

Photoluminescence and optical absorption spectra in Tb_2O_3 - Y_2O_3 mixed-crystals

Yutaro Chibana, Hisaya Oda and Akio Yamanaka*

Graduate School of Photonics Science, Chitose Institute of Science and Technology, 758-65 Bibi, Chitose, Hokkaido 066-8655, Japan

We have grown single-crystals of $(Tb_xY_{1-x})_2O_3$ with $x \leq 0.6$ by the floating zone method. The obtained crystals are substitutional solid solutions of Tb_2O_3 and Y_2O_3 , and their crystal structure is of the cubic C-type. Optical spectroscopy reveals that the absorption band, originated from $4f^8 \rightarrow 4f^75d^1$ transitions of Tb^{3+} , grows inside the optical band gap of Y_2O_3 . However, the excitation to this band is not effective for emissions of the $4f$ -electrons, except for low Tb-concentrations. In contrast, the blue-green and violet-UVA excitations are sufficient, at least, up to $x=0.3$.

Key words: $(Tb_xY_{1-x})_2O_3$, Solid solution, Optical spectroscopy, Optical band gap.

Introduction

Yttrium-oxide (Y_2O_3) is one of rare earth sesquioxides RE_2O_3 and an excellent host material for phosphor application, because it is chemically stable, optically isotropic and optically transparent in the wide wavelength range. It is known that Tb-doped Y_2O_3 exhibits green emissions, originated from the f^7f transition of Tb^{3+} ions [1]. The emission is strongest for Tb-concentration of a few mol%, resulted from concentration quenching of the luminescence. Recently, nanocrystals of highly Tb-doped Y_2O_3 and of undiluted Tb_2O_3 have attracted a considerable attention [2-4]. This is because significant modification of the phonon density of states in a nanocrystal is expected to reduce non-radiative relaxation of luminescence and, as a result, enhance the quantum efficiency of the phosphor. Furthermore, Tb_2O_3 has been considered for potential use as a high- k dielectric material for memory applications [5, 6].

Considering the above situation in mind, we have attempted to grow bulk-size single-crystals of Tb_2O_3 - Y_2O_3 by the floating zone technique. In this paper we report results of the photoluminescence and optical absorption measurements performed in the mixed-crystals.

Results and Discussion

Crystal growth and characterization

Mixed-crystals of $(Tb_xY_{1-x})_2O_3$ (abbreviated hereafter as TbYO) were grown by the floating-zone (FZ) method. Appropriate amounts of high-purity commercial powders of Tb_2O_3 (Kojundo Chemical Laboratory, 99.9%) and Y_2O_3 (Furuuchi Chemical, 99.99%) were well mixed and compressed into a rod in the hydrostatic pressure of

30 MPa. The raw material rod was not sintered to avoid the oxidation of Tb^{3+} ions to the non-luminescent Tb^{4+} ones. TbYO was melt-grown from the rod in a FZ furnace (Canon Machinery, SC-M50XS). A Xe discharge lamp was employed as the light source, because the rare earth sesquioxides have higher melting points (~ 2700 K) than the maximum temperature (~ 2300 K) of a conventional FZ furnace, equipped with halogen lamps [7]. In order to remove the residual O_2 in the raw material rod, the crystal growth was performed in a reduced atmosphere consisting of Ar(92%)- H_2 (8%) mixture. The growth rate was 5 mm/hr. Single-crystalline samples of TbYO were successfully obtained for $x \leq 0.6$. Their dimensions are 3-5 mm in diameter and 20-40 mm in length. For higher concentrations the samples were badly cracked during post growth cooling, probably, due to the structural phase transitions [8].

The crystalline structures of TbYO were analyzed by X-ray powder diffraction (XRD) using a diffractometer (Rigaku, RINT2000). The observed XRD patterns are very similar to those of Y_2O_3 and Tb_2O_3 , indicating the cubic C-type structure of TbYO. The samples were also analyzed by a Raman microscope (Renishaw, inVia). The 785 nm line from a laser diode was employed as the light source, because there are no absorption and luminescence of Tb^{3+} in the range of 700-1500 nm. The Raman spectrum of TbYO is very similar to those of Y_2O_3 and other sesquioxides of the cubic C-type, reported in the literature [9]. In order to consider the x -dependence of the Raman scattering, we have analyzed the spectrum in terms of a Lorentz function and estimated the mode frequency. Fig. 1 displays the frequency Ω_{TbYO} of the strongest Raman band at 370 cm^{-1} . It turns out that the frequency Ω_{TbYO} well follows the solid line, expected from the Vegard's law $\Omega_{TbYO} = x \cdot \Omega_{TbO} + (1-x) \cdot \Omega_{YO}$. Here $\Omega_{TbO} = 367.6\text{ cm}^{-1}$ and $\Omega_{YO} = 378.2\text{ cm}^{-1}$, plotted as open circles in Fig. 1, have been measured in raw powders of Tb_2O_3 and Y_2O_3 , respectively. The behavior is typical for

*Corresponding author:
Tel : +81-123-27-6114
Fax: +81-123-27-6114
E-mail: a-yamana@photon.chitose.ac.jp

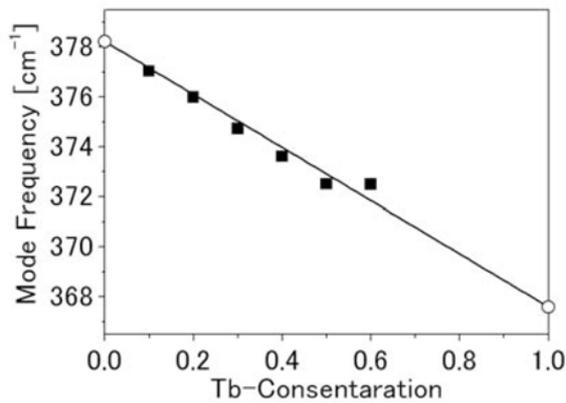


Fig. 1. Frequency of the 370 cm^{-1} mode in $(Tb_xY_{1-x})_2O_3$ mixed-crystals as a function of Tb-concentration x . The solid line displays the Vegard's law.

substitutional solid solutions [10]. It should be noted that no inhomogeneous broadening of the Raman band is detected.

Optical absorption and photoluminescence

Optical absorption spectra were recorded by UV-VIS-NIR spectrometer (Jasco, V-670) and FT-IR spectrometer (Shimadzu, FTIR-8700). The samples were sliced into disks by a diamond cutter and polished by diamond suspension and colloidal silica. Fig. 2 illustrates the absorption spectra of TbYO with several Tb-concentrations. TbYO(0.003), namely Tb(0.3%)-doped Y_2O_3 , shows a striking absorption band above 3.8 eV ($\sim 330\text{ nm}$), well below the optical band gap of 5.6 eV (220 nm) in Y_2O_3 [11]. This UV absorption agrees nicely with the absorption band ($4\sim 5\text{ eV}$) observed in the excitation spectrum of Tb-doped Y_2O_3 [12]. In TbYO(0.5) the absorption edge should be located at $3.2\sim 3.5\text{ eV}$. This value agrees roughly with the band gap of $E_g = 3.8\text{ eV}$ observed in Tb_2O_3 powder [13] and $E_g = 2.8\text{ eV}$ in C-type Tb_2O_3 films [6]. The band gap of Tb_2O_3 is understood to originate the transition from the filled Tb- $4f$ state to the unoccupied Tb- $5d$ conduction band [14, 15]. It is natural to attribute the UV-absorption band in TbYO to the $4f^8 \rightarrow 4f^75d^1$ transitions.

As shown in Fig. 2, TbYO has absorption bands around 2.6 eV (480 nm) and 3.3 eV (380 nm), originated from the $^7F_6 \rightarrow ^5D_4$ and $^7F_6 \rightarrow ^5D_3$ transitions, respectively. Small peaks around 3.5 eV (350 nm) might be due to the $^7F_6 \rightarrow ^5D_2$ one. Similarly, the $^7F_6 \rightarrow ^7F_j$ ($j=1, \dots, 5$) transitions take place as absorption bands in the infrared region. Each band consists of many sharp peaks, as the result of the Stark splitting of the f -states [16]. The absorption coefficient α of each peak increases smoothly with x , at least, up to $x=0.4$. This fact indicates that the absorption is proportional to the number of Tb^{3+} ions.

Fig. 3 illustrates the luminescence spectrum of TbYO(0.3), where the excitation photon energy are 3.87 eV (320 nm), 3.25 eV (380 nm) and 2.56 eV (484 nm), corresponding to the $4f^8 \rightarrow 4f^75d^1$, $^7F_6 \rightarrow ^5D_3$

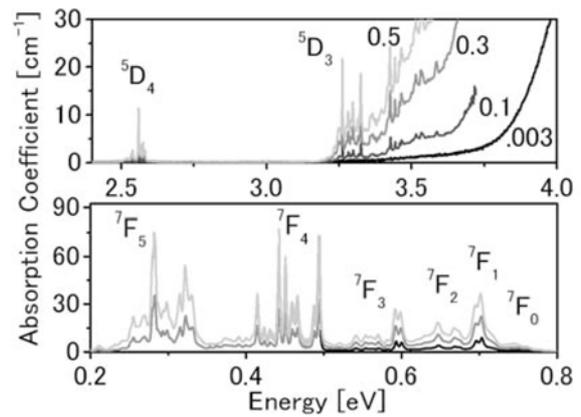


Fig. 2. Absorption spectra of $(Tb_xY_{1-x})_2O_3$ with $x = 0.003, 0.1, 0.3$ and 0.5 .

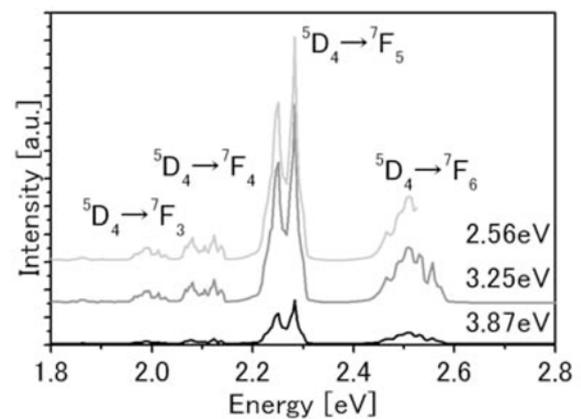


Fig. 3. Photoluminescence spectra of $(Tb_xY_{1-x})_2O_3$ with $x = 0.3$.

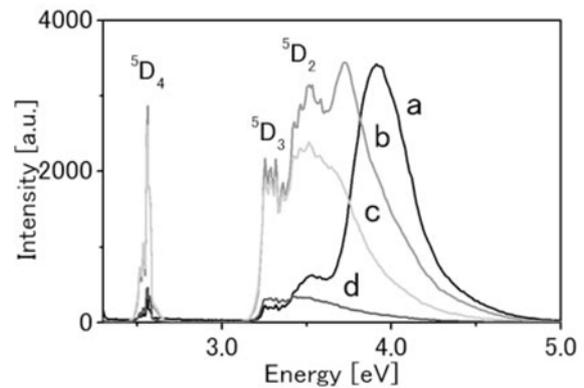


Fig. 4. Excitation spectra of $(Tb_xY_{1-x})_2O_3$ with (a) $x = 0.003$, (b) 0.1 , (c) 0.3 and (d) 0.5 , measured by the intense emission peak at 2.28 eV .

and $^7F_6 \rightarrow ^5D_4$ transitions, respectively. The $^5D_4 \rightarrow ^7F_j$ ($j=3\sim 6$) emissions are clearly observed in the range of $1.9\text{ eV} \sim 2.6\text{ eV}$ ($650\text{ nm} \sim 470\text{ nm}$). The $^7F_6 \rightarrow ^5D_3$ and $^7F_6 \rightarrow ^5D_4$ excitations give rise to rather strong emissions as compared to the UV-excitation. To understand this behavior, we have measured the excitation spectrum of the most intense emission of the $^5D_4 \rightarrow ^7F_5$ transition at 2.28 eV (544 nm). Fig. 4 shows the results. The excitation spectrum of TbYO(0.3), spectrum c, has a maximum

intensity at 2.56 eV (484 nm), blue-green excitation. TbYO(0.3) is also effective for violet-UVA excitation, because the intensity of the excitation spectrum is rather strong for the ${}^7F_6 \rightarrow {}^5D_3$ excitation. An optimal Tb-concentration for the blue-green or violet-UVA excitation should be $x = 0.1 \sim 0.3$.

The optimal Tb-concentration estimated above is quite different from the value of a few mol% for Tb-doped Y_2O_3 . We attribute this difference to the x -dependence of the excitation spectrum. As can be seen in Fig. 4, the excitation spectrum of TbYO(0.003), spectrum a, shows a strong and broad peak at about 3.9 eV, which corresponds to the UV-band observed in the absorption spectrum. With increasing x , the broad peak moves to a lower energy. As a result, the excitation spectrum is greatly suppressed at higher energies above 4 eV (below 300 nm). In other word, the optimal concentration for the luminescence depends on the excitation energy. Finally, it is noted that the excitation spectrum is very weak for $x \geq 0.5$, although the strong absorption of the $f-d$ and $f-f$ transitions is observed (Fig. 2). This fact implies that formation of the $5d$ -conduction band accompanies with the remarkable increase of the non-radiative decay for the photo-excited electrons. To consider this problem, further investigation is required.

Summary

We have studied the optical absorption and photoluminescence in the mixed-crystals of $(Tb_xY_{1-x})_2O_3$, grown by the floating zone method. The obtained crystals are substitutional solid solutions of Tb_2O_3 and Y_2O_3 , and their crystal structure is of the cubic C-type. The $4f^8 \rightarrow 4f^75d^1$ transitions of Tb^{3+} lead to the absorption band inside the optical band gap of Y_2O_3 . The photo-excitation to the $4f^8 \rightarrow 4f^75d^1$ transitions leads to the strong emissions of the $4f$ -electrons, only for low Tb-

concentrations. In contrast, the blue-green and violet-UVA excitations are sufficient for higher Tb-concentrations.

References

1. Phosphor Handbook, edited by S. Shionoya, W.M. Yen, and H. Yamamoto (CRC Press, Northwest London, 2006).
2. M.A. Flores-Gonzalez, G. Ledoux, S. Roux, K. Lebbou, P. Perriat, and O. Tillement, *J. Solid State Chem.* 178 (2005) 989-997.
3. Q. Chen, W. Zhang, and X. Huang, *J. Lumin.* 126 (2007) 309-313.
4. A.B. Panda, G. Glaspell, and M.S. El-Shall, *J. Phys. Chem. C* 111 (2007) 1861-1864.
5. T. Pan, F. Chen, and J. Jung, *J. Appl. Phys.* 108 (2010) 074501.
6. N.W. Gray, M.C. Prestgard, and A. Tiwari, *Appl. Phys. Lett.* 105 (2014) 222903.
7. H. Tsuiki, K. Kitazawa, T. Masumoto, K. Shiroki, and K. Fueki, *J. Crystal Growth* 49 (1980) 71-76.
8. M. Zinkevich, *Prog. Mater. Sci.* 52 (2007) 597-647.
9. A. Ubaldini, and M. M. Carnasciali, *J. Alloy Compd.* 454 (2008) 374-378.
10. J.-C. Panitz, J.-C. Mayor, B. Grob, and W. Durisch, *J. Alloy Compd.* 303-304 (2000) 340-344.
11. W.C. Wang, M. Badylevich, V.V. Afanas'ev, A. Stesmans, C. Adelman, S. Van Elshocht, J. A. Kittl, M. Lukosius, C. Walczyk, and C. Wenger, *Appl. Phys. Lett.* 95 (2009) 132903.
12. M. Back, A. Massari, M. Boffelli, F. Gonella, P. Riello, D. Cristofori, R. Ricco, and F. Enrichi, *J. Nanopart. Res.* 14 (2012) 792.
13. A. Prokofiev, A. Shelykh, and B. Melekh, *J. Alloy Compd.* 242 (1996) 41-44.
14. L. Petit, A. Svane, Z. Szotek, and W.M. Temmerman, *Phys. Rev. B* 72 (2005) 205118.
15. R. Gillen, S.J. Clark and J. Robertson, *Phys. Rev. B* 87 (2013) 125116.
16. J.B. Gruber, K.L. Nash, R.M. Yow, D.K. Sardar, U.V. Valiev, A.A. Uzokov, and G.W. Burdick, *J. Lumin.* 128 (2008) 1271-1284.