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Photoluminescence and Scintillation Properties of Tb:$GdTaO_4$ Crystals

Daisuke Nakauchi,* Takumi Kato, Noriaki Kawaguchi, and Takayuki Yanagida

Division of Materials Science, Nara Institute of Science and Technology (NAIST),
8916-5 Takayama, Ikoma, Nara 630-0192, Japan

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Tb-doped $GdTaO_4$ crystals were synthesized to investigate their photoluminescence and scintillation properties. Tb:$GdTaO_4$ exhibits photo- and radioluminescence characterized by several sharp peaks due to 4f–4f transitions of Tb^{3+}. The photo- and radioluminescence decay time constants are 500–900 μs. The values become short with increasing Tb concentration and are typical for the 4f–4f transitions of Tb^{3+}. From the quantum yield (*QY*), radioluminescence spectra, and pulse height under ^{137}Cs γ-rays, the 1% Tb:$GdTaO_4$ crystal shows the highest scintillation output among the samples.

1. Introduction

Scintillators convert incident ionizing radiation into UV–visible photons to measure indirectly ionizing radiation dose and energy, and they have been used in various applications such as medicine,[1] monitoring,[2,3] security,[4] and well-logging.[5] The interaction cross section against photons with high energy such as X-rays and γ-rays strongly depends on the density and atomic number of materials, and a heavy scintillator is advantageous for X- and γ-ray detection. To date, $Bi_4Ge_3O_{12}$ (BGO)[6,7] and $CdWO_4$[8,9] have been widely used for X- and γ-ray detection in practice, while their scintillation output and decay are not desirable compared with those of other commercial scintillators.[10–12]

Gadolinium tantalate ($GdTaO_4$) is an attractive novel host of scintillators because its density (8.8 g/cm^3) is superior to those of practical oxide scintillators (7.1 g/cm^3 for BGO and 7.9 g/cm^3 for $CdWO_4$). Hence, $GdTaO_4$ is a potential candidate of X- and γ-ray scintillators with a large interaction cross section.[13–16] To date, there have been many reports on the scintillation properties of rare-earth tantalates doped with Eu or Tb ions, and strong luminescence was observed in the visible range;[17–19] however, most of the studied tantalates have been polycrystals. In most applications, a single-crystalline form has been used for X- and γ-ray detection because the interaction probability is dependent on the volume and density of the scintillator, so most of the recent papers on scintillators have been for single-crystalline forms.[20–23] Although the scintillation properties of undoped $GdTaO_4$ single crystals have been

*Corresponding author: e-mail: nakauchi@ms.naist.jp
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recently reported,[24,25] there is still room for research on the performance of rare-earth-doped $GdTaO_4$ single crystals. Previously, we prepared rare-earth-doped $GdTaO_4$ bulk crystals and investigated their scintillation properties. Ce could not activate the $GdTaO_4$ host,[26] while the Pr-doped host showed a reasonable quantum yield (*QY*) and an observable photoabsorption peak under ^{137}Cs.[27] In this study, we focused on Tb-doped $GdTaO_4$ as a high-density scintillator, and single crystals were synthesized to investigate the scintillation properties.

2. Materials and Methods

$GdTaO_4$ crystals doped with Tb (0.1, 1, and 3%) were prepared by the floating zone (FZ) method (FZD0192, Canon Machinery), which is suitable for the fast crystal growth of oxide compounds.[28–33] Mixed Gd_2O_3 (99.99%), Ta_2O_5 (99.99%), and Tb_4O_7 (99.99%) powders were formed and sintered at 1100 °C for 8 h to synthesize a ceramic rod. After that, FZ growth was conducted with a pull-down speed of 5 mm/h. Powder X-ray diffraction (XRD) patterns were obtained using a diffractometer (MiniFlex600, Rigaku) in order to clarify the crystal phase. The X-ray source was a micro-focus X-ray tube with a CuKα target operated at 40 kV and 15 mA. Quantaurus-QY (C11347, Hamamatsu Photonics) was used for 3D PL spectra as well as *QY* measurements. To identify the emission origin, PL decay curves were measured using Quantaurus-τ (C11367, Hamamatsu Photonics). X-ray-induced radioluminescence (XRL) spectra and decay curves were evaluated using a laboratory-made setup.[34,35] The irradiation source was an X-ray generator (XRB80N100/CB, Spellman) equipped with an ordinary X-ray tube with a W anode target and Be window. During the measurements, the X-ray generator was supplied with a bias voltage of 60 kV and a tube current of 1.2 mA. For pulse height analyses, a photomultiplier tube (PMT) (R7600U-200, Hamamatsu Photonics) was used with the same nuclear instrumentation modules as reported previously,[34] and the shaping time was 10 μs for the samples.

3. Results and Discussion

Photographs of the crystal samples are shown in Fig. 1. The samples look pale brown under room light and exhibit bright green light under a UV lamp (254 nm). A fraction of each sample was crushed into a crystalline powder for powder XRD analyses. Figure 2 shows the XRD patterns of the samples and a reference (ICSD–109186). The diffraction peaks are in good agreement with the reference with a monoclinic symmetry [space group: $P2/a$[36,37]] and demonstrate that the samples contain no impurity phase.

Figure 3 shows the PL 3D spectrum of the 1% Tb-doped sample; all the samples show almost the same spectral features. The samples show PL with sharp emission signals in the range of 490–650 nm. Since the observed wavelengths are consistent with those in other Tb-doped samples,[38] they are due to 4f–4f transitions of Tb^{3+}. The excitation signals are observed at ~300 nm, which are attributed to the overlap between the host absorption and the 4f–5d transitions of Tb^{3+}.[39] The *QY* values of the 0.1, 1, and 3% Tb-doped samples are 22.5, 53.6, and 46.2%, respectively; the 1% doped sample shows the highest *QY* among the prepared samples. Figure 4

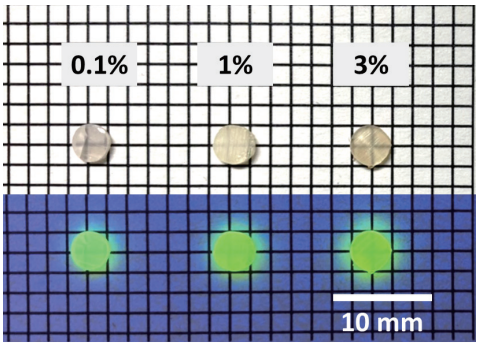

Fig. 1. (Color online) Photographs of Tb:$GdTaO_4$ samples under room light and UV light.

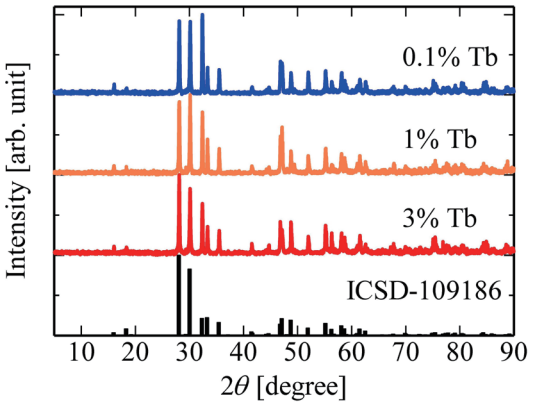

Fig. 2. (Color online) Powder XRD patterns of Tb:$GdTaO_4$ and ICSD reference.

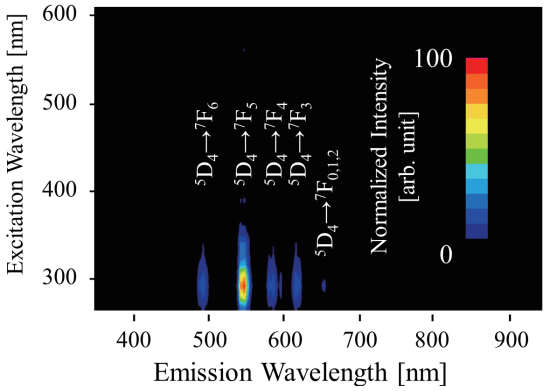

Fig. 3. (Color online) PL 3D spectrum of 1% Tb:$GdTaO_4$.

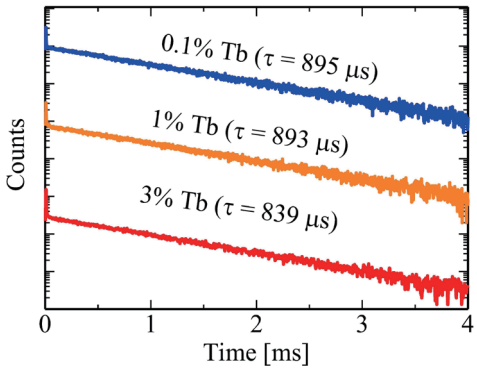

Fig. 4. (Color online) PL decay curves of Tb:$GdTaO_4$.

shows the PL decay curves monitored at 550 nm under excitation at 256 nm. The decay curves are approximated by one exponential function with decay time constants (τ) of 656, 636, and 590 μs for the 0.1, 1, and 3% Tb-doped samples, respectively. All the constants are consistent with the 4f–4f transitions of Tb^{3+}.[40] The decay time monotonically decreases with increasing Tb concentration owing to concentration quenching.

Figure 5 shows the XRL spectra. All the Tb:$GdTaO_4$ samples show sharp peaks in the range of 380–650 nm due to the 4f–4f transitions of Tb^{3+}, which are similar to those in the PL spectra. The emission intensity increases in the order of 0.1, 3, and 1% doped samples. Figure 6 shows the XRL decay curves; all the decay curves can be fitted by one exponential function. As well as for the PL decay, the decay time constant decreases as the Tb concentration increases owing to concentration quenching. The obtained XRL decay time constants are shorter than the PL decay time constants. In general, PL occurs by excitation and relaxation processes only at a luminescence center, while XRL is known to include ionization and transportation from a host to a luminescence center as well as the emission process. Hence, the XRL decay time often

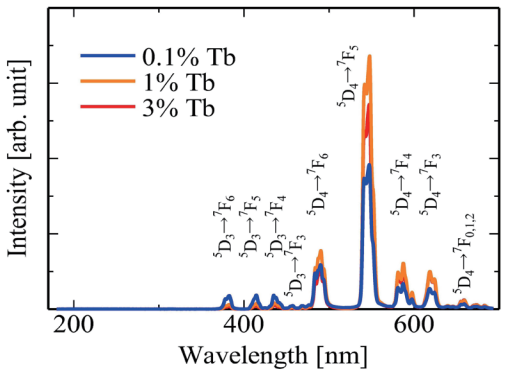

Fig. 5. (Color online) XRL spectra of Tb:$GdTaO_4$.

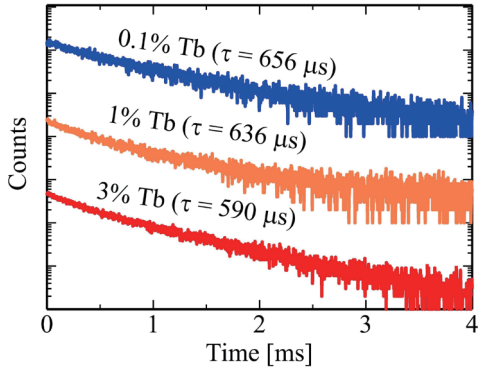

Fig. 6. (Color online) XRL decay curves of Tb:$GdTaO_4$.

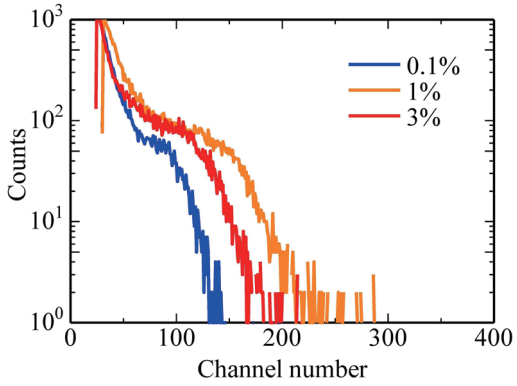

Fig. 7. (Color online) Pulse height spectra measured using Tb:$GdTaO_4$ under ^{137}Cs γ-rays.

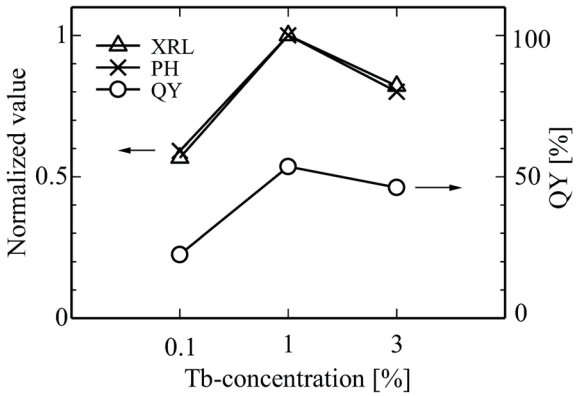

Fig. 8. Dopant concentration dependence of *QY*, normalized XRL intensity, and normalized pulse height channel.

becomes long in comparison with that of PL, which is not true in the present case. The phenomenon is interpreted to be due to the excitation density being considerably higher in XRL than in PL, so interactions between the multiple excitation states cause quenching. Such behavior can be observed in some material systems reported elsewhere.[41–44]

Figure 7 shows the pulse height of γ-rays (662 keV) from ^{137}Cs measured by using the Tb:$GdTaO_4$ samples. Although all the samples show significant signals due to γ-rays, a photoabsorption peak cannot be clearly distinguished from Compton signals because of the long decay time of sub-millisecond order. The pulse height spectra suggest that the 1% doped sample shows the highest scintillation output. Figure 8 summarizes the *QY*, normalized XRL intensity, and normalized pulse height channels. All the values show almost the same trend and demonstrate that the 1% doped sample has the highest values among the doped samples. The results suggest that all the samples have almost the same energy transfer efficiency on the basis of the equation of scintillation efficiency $\eta = \beta SQ$, where η is the total scintillation efficiency and β, S, and Q are the efficiencies of the conversion, transfer, and luminescence processes, respectively.

4. Conclusions

Tb:$GdTaO_4$ crystals were prepared by the FZ method, and the PL and scintillation properties were evaluated. Tb:$GdTaO_4$ shows several sharp emission peaks in the range of 380–650 nm due to Tb^{3+} with the decay time constant on the order of 100 μs. In the pulse height spectra of γ-rays from ^{137}Cs, the 1% doped sample shows the highest channel among the samples. The obtained PL, XRL, and pulse height results suggest that the optimum Tb concentration is 1%.

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