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Visible emission and energy transfer in Tb³⁺/Dy³⁺ co-doped phosphate glasses

Yan Sun ^{1,2}, Fei Yu ^{1,3,*}, Meisong Liao ¹, Juping Ma ^{1,2}, Xin Wang ¹, Dongbing He ¹, Weiqing Gao ⁴,
Jonathan Knight ⁵, Lili Hu ^{1,3,*}

¹ Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics,
Chinese Academy of Sciences, Shanghai 201800, China

² Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of
Sciences, Beijing 100049, China

³ Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024,
China

⁴ Department of Optical Engineering, Hefei University of Technology, Hefei 230601, China

⁵ Centre for Photonics and Photonic Materials, Department of Physics, University of Bath, Claverton
Down, Bath, BA2 7AY, United Kingdom

Abstract: In this work, we systematically study spectroscopic properties of Tb³⁺/Dy³⁺ co-doped phosphate glasses in the visible spectral region and explore the sensitization role of Dy³⁺ in the enhancement of visible fluorescence of Tb³⁺ ions. Judd–Ofelt parameters Ω_2 and Ω_4/Ω_6 of the phosphate glass as host for Tb³⁺ are calculated as $21.60 \times 10^{-20} \text{ cm}^2$ and 0.73 respectively based on the measured spectral absorption. Multiple energy transfer routes from Dy³⁺ to Tb³⁺ and their efficiencies are characterized and the enhanced fluorescence properties of Tb³⁺ are investigated, including the emission spectral strength and the spontaneous emission lifetime as functions of Dy³⁺ doping concentration. The efficient non-radiative energy transfer processes between Dy³⁺ and Tb³⁺ allow a moderate concentration level of Tb³⁺ to achieve favorably stronger spectral absorption at blue and ultraviolet wavelengths but almost negligible up-conversion. Tb³⁺/Dy³⁺ co-doped phosphate glass shows promising potential for phosphors and lasing operation at visible wavelengths.

Keywords: Dy³⁺/Tb³⁺; phosphate glass; luminescence; energy transfer process

* Corresponding author.

E-mail address: yufei@siom.ac.cn (F. Yu), hulili@siom.ac.cn (L. Hu)

1. Introduction

In recent years, visible luminescence of Tb^{3+} ions doped in crystal, ceramic and glass, has found various applications in display techniques, visible light communication and medical treatment ¹⁻⁶. Particularly, lasing operation in the visible spectral region has already been demonstrated in Tb^{3+} doped crystals, e.g. CaF_2 ⁷, LiLuF_4 ⁷, LiYF_4 ⁸, LaF_3 ⁹, KY_3F_{10} ⁹, BaY_2F_8 ⁹, BaLu_2F_4 ⁹ as well as in fluoride glass fibers ¹⁰⁻¹².

Tb^{3+} doped fluoride glass was investigated for visible luminescence since 1989 ¹³. Generally, the low-energy phonon density distribution of the fluoride glass mitigates the cross relaxation processes, which is favorable for a high concentration of rare-earth ions, and makes it an attractive material for gain fiber ¹⁰⁻¹². ¹⁴. In 2007, Tb^{3+} doped fluoride glass of 1 wt% concentration realized a gain of 5.3 dB at 540 nm wavelength ¹¹. In 2008, the first continuous-wave laser operation at 542 nm in a fluoride glass fiber was reported where 1.6 mW output power with 8.4 % slope efficiency was measured ¹².

Visible emissions in rare-earth ions doped oxide glasses usually suffer from degradation of emission strength due to the cross relaxation effect ¹⁵. Uniquely, Tb^{3+} ions with $^5\text{D}_4$ -multiplet are regarded as a promising doping candidate which is assumed to be largely absent from cross relaxation processes due to the lack of acceptor levels. The feasibility of doping Tb^{3+} ion in phosphate ¹⁶, silicate ¹⁷, and borate ¹⁸ glasses has been explored. Unfortunately the weak absorption cross section of Tb^{3+} around 10^{-22} cm^2 in the blue spectral region ⁹ challenges its practical application.

Among oxide glasses, phosphate glasses are known for high transparency, high solubility of rare-earth ions, low photo-darkening and mature manufacturing technology ¹⁹⁻²¹. Although in principle phosphate glasses allow a much higher doping concentration of Tb^{3+} , multi-photon absorption ⁹ counterbalances the benefits of increased dopant concentration in practice. To address the dilemma, Dy^{3+} assisted energy transfer (ET) process has been proposed to enhance the visible fluorescence of Tb^{3+} under a moderate

concentration level and investigated in hosts of borate ²², silicate ²³ oxyfluorosilicate ²⁴ glasses, which indicated Dy³⁺ ion as a good sensitizer for the visible emission of Tb³⁺ ions.

In the previous studies of Dy³⁺/Tb³⁺ co-doped phosphate glasses 25-27, the potential of using Dy³⁺ to sensitize Tb³⁺ in phosphate glass for visible lasing application still remained unexplored. In this work, we focus on the spectroscopic properties of Tb³⁺ ions in Dy³⁺/Tb³⁺ co-doped phosphate glasses, and systematically characterize the dependence of spectral and temporal properties of Tb³⁺ emission on pump wavelength and Dy³⁺ concentration, which are key to understand the sensitization effect of Dy³⁺ ions. Energy transfer routes and corresponding efficiencies between Dy³⁺ and Tb³⁺ ions are investigated based on experimental measurement of enhanced absorption, excitation and fluorescence spectra of Tb³⁺ ions in the Dy³⁺/Tb³⁺ co-doped phosphate glass. We experimentally confirm much higher Judd–Ofelt parameters and longer lifetime of Tb³⁺ in our phosphate glass, with a promising potential for laser operation at visible wavelengths.

2. Glass synthesis and characterization methodology

2.1 Glass synthesis

The sample glasses are fabricated by composition (in mol%) of 65P₂O₅-15Al₂O₃-10K₂O-(10-x-y)Y₂O₃-xTb₂O₃-yDy₂O₃ (x=1, y=0, 0.1, 0.5, 1, 2; x=0, y=1; x=0, 0.5, 1, 2, 4, y=0.5) which are denoted as T1, T1D0.1, T1D0.5, T1D1 and T1D2, respectively), as listed in Table 1. Analytical reagents P₂O₅, Al₂O₃, K₂CO₃ and high purity Tb₂O₃, Dy₂O₃ (99.99 wt.% Aladdin Chemical Co.) were used as raw materials. Compounds were well mixed and melted in platinum crucibles at 1150°C for 2 h in the atmosphere, cast onto a preheated steel plate, and then annealed at 450°C for 3 h. The prepared glass samples (15 mm × 15 mm × 1.2 mm each) were double-polished for characterization.

Table 1. Composition of Tb³⁺/Dy³⁺ co-doped phosphate glasses.

Glass compositions (mol%)

Samples	P ₂ O ₅	Al ₂ O ₃	K ₂ O	Y ₂ O ₃	Tb ₂ O ₃	Dy ₂ O ₃
T1	65	15	10	9	1	-
T1D0.1	65	15	10	8.9	1	0.1
T1D0.5	65	15	10	8.5	1	0.5
T1D1	65	15	10	8	1	1
T1D2	65	15	10	7	1	2
D1	65	15	10	9	-	1
D0.5	65	15	10	9.5	-	0.5
T0.5D0.5	65	15	10	9	0.5	0.5
T2D0.5	65	15	10	7.5	2	0.5
T4D0.5	65	15	10	5.5	4	0.5

2.2 Measurement method

Phases of the samples were characterized by X-ray diffraction (XRD, Rigaku RINT-2000) with Cu K α radiation (0.154 nm). The element distribution of samples was characterized by JXA8230 electron probe microscopy analysis (EPMA). Scanning electron microscopy (SEM) images of samples were acquired on an SU1080 microscopy (Hitachi, Japan). The refractive index was measured by a waveguide prism coupling instrument 1010/M (Metricon Co., USA). The absorption spectra of Dy³⁺/Tb³⁺ co-doped phosphate glass samples were measured with a UV/VIS/NIR spectrophotometer (Perkin Elmer Lambda 900) using Xe discharged lamp as light source. The excitation, emission spectra and fluorescence lifetime of samples were obtained by using an Edinburg FL920-type spectrophotometer. All measurements were carried out at room temperature.

3. Characterization and discussion

3.1 Dopant distribution in samples

The XRD patterns of all Dy³⁺/Tb³⁺ co-doped phosphate glasses are shown in Fig. 1, and a broad refraction peak at around $2\theta = 25^\circ$ was observed in all glass samples. Based on the study on the fundamentals of amorphous solids²⁸, the broad refraction peak is ascribed to the immaterial orientation of the amorphous glass with regard to the X-ray beam as there is no any crystalline plane. The diffraction angle 2θ is related to the region of local random network in glasses (from Bragg's law: $\lambda = 2d \sin\theta$). We pick T1D1 and

characterize 2D elemental distributions of P, O, Al and K shown in Fig. 2a–e, whereas the signals of low-concentrated Tb^{3+} and Dy^{3+} were too weak to detect. To further examine the dopant uniformity, we use EPMA to scan sample T1D2 and homogeneous distributions of Tb^{3+} and Dy^{3+} ions in Fig. 2f.

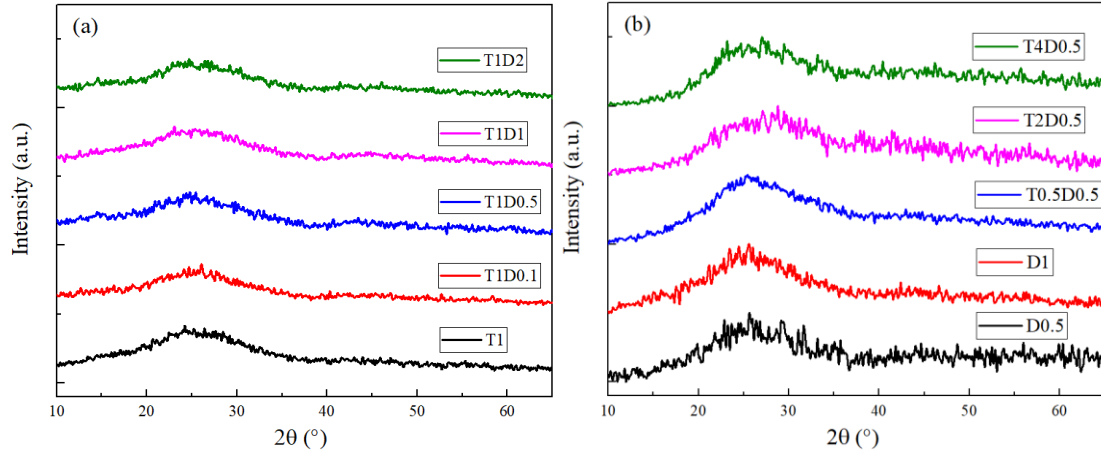


Fig. 1. XRD patterns of $\text{Tb}^{3+}/\text{Dy}^{3+}$ co-doped phosphate glasses.

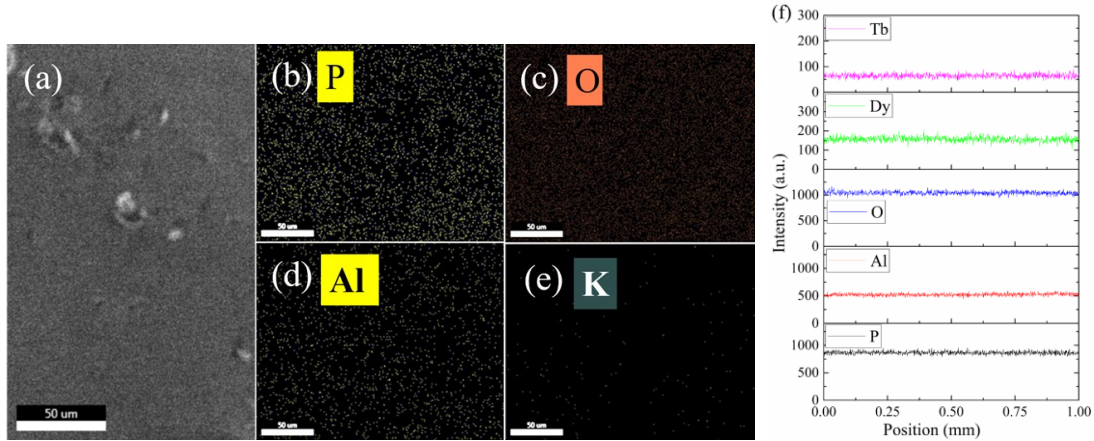


Fig. 2. (a) SEM images of glass surface and two-dimensional elemental distributions of (b) P, (c) O, (d) Al and (e) K in the T1D1 sample, and (f) line scan of P, Al, O, Dy and Tb in sample T1D2.

3.2 Absorption measurement and Judd–Ofelt analysis

The measured absorption spectra of all glass samples in the wavelength range from 300 to 2500 nm are shown in Fig. 3a and b. Absorption peaks of Tb^{3+} ions in Dy^{3+} free sample T1 locate at 338, 350, 359, 366, 377, 485, 1885, 1903 and 2209 nm corresponding to transitions from ground state $^7\text{F}_6$ to excited states of $^5\text{L}_7$, $^5\text{L}_9$, $^5\text{G}_5$, $^5\text{L}_{10}$, $^5\text{D}_3$, $^5\text{D}_4$, $^7\text{F}_1$, $^7\text{F}_2$ and $^7\text{F}_3$, respectively. Absorption in $\text{Dy}^{3+}/\text{Tb}^{3+}$ co-doped samples at 350, 364, 377, 386, 425, 452, 472 and 1682 nm is due to transitions of Dy^{3+} ions from ground state $^6\text{H}_{15/2}$ to the $^4\text{M}_{15/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{13/2}$, $^4\text{F}_{7/2}$, $^4\text{G}_{11/2}$, $^4\text{I}_{15/2}$, $^4\text{F}_{9/2}$ and $^6\text{H}_{11/2}$ excited states, as illustrated by the energy level diagrams

²⁵ in Fig. 3c. In the single dopant samples, Dy³⁺ ions present much stronger absorption than Tb³⁺ ions at the same concentration level at UV and blue wavelengths. By comparing Fig. 3a and b, Tb³⁺ ions show higher absorption at infrared wavelength region, whereas Dy³⁺ ions exhibit much stronger absorption at UV and blue wavelengths.

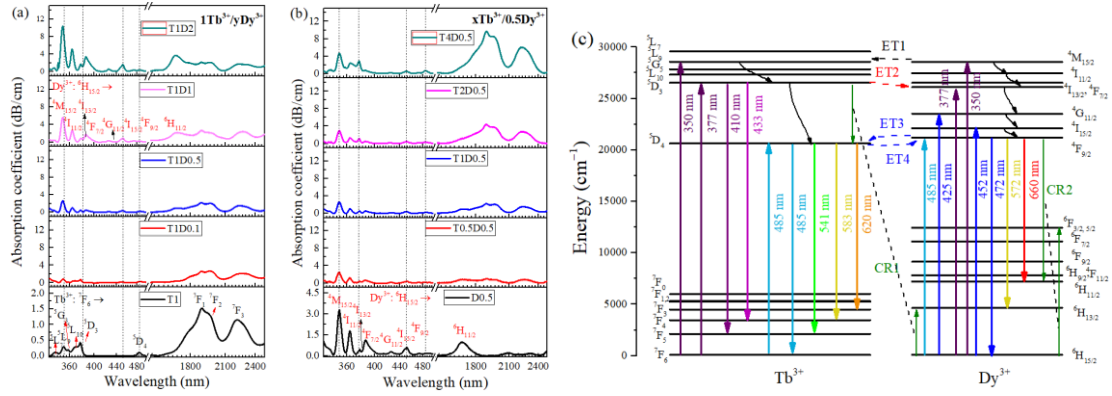


Fig. 3. Measured absorption spectra of (a) 1Tb³⁺/yDy³⁺ (y=0, 0.1, 0.5, 1, 2), (b) xTb³⁺/0.5Dy³⁺ (x=0, 0.5, 1, 2, 4) in phosphate glasses, and (c) energy level diagrams of Tb³⁺ and Dy³⁺ ions with possible transfer routes in between ²⁵.

Table 2 summarizes absorption cross-sections (σ_a) of Dy³⁺ and Tb³⁺ ions at different wavelengths calculated by $\sigma_a = 2.303OD(\lambda)/NI$, in which $OD(\lambda)$ is optical density obtained from the spectrophotometer, l the thickness of samples, N the concentration ($N = \rho m_w N_A / M_w$, ρ is density of sample, m_w weight concentration of dopant ions, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ Avogadro number, M_w molar mass). Dy³⁺ ions present a stronger absorption at 350 nm by an order of magnitude than that of Tb³⁺ ions in phosphate glasses. Four possible energy transfer routs ^{23, 25}, ET1 (Dy³⁺: ⁴M_{15/2} + Tb³⁺: ⁷F₆ → Dy³⁺: ⁶H_{15/2} + Tb³⁺: ⁵L₉), ET2 (Tb³⁺: ⁵D₃ + Dy³⁺: ⁶H_{15/2} → Tb³⁺: ⁷F₆ + Dy³⁺: ⁴F_{7/2} + phonon), ET3 and 4 (Dy³⁺: ⁴F_{9/2} + Tb³⁺: ⁷F₆ ↔ Dy³⁺: ⁶H_{15/2} + Tb³⁺: ⁵D₄ + phonon) shown in Fig. 3c, makes it possible to sensitize Tb³⁺ ions in phosphate glass for visible emission by Dy³⁺ ions co-doping.

Table 2. Absorption cross-sections σ_a of Tb³⁺ and Dy³⁺ ions at UV and visible wavelengths

Transitions	Wavelength (nm)	$\sigma_a (\times 10^{-22} \text{ cm}^2)$ of Tb ³⁺	$\sigma_a (\times 10^{-22} \text{ cm}^2)$ of Dy ³⁺
Tb ³⁺ : ⁷ F ₆ → ⁵ L ₉	350	2.9	
Tb ³⁺ : ⁷ F ₆ → ⁵ D ₃	377	4.3	

Tb ³⁺ : ⁷ F ₆ → ⁵ D ₄	485	1.1	
Dy ³⁺ : ⁶ H _{15/2} → ⁴ M _{15/2}	350		62.8
Dy ³⁺ : ⁶ H _{15/2} → ⁴ I _{11/2}	364		35.1
Dy ³⁺ : ⁶ H _{15/2} → ⁴ I _{13/2}	377		9.6
Dy ³⁺ : ⁶ H _{15/2} → ⁴ I _{15/2}	452		8.9
Dy ³⁺ : ⁶ H _{15/2} → ⁴ F _{9/2}	485		2.3

Based on Judd–Ofelt (J–O) theory^{29, 30}, the experimental strength (f_{exp}) of transitions can be calculated

from absorption spectra by the following equation:

$$f_{\text{exp}} = \frac{2.303mc^2}{\pi Nle^2 \bar{\lambda}^2} \int \log_{10} \left(\frac{I(\lambda)}{I_0} \right) d\lambda \quad (1)$$

where m is the electron mass, e the charge, c the velocity of light in vacuum, and $\bar{\lambda}$ the mean wavelength of the transition photon. The theoretical oscillator strength (f_{cal}) of radiative $4f \rightarrow 4f$ transitions from an initial J to a final J' states can be calculated:

$$f_{\text{cal}}(J; J') = \frac{8\pi^2 mc}{3h(2J+1)\bar{\lambda}} \left[\frac{(n^2+2)^2}{9n} S_{\text{ed}}(J; J') + n S_{\text{md}}(J; J') \right] \quad (2)$$

$$S_{\text{ed}}(J; J') = \sum_{t=2,4,6} \Omega_t \left| \left\langle (S, L)J \left\| U^t \right\| (S', L')J' \right\rangle \right|^2 \quad (3)$$

$$S_{\text{md}}(J, J') = \left(\frac{h}{4\pi mc} \right)^2 \sum_{t=2,4,6} \left| \left\langle (S, L)J \left\| \bar{L} + 2\bar{S} \right\| (S', L')J' \right\rangle \right|^2 \quad (4)$$

where n is the refractive index of the host, the terms $\left| \left\langle (S, L)J \left\| U^t \right\| (S', L')J' \right\rangle \right|^2$ are the double-reduced matrix elements of unit tensor operators that are considered to be independent of host materials and its values of Tb³⁺ ions are given by Carnall et al.³¹, and Ω_t ($t=2, 4, 6$) are the J–O parameters that can be calculated by a least-square fitting approach. Table 3 shows good agreement between f_{exp} and f_{cal} . The root-mean-square deviation (δ_{rms}) is $\pm 0.12 \times 10^{-6}$ implying a good quality of fitting. It is noted that J–O parameters of Tb³⁺ ions in T1 sample are calculated from the absorption bands of ⁷F₆ → ⁵D₄ and ⁷F_{1,2,3} (shown in Fig. 3a) rather than the absorption in the blue region (300–400 nm) where the absorption features are too complex to calculate^{32, 33}.

Table 3. Peak wavelength of absorption bands of Tb^{3+} ions in T1 sample as well as the experimental f_{exp} and calculated f_{cal} oscillator strengths.

Transition	λ_{peak} (nm)	$f_{\text{exp}} (\times 10^{-6})$	$f_{\text{cal}} (\times 10^{-6})$
${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$	484	0.060	0.060
${}^7\text{F}_6 \rightarrow {}^7\text{F}_1$	1895	0.585	0.495
${}^7\text{F}_6 \rightarrow {}^7\text{F}_2$	1903	0.540	0.620
${}^7\text{F}_6 \rightarrow {}^7\text{F}_3$	2209	0.645	0.629
$\delta_{\text{rms}} = \pm 0.12 \times 10^{-6}$			

Table 4 compares the J–O parameters of Tb^{3+} in our T1 sample with other reported host materials^{18, 32–}

³⁵. The parameter Ω_2 reflects directly the asymmetry of local environment around Tb^{3+} ions and the covalence degree between Tb^{3+} and ligand ions. The spectroscopic quality factor Ω_4/Ω_6 is important for evaluating the stimulated emission behavior³⁴. A higher values of Ω_2 parameter ($21.60 \times 10^{-20} \text{ cm}^2$) and Ω_4/Ω_6 ratio of 0.73 for Tb^{3+} ions are obtained in our phosphate glass (T1 sample) than those reported in previous studies, implying that a stronger local electric field results in a higher degree of asymmetry around the rare-earth ions and gives rise to a more efficient stimulated emission of Tb^{3+} ions in our phosphate glass.

Table 4. Comparison of Judd–Ofelt parameters of Tb^{3+} ions in different host materials.

Host materials	$\Omega_2 (10^{-20} \text{ cm}^2)$	$\Omega_4 (10^{-20} \text{ cm}^2)$	$\Omega_6 (10^{-20} \text{ cm}^2)$	Ω_4/Ω_6	Reference
Lead borate glass	13.23	1.23	2.96	0.42	32
Lead telluroborate glass	11.98	2.87	10.51	0.27	33
Zinc borophosphate glass	11.26	1.02	3.00	0.34	34
Borate glass	6.95	1.28	2.91	0.44	18
Fluoride glass	13.40	2.15	4.90	0.44	35
Phosphate glass (T1)	21.60	1.56	2.15	0.73	Our work

3.3 Excitation and luminescence measurement

Figure 4 compares the measured excitation spectra of the T1 and T1D0.5 samples by monitoring the emission at 541 nm, as well as D1 sample monitored at 572 nm. According to Fig. 4, we select 350, 377 and 485 nm as pumping wavelengths, corresponding to Tb^{3+} : ${}^7\text{F}_6 \rightarrow {}^5\text{L}_9$ + Dy^{3+} : ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{15/2}$, Tb^{3+} : ${}^7\text{F}_6 \rightarrow {}^5\text{D}_3$ + Dy^{3+} : ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{7/2}$ and Tb^{3+} : ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$ + Dy^{3+} : ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{9/2}$, respectively, and investigate the fluorescence of Tb^{3+} ions as a function of Dy^{3+} concentration. The corresponding emission spectra are shown in Fig. 5.

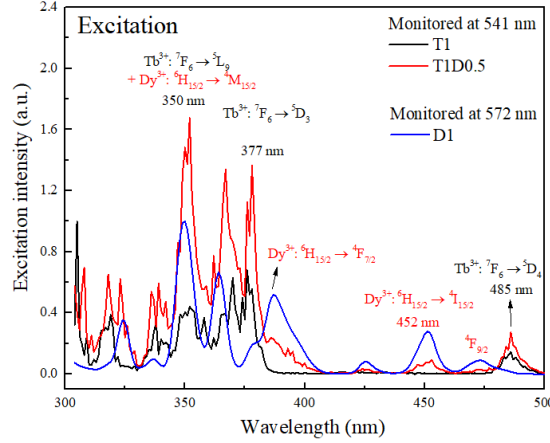


Fig. 4. Excitation spectra of the samples T1 and T1D0.5 by monitoring emission at 541 nm as well as D1 sample monitored at 572 nm.

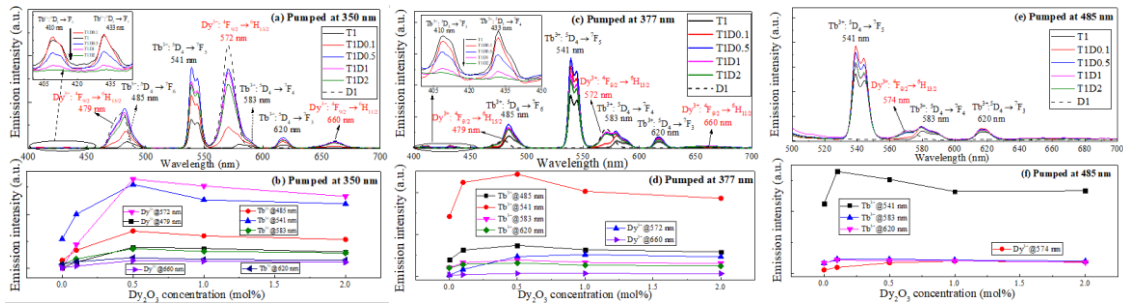


Fig. 5. Emission spectra of 1Tb³⁺/yDy³⁺ (y=0, 0.1, 0.5, 1, 2) co-doped phosphate glasses pumped by (a) 350 nm, (c) 377 nm and (e) 485 nm, and the corresponding trends of main emission intensities as a function of Dy³⁺ concentration pumped by (b) 350 nm, (d) 377 nm and (f) 485 nm, respectively.

In Fig. 5a, the emission of Tb³⁺ ions peaked at 541 nm is observed in T1 and much enhanced after introducing Dy³⁺ ions. By pumping at 350 nm wavelength, Tb³⁺ ions have a rapid thermal relaxation that would populate ⁵D₃ from ⁵L₉²⁵, and subsequently radiate to ⁷F₅ and ⁷F₄ states, giving rise to emission peaked at 412 and 435 nm, respectively (as shown in Fig. 3c). Meanwhile, electrons in ⁵D₃ state of Tb³⁺ would non-radiatively quench to ⁵D₄ state by multi-phonon relaxation or cross relaxation (CR) processes, and then radiate to ⁷F₆, ⁷F₅, ⁷F₄ and ⁷F₃ states corresponding the emissions peaked at 485, 541, 583 and 620 nm, respectively. Under pumping at 350 nm, Dy³⁺ ions are excited to ⁴M_{15/2} state and found quickly quenched to ⁴F_{9/2} state by thermal relaxation, and then radiate to ⁶H_{15/2}, ⁶H_{13/2} and ⁶H_{11/2} states which give rise to emissions at 479, 572 and 660 nm respectively. The introduction of Dy³⁺ ions helps population of Tb³⁺: ⁵D₃ state through the ET1 process (shown in Fig. 3c) efficiently. From the enhanced emission at 485, 541 and

620 nm wavelengths (derived from Tb^{3+} : $^5\text{D}_4$ state shown in Fig. 5a), we confirm a more efficient energy transfer process ET3 (shown in Fig. 3c) from Dy^{3+} ions to populate the Tb^{3+} : $^5\text{D}_4$ state. It is noted that the ET2 and CR1 (Tb^{3+} : $^5\text{D}_3 + \text{Dy}^{3+}$: $^6\text{H}_{15/2} \rightarrow \text{Tb}^{3+}$: $^5\text{D}_4 + \text{Dy}^{3+}$: $^6\text{H}_{13/2} + \text{phonon}$, shown in Fig. 3c) processes can reduce the emission strengths at 410 and 433 nm wavelengths, when Dy_2O_3 doping concentration is more than 0.5 mol%.

The emissions strength of Tb^{3+} reaches the maximum in all samples when introducing Dy^{3+} at 0.5 mol% Dy_2O_3 concentration. As the doping concentration of Dy^{3+} rises further, emission intensities of both Dy^{3+} and Tb^{3+} ions in T1D1 and 2 samples are declined and maintained, and we ascribe it to the counterbalance out of concentration quenching effect³⁶, in which the ET4 process from Tb^{3+} to Dy^{3+} ions, and possible CR2 (Dy^{3+} : $^4\text{F}_{9/2} + ^6\text{H}_{15/2} \rightarrow ^6\text{H}_{11/2} + ^6\text{F}_{3/2}$ shown in Fig. 3c) occurred between Dy^{3+} ions³⁷, resulted in the inefficient emission behaviors of Tb^{3+} and Dy^{3+} ions respectively.

Similar to 350 nm pumping wavelength, 377 nm pump will excite Tb^{3+} : $^5\text{D}_3$ state, radiating to $^7\text{F}_5$ (412 nm) and $^7\text{F}_4$ (435 nm) states, meanwhile the ET2, ET3 and CR1 processes populate the Tb^{3+} : $^5\text{D}_4$ state, radiating to $^7\text{F}_6$ (485 nm), $^7\text{F}_5$ (541 nm), $^7\text{F}_4$ (583 nm) and $^7\text{F}_3$ (620 nm) states. Emissions peaked at 485, 541, 583 and 620 nm show almost the same trends as that by pumping at 350 nm. For Dy^{3+} ions, a thermal relaxation will populate $^4\text{F}_{9/2}$ from $^4\text{F}_{7/2}$ (377 nm) states as shown in Fig. 3c, and generate 479, 572 and 660 nm emissions. The weak emissions of Dy^{3+} ions can be attributed to its lower absorption at 377 nm as shown in Table 1 and Fig. 4.

In Fig. 5e, the main emission at 541 nm is generated by pumping $\text{Tb}^{3+}/\text{Dy}^{3+}$ co-doped phosphate glasses with 485 nm. The Tb^{3+} : $^5\text{D}_4$ state is populated by 485 nm pump and ET3 process from Dy^{3+} ions, radiating to $^7\text{F}_6$ (485 nm), $^7\text{F}_5$ (541 nm), $^7\text{F}_4$ (583 nm) and $^7\text{F}_3$ (620 nm) states. The maximum emission of Tb^{3+} appears in the T1D0.1 sample and the concentration quenching effect takes place for Dy_2O_3 concentration more

than 0.5 mol%, which are attributed to the lower absorption cross-sections of both Tb^{3+} and Dy^{3+} ions at 485 nm. It can be concluded for Dy^{3+} ions that all the pumping wavelengths (350, 377 and 485 nm) populate the $\text{Dy}^{3+}: {}^4\text{F}_{9/2}$ state, and generate emissions peaked at 479, 572 and 660 nm. Besides, 350 nm is the most efficient pump wavelength for both the 541 nm emission of Tb^{3+} and 572 nm emission of Dy^{3+} ions in $\text{Tb}^{3+}/\text{Dy}^{3+}$ co-doped phosphate glasses.

3.4 Fluorescence lifetimes of Tb^{3+} ion

The fluorescence decay curve of $\text{Tb}^{3+}: {}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition emitting at around 541 nm are measured as a function of Dy^{3+} concentrations under excitations of 350, 485 and 452 nm respectively, shown in Fig. 6. Using a logarithmic scale for the axis of emission intensity we confirm an almost linear fluorescence decay as function of time, indicating an exponential decay behavior. As shown in Fig. 6d, the longest lifetime of $\text{Tb}^{3+}: {}^5\text{D}_4$ state is found in T1D0.1 with 0.1 mol% Dy_2O_3 concentration for all pump wavelengths, which we ascribed to the ET3 process, whereas the slightly decreased lifetime³⁸ is attributed to the ET4 and CR2 processes shown in Fig. 3c. The trends of lifetime of $\text{Tb}^{3+}: {}^5\text{D}_4$ level as function of Dy^{3+} concentration almost show no dependence on pumping wavelengths as illustrated in Fig. 6d.

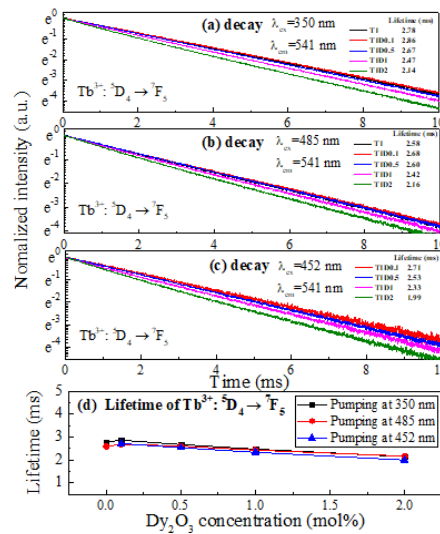


Fig. 6. Decay curves of transition $\text{Tb}^{3+}: {}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ pumped at (a) 350 nm, (b) 485 nm and (c) 452 nm, and (d) the calculated lifetime as a function of Dy^{3+} concentration.

Table 5. Measured lifetime of the $\text{Tb}^{3+}: {}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition in our work (pumped by 350 nm) and

reported literatures.

Host	Tb ₂ O ₃ concentration (mol%)	Lifetime (ms)	Reference
Lead borate glass	1.0	1.76	32
Lead telluroborate glass	1.0	0.83	33
Zinc borophosphate glass	0.9	1.89	34
Fluoride glass	0.5	1.21	35
T1	1.0	2.78	Our work
T1D0.1	1.0	2.86	Our work
T1D0.5	1.0	2.67	Our work
T1D1	1.0	2.47	Our work
T1D2	1.0	2.14	Our work

Table 5 compares the measured lifetime of Tb³⁺: ⁵D₄→⁷F₅ transition in various host materials ³²⁻³⁵. The

longest 2.86 ms lifetime of Tb³⁺: ⁵D₄ is measured in T1D0.1 sample.

3.5 Energy transfer efficiency and mechanism

The results of Fig. 4–6 show how the concentration of Dy³⁺ ions affect the visible emission properties and fluorescence lifetime of Tb³⁺ under the excitation of different pumping wavelength. To further investigate the energy transfer efficiency from Dy³⁺ to Tb³⁺ ions, we focus on the emission and fluorescence lifetime of xTb³⁺/0.5Dy³⁺ (x=0, 0.5, 1, 2, 4) co-doped glass samples by pumping at 425 nm where Tb³⁺ presents no absorption.

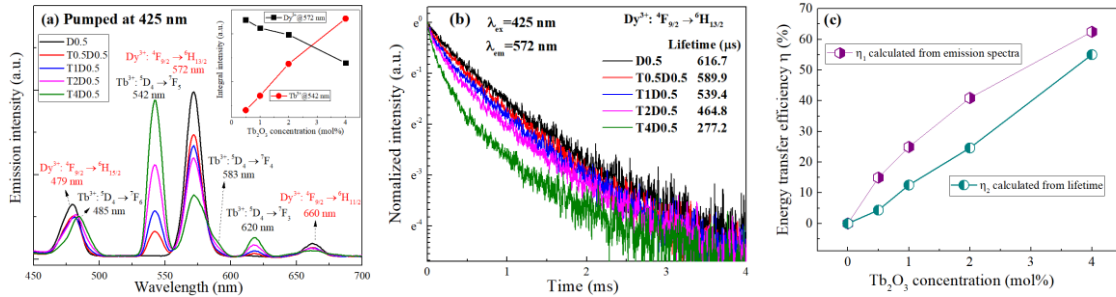


Fig. 7. (a) Emission spectra of xTb³⁺/0.5Dy³⁺ (x=0, 0.5, 1, 2, 4) co-doped phosphate glasses pumped by 425 nm, and the inset is the trends of main emission intensities, and (b) the decay curves of transition ⁴F_{9/2}→⁶H_{13/2} of Dy³⁺ pumped by 425 nm, inset shows the energy transfer efficiency from Dy³⁺ to Tb³⁺ ions as a function of Tb³⁺ concentration.

Under excitation, Dy³⁺: ⁴G_{11/2} state is populated and quickly relaxed by transferring energy to ⁴F_{9/2} state, and radiate to ⁶H_{15/2} (479 nm), ⁶H_{13/2} (572 nm) and ⁶H_{13/2} (660 nm) states as shown in Fig. 3c and Fig. 7a.

Through ET3 process, Tb³⁺: ⁵D₄ state is excited with fluorescence emissions peaked at 541, 583 and 620

nm shown in Fig. 7a. After introducing Tb³⁺ ions, the energy transfer process ET3 populates the Tb³⁺: ⁵D₄ state and gives rise to an increased emissions strength of Tb³⁺ at all wavelengths when Tb³⁺ concentration rises. Based on the emission spectra, the energy transfer efficiency from Dy³⁺ to Tb³⁺ ions is defined by $\eta_1 = 1 - I_{Dy}/(I_{Dy} + I_{Tb})$ ³⁹, where I_{Dy} and I_{Tb} are the integrated intensities of Dy³⁺ and Tb³⁺ ions, respectively, and the calculated results are plotted in Fig. 7c. We obtained the increasing energy transfer efficiency from Dy³⁺ to Tb³⁺ ions as a function of Tb³⁺ concentration in our phosphate glasses, which are 15.0 %, 24.9 %, 40.9 % and 62.5 % for the T0.5D0.5, T1D0.5, T2D0.5 and T4D0.5 samples, respectively.

To complete our measurement, the decay curves of the transition Dy³⁺: ⁴F_{9/2} → ⁶H_{13/2} (572 nm) under excitation at 425 nm are measured as a function of Tb³⁺ ions concentration shown in Fig. 7b. A non-exponential decay behavior of Dy³⁺ after introducing Tb³⁺ ions, especially in the T4D0.5 sample, which confirms the energy transfer processes between Dy³⁺ and Tb³⁺ ions. The average lifetimes are calculated by

25

$$\tau = \frac{\int_0^{\infty} tI(t)dt}{\int_0^{\infty} I(t)dt} \quad (5)$$

where $I(t)$ is the emission intensity as function of time t . The lifetime of Dy³⁺ declined from 616.7 μs (D0.5 sample) to 277.2 μs (T4D0.5 sample) as listed in Table 6. Based on the fluorescence lifetime of Dy³⁺, the energy transfer efficiency from Dy³⁺ to Tb³⁺ ions can be also calculated by ^{25, 40, 41} $\eta_2 = 1 - \tau/\tau_0$, in which τ_0 and τ represent lifetime of donor in the absence and presence of acceptor, respectively) and the calculated results are plotted in Fig. 7c, which are 4.4 %, 12.5 %, 24.6 % and 55.0 % as a function of Tb³⁺ concentration for the T0.5D0.5, T1D0.5, T2D0.5 and T4D0.5 samples, respectively. Both η_1 and η_2 values show a similar increasing trend as function of Tb³⁺ ions and the results in our phosphate glasses are on the same level as those found in other host materials ^{25, 40}, indicating an efficient sensitizer of Dy³⁺ ion for the visible emission

of Tb³⁺ ions in our phosphate glasses.

Based on Dexter's energy transfer expressions of multipolar interactions⁴² and Reisfeld's approximation⁴³, the donor-acceptor energy transfer probability (P_{DA}) is defined as $P_{DA} = (1/\tau_d)(\eta_0/\eta - 1)$, in which τ_d is lifetime of donor, η_0 and η are the luminescence quantum efficiencies of donor in the absence and presence of acceptor. The η_0/η can be approximately calculated by^{25, 41, 43}

$$\frac{\eta_0}{\eta} \approx \frac{I_0}{I} \propto C^{\frac{n}{3}} \quad (6)$$

where I_0 and I are the emission intensities of Dy³⁺ (572 nm) in the absence and presence of Tb³⁺ ions, respectively, C is the total concentration of Dy³⁺ and Tb³⁺ ions, and $n = 6, 8$ and 10 responding to electric dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively. By linear fitting the dependence of I_0/I on $C^{n/3}$ as shown in Fig. 8, we obtained a linear relationship with the optimum $R^2 = 99.98\%$ only when $n=6$, which indicates a dominant electric dipole-dipole interaction mechanism responsible for the energy transfer from Dy³⁺ to Tb³⁺ ions in our phosphate glasses. Table 6 summarized the calculated results discussed above, and in conclusion we obtained an increasing η_T and P_{DA} from Dy³⁺ to Tb³⁺ ions as a function of Tb³⁺ concentration under excitation at 425 nm. The chromaticity coordinate of emissions in xTb³⁺/0.5Dy³⁺ ($x=0, 0.5, 1, 2, 4$) co-doped samples excited at 425 nm in CIE1931 diagram (Fig. 9a) present a yellow-to-green light shift when Tb³⁺ concentration rises, indicating a potential application of using our glasses for color adjustable phosphors. Furthermore, we irradiate our Tb³⁺/Dy³⁺ co-doped phosphate glass by using a 450 nm multi-mode laser diode (pumping Dy³⁺) as shown in Fig. 9b, and obtained a total reflection of green light in the glass, demonstrating a promising potential of using our Tb³⁺/Dy³⁺ co-doped phosphate glass for lasing operation at visible wavelengths.

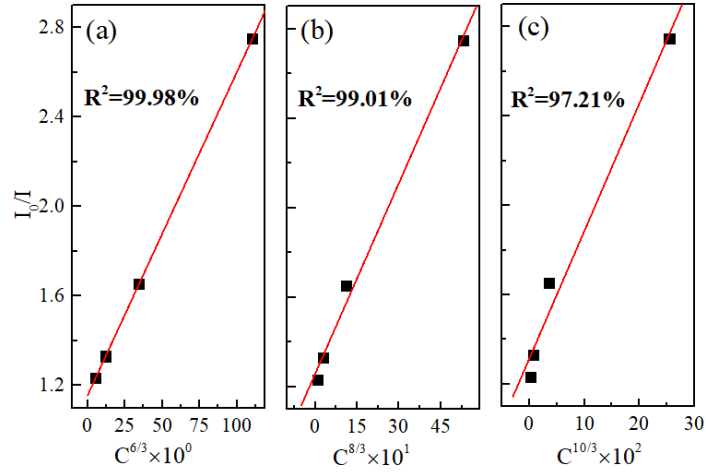


Fig. 8. Dependence of I_0/I on (a) $C^{6/3}$, (b) $C^{8/3}$ and (c) $C^{10/3}$.

Table 6. Measured lifetime τ of the $\text{Dy}^{3+}: {}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition, energy transfer efficiencies η_T and probabilities (P_{DA}) as a function of Tb^{3+} concentration under excitation at 425 nm.

Samples	τ (μs)	η_T (%)	I_0/I	P_{DA} (s^{-1})
D0.5	616.7			
T0.5D0.5	589.9	4.4	1.23	580.9
T1D0.5	539.4	12.5	1.33	874.1
T2D0.5	464.8	24.6	1.65	1405.2
T4D0.5	277.2	55.0	2.75	5795.3

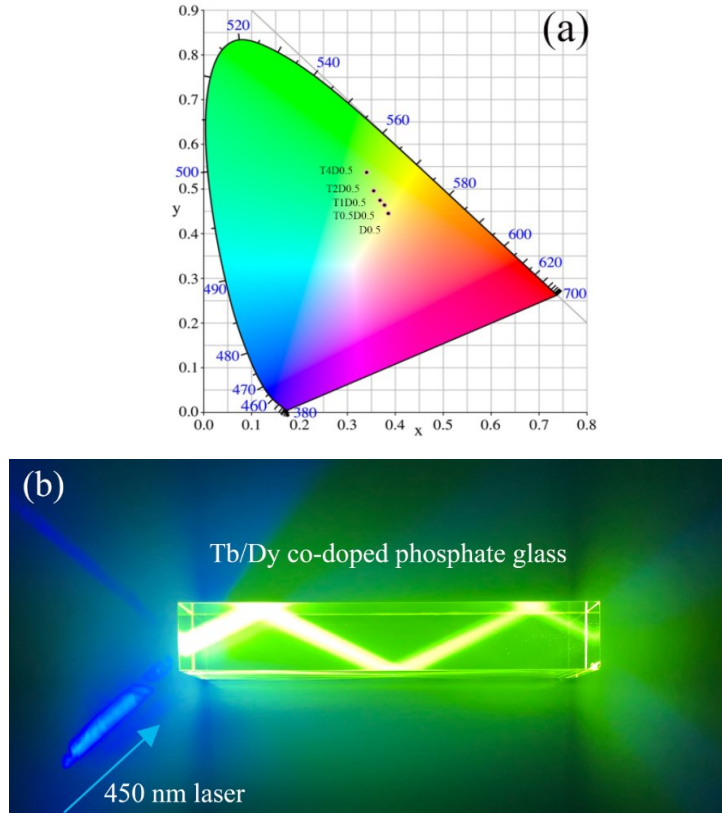


Fig. 9. (a) Chromaticity coordinates of emissions of $x\text{Tb}^{3+}/0.5\text{Dy}^{3+}$ ($x=0, 0.5, 1, 2, 4$) co-doped samples

excited at 425 nm in CIE1931 diagram (b) photograph of Tb³⁺/Dy³⁺ co-doped phosphate glass under irradiation of 450 nm laser diode.

4. Conclusions

In this paper, we study the role of sensitization of Dy³⁺ ions played in the enhanced visible emission of Tb³⁺ ions in phosphate glasses at various pump wavelengths. We confirm that in the host of phosphate glass, the Judd–Ofelt parameters Ω_2 and Ω_4/Ω_6 for Tb³⁺ ions could reach up to $21.60 \times 10^{-20} \text{ cm}^2$ and 0.73 respectively, highest among all glass hosts as far as we learn. The visible emission (peaked at 485 and 541 nm) of Tb³⁺ ions can be much enhanced by the sensitization effect of Dy³⁺ under the excitation of 350 and 377 nm with an optimum Dy³⁺/Tb³⁺ ions concentration ratio of 0.5:1. The maximum lifetime of Tb³⁺: ⁵D₄ (2.86 ms) is measured for the concentration of Dy₂O₃ around 0.1 mol%. The energy transfer efficiency η_T from Dy³⁺ to Tb³⁺ is demonstrate an electric dipole-dipole interaction between them and also found a maximum η_T of 55.0% for 4:0.5 ratio of Tb³⁺/Dy³⁺ at 425 nm wavelength for pumping. Our studies demonstrate a promising potential of Dy³⁺/Tb³⁺ co-doped phosphate glasses for highly efficient visible phosphors and lasing applications.

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