

Growth and Luminescence of M-Type GdTaO_4 and $\text{Tb}:\text{GdTaO}_4$ Scintillation Single Crystals

Wenpeng Liu, Qingli Zhang, Wenlong Zhou, Changjiang Gu, and Shaotang Yin

Abstract—M-type GdTaO_4 and $\text{Tb}:\text{GdTaO}_4$ bulk single crystals were first grown by Czochralski method. Transmission, excitation, emission spectra and luminescence decay curves of them were measured. The refractive indices of GdTaO_4 were calculated with its transmission spectrum and fitted with Sellmeier equation. GdTaO_4 shows Gd^{3+} absorption and defect luminescence, Tb^{3+} exhibits its typical absorption and luminescence in GdTaO_4 . The luminescence decay times of GdTaO_4 and $\text{Tb}:\text{GdTaO}_4$ were also determined by fitting luminescence decay curves with single-exponential function.

Index Terms— GdTaO_4 , luminescence, refractive index, scintillator.

I. INTRODUCTION

AS the urgent needs in high energy physics experiments and nuclear medical imaging, scintillation crystals with high density and fast decay character have attracted increasing interest since the last decade. Rare earth activated crystals have been found very useful as detectors in these fields. As a potential efficient host for X-ray luminescence material, GdTaO_4 has attracted more attentions for a long time. It usually exhibits two modifications, one belonging to space group $I2/a$ or M-type and the other belonging to space group $P2_1/a$ or M'-type [1]. Luminescence properties of rare earth tantalate phosphors have been reported extensively, and this type phosphors show excellent scintillation performance [2]–[5]. Eu^{3+} doped GdTaO_4 shows efficient red emission, and the luminescence can be highly enhanced by codopant ions [6]–[8]. Tb^{3+} activated GdTaO_4 also exhibits efficient green emission under UV excitation and is a promising phosphor for X-ray intensifying screen. In addition, GdTaO_4 phosphor possesses many advantages, such as high density (8.84 g/cm^3), stable chemical properties, strong irradiation hardness and good X-ray absorption [9]. However, most of research is only in polycrystalline samples of rare-earth tantalates, and there is no work on the growth and performance of big bulk single crystals of them, which can be practically applied.

In the present paper, the GdTaO_4 and $\text{Tb}:\text{GdTaO}_4$ bulk single crystals were grown by Czochralski method, the optical absorption, refractive indices and luminescence spectra of them are also described. To our knowledge, GdTaO_4 bulk single

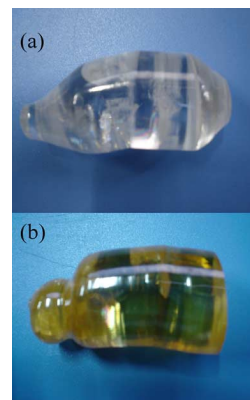


Fig. 1. Photograph of M-type GdTaO_4 (a) and $\text{Tb}:\text{GdTaO}_4$ (b).

crystal growth by Czochralski method is reported for the first time in the literature.

II. EXPERIMENTAL DETAILS

GdTaO_4 and $\text{Tb}:\text{GdTaO}_4$ bulk single crystals were grown by Czochralski method with an automatic diameter controlled (ADC) Czochralski growth system. The Gd_2O_3 (99.995%), Ta_2O_5 (99.99%) and Tb_4O_7 (99.99%) were used as raw materials and they were weighted according to the stoichiometric and designed compositions, and the Tb concentration was 1at% in $\text{Tb}:\text{GdTaO}_4$. Then they were mixed thoroughly and pressed into disks. After sintering at 1250°C for 24 h in air, raw materials were loaded into an iridium crucible.

As GdTaO_4 is a new material, so the seed was first pulled from GdTaO_4 melt with iridium wire in N_2 atmosphere. Then the seed was used to grow GdTaO_4 crystal. After several times, good quality $\langle 100 \rangle$ -oriented GdTaO_4 seed was obtained. And transparent GdTaO_4 and $\text{Tb}:\text{GdTaO}_4$ with diameter of 25 mm were grown successfully using the $\langle 100 \rangle$ -oriented seed, as shown in Fig. 1. By X-ray diffraction measurement, both the crystals were determined as M-type GdTaO_4 single phase. The as-grown crystals were annealed in air at 1500°C for 72 h in order to eliminate the residual stress. Samples were cut from the post-annealing crystals perpendicular to the $\langle 010 \rangle$ axis and polished on both sides with 2 mm in thickness.

The absorption spectrum in the range of 200–2200 nm was recorded by a PE lambda 900 spectrophotometer and the spectral interval was 1 nm. A Fluorolog-3-Tan Steady-state/lifetime spectrofluorometer was used to measure the excitation, emission spectra and the luminescence lifetime. All of the measurements were performed at room temperature.

Manuscript received May 07, 2009; revised September 05, 2009; accepted September 25, 2009. Date of current version June 16, 2010. This work was supported in part by the National Natural Science Foundation of China under Grant 50772112, 90922003 and Grant 50872135, and in part by the Anhui Provincial Natural Science Foundation under Grant 08040106820.

The authors are with Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China (e-mail: wpliu@aiofm.ac.cn).

Color versions of one or more of the figures in this paper are available online at <http://ieeexplore.ieee.org>.

Digital Object Identifier 10.1109/TNS.2009.2037320

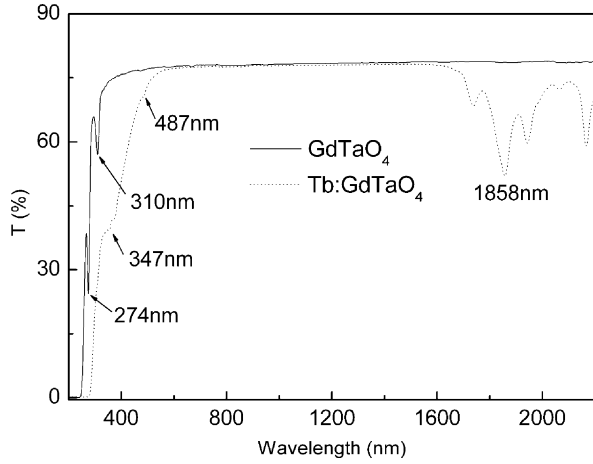


Fig. 2. Transmission spectra of GdTaO₄ and Tb:GdTaO₄.

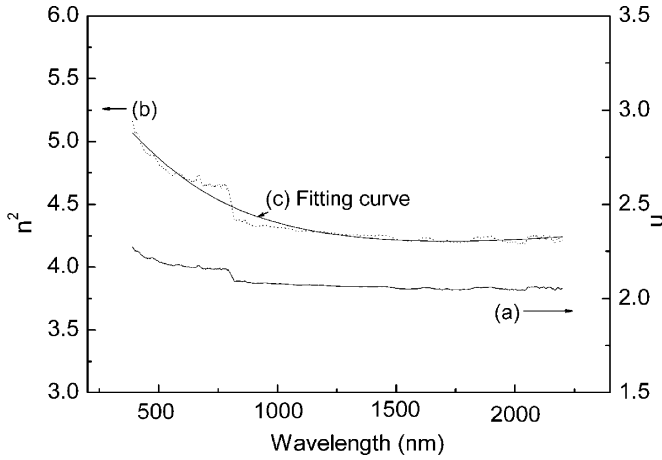


Fig. 3. Refractive indices (a), refractive indices square (b) of GdTaO₄ calculated from its transmission spectrum and fitting curve (c) with sellmeier equation.

III. RESULTS AND DISCUSSION

A. Transmission Spectra of GdTaO₄ and Tb:GdTaO₄

The transmission spectra of GdTaO₄ and Tb:GdTaO₄ are shown in Fig. 2. Two peaks at 310 nm and 274 nm are found in the transmission spectrum of GdTaO₄, which are attributed to the $^8S_{7/2} \rightarrow ^6P_J$ transition and $^8S_{7/2} \rightarrow ^6I_J$ transition of Gd³⁺, respectively. In the transmission spectrum of Tb:GdTaO₄, the spectra between 2200 and 1700 nm represent transitions from the ground-state multiplet manifold 7F_6 to 7F_3 , 7F_2 , 7F_1 and 7F_0 of Tb³⁺ [10], the spectra between 487 and 347 nm include the transitions from the ground-state multiplet 7F_6 to multiplet 5D_4 , 5D_3 , 5G_6 , $^5L_{10}$, 5G_5 , 5D_2 , 5G_4 , and 5L_9 of Tb³⁺ and perhaps also some color centers absorption that needs further study.

B. The Refractive Index of GdTaO₄

Refractive index is an essential parameter of crystal, and there are many methods to measure it, such as the least deflection angle method, auto-collimation method, V-prism method and absorption spectrum method. Among these, the absorption method is a simple method, it has some advantages such as

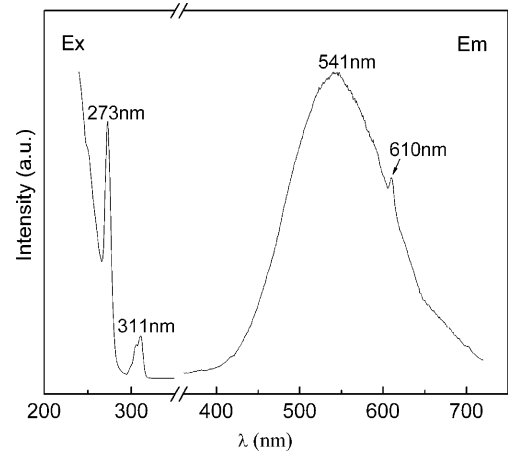


Fig. 4. Excitation and emission spectra of GdTaO₄ crystal ($\lambda_{em} = 541$ nm, $\lambda_{ex} = 311$ nm).

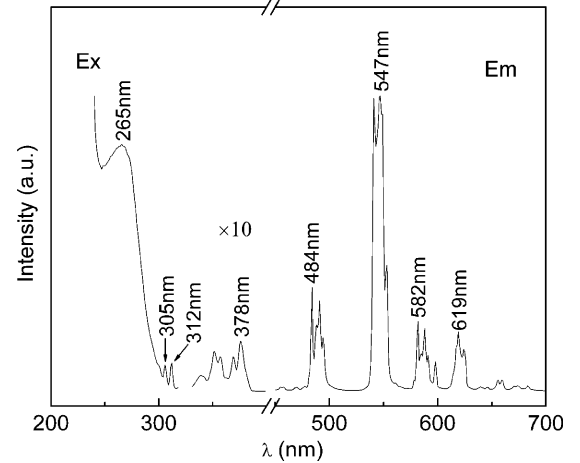


Fig. 5. Excitation and emission spectra of Tb:GdTaO₄ crystal ($\lambda_{em} = 547$ nm, $\lambda_{ex} = 378$ nm).

no strict demand for the sample size, no measurement range restriction and is easy to operate and can obtain refractive indices within a spectral range [12].

The relationship of crystal transmission $T = I/I_0$, reflex indices R and absorption coefficient α can be described as

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad (1)$$

where d is the thickness of the crystal sample,

$$R = \left(\frac{n-1}{n+1} \right)^2. \quad (2)$$

In the transparent range of crystal, $\alpha = 0$, formula (1) can be simplified as

$$T = \frac{(1-R)^2}{1-R^2} = \frac{1-R}{1+R}. \quad (3)$$

From the above formulas (2) and (3), we can obtain

$$R = \frac{1-T}{1+T} \quad (4)$$

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}. \quad (5)$$

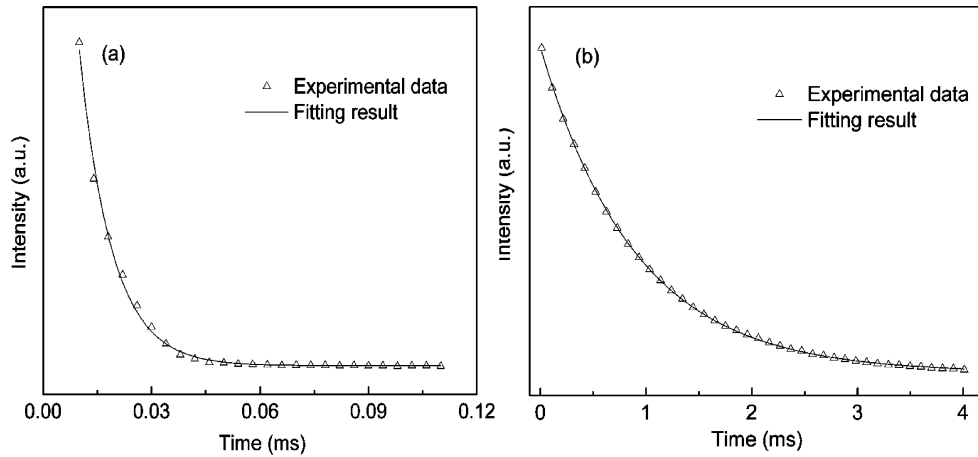


Fig. 6. Luminescence decay curves of GdTaO₄ (a) and Tb:GdTaO₄ (b).

So the refractive indices of crystals can be calculated using the transmission data in the $\alpha = 0$ range.

For GdTaO₄ belongs to monoclinic crystal, so the orientation of the crystallographic axis (a, b, c) is not entirely the same with that of the optical indicatrix axis (X, Y, Z), and only the b axis is parallel to Y axis [11]. So the samples were cut from the post-annealing crystals perpendicular to the $\langle 010 \rangle$ axis.

It can be seen that α equal 0 in the range of 500–2100 nm in the absorption spectrum of GdTaO₄ in Fig. 2, so we chose the transmission data in this range to calculate the refractive indices of GdTaO₄. The calculated results of refractive indices can be fitted with the following Sellmeier equation

$$n^2(\lambda, T) = A(T) + \frac{B(T)}{\lambda^2 - C(T)} - D(T)\lambda^2. \quad (6)$$

And the fitting curve with this equation is shown in Fig. 3, the fitted results are $A = 3.89546$, $B = 0.53175 \mu\text{m}^2$, $C = -0.30491 \mu\text{m}^2$, $D = -0.05039(\mu\text{m}^2)^{-1}$.

C. Emission and Excitation Spectra of GdTaO₄ and Tb:GdTaO₄

Fig. 4 presents excitation and emission spectra of GdTaO₄ crystal ($\lambda_{\text{em}} = 541 \text{ nm}$, $\lambda_{\text{ex}} = 311 \text{ nm}$). In the excitation spectrum of GdTaO₄, the sharp lines peaked at 273 nm and 311 nm are assigned to the $^8S_{7/2} \rightarrow ^6I_J$ and $^8S_{7/2} \rightarrow ^6P_J$ transitions of Gd³⁺, respectively. The strong band shorter than 266 nm is due to the $\text{O}^{2-} \rightarrow \text{Ta}^{5+}$ charge transfer transition [13]. As shown in the emission spectrum of GdTaO₄ in Fig. 4, there are one strong band around 541 nm, which may be caused by defects in the tantalate group surroundings (F-type centers) [14], and a sharp peak at 610 nm superposed on the band corresponding to the Eu³⁺ impurity.

Fig. 5 presents excitation and emission spectra of Tb:GdTaO₄ crystal ($\lambda_{\text{em}} = 547 \text{ nm}$, $\lambda_{\text{ex}} = 378 \text{ nm}$). Two strong bands around 265 nm and shorter than 250 nm and some weak bands in 300–400 nm (the intensity of the excitation spectrum in 330–400 nm was multiplied by 10) are observed in the excitation spectrum of Tb:GdTaO₄. The band shorter than 250 nm is due to the $\text{O}^{2-} \rightarrow \text{Ta}^{5+}$ charge transfer transition [13], the band around 265 nm is due to transitions from the lower levels of the $4f^8$ single configuration of Tb³⁺

to the levels of the $4f^75d$ mixed configuration of Tb³⁺. The sharp lines peaked at 305 nm and 312 nm are assigned to the transitions from $^8S_{7/2}$ level to different 6P_J levels of Gd³⁺. Many weak peaks in 300–400 nm range are from the $4f - 4f$ transition of Tb³⁺, and the excitation at 378 nm is the strongest corresponding to $^7F_6 \rightarrow ^5D_3$ transition of Tb³⁺. Under 378 nm excitation, the emission spectrum of Tb:GdTaO₄ exhibits typical Tb³⁺ emission due to the $^5D_4 \rightarrow ^7F_J$ ($J = 6, 5, 4, 3$) transitions, which are $^5D_4 \rightarrow ^7F_6$ (484 nm), $^5D_4 \rightarrow ^7F_5$ (547 nm), $^5D_4 \rightarrow ^7F_4$ (582 nm), $^5D_4 \rightarrow ^7F_3$ (619 nm) transitions, respectively. Among them, the emission at 547 nm is the strongest.

D. Luminescence Decay Times of GdTaO₄ and Tb:GdTaO₄

Luminescence decay curves of GdTaO₄ and Tb:GdTaO₄ are shown in Fig. 6(a) and (b), and the monitored emission wavelength were 541 nm for GdTaO₄ and 547 nm for Tb:GdTaO₄, respectively. The luminescence decay time can be obtained by fitting the luminescence decay curves with single-exponential function: $I = I_0 \exp(-t/\tau)$ (I_0 is the initial intensity at $t = 0$, τ is the luminescence decay time). By this fitting, the luminescence decay times (τ) of GdTaO₄ and Tb:GdTaO₄ were determined as 0.009 ms and 0.901 ms, respectively.

IV. CONCLUSIONS

M-type GdTaO₄ and Tb:GdTaO₄ bulk single crystals were first grown by Czochralski method successfully. GdTaO₄ shows Gd³⁺ absorption at 274 and 310 nm and defect luminescence band at 541 nm, Tb:GdTaO₄ exhibits Tb³⁺ and color centers absorption between 487 and 347 nm and typical Tb³⁺ luminescence in which 547 nm is the strongest. The refractive indices of GdTaO₄ were calculated with the transmission spectrum and fitted with Sellmeier equation. The luminescence decay times of GdTaO₄ and Tb:GdTaO₄ were also determined as 0.009 ms and 0.901 ms, respectively.

REFERENCES

- [1] R. A. Silva, G. Tirao, C. Cusatis, and J. P. Andreetta, "Growth and structural characterization of M-type GdTaO₄ single crystal fiber," *J. Cryst. Growth.*, vol. 274, no. 3–4, pp. 512–517, Feb. 2005.
- [2] G. Blasse, G. J. Dirksen, L. H. Brixner, and M. K. Crawford, "Luminescence of materials based on LuTaO₄," *J. Alloy. Comp.*, vol. 209, no. 1–2, pp. 1–6, Jul. 1994.

- [3] B. Li, Z. Gu, J. Lin, and M.-Z. Su, "X-ray luminescence properties of rare-earth doped orthotantalate," *Mater. Res. Bull.*, vol. 35, no. 12, pp. 1921–1931, Sep. 2000.
- [4] S. L. Issler and C. C. Torardi, "Solid state chemistry and luminescence of X-ray phosphors," *J. Alloy. Comp.*, vol. 229, no. 1, pp. 54–65, Oct. 1995.
- [5] L. H. Brixner and H.-Y. Chen, "On the structural and luminescence properties of the $M'LnTaO_4$ rare earth tantalates," *J. Electrochem. Soc.*, vol. 130, no. 12, pp. 2435–2443, Dec. 1983.
- [6] M. Gu, L. H. Xiao, X. L. Liu, R. Zhang, B. J. Liu, and X. Xu, "Highly enhanced luminescence of $GdTaO_4:Eu^{3+}$ phosphors by codoping with Zn^{2+} ions," *J. Alloy. Comp.*, vol. 426, no. 1-2, pp. 390–394, Dec. 2006.
- [7] B. Li, Z. N. Gu, J. H. Lin, and M. Z. Su, "X-ray luminescence properties of rare-earth doped orthotantalate," *Mater. Res. Bull.*, vol. 35, no. 12, pp. 1921–1931, Sep. 2000.
- [8] X. L. Liu, K. Han, M. Gu, L. H. Xiao, C. Ni, S. M. Huang, and B. Liu, "Effect of codopants on enhanced luminescence of $GdTaO_4:Eu^{3+}$ phosphors," *Solid State Commun.*, vol. 142, no. 12, pp. 680–684, Jun. 2007.
- [9] C. W. E. van Eijk, "Inorganic-scintillator development," *Nucl. Instrum. Meth. Phys. Res. A.*, vol. 460, no. 1, pp. 1–14, Mar. 2001.
- [10] J. B. Gruber, K. L. Nash, R. M. Yow, D. K. Sardar, U. V. Valiev, A. A. Uzokov, and G. W. Burdick, "Spectroscopic and magnetic susceptibility analyses of the 7F_J and 5D_4 energy levels of $Tb^{3+}(4f^8)$ in $TbAlO_3$," *J. Lumin.*, vol. 128, no. 8, pp. 1271–1284, Aug. 2008.
- [11] X. G. Guan, P. Z. Fu, S. M. Wan, H. Q. Zhou, Y. C. Wu, and C. T. Chen, "Growth and orientation of $CaLa_2B_{10}O_9$ (LCB) crystal," (in Chinese) *J. Synth. Cryst.*, vol. 31, no. 4, pp. 333–336, Aug. 2008.
- [12] Q. L. Zhang, S. T. Yin, Z. B. Wang, D. L. Sun, and S. M. Wan, "A simple method to measure crystal refractive indices with an absorption spectrum," (in Chinese) *J. Synth. Cryst.*, vol. 36, no. 1, pp. 110–113, Feb. 2007.
- [13] G. Blasse and A. Bril, "Luminescence phenomena in compounds with fergusonite structure," *J. Lumin.*, vol. 3, no. 2, pp. 109–131, Sep. 1970.
- [14] L. I. Kazakova, L. S. Bykov, and A. B. Dubovsky, "The luminescence of rare-earth tantalate single crystals," *J. Lumin.*, vol. 72–74, pp. 211–212, Jun. 1997.