefore, the Yb:GAGG crystal was successfully grown.

Transmittance spectrum of the Yb:GAGG crystal between 200 and 900 nm is shown in Fig. 5. Two Gd^{3+} absorption bands were also observed around 276 nm and 310 nm, and they were ascribed to Gd^{3+} 4f – 4f transitions from its ground state ^8S to the other excited states [8]. Large drop around 220 nm would be due to charge transfer transition related to Yb^{3+} [9]. The infra-red transmittance spectrum of the sample is shown in Fig. 6. Two absorption peaks were observed around 940 and 970 nm, and they could be ascribed to Yb^{3+} 4f – 4f transition from its ground state $^2\text{F}_{5/2}$ to excited state $^2\text{F}_{7/2}$ as shown in Fig. 7 [5],[6]. These two transmittance measurements showed Yb:GAGG crystal was highly transparent in the transparency region of the human tissue. This enables the scintillation light to be detected from outside of the human body.

Photoluminescence spectrum of this material under the Xe lamp excitation at 940nm is shown in Fig. 8. Two luminescence peaks observed around 970 and 1030 nm, were ascribed to the Yb^{3+} transition from its $^5\text{F}_{5/2}$ to $^5\text{F}_{7/2}$ levels [5][6].

An X-ray excited radio-luminescence spectrum of the sample is shown in Fig. 9. Two bands were observed around 970 and 1030 nm, which corresponds to the above described photoluminescence emission spectrum. They can be again ascribed to the Yb^{3+} 4f – 4f transition from its $^2\text{F}_{5/2}$ to ground $^2\text{F}_{7/2}$ state [5][6]. The reabsorption of these scintillation photons is negligible due to the high transmittance around 1030 nm,

as shown in Fig. 6. Moreover, it is necessary to emphasize that these photons can easily penetrate the human tissue. Thus, Yb:GAGG crystal can be used as infra-red scintillator in radiation monitoring applications in medicine. Yb:GAGG crystal has its own high effective atomic number and non-hygrosopic nature, and therefore Yb:GAGG can be one of the candidates for new implantable radiation monitors.

4. Conclusion

1-mol%-Yb-doped $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (Yb:GAGG) crystal was successfully grown by a micro-pulling down method. Powder XRD measurement and chemical analysis with a field-emission scanning electron microscope and wavelength dispersive spectrometer determined its garnet structure and average composition of $\text{Yb}_{0.03 \pm 0.01}\text{Gd}_{2.99 \pm 0.07}\text{Al}_{2.21 \pm 0.08}\text{Ga}_{2.64 \pm 0.09}\text{O}_{12.10 \pm 0.09}$. In addition, the transmittance measurements showed that the sample was highly transparent from 650 to 1200 nm. The infra-red photoluminescence was detected at 970 and 1030 nm under the 940 nm excitation with a Xe lamp. The X-ray excited radio-luminescence spectrum showed infra-red scintillation peaks at 970 and 1030 nm related to Yb^{3+} 4f - 4f transitions. Yb:GAGG material can a possible candidate for an implantable infra-red scintillator in the medical radiation monitoring.

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Figure Caption

Fig. 1 A schematic of implantable real-time dosimeter system.

Fig. 2 Photograph of the as-grown Yb:GAGG crystal prepared by the micro-pulling down method.

Fig. 3 Powder X-ray diffraction pattern of Yb:GAGG sample (X-ray Source Target: Cu).

Fig. 4 Composition distribution of the as-grown Yb:GAGG crystal along its growth direction.

Fig. 5 Transmittance spectrum of Yb:GAGG crystal between 200 nm to 900 nm at room temperature.

Fig. 6 Infra-red transmittance spectrum of Yb:GAGG crystal at room temperature. Two absorption peaks around 940 and 970 nm corresponded with the transition (1) and (2) of Yb^{3+} in Fig. 7, respectively.

Fig. 7 Energy level diagram of Yb^{3+} in the $\text{Y}_3\text{Al}_5\text{O}_{12}$ garnet crystal [5], [6].

Fig. 8 Infra-red photoluminescence spectrum of Yb:GAGG crystal excited with a Xe lamp at room temperature. Two luminescence peaks around 970 and 1030 nm corresponded with the transition (3) and (4) of Yb^{3+} in Fig. 7, respectively.

Fig. 9 X-ray excited radio-luminescence spectrum of Yb:GAGG crystal in NIR optical window region at room temperature. Two scintillation emission peaks around 970 and 1030 nm corresponded with the transition (3) and (4) of Yb^{3+} in Fig. 7, respectively.

Figure1

Figure2

Figure3

Figure5

Figure6

Figure 7

Figure8

Figure9