Scintillation properties of Dy-doped TeO$_2$–Al$_2$O$_3$–BaO glasses

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We investigated photoluminescence (PL) and scintillation properties of Dy-doped tellurite glasses [80TeO$_2$–5Al$_2$O$_3$–(15 – x)BaO–xDy$_2$O$_3$ (x = 0.1–0.5)]. The Dy-doped tellurite glasses were prepared by the conventional melt-quenching method. In PL, all the Dy-doped tellurite glasses showed sharp emission peaks at approximately 575, 660 and 755 nm originated from the 4f–4f transition of Dy$^{3+}$. The 0.5 and 1.0 % Dy-doped tellurite glasses exhibited high PL intensities under 450 nm excitation light. In scintillation, the Dy-doped tellurite glasses showed emissions peaking at approximately 485, 585 and 665 nm due to the 4f–4f transitions of Dy$^{3+}$, and the 1.0 % Dy-doped tellurite glass exhibited the highest scintillation intensity. Furthermore, the PL and scintillation decay time constants of the Dy-doped tellurite glasses were about 12.6–367 and 30.2–248 μs, respectively. These decay time constants were typical values for the 4f–4f transition of Dy$^{3+}$. In addition, the Dy-doped tellurite glasses showed moderate afterglow levels of about 289–751 ppm, and the afterglow level of the 1.0 % Dy-doped tellurite glass (289 ppm) was almost comparable to that of a commonly used inorganic scintillator Tl-doped CsI.

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1. Introduction

A scintillator is a kind of luminescent material for the measurement of high-energy ionizing radiation (e.g. X-ray, α-ray), and it has a capability of converting a single quantum of the radiation into several thousands of low-energy photons such as ultraviolet photons. A scintillator has been widely used in various fields such as medicine, security and high energy physics. In general, a high light yield, a high detection efficiency, radiation hardness, a low afterglow level and a fast decay time are important requirements for scintillator applications. There is no one which meets all the requirements of all applications, thus it is necessary to select the scintillator according to the applications. Up to now, single-crystalline scintillators are often used in practice owing to their high light yield. For example, Ce-doped Gd$_2$SiO$_5$, CdWO$_4$, Tl-doped CsI single crystals are utilized for scintillator applications such as medical imaging systems and security scanners.

Recently, glass materials have attracted much attentions due to their practical advantages such as low cost, ease of shape processing and flexible chemical composition. Ce-doped 34Li$_2$O–5MgO–10Al$_2$O$_3$–51SiO$_2$ glass (6Li-glass) is an example of a conventional glass scintillator used in practice. 6Li-glass shows an emission peak at 395 nm originating from the 5d–4f transition of Ce$^{3+}$. In this glass, 6Li is incorporated into the glass host with an aim to detect thermal neutrons since 6Li has a high cross-section against thermal neutrons. Furthermore, scintillation properties of various oxide glasses (e.g. SiO$_2$, P$_2$O$_5$, B$_2$O$_3$, and GeO$_2$) have been investigated for scintillators so far. For instance, Tb-doped NaPO$_3$–Al(P0$_3$)$_3$ glasses show a high quantum efficiency (QE) over 0.9, and the scintillation peaks ascribed to the 4f–4f transition of Tb$^{3+}$ are clearly observed across 380–620 nm under X-ray irradiation.

Unlike the above glass materials, we focused on tellurite glasses for scintillator applications. The tellurite glasses can be potential materials that show a high light yield and a high detection efficiency against high energy X-ray and gamma-ray because of their low phonon energy (700–800 cm$^{-1}$) and high effective atomic number compared with conventional glass materials. Up to now, scintillation properties of several tellurite glasses doped with an impurity such as Eu and Nd have been evaluated. For example, Eu-doped TeO$_2$–Al$_2$O$_3$–BaO tellurite glasses with a high QE of 0.7 in photoluminescence (PL) show intense scintillation peaks attributed to the 4f–4f transitions of Eu$^{3+}$. In addition, the afterglow levels of the Eu-doped tellurite glasses are in the range of 180–245 ppm, which is on the same order as that of Tl-doped CsI.

In this study, we prepared TeO$_2$–Al$_2$O$_3$–BaO glasses doped with different concentrations of Dy (0.1, 0.5, 1.0 and 5.0 mol %) by the conventional melt-quenching method.

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method. Dy$^{3+}$ is one of the common luminescence centers because of the intense emissions originating from the 4f–4f transitions of Dy$^{3+}$.$^{18-21}$ and the emission wavelengths of Dy$^{3+}$ should be suitable for the detection using Si-photodiode sensors. Up to now, several studies on the scintillation properties of Dy-doped glasses have been reported so far. For instance, the Dy-doped Gd$2$O$_3$–CaO–SiO$_2$–B$_2$O$_3$ glasses exhibit efficient scintillation due to the 4f–4f transitions of Dy$^{3+}$.$^{19}$ To the best of our knowledge, there are few reports on the scintillation properties of Dy-doped tellurite glasses. After the preparation of the Dy-doped tellurite glasses, we investigated the PL and scintillation properties, comprehensively.

2. Experimental methods

The Dy-doped $80$TeO$_2$–$5$Al$_2$O$_3$–$(15-x)$BaO–$x$Dy$_2$O$_3$ ($x = 0.1–5.0$) glasses were fabricated by the conventional melt-quenching method. TeO$_2$, Al$_2$O$_3$, BaCO$_3$ and Dy$_2$O$_3$ were mixed in the above chemical composition, and the mixture in an alumina crucible was sintered at $950$ °C for $1$ h in an electric furnace. Subsequently, the melted compound was quenched on a preheated stainless plate at $300$ °C to obtain the Dy-doped tellurite glasses. All of the obtained glasses were mechanically polished, and their thickness was fixed to be approximately $1.5$ mm.

The glass-transition temperatures ($T_g$) were examined using differential thermal analysis (TG-DTA2000S, Bruker) at a heating rate of $10$ °C/min. The in-line transmittance spectra were obtained by a spectrophotometer (V670, JASCO) covering a spectral region of $300–800$ nm. PL excitation/emission contour spectra, and $QE$ values were evaluated using a quantum yield spectrometer (Quantaurus QY, C11347 Hamamatsu). The excitation and emission wavelengths measured were across $250–500$ and $200–900$ nm, respectively. The PL decay curves were obtained by a fluorescence lifetime spectrometer (Quantaurus $\tau$, C11367 Hamamatsu). The excitation and monitoring wavelengths in this measurement were $340$ and $575$ nm, respectively. The X-ray induced scintillation spectra were recorded using an original setup.$^{22}$ In this measurement, the X-ray generator was operated with the bias voltage of $80$ kV and current of $1.2$ mA. The measurements of scintillation decay profile and afterglow profile were performed using an afterglow characterization system.$^{23}$ The voltage of the X-ray tube equipped with this system was $30$ kV and the spectral sensitivity of photomultiplier tube used in this measurement was from $160$ to $650$ nm.

3. Results and discussion

Figure 1 shows a photograph of the Dy-doped tellurite glasses under room light. The thickness and weight of these tellurite glasses were about $1.5 \pm 0.03$ mm and $0.47 \pm 0.03$ g, respectively. All the Dy-doped tellurite glasses were visibly transparent, and the stripe patterns on the back of the Dy-doped tellurite glasses were observed. The color of the Dy-doped tellurite glasses varied gradually from colorless to yellow as the concentration of Dy increased.

The $T_g$ values of the Dy-doped tellurite glasses are shown in Table 1. The $T_g$ values of the Dy-doped tellurite glasses were $401$ °C (Dy0.1 %), $401$ °C (Dy0.5 %), $405$ °C (Dy1.0 %) and $420$ °C (Dy5.0 %), and the $5.0 \%$ Dy-doped tellurite glass showed the highest $T_g$ value among the Dy-doped tellurite glasses. This should be due to a high concentration of Dy$_2$O$_3$ with high melting temperature (TeO$_2$: $732$ °C, Al$_2$O$_3$: $2072$ °C, BaO: $1923$ °C, Dy$_2$O$_3$: $2408$ °C).$^{24}$

Figure 2 represents the in-line transmittance spectra of the Dy-doped tellurite glasses. These transmittances in a wavelength range of $500–800$ nm for the Dy-doped tellurite glasses were approximately $60–75\%$, which were almost the same as the reported values for the Eu-doped and Nd-doped tellurite glasses.$^{16,17}$ The significant difference in the transmittance was not observed among the Dy-doped tellurite glasses. In addition, the $0.5–5.0 \%$ Dy-doped tellurite glasses showed absorption bands at approximately $365, 390, 430, 450, 475$ and $750$ nm. These absorptions

![Figure 1](image1.png)

![Figure 2](image2.png)
were assigned to the 4f-4f transition of Dy$^{3+}$ according to the past studies. The absorption intensity increased as the Dy concentration increased. In addition, the absorption edge of the Dy-doped tellurite glasses remained constant, regardless of the concentrations of Dy.

**Table 2. QE values of the Dy-doped tellurite glasses**

| Excitation wavelength | 380 nm | 400 nm | 450 nm |
|-----------------------|--------|--------|--------|
| Dy 0.1%               | 0.016 ± 0.02 | 0.020 ± 0.02 | 0.11 ± 0.02 |
| Dy 0.5%               | 0.039 ± 0.02 | 0.047 ± 0.02 | 0.19 ± 0.02 |
| Dy 1.0%               | 0.039 ± 0.02 | 0.043 ± 0.02 | 0.16 ± 0.02 |
| Dy 5.0%               | 0.006 ± 0.02 | 0.007 ± 0.02 | 0.01 ± 0.02 |

Here, $pho_{Abs}$ is the number of absorbed photons and $pho_{Emi}$ is the number of emitted photons. According to Table 2, large QE values were observed under excitation wavelength of 450 nm, which corresponded to the wavelength of absorption band ($^6H_{15/2} \rightarrow ^4I_{15/2}$). The QE values under 450 nm excitation light were 0.11 ± 0.02 (Dy0.1%), 0.19 ± 0.02 (Dy0.5%), 0.16 ± 0.02 (Dy1.0%), and 0.01 ± 0.02 (Dy5.0%). The 0.5 and 1.0% Dy-doped tellurite glasses showed high QE values among the evaluated glasses, but the difference in the QE values between the 0.5 and 1.0% Dy-doped tellurite glasses could not be determined with the spectrometer used. In addition, the QE value of the 0.5% Dy-doped tellurite glasses was found to be higher than that of the Nd-doped tellurite glasses (about 0.1), whereas it was lower than that of the Eu-doped tellurite glasses (about 0.7).

Figure 3 shows the PL decay time profiles of the Dy-doped tellurite glasses. In this measurement, the excitation and monitoring wavelengths were 340 and 575 nm, respectively. The PL decay time constants of the Dy-doped tellurite glasses were derived by assuming two exponential decay functions since two decay time components were observed due to an energy migration process from a donor ion (excited Dy$^{3+}$ ion) to an acceptor ion (not excited Dy$^{3+}$ ion) in the past studies on Dy-doped compounds. The obtained faster and slower PL decay time constants of Dy-doped tellurite glasses were 167, 367 µs (Dy0.1%), 109, 316 µs (Dy0.5%), 94.6, 300 µs (Dy1.0%), and 12.6, 61.6 µs (Dy5.0%), respectively. These constants were typical for those of the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions of Dy$^{3+}$. The PL decay time constants decreased as the concentration of Dy increased possibly due to the concentration quenching.

Figure 4 represents the X-ray induced scintillation spectra of the Dy-doped tellurite glasses. All the Dy-doped tellurite glasses showed sharp emission peaks at approximately 485, 585 and 665 nm. From the previous
studies, these emission peaks at 485, 585 and 665 nm were assigned to the $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$, and $^4F_{9/2} \rightarrow ^6H_{11/2}$ transitions of Dy$^{3+}$, respectively.\(^{18)}\)

The 1.0% Dy-doped tellurite glass exhibited the highest scintillation intensity among the tested glasses. Generally, the scintillation intensity ($LI$) is expressed by the following formula,

$$LI \propto N_{e-h}SQ = \frac{E_r}{\beta E_g} SQ$$

where $N_{e-h}$ is the number of electron–hole pairs generated by X-ray irradiation, $S$ is an energy transfer efficiency, $Q$ is a QE for final luminescence process, $E_r$ is an energy of radiation, $E_g$ is a bandgap energy of the compounds and $\beta$ is a constant of typically 2–3.\(^{29)}\) Based on the results of PL and scintillation spectra, the 0.5 and 1.0% Dy-doped tellurite glasses showed high QE values and X-ray scintillation intensities. Therefore, it suggests that the QE values mainly affected the scintillation intensity. Meanwhile, the scintillation intensity of the 1.0% Dy-doped tellurite glass was found to be higher than that of the 0.5% Dy-doped tellurite glass. The causes of the difference in the results between ultraviolet and X-ray irradiation were unclear, and the efficiency of the energy transfer $S$ might have a little effect on the scintillation intensity because the bandgap energy of the glass host should be almost equal according to the absorption edge as shown in Fig. 2.

**Figure 7** shows the scintillation decay profiles of the Dy-doped tellurite glasses. The scintillation decay time constants were derived from a sum of two exponential decay functions as well as PL decay time profiles. The decay time of the faster and slower components for the Dy-doped tellurite glasses were 39.1, 248 $\mu$s (Dy0.1%), 25.5, 203 $\mu$s (Dy0.5%), 23.5, 157 $\mu$s (Dy1.0%), and 4.95, 30.2 $\mu$s (Dy5.0%). These scintillation decay time constants should be ascribed to the 4f–4f transitions of Dy$^{3+}$. Furthermore, they became shorter as the concentration of Dy increased, and the results were consistent with those in PL as shown in Fig. 5. In addition, the decay time constants in scintillation were shorter than that in PL. In general, scintillation decay time is longer than PL one because of the additional processes such as the energy transfer process as mentioned above.\(^{30)}\) In this case, the energy transfer and quenching of excited state should compete in the Dy-doped tellurite glasses. In PL, there is little interaction among the Dy$^{3+}$ ions in the tellurite glasses because only 4f electrons in Dy$^{3+}$ are excited. On the other hand, in scintillation, this interaction could not be neglected and quenching processes would be dominant since many secondary electrons are excited in a spatial scale of 10–100 nm in scintillation. This should be the reason why the scintillation decay time was shorter than PL decay time in the Dy-doped tellurite glasses.\(^{16),31)}\)

The afterglow profiles of the Dy-doped tellurite glasses are represented in **Fig. 8**. The afterglow level ($I_{AG}$) was evaluated by the following formula.\(^{16)}\)

$$I_{AG} [\%] = 100 \times \left( \frac{I_2 - I_{BG}}{I_1 - I_{BG}} \right)$$

Here, $I_1$ is the averaged scintillation intensity during X-ray irradiation, $I_2$ is the averaged intensity around 20 ms after the X-ray was stopped, and $I_{BG}$ is the background intensity.

**Fig. 5.** PL decay profile of Dy-doped tellurite glasses.

**Fig. 6.** Scintillation spectra of Dy-doped tellurite glasses under X-ray irradiation.
The obtained afterglow levels of the Dy-doped tellurite glasses were 751 ppm (0.1% Dy), 431 ppm (0.5% Dy), 289 ppm (1.0% Dy), and 454 ppm (5.0% Dy). The afterglow levels were on a same order levels of the common inorganic scintillator Tl-doped CsI and the previously reported Eu-doped TeO$_2$–Al$_2$O$_3$–BaO glasses, but they were ten times higher than those of Bi$_4$Ge$_3$O$_12$ and CdWO$_4$, which are famous for low afterglow levels.\textsuperscript{16,23} In scintillation, there are complicate trapping and detrapping processes, which affect the afterglow level on about millisecond order. It is suggested that some trapping centers involving the afterglow level could be generated in the Dy-doped tellurite glasses.

4. Conclusion

The Dy-doped tellurite glasses having a chemical composition of 80TeO$_2$–5Al$_2$O$_3$–(15 – x)BaO–xDy$_2$O$_3$ were prepared by the conventional melt quenching method, and their PL and scintillation properties of these tellurite glasses were investigated, systematically. In PL, the 0.5 and 1.0% Dy-doped tellurite glasses showed high intensities and the decay time constants derived by the 4f–4f transitions of Dy$^{3+}$ were in the range of 12.6–367μs. As scintillation properties, the 1.0% Dy-doped tellurite glass showed the highest scintillation intensity, and all the tellurite glasses had scintillation decay times in the range of 4.95–302μs. In addition, the obtained afterglow levels were several hundred ppm, and the 1.0% Dy-doped tellurite glass exhibited the lowest value, which was comparable to that of Tl-doped CsI. In the future, it is interesting to investigate the effect of doping with other rare earth ions into tellurite glasses with an aim to enhance scintillation light yield and decrease afterglow levels for scintillator applications.

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References
1) M. J. Weber, \textit{Nucl. Instrum. Meth. A}, 527, 9–14 (2004).
2) C. W. E. van Eijk, \textit{Nucl. Instrum. Meth. A}, 460, 1–14 (2001).
3) D. Mannes, F. Schmid, J. Frey, K. Schmidt-Ott and E. Lehmann, \textit{Phys. Proc.}, 69, 653 (2015).
4) T. Yanagida, Y. Fujimoto, S. Kuroswa, K. Kamada, H. Takahashi, Y. Fukazawa, M. Nikl and V. Chani, \textit{Jpn. J. Appl. Phys.}, 52, 076401 (2013).
5) T. Itoh, T. Yanagida, M. Kokubun, M. Sato, R. Miyawaki, K. Makishima, T. Takahisa, T. Tanaka, K. Nakazawa, T. Takahashi, N. Shimura and H. Ishibashi, \textit{Nucl. Instrum. Meth. A}, 579, 239–242 (2007).
6) C. W. E. van Eijk, \textit{Phys. Med. Biol.}, 47, 85–106 (2002).
7) R. Hawrami, A. R. Fatah and K. A. Faraj, \textit{J. Asian Sci. Res.}, 1, 131–138 (2011).
8) W. W. Moses, S. E. Derenzo, M. J. Weber, A. K. Raychaudhuri and F. Cerrina, \textit{J. Lumin.}, 59, 89–100 (1990).
9) Y. Oshima, T. Yasumune, T. Masuda, K. Maehata, K. Ishibashi and T. Ueno, \textit{Prog. Nucl. Sci. Technol.}, 1,
10) T. Yanagida, N. Kawaguchi, Y. Fujimoto, K. Fukuda, Y. Yokota, A. Yamazaki, K. Watanabe, J. Pejchal, A. Uritani, T. Iguchi and A. Yoshikawa, Opt. Mater., 33, 1243–1247 (2011).
11) G. Okada, S. Kasap and T. Yanagida, Opt. Mater., 61, 15–20 (2016).
12) H. Masai, Y. Hino, T. Yanagida and Y. Fujimoto, Opt. Mater., 42, 381–384 (2015).
13) Y. Isokawa, S. Hirano, N. Kawano, G. Okada, N. Kawaguchi and T. Yanagida, Opt. Mater., 487, 1–6 (2018).
14) L. Liu, C. Shao, Y. Zhang, X. Liao, Q. Yang, L. Hu and D. Chen, J. Lumin., 176, 1–5 (2016).
15) N. Kawano, M. Akastuka, H. Kimura, G. Okada, N. Kawaguchi and T. Yanagida, Radiat. Meas., 117, 52–56 (2018).
16) N. Kawano, H. Kimura, A. Horimoto, K. Shinozaki and T. Yanagida, J. Mater. Sci.-Mater. El., 30, 11468–11474 (2019).
17) N. Kawano, H. Kimura, D. Nakauchi, K. Shinozaki and T. Yanagida, Solid Stat. Sci., 100, 10611 (2020).
18) J. Kaewkhao, N. Wantana, S. Kaewjaeng, S. Kothan and H. J. Kim, J. Rare Earth., 34, 583–589 (2016).
19) E. Kaewnuam, N. Wantana, H. J. Kim and J. Kawewkhao, J. Non-Cryst. Solids, 464, 96–103 (2017).
20) N. Wantana, Y. Ruangtaweep, W. Kaewnuam, S. G. Kang, H. J. Kim, S. Kothan and J. Kaewkhao, Solid State Sci., 101, 106135 (2020).
21) T. Kato, D. Nakauchi, N. Kawaguchi and T. Yanagida, Optik, 207, 164433 (2020).
22) T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi and T. Yanagitani, Opt. Mater., 35, 2480–2485 (2013).
23) T. Yanagida, Y. Fujimoto, T. Ito, K. Uchiyama and K. Mori, Appl. Phys. Express, 7, 062401 (2014).
24) A. Torimoto, H. Masai, G. Okada, N. Kawaguchi, T. Yanagida and T. Ohkubo, J. Lumin., 197, 98–103 (2018).
25) T. A. Lodia, N. F. Dantas, T. S. Gonçalvesb, A. S. S. deCamargob, F. Pedrocchia and A. Steimacher, J. Lumin., 207, 378–385 (2019).
26) P. Kantuptim, M. Akastuka, D. Nakauchi, T. Kato, N. Kawaguchi and T. Yanagida, Radiat. Meas., 134, 106320 (2020).
27) R. Liu, M. Chen, X. Zhu, Y. Zhou, F. Zeng and Z. Su, J. Lumin., 226, 117378 (2020).
28) S. A. Saleem, B. C. Janalaliah, M. Jayaimhadri, A. Srinivasarao K. Jang and L. Rama Murthy, J. Quant. Spectrosc. Ra., 112, 78–84 (2011).
29) D. J. Robbins, J. Electrochem. Soc., 127, 2694–2702 (1980).
30) M. Koshimizu, K. Iwamatsu, M. Taguchi, S. Kurashima, A. Kimura, T. Yanagida, Y. Fujimoto, K. Watanabe and K. Asai, J. Lumin., 169, 678–681 (2016).
31) D. Nakauchi, G. Okada, M. Koshimizu and T. Yanagida, J. Lumin., 176, 342–346 (2016).