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A new melilite-type rare-earth borate CdTbGaB₂O₇ and multicolor tunable emission in the CdTb_{1-x}Sm_xGaB₂O₇ (0 ≤ x ≤ 0.2) phosphors†

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A new mixed metal borate, CdTbGaB₂O₇, was successfully synthesized using the high-temperature solution method and its crystal structure was determined by single-crystal X-ray diffraction with the following unit-cell data: $P\bar{4}2_1m$, $a = b = 7.3487(1) \text{ \AA}$, $c = 4.7247(1) \text{ \AA}$, $V = 255.150(9) \text{ \AA}^3$, and $Z = 2$. It belongs to a new member of the melilite family, which features a 3D framework consisting of alternately stacked $[\text{Ga}(\text{B}_2\text{O}_7)]_n^{5n-}$ tetrahedral layers and $(\text{Cd}^{2+}/\text{Tb}^{3+})$ cationic layers that are interconnected via B(Ga)–O–(Cd/Tb) bridges. In addition, the solid solutions of CdTb_{1-x}Sm_xGaB₂O₇ (0 ≤ x ≤ 0.2) were prepared via the solid-state reaction method. The combined techniques of XRD, SEM, IR/Raman, XPS and PLE/PL were employed to characterize the products. It was found that the CdTb_{1-x}Sm_xGaB₂O₇ phosphors simultaneously showed green emission of Tb³⁺ at 545 nm and orange emission of Sm³⁺ at 603 nm under excitation at 370 nm. The emission color can be adjusted from green to orange-red by varying the Sm³⁺ doped content via an energy transfer mechanism. For CdTb_{0.995}Sm_{0.005}GaB₂O₇, a QY of 13.22% was obtained, and its emission intensity at 423 K was 94% of that at 303 K. These results show that the prepared materials can act as potential color-tunable phosphors for UV w-LEDs.

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1. Introduction

Melilites include a large class of natural and synthetic compounds, whose general formula is A₂XZ₂O₇, where A cations (A = Na, Ca, Sr, Ba, Cd, Pb, Y, Ln) are sandwiched between XZ₂O₇ tetrahedral layers (X = Be, Mg, Co, Fe, Mn, Cu, Zn, Cd, Al, Ga; Z = Be, B, Al, Ga, Si, Ge).¹ The melilite-like compounds have been extensively investigated in the past due to their crystal chemical properties and potential applications. For example, crystallographic studies indicated that the stability of the melilite structure depends strongly on the degree of the size misfit between the tetrahedral layers and the interlayer cations.²

As far as their application prospects are concerned, some Si (or Ge)-based melilites may act as potential microwave dielectric materials.³ Doped with Nd³⁺, crystals of the melilite family, *e.g.* Ca₂Ga₂SiO₇, Ba₂MgGe₂O₇ and Ba₂ZnGe₂O₇, were successfully used in high-power lasers, both with Xe-flash lamp pumping and with laser-diode pumping.^{4–6}

The mineral okayamalite, Ca₂SiB₂O₇, was first discovered by Giuli *et al.* in 2000, which is the only melilite borate known at early times.⁷ Subsequently, Barbier *et al.* conducted a systematic survey of several MO–Bi₂O₃ (and Ga₂O₃)–B₂O₃ systems and found three new diborate members of this family, including Bi₂ZnB₂O₇, CaBiGaB₂O₇, and CdBiGaB₂O₇ (only unit-cell data were provided for the last borate).⁸ Among them, two Ga-containing compounds crystallize with the normal tetragonal melilite structure, whereas the Zn-containing phase adopts a unique orthorhombic superstructure of melilite. The attempted solid-state syntheses of the other melilites, such as Bi₂MB₂O₇ (M = Be, Mg, Co), MBiGaB₂O₇ (M = Mg, Sr, Ba), CaBiMB₂O₇ (M = B, Al, In), and MBiZnB₂O₇ (M = Y, Nd, Yb), were unsuccessful. The preliminary measurements of second-harmonic generation (SHG) efficiencies (d_{eff}) on powder samples yielded values of 4.0 (Bi₂ZnB₂O₇) and 1.6 (CaBiGaB₂O₇) relative to a KH₂PO₄ (KDP) standard. The larger efficiency of Bi₂ZnB₂O₇ was ascribed to the presence of planar BO₃ groups and a higher concentration of the heavy and polarizable Bi³⁺ cations in its crystal structure. Soon after, relatively large single crystals of Bi₂ZnB₂O₇ were successfully grown from a high-temperature melt by the top-seeded method, which reveals

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† Electronic supplementary information (ESI) available: The X-ray crystallographic file for CdTbGaB₂O₇ in CIF format; atomic coordinates, equivalent isotropic and anisotropic displacement parameters; selected bond distances and angles; correlation table of B₂O₇ between the site group of the molecule (C_{2v}) and the factor group of the crystal (D_{2d}); Rietveld refinement results of CdTb_{1-x}Sm_xGaB₂O₇ (0 ≤ x ≤ 1); the SEM image and EDX results of the CdTbGaB₂O₇ single-crystal; Rietveld refinements of powder X-ray diffractograms of CdTb_{1-x}Sm_xGaB₂O₇ (0.001 ≤ x ≤ 0.2); IR, Raman, XPS and UV-vis absorption spectra; the excitation line of BaSO₄ and the PL spectrum of the CdTb_{0.995}Sm_{0.005}GaB₂O₇ phosphor. CCDC 2253832. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3ra03002d>



that this borate is a promising candidate for nonlinear optical (NLO) materials.⁹ This Zn-containing melilite diborate is still of current interest due to its potential value as a host to prepare different kinds of luminescent materials. For instance, Tb³⁺, Sm³⁺, Eu³⁺ and Dy³⁺-doped Bi₂ZnB₂O₇ phosphors were synthesized and their luminescent properties were investigated.^{10–12} When active laser medium (such as Er³⁺, Nd³⁺ or Pr³⁺ ions) are doped into this crystal structure, the obtained crystals may show both luminescence and NLO properties, which makes them very attractive for the new generation of laser frequency converters, the representative crystals including Bi₂ZnOB₂O₆:Yb³⁺/Er³⁺, Bi₂ZnOB₂O₆:Nd³⁺ and Bi₂ZnOB₂O₆:Pr³⁺.^{13–15} In addition, not long ago, two new melilite-type borogermanates, Ca₂GeB₂O₇ and Ca_{1.78}Cd_{0.22}GeB₂O₇, were also reported, among which Ca₂GeB₂O₇ has a short UV cutoff edge (<200 nm), indicating its potential as an optical material in the UV or DUV region.¹⁶ The compounds mentioned above are the only borates with melilite structure reported so far. In contrast to many investigations on Bi₂ZnB₂O₇, there are no studies of CaBiGaB₂O₇ and CdBiGaB₂O₇ as promising hosts for luminescence applications, and also, there are no reports on rare-earth analogues of these borates in the literature.

It is well known that Tb³⁺ ions usually generate green emission arising from the ⁵D₄ → ⁷F_J (*J* = 6, 5, 4, 3) transitions, while Sm³⁺ ions emit orange-red light due to the ⁴G_{5/2} → ⁶H_J (*J* = 5/2, 7/2, 9/2, 11/2) transitions.¹⁷ In Tb³⁺/Sm³⁺ co-doped systems, terbium plays the role of a sensitizer, and samarium is an activator. The energy transfer from Tb³⁺ to Sm³⁺ occurs, which makes it possible to achieve the multicolor tunable luminescence from green to orange-red by simply adjusting the ratio of these two ions. With these materials, it will be more convenient to control the color output according to the practical application requirements. Therefore, the study of Tb³⁺/Sm³⁺ co-doped phosphors is not only of theoretical but also of practical significance, and some previously reported examples are KBaY(MoO₄)₃:Ln³⁺ (Ln³⁺ = Tb³⁺, Eu³⁺, Sm³⁺, Tb³⁺/Eu³⁺, Tb³⁺/Sm³⁺), CaLa₂(MoO₄)₄:Tb³⁺/Sm³⁺, and Ba₃La(PO₄)₃:Tb³⁺/Sm³⁺.^{18–20}

In the process of exploring new borate materials to study their structure–property relationships, we found that Bi³⁺ in CdBiGaB₂O₇ can be completely replaced by Tb³⁺, resulting in a new melilite diborate, CdTbGaB₂O₇. Insofar as we know, it represents the first quaternary compound within CdO–Ln₂O₃–Ga₂O₃–B₂O₃ (Ln = trivalent rare-earth cations) system, and it is also the only rare-earth borate of the melilite family known to date. In this work, we first performed the synthesis and characterization of CdTbGaB₂O₇, then introduced Sm³⁺ into CdTbGaB₂O₇ to prepare CdTb_{1–x}Sm_xGaB₂O₇ solid solutions (*x* = 0–0.2), and further studied the luminescence properties and energy transfer of Sm³⁺ doped CdTbGaB₂O₇. The obtained results suggest that this type of novel phosphors could serve as a multi-color component in UV w-LEDs.

2. Experimental section

2.1. Materials and methods

All chemicals, including CdCO₃ (A.R.), Tb₄O₇ (99.99%), Tb(NO₃)₃·6H₂O (A.R.), Sm₂O₃ (99.99%), Ga₂O₃ (99.99%) and

H₃BO₃ (A.R.), were commercially available from Sinopharm Chemical Reagent Co. Ltd and used without further purification. The XRD plots were recorded on a Bruker AXS D8 ADVANCE diffractometer equipped with Cu K_{α1} radiation (*λ* = 1.5406 Å) operating at 40 kV and 40 mA. Surface morphology and element compositions of the synthetic product were characterized by a Hitachi SU8020 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer (EDX). The Infrared (IR) spectra were measured with a Bruker VERTEX70 FT-IR spectrometer using the KBr pellet method. The Raman studies were carried out using a Renishaw InVia Raman spectrometer equipped with a confocal DM 2500 Leica optical microscope, a thermoelectrically cooled CCD as a detector, and He/Ne laser as an exciting source working at 633 nm. The X-ray photoelectron spectroscopy (XPS) measurements were done by a Thermo ESCALAB 250xi spectrometer equipped with Al K_α (*hν* = 1486.6 eV) as an excitation source. The UV-vis absorption spectra were monitored using a Hitachi UH4150 spectrophotometer equipped with an integrating sphere attachment. The excitation and emission spectra as well as decay kinetics were investigated using an Edinburgh FLS 1000 system equipped with a 450 W Xe lamp and a 60 W μF flash lamp. Quantum yield (QY) and temperature-dependent emission spectra were determined by the same spectrometer with a BaSO₄-coated integrating sphere and a temperature controlling system, respectively.

2.2. Synthetic procedures

Single crystals of CdTbGaB₂O₇ were grown by the high-temperature solution method. In a typical procedure, a powder mixture of 0.5464 g CdCO₃, 0.1974g Tb₄O₇, 0.4950 g Ga₂O₃ and 0.2612 g H₃BO₃ (molar ratio 12 : 1 : 10 : 16) was thoroughly ground and placed in a Pt crucible. The mixture was slowly heated to 950 °C in a muffle furnace, and maintained at this temperature for 6 h to ensure that the raw materials are completely melted and uniformly mixed. Subsequently, the solution temperature was decreased, first to 700 °C at a rate of 1.5 °C h^{–1}, then to 400 °C at 5.0 °C h^{–1}, and finally to room temperature at 20 °C h^{–1}. Many colorless, transparent, block-shaped crystals were obtained. Energy-dispersive X-ray analysis in a scanning electron microscope confirmed that the crystal contains the elements Cd, Tb, Ga, and O with an approximate atomic ratio of 10.44 : 8.25 : 6.65 : 74.66, which is close to its ideal composition of 1 : 1 : 1 : 7 (B is too light to be detected, see Fig. S1†).

The powder samples of CdTb_{1–x}Sm_xGaB₂O₇ (*x* = 0, 0.001, 0.002, 0.005, 0.01, 0.05, 0.1, 0.2, and 1) were obtained through solid-state reactions of the calculated amounts of CdCO₃, Tb(NO₃)₃·6H₂O, Sm₂O₃, Ga₂O₃, and H₃BO₃. The well-ground samples were first preheated at 500 °C for 12 h and then sintered at 800 °C for 120 h with several intermediate re-mixings. Finally, the as-synthesized samples were ground into fine powder and their phase purity was checked by powder X-ray diffraction.

2.3. Single-crystal X-ray diffraction

Single-crystal diffraction data were collected at room temperature on an Agilent Super Nova diffractometer equipped with



Table 1 Crystallographic data for CdTbGaB₂O₇^a

Formula	CdTbGaB ₂ O ₇
Formula weight	474.66
Space group	<i>P</i> $\bar{4}$ 2 ₁ <i>m</i> (No. 113)
<i>a</i> (Å)	7.3487(1)
<i>c</i> (Å)	4.7247(1)
<i>V</i> (Å ³)	255.150(9)
<i>Z</i>	2
<i>d</i> _{calc} (g cm ⁻³)	6.178
μ (mm ⁻¹)	23.062
2 θ _{max} (°)	69.94
Unique reflections	620
Observed [<i>I</i> ≥ 2 σ (<i>I</i>)]	598
No. of variables	35
GOF on <i>F</i> _o ²	1.092
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0221/0.0443
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0236/0.0449
$\Delta\rho$ _{max} , $\Delta\rho$ _{min} (e Å ⁻³)	1.528, -1.379

^a *R*₁ = $\sum||F_o| - |F_c||/\sum|F_o|$ and *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ for *F*_o² > 2 σ (*F*_o²).

a Mo X-ray source ($\lambda = 0.71073$ Å). The data collection and reduction were performed with the CrysAlisPro software, and absorption corrections were made by the multi-scan method.²¹ The crystal structure was established by Direct Methods and subsequently refined by the full-matrix least-squares method on *F*² on the basis of SHELX-2018.²² All atoms were refined anisotropically and the final difference Fourier synthesis did not reveal any significant residual peaks.

Refinements of atomic occupancy parameters indicated that Cd and Tb atoms reside in the same atomic site (Wyckoff 4e) with the composition Cd_{0.5}Tb_{0.5}, which is not surprising since Cd²⁺ and Tb³⁺ have similar cationic radii (1.10 Å for Cd²⁺ vs. 1.04 Å for Tb³⁺, CN = 8) and coordination geometries.²³ For this (Cd/Tb) site, no abnormally large displacement parameters were observed, and the largest principal anisotropic displacement parameter [*U*₁₁ = *U*₂₂ = 0.01079(11) Å²] was only about 1.3 times of the smallest one [*U*₃₃ = 0.00832(13) Å²] (Table S2†). Therefore, it is not necessary to split (Cd/Tb) into two positions. In addition, the single-crystal XRD data did not show a symmetry lower than tetragonal or a larger unit cell that would allow the ordering of Cd²⁺/Tb³⁺. Finally, the disorder model was adopted. The flack parameter of this compound was refined to be -0.12(4). The program PLATON was used to check the positional parameters,²⁴ and no higher symmetries were found. Details of unit-cell parameters, data collection and structure refinements are summarized in Table 1. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters are given in Tables S1 and S2† and selected bond lengths and angles in Table S3.†

3. Results and discussion

3.1. Crystal structure description

CdTbGaB₂O₇ is a new member of the melilite series, and it is also the only rare-earth borate of this family known so far. In this structure, two BO₄ tetrahedra first share a corner to form

a diborate group, [B₂O₇]⁸⁻. Each [B₂O₇]⁸⁻ dimer is linked to four different GaO₄ tetrahedra, and, likewise, each GaO₄ tetrahedron is connected to four neighboring [B₂O₇]⁸⁻ groups *via* common O atoms to form a 2D infinite [Ga(B₂O₇)_n]⁵ⁿ⁻ layer extending in the (001) plane [see Fig. 1(b)]. These gallium borate anionic layers are stacked along the crystallographic *c*-axis direction, and (Cd²⁺/Tb³⁺) cations are placed in the square antiprismatic cavities between the layers to hold them together *via* (Cd/Tb)-O bonds, thus obtaining a 3D [CdTbGa(B₂O₇)_n] framework [Fig. 1(a)].

As shown in Table S1,† the asymmetric unit of CdTbGaB₂O₇ contains one disordered (Cd/Tb), one Ga, one B and three O sites. Among them, each (Cd/Tb) has eight O nearest-neighbors arranged into a distorted square antiprism [Fig. 1(c)]. The (Cd/Tb)-O distances fall in the range of 2.305(4)-2.547(3) Å, with an average of 2.430 Å (Table S3†), which lies between 2.42 and 2.48 Å computed from crystal radii sums of Tb³⁺ and O²⁻ as well as Cd²⁺ and O²⁻ for 8-fold coordination, respectively.²³ These distances also correspond to those found in α -CdUO₄, CdPd₃O₄ and Ba₂CdTb₂(BO₃)₄, where 8-coordinated Cd²⁺ or Tb³⁺ exist.²⁵⁻²⁷ Both Ga and B atoms adopt a tetrahedral coordination configuration. However, the Ga atom is located on the $\bar{4}$ axis, thereby resulting in four equal Ga-O bond lengths of 1.824(3) Å and two groups of O-Ga-O bond angles of 107.90(10)° and 112.7(2)°, while the B atom lies on a mirror plane, giving three groups of B-O distances of 1.419(7), 1.492(7) and 1.525(5) Å and four groups of O-B-O angles of 114.6(5)°, 116.1(3)°, 102.6(3)° and 102.9(4)°. The average O-Ga-O and O-B-O angles are 109.5° and 109.15°, respectively, indicating that the GaO₄ tetrahedron is rather regular, while the BO₄ is somewhat deformed (Table S3†). Similar GaO₄ and BO₄ groups have already been identified in K₂Ga₂O(BO₃)₂ and In₄O₂B₂O₇, respectively.^{28,29} Furthermore, the calculated bond valence sums are 3.10 for Ga³⁺ and 2.92 for B³⁺, respectively, close to their expected values, indicating the validity of the structure.³⁰

In the literature, several compounds with the chemical formula containing “B₂O₇” are known, which have various structure types from extended 2D layers to 3D frameworks. For example, all Bi₂CaB₂O₇, Bi₂SrB₂O₇ and Bi_{1.48}Eu_{0.52}Pb_{0.5}Sr_{0.5}B₂O₇ contain topologically identical 2D [A₂MO(BO₃)₂] [A = Bi, (Bi/Eu); M = Ca, Sr, (Pb/Sr)] layers built of corner-sharing [BO₃]³⁻ triangles and [MO₆]¹⁰⁻ trigonal prisms with [A₂O]⁴⁺ groups accommodated within six-membered rings. However, the Ca and Sr compounds take an acentric structure with space groups *Pna*2₁ and *P6*₃, respectively, while the (Pb/Sr) phase crystallizes in the centrosymmetric *R3c* group.^{31,32} BaAl₂B₂O₇ also has a layered structure, but being built up from [BO₃]³⁻ triangles and [Al₂O₇]⁸⁻ groups, and the latter consists of two corner-sharing AlO₄ tetrahedra.³³ Bi₂ZnB₂O₇ contains both tetrahedral [B₂O₇]⁸⁻ and triangular [B₂O₅]⁴⁻ diborate groups, which are alternately arranged in the *a* and *b* directions, and further bridged by tetrahedral Zn²⁺ centers through sharing three O atoms of each ZnO₄ tetrahedron to generate a 2D [Zn₂O₂(B₂O₇)(B₂O₅)_n]¹²ⁿ⁻ layer. These zinc borate anionic layers are held together by the octahedrally coordinated Bi³⁺ cations to create a 3D framework.⁸ This is different from the case of CdTbGaB₂O₇, where the 3D network is only composed of [B₂O₇]⁸⁻



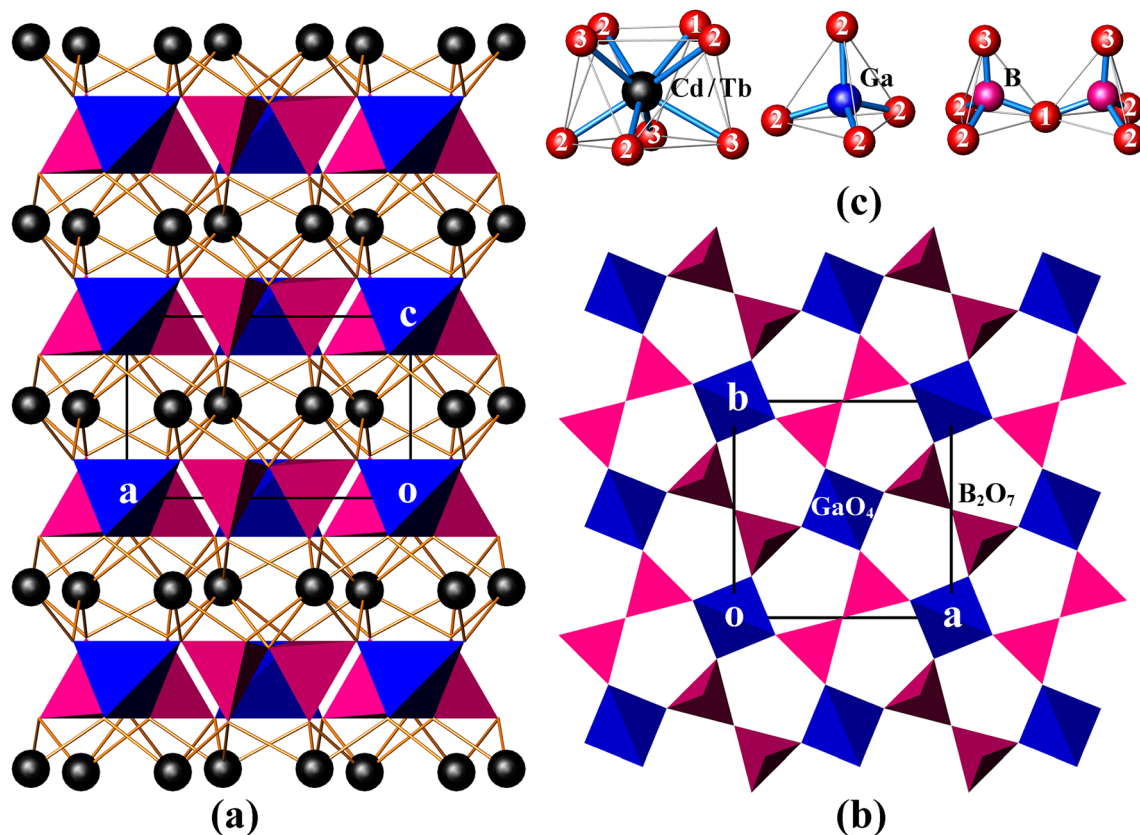


Fig. 1 The unit cell of CdTbGaB₂O₇ projected along [010] (a), the [Ga(B₂O₇)_n]⁵ⁿ⁻ layer viewed along [001] (b), and the coordination environment of each cation site (the numbers correspond to the oxygen atom designations) (c). (Cd/Tb): black spheres; GaO₄: blue tetrahedra; BO₄: magenta tetrahedra.

tetrahedral dimers, GaO₄ tetrahedra, and 8-coordinated (Cd²⁺/Tb³⁺) cations, and each GaO₄ corner-shares with four [B₂O₇]⁸⁻ units. It is the differences in the fundamental building blocks and their connection modes that make these structures significantly different, which enriches the structural chemistry of borates.

3.2. IR and Raman spectra

CdLnGaB₂O₇ (Ln = Tb, Sm) crystallizes in the tetragonal space group $P4_21m$ (D_{2d}^3 , No. 113), and its primitive cell comprises two B₂O₇ “pyro” units. A free B₂O₇ group is composed of two corner-shared BO₄ tetrahedra, which can be described as two BO₃ groups connected by a bent B^oB bridge, as shown in Fig. 1(c). In analogy with pyrophosphate and pyrogermanate groups (P₂O₇ and Ge₂O₇),^{34–36} the 21 internal modes of the free B₂O₇ group with C_{2v} symmetry can be subdivided into: A₁ + B₁ symmetric and A₁ + A₂ + B₁ + B₂ antisymmetric stretching modes of the BO₃ groups [$\nu_s(\text{BO}_3)$ and $\nu_{as}(\text{BO}_3)$, respectively]; A₁ symmetric and B₁ antisymmetric stretching modes of the B^oB bridge [$\nu_s(\text{B}^o\text{B})$ and $\nu_{as}(\text{B}^o\text{B})$, respectively]; A₁ bending mode of the B^oB bridge [$\delta(\text{B}^o\text{B})$]; A₂ + B₂ rocking modes of the BO₃ groups [$\rho(\text{BO}_3)$]; and 3A₁ + 2A₂ + 3B₁ + 2B₂ O–B–O bending modes [$\delta(\text{BO}_3)$] (see the correlation diagram presented in Table S4[†]). In the crystal, these modes will give rise to 7A₁ + 4A₂ + 4B₁ + 7B₂ + 10E internal modes. Translational (T[†]) and librational (L)

modes of free B₂O₇, *i.e.* A₁ + B₁ + B₂ and A₂ + B₁ + B₂, transform in crystal into A₁ + B₂ + 2E and A₂ + B₁ + 2E external modes, respectively. In addition, the disordered (Cd/Tb) atoms occupy the 4e Wyckoff positions of C_s symmetry and Ga atoms the 2a positions of S₄ symmetry (Table S1[†]). These atoms contribute totally with 2A₁ + A₂ + 2B₁ + 3B₂ + 5E translational modes. By adding all these modes and subtracting three acoustic modes (B₂ + E), the following optical vibrational modes of the crystal can be obtained: $\Gamma_{\text{optic}} = 10A_1 + 6A_2 + 7B_1 + 10B_2 + 18E$, in which E modes are twofold degenerated and often observed as one frequency. Among these modes, B₂ and E are both IR- and Raman-active, A₁ and B₁ are Raman-active only, and A₂ is silent. This analysis shows that 63 modes in the Raman spectrum (10A₁ + 7B₁ + 10B₂ + 18E) and 46 modes in the IR spectrum (10B₂ + 18E) are expected to be observed, resulting in 45 Raman and 28 IR frequencies, respectively. Due to the large number of modes and the overlap of some modes, a precise assignment of the individual bands to specific vibrational modes is difficult, but a rough assignment of groups is possible for both IR and Raman spectra.

Fig. S2[†] shows the room-temperature IR and Raman spectra of the CdLnGaB₂O₇ (Ln = Tb, Sm) samples. Due to experimental limitations, IR characterization below 500 cm⁻¹ is not possible. Two compounds exhibit similar spectral profiles, reflecting their isostructural features. The tentative band assignments are



based on literature data,^{29,37–39} and the frequencies of the B₂O₇ group are assigned according to the characteristic vibrations of the B^OB bridge and the terminal BO₃ groups. The bands due to the antisymmetric BO₃ terminal stretching vibrations of the B₂O₇ group [$\nu_{\text{as}}(\text{BO}_3)$] and the antisymmetric B^OB bridge stretching modes [$\nu_{\text{as}}(\text{B}^{\text{O}}\text{B})$] are observed in the high-frequency region of 1250–900 cm⁻¹. The intensities of these bands are generally greater in infrared than in Raman spectra.³⁸ The strong Raman bands at about 787 (795) cm⁻¹ are assigned to the symmetric stretching of the terminal BO₃ groups [$\nu_{\text{s}}(\text{BO}_3)$], while in infrared spectra, these vibrations are clearly observed in the region of 800–840 cm⁻¹. The IR bands near 704 (719) cm⁻¹ can be attributed to the stretching vibrations of GaO₄ tetrahedra,^{40,41} which matches with the peaks at 668 (676) cm⁻¹ in the Raman spectra. The absorption bands at 600–300 cm⁻¹ correspond to the $\delta(\text{B}^{\text{O}}\text{B})$ and $\delta(\text{BO}_3)$ bending modes, and the bending vibrations of the GaO₄ tetrahedra also appear in this area, making it difficult to assign the bands below 600 cm⁻¹.^{39,42} Thus, the IR and Raman spectra confirm the presence of B₂O₇ tetrahedral dimers and four-coordinated Ga³⁺ ions, in accordance with the results obtained from the single-crystal XRD analyses.

3.3. UV-vis absorption spectra

Fig. S3† shows the UV-visible absorption spectra of CdLnGaB₂O₇ (Ln = Tb, Sm) (converted from diffuse reflectance data). The spectrum of the Tb compound shows a wide absorption band superimposed with several weak absorption peaks below 500 nm, which are mainly attributed to the inter-configurational 4f–5d transitions and intra-configurational 4f–4f transitions of the Tb³⁺ ions, i. e. ⁷F₆ → ⁵L₈ at 352 nm, ⁷F₆ → ⁵L₁₀ at 370 nm, ⁷F₆ → ⁵D₃ at 377 nm and ⁷F₆ → ⁵D₄ at 489 nm, respectively.⁴³ For CdSmGaB₂O₇, there is a strong absorption band below 300 nm with maxima at about 224 nm, which is mainly ascribed to the ligand (O²⁻) to metal charge transfer (CT) transition. In the region between 300 and 500 nm, a series of sharp absorption peaks were observed at about 317, 346, 363, 377, 405, 418, 444, 465, 472, and 483 nm, which can be assigned to the ⁶H_{5/2} → ⁴F_{11/2}, ⁶H_{5/2} → ³H_{7/2}, ⁶H_{5/2} → ⁴F_{9/2}, ⁶H_{5/2} → ⁴D_{5/2}, ⁶H_{5/2} → ⁴K_{11/2}, ⁶H_{5/2} → ⁴M_{19/2}, ⁶H_{5/2} → ⁴G_{9/2} + ⁴I_{15/2}, ⁶H_{5/2} → ⁴F_{5/2}, ⁶H_{5/2} → ⁴I_{11/2}, ⁶H_{5/2} → ⁴M_{15/2} transitions, respectively, as found in the PLE spectrum [Fig. 4(b)].^{44,45}

The optical band gap (E_{g}) can be estimated with the help of Tauc's relation:⁴⁶

$$\alpha h\nu = A(h\nu - E_{\text{g}})^n$$

where α , h , ν , A and E_{g} stand for absorption coefficient, Planck's constant, light frequency, proportionality constant and band gap, respectively. n is a constant related to the transition ($n = 1/2$ and 2 for direct and indirect allowed transitions, respectively). If the absorption coefficient α is replaced by the absorbance obtained from the UV-vis spectrum, $(\alpha h\nu)^{1/n}$ is plotted against the photon energy ($h\nu$), and on this basis, a line tangent to the inflection point of the curve is further drawn, the intercept of the tangent to the x-axis will give a good approximation of the band gap energy. In the present case, the indirect and direct

band gaps are estimated to be 4.10 and 4.33 eV for CdTbGaB₂O₇, whereas they are 3.82 (indirect) and 4.87 eV (direct) for CdSmGaB₂O₇, respectively, as shown in the insets of Fig. S3.† These bandgap values are similar to those previously reported in other Tb- and Sm-containing borates, such as K₃Li₃Tb₇(BO₃)₉ [4.19 (indirect) and 4.55 (direct) eV] and K₃Sm₃(BO₃)₄ [4.99 (direct) eV].^{47,48}

3.4. Phase purity and morphology

In order to check the correctness of the single-crystal structure, additional Rietveld refinements of powder XRD data from CdTb_{1-x}Sm_xGaB₂O₇ ($x = 0$ and 1) were carried out using TOPAS software.⁴⁹ In the refining process, the single-crystal data of the Tb phase were employed as the initial model, a total of 51 parameters were refined, including 47 profile and 4 structure ones. The final refinement patterns are depicted in Fig. 2(a) and (b), where the low R -factors and the small differences between the measured and calculated data were obtained, indicating good fitting quality and high phase purity. Although the cell dimensions of CdTbGaB₂O₇ from Rietveld refinements [$a = b = 7.3437(1)$ Å, $c = 4.7201(1)$ Å, and $V = 254.558(8)$ Å³] are somewhat smaller than the single-crystal data [Table 1], their relative deviations are less than 0.5%, revealing that the determined structure should be quite credible.

Powder XRD patterns of the as-prepared CdTb_{1-x}Sm_xGaB₂O₇ ($0 \leq x \leq 1$) samples are presented in Fig. 2(c). All experimental diagrams agree well with the simulated pattern of CdTbGaB₂O₇, indicating that doping of Sm³⁺ ions did not generate any distinct impurity or induce significant changes in the host structure. In addition, the enlargement of the reflections in the range of $2\theta = 32.8^\circ$ – 33.4° is shown in the right part of Fig. 2(c), where a continuous left-shift of the representative peak (121) can be clearly observed with increasing Sm³⁺ content in CdTb_{1-x}Sm_xGaB₂O₇. In fact, as we discussed earlier, Cd and Tb atoms in CdTbGaB₂O₇ are statistically distributed over one atomic site, and each (Cd/Tb) is surrounded by eight oxygen atoms, forming a distorted (Cd/Tb)O₈ polyhedron, while Ga and B atoms are completely ordered and tetrahedrally coordinated with oxygen atoms. Considering the ionic radii and coordination number (CN) of Cd²⁺ (1.10 Å, CN = 8), Tb³⁺ (1.040 Å, CN = 8), Sm³⁺ (1.079 Å, CN = 8), Ga³⁺ (0.47 Å, CN = 4) and B³⁺ (0.11 Å, CN = 4),²³ it is reasonable to believe that the doped Sm³⁺ ions will replace Tb³⁺ and occupy (Cd/Tb) sites randomly in the host, which will lead to lattice expansion, thus shifting the diffraction peaks to smaller 2θ values according to the Bragg equation.

The ionic radii for eightfold coordinated Tb³⁺ and Sm³⁺ differ only by 3.75% and both fully concentrated Tb³⁺ and Sm³⁺ compounds are isostructural. Therefore, it is expected that there is a solid solution series whose lattice constants are linearly related to the Sm³⁺/Tb³⁺ ratio. In order to confirm this point, Rietveld refinements of powder XRD profiles were also performed on CdTb_{1-x}Sm_xGaB₂O₇ ($x = 0.001, 0.002, 0.005, 0.01, 0.05, 0.1$ and 0.2), as shown in Fig. S4.† For these refinements, the atomic coordinates of Ga, B and O sites, atomic occupancies, and isotropic thermal displacement factors were fixed, while the atomic coordinates of the (Cd/Tb/Sm) site and cell



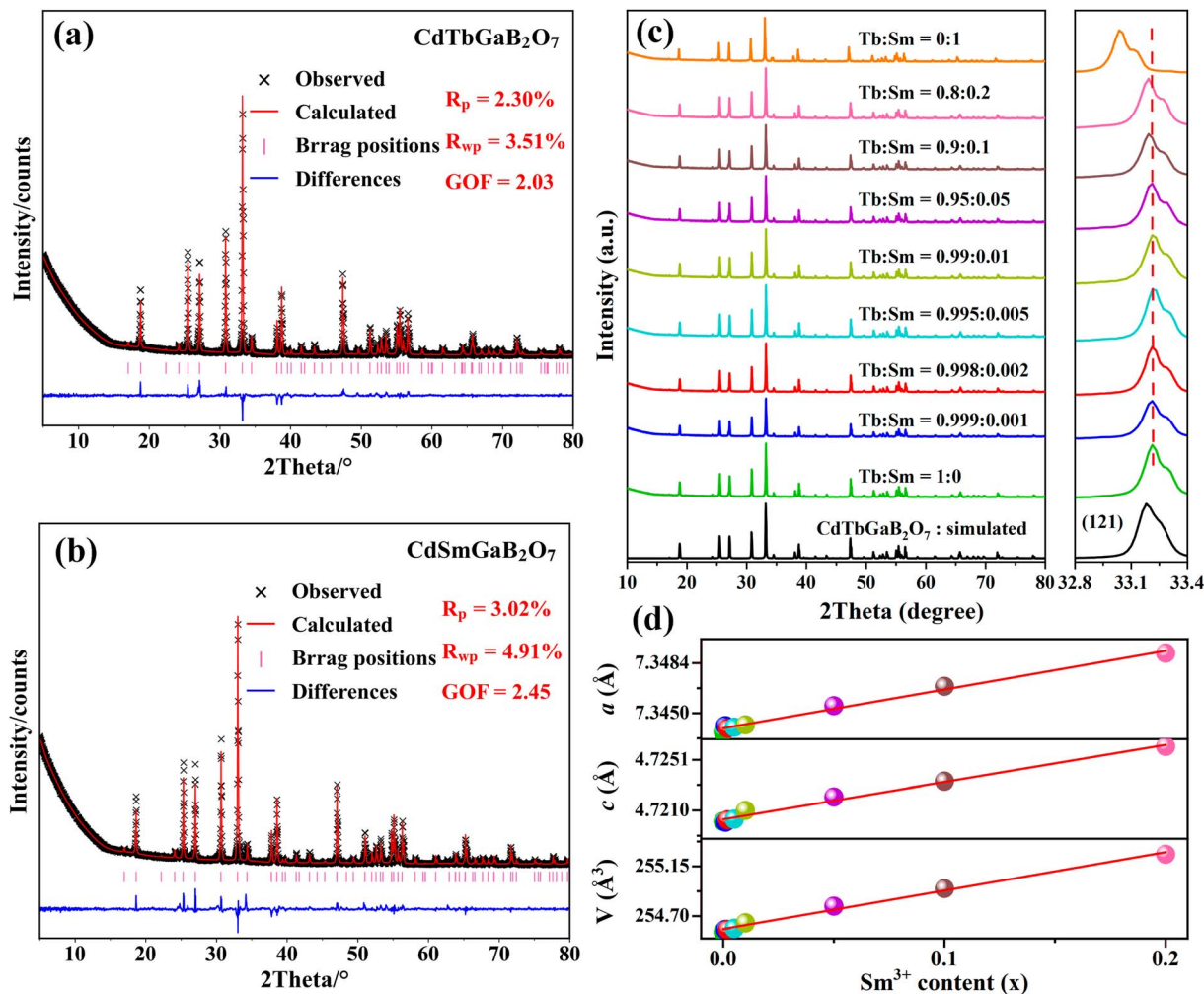


Fig. 2 (a and b) Rietveld refinements of the XRD files for $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ ($x = 0$ and 1). (c) XRD patterns of the $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ ($0 \leq x \leq 1$) phosphors. (d) The cell parameters (a , c , and V) obtained by Rietveld refinements against the Sm^{3+} concentration (x).

parameters were refined along with other parameters. The lattice parameters and atomic coordinates of all species obtained from Rietveld fitting are summarized in Tables S5 and S6,[†] while the lattice parameters for $0 \leq x \leq 0.2$ were plotted as a function of the dopant Sm^{3+} concentration (x) in Fig. 2(d). Obviously, cell parameters, including axis lengths (a and c) and volume (V), increase linearly with the incorporation of Sm^{3+} , as predicted by Vegard law. This phenomenon can be explained by the larger ionic radius of Sm^{3+} compared to that of Tb^{3+} , which is strong evidence of the successful cationic substitution.

The SEM images of the representative phosphor $\text{CdTb}_{0.995}\text{Sm}_{0.005}\text{GaB}_2\text{O}_7$ are illustrated in Fig. 3. The particles exhibit irregular shapes in the agglomerated form with several microns in size. They are typical products prepared by the high-temperature solid state reaction. Besides, the EDX spectrum reveals that in addition to Au as a coating element, there are expected elements in the studied sample, including Cd, Tb, Sm, Ga and O (B is too light to be detected). The elemental mappings demonstrate that all constituent elements are evenly distributed among the selected particle. Hence, the successful doping

of Sm^{3+} into the $\text{CdTbGaB}_2\text{O}_7$ matrix to form a homogenous phase can be verified based on the XRD and EDX results.

3.5. XPS spectra

XPS was performed to determine the surface chemical components of the phosphor $\text{CdTb}_{0.995}\text{Sm}_{0.005}\text{GaB}_2\text{O}_7$. Fig. S5(a)[†] depicts a typical survey scan in the range of 1350–0 eV, which contains Cd 3p, 3d, 4d, Tb 3d, 4d, Ga 2p, 3d, B 1s, O 1s and C 1s core levels along with Ga and O Auger peaks, confirming the sample composition. The presence of C can be ascribed to the expected adsorption of adventitious carbon from XPS instrument itself, and the C 1s peak of 284.6 eV was used as a standard to adjust other peaks. To further inspect the chemical state of each element, narrow scan XPS measurements were done, and the results are shown in Fig. S5(b)–(g).[†] One can see that there are two distinct peaks at 411.62 and 404.79 eV in Fig. S5(b),[†] which are assigned to Cd 3d_{3/2} and 3d_{5/2} core levels, and can be used as a fingerprint to identify the existence of Cd²⁺.⁵⁰ The Tb 3d XPS spectrum is depicted in Fig. S5(c),[†] where two strong peaks associated with Tb 3d_{3/2} and 3d_{5/2} were clearly observed at



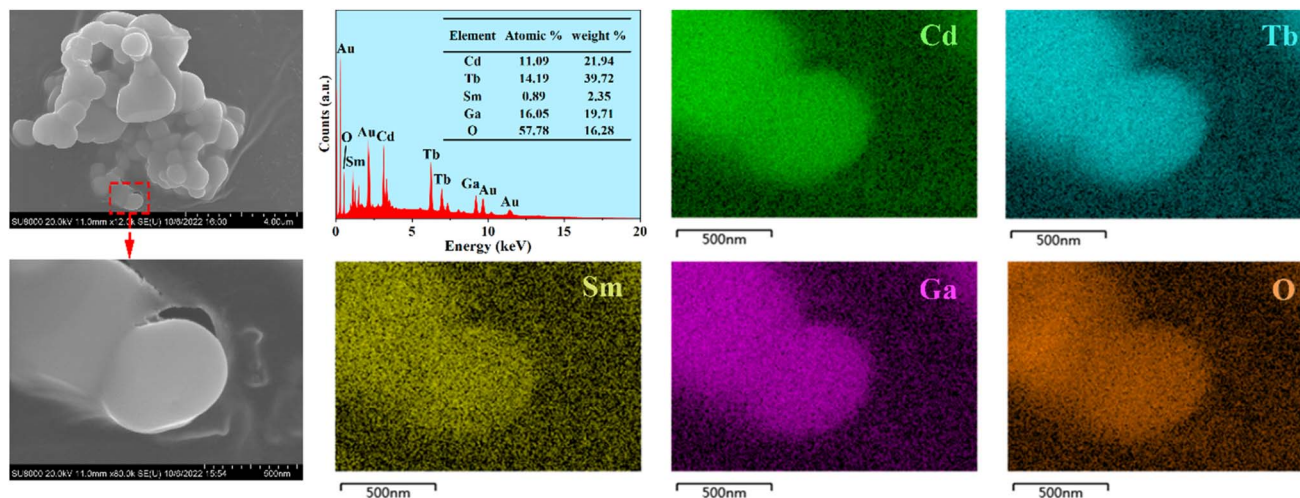


Fig. 3 FE-SEM images, typical EDS results, and elemental mapping of the CdTb_{0.995}Sm_{0.005}GaB₂O₇ phosphor. Note that a thin layer of Au was evaporated on the sample surface to provide conductivity prior to SEM inspection.

1278.71 and 1243.76 eV. These binding energies and their differences confirm the +3 valence state of Tb in the doped system.⁵¹ In Fig. S5(d),† although the Sm 4d XPS signal is relatively weak because of the very low dopant concentration in the phosphor, it can be deconvoluted into three components, corresponding to Sm 4d_{3/2} (~134.29 eV), 4d_{5/2} (~130.98 eV) and a satellite peak (127.87 eV), respectively, similar to the earlier results obtained for β-RbSm(MoO₄)₂.⁵² This indicates that the doped Sm element predominantly maintains the state of Sm³⁺ in the CdTbGaB₂O₇ matrix. Furthermore, the Ga 3p spectrum is composed of doublet components at 108.58 eV (Ga 3p_{1/2}) and 104.96 eV (Ga 3p_{3/2}) with the spin-orbit splitting of ~3.62 eV, indicating that Ga appears as +3 valence.⁵³ The B 1s spectrum was fitted to a single peak, which is attributed to the B atoms bonded to oxygen atoms (B–O) in borates, and its binding energy of 191.57 eV is in good accord with the literature report.⁵⁴ The O 1s spectrum can be resolved into two components, of which the main peak at 530.95 eV usually denotes the presence of structural oxide (O²⁻), while the shoulder peak at 532.77 eV corresponds to the oxygen in adsorbed water (H₂O) at the sample surface.⁵⁵ No other impurity peaks have been identified from the XPS spectra, supporting the aforementioned XRD and EDX analyses. All these observations ensure the successful cationic substitution, after which a systematic investigation of the photoluminescence properties of the CdTb_{1-x}Sm_xGaB₂O₇ phosphors was conducted.

3.6. PLE and PL spectra

Fig. 4(a) shows the typical photoluminescence excitation (PLE) and emission (PL) spectra of the CdTbGaB₂O₇ phosphor. The PLE spectrum obtained by monitoring 545 nm emission (Tb³⁺: ⁵D₄ → ⁷F₅) consists of two strong broad bands below 300 nm, along with many sharp peaks in the higher wavelength region. The strong broadband centered at ~248 and 286 nm can be attributed to the spin-allowed (⁷F₆–⁷D_J) and spin-forbidden (⁷F₆–⁹D_J) 4f⁸ → 4f⁷5d¹ inter-configurational Tb³⁺ transitions, respectively.⁵⁶ The other excitation peaks appearing at 318, 343,

352, 370, 377, and 485 nm correspond to the parity- and spin-forbidden 4f–4f transitions of the Tb³⁺ ion, that is, from the ⁷F₆ ground state to the excited states of ⁵D₀, ⁵L₆, ⁵L₈, ⁵L₁₀, ⁵D₃, and ⁵D₄ levels, as labelled in Fig. 4(a).⁴³ The PL spectrum recorded under the excitation of 370 nm gives four sets of characteristic optical transitions of Tb³⁺, namely ⁵D₄ → ⁷F_J (J = 6, 5, 4, and 3) at approximately 491, 545, 587 and 623 nm, respectively. The transition of ⁵D₄ → ⁷F₅ at ~545 nm is the most prominent, which explains the strong green emission of CdTbGaB₂O₇. As expected, no emission coming from ⁵D₃ level has been observed due to the fast cross relaxation processes [Tb³⁺ (⁵D₃) + Tb³⁺ (⁷F₆) → Tb³⁺ (⁵D₄) + Tb³⁺ (⁷F₀)] present in fully concentrated terbium materials.⁵⁷

The PLE and PL spectra of the CdSmGaB₂O₇ phosphor are presented in Fig. 4(b). The PLE spectrum monitored with 603 nm emission exhibits a broadband near 250 nm together with multiple sharp peaks at 319, 346, 362, 377, 405, 440, 474, 502 and 528 nm, which are associated with the O²⁻ → Sm³⁺ charge-transfer transition and the characteristic Sm³⁺ f–f transitions: ⁶H_{5/2} → ⁴F_{11/2}, ⁶H_{5/2} → ³H_{7/2}, ⁶H_{5/2} → ⁴F_{9/2}, ⁶H_{5/2} → ⁴D_{5/2}, ⁶H_{5/2} → ⁴K_{11/2}, ⁶H_{5/2} → ⁴G_{9/2}, ⁶H_{5/2} → ⁴I_{11/2}, ⁶H_{5/2} → ⁴G_{7/2} and ⁶H_{5/2} → ⁴F_{3/2}, respectively.^{44,45} The presence of the intense absorption bands from 350 to 490 nm suggests that CdSmGaB₂O₇ can be used as a potential phosphor for UV/NUV LED lighting. When the phosphor is exposed to 405 nm radiation, it emits luminescence at about 564, 603, 646, and 705 nm, assigned to the ⁴G_{5/2} → ⁶H_J (J = 5/2, 7/2, 9/2, 11/2) transitions of Sm³⁺, respectively. Among them, ⁴G_{5/2} → ⁶H_{5/2} and ⁴G_{5/2} → ⁶H_{9/2} are purely magnetic dipole (MD) and electric dipole (ED) allowed transitions, respectively, while ⁴G_{5/2} → ⁶H_{7/2} is a MD allowed one but also ED dominated. Generally speaking, the integral intensity ratio of the ED/MD transitions [R = I(⁴G_{5/2} → ⁶H_{9/2})/I(⁴G_{5/2} → ⁶H_{5/2})] is used to assess the symmetry nature of trivalent 4f ions. In this work, the R value was calculated as 1.45 (>1), implying that Sm³⁺ ions are located in the low symmetry sites. In fact, our structural analysis reveals that Sm³⁺ will replace Tb³⁺ and share the Wyckoff



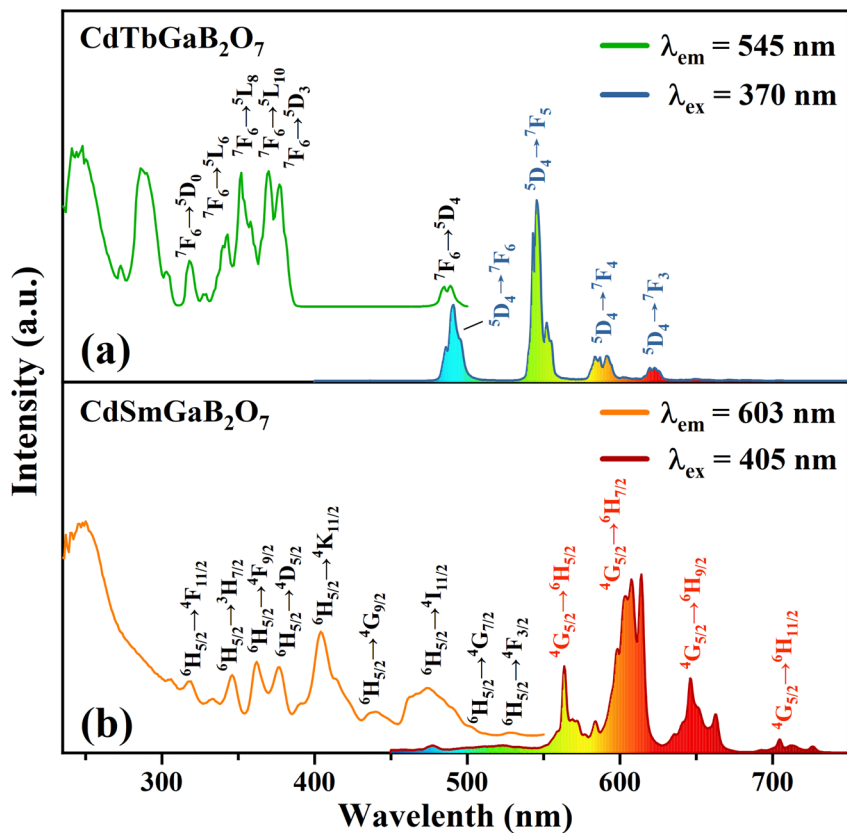


Fig. 4 The PLE and PL spectra of CdTbGaB₂O₇ (a) and CdSmGaB₂O₇ (b).

4e site with Cd²⁺, which is on a mirror plane without inversion center, as shown in Table S1† and Fig. 1(c).

The PLE spectra of the CdTb_{1-x}Sm_xGaB₂O₇ phosphors with different Sm³⁺ concentrations are shown in Fig. 5(a) and (b). By monitoring the Tb³⁺ emission at 545 nm (5D₄ → 7F₅), the PLE spectra show the f-d and f-f transitions of Tb³⁺ and the excitation intensity decreases remarkably and steadily towards a higher Sm³⁺ content and finally becomes negligible at $x = 0.2$, suggesting the presence of efficient Tb³⁺ → Sm³⁺ energy transfer. It is noteworthy that Sm³⁺ excitation peaks were undetectable in each case, which ascertains the fact that there was no possibility of energy transfer from Sm³⁺ to Tb³⁺. On the other hand, the PLE spectra monitored with the 603 nm emission (Sm³⁺: 4G_{5/2} → 6H_{7/2}) contain not only the characteristic excitation peak of Sm³⁺ at 405 nm, but also those of Tb³⁺ originated from f-d and f-f transitions, with the latter dominating the PLE spectra, which further confirms the efficient Tb³⁺ → Sm³⁺ energy transfer. Besides, the intensities of the Tb³⁺ excitation transitions (e.g., 7F₆ → 5L₁₀ at 370 nm) successively increase with increasing Sm³⁺ concentration up to $x = 0.005$ and then decrease, implying the occurrence of concentration quenching at $x > 0.005$.

The influence of Sm³⁺ content on the PL spectra of CdTb_{1-x}Sm_xGaB₂O₇ were also studied, as shown in Fig. 5(c) and (d). As expected, upon excitation at 370 nm (Tb³⁺: 7F₆ → 5L₁₀), CdTbGaB₂O₇ displays only the characteristic emissions of Tb³⁺. With the doping of Sm³⁺ ions, besides Tb³⁺ emissions at 491 (5D₄ → 7F₆) and 545 nm (5D₄ → 7F₅), the characteristic

emissions of Sm³⁺ at 603 nm (4G_{5/2} → 6H_{7/2}) and 646 nm (4G_{5/2} → 6H_{9/2}) can also be observed. Furthermore, as the Sm³⁺ concentration increases, the emission intensity of Tb³⁺ at 545 nm first decreases rapidly, and then remains at a relative low value with little difference, as illustrated in the inset of Fig. 5(c). At the same time, the emission intensity of Sm³⁺ at 603 nm increases initially until the Sm³⁺ concentration reaches $x = 0.005$, reflecting the result of energy transfer from Tb³⁺ to Sm³⁺. However, once the Sm³⁺ content is further increased to beyond $x = 0.005$, the concentration quenching occurs between Sm³⁺ ions, resulting in a decrease in the emission intensity. In addition, the PL spectra under direct excitation of the Sm³⁺ 4f levels at 405 nm (Sm³⁺: 6H_{5/2} → 4K_{11/2}) yield only the emission peaks of Sm³⁺ and not those of Tb³⁺, further confirming the absence of energy transfer from Sm³⁺ to Tb³⁺. In this case, the emission intensity of Sm³⁺ first increases until $x = 0.05$ and then appears a downfall, which is consistent with the trend of Sm³⁺ characteristic excitation peak at 405 nm in the PLE spectra monitored at 603 nm emission of Sm³⁺ [Fig. 5(b)]. However, it is different from the situation observed in the 370 nm indirect excitation *via* the energy transfer from Tb³⁺ to Sm³⁺, where the optimal Sm³⁺ doped content is $x = 0.005$. As everyone knows, the PL spectrum is strongly affected by the excitation wavelength.⁵⁸ The fact that indirect and direct excitation leads to different quenching concentrations has already been reported in some other phosphors, such as Ba₃BiPbY_{1-x}Eu_xO(BO₃)₄, CeO₂:Eu³⁺ and SnO₂:Eu³⁺.⁵⁹⁻⁶¹



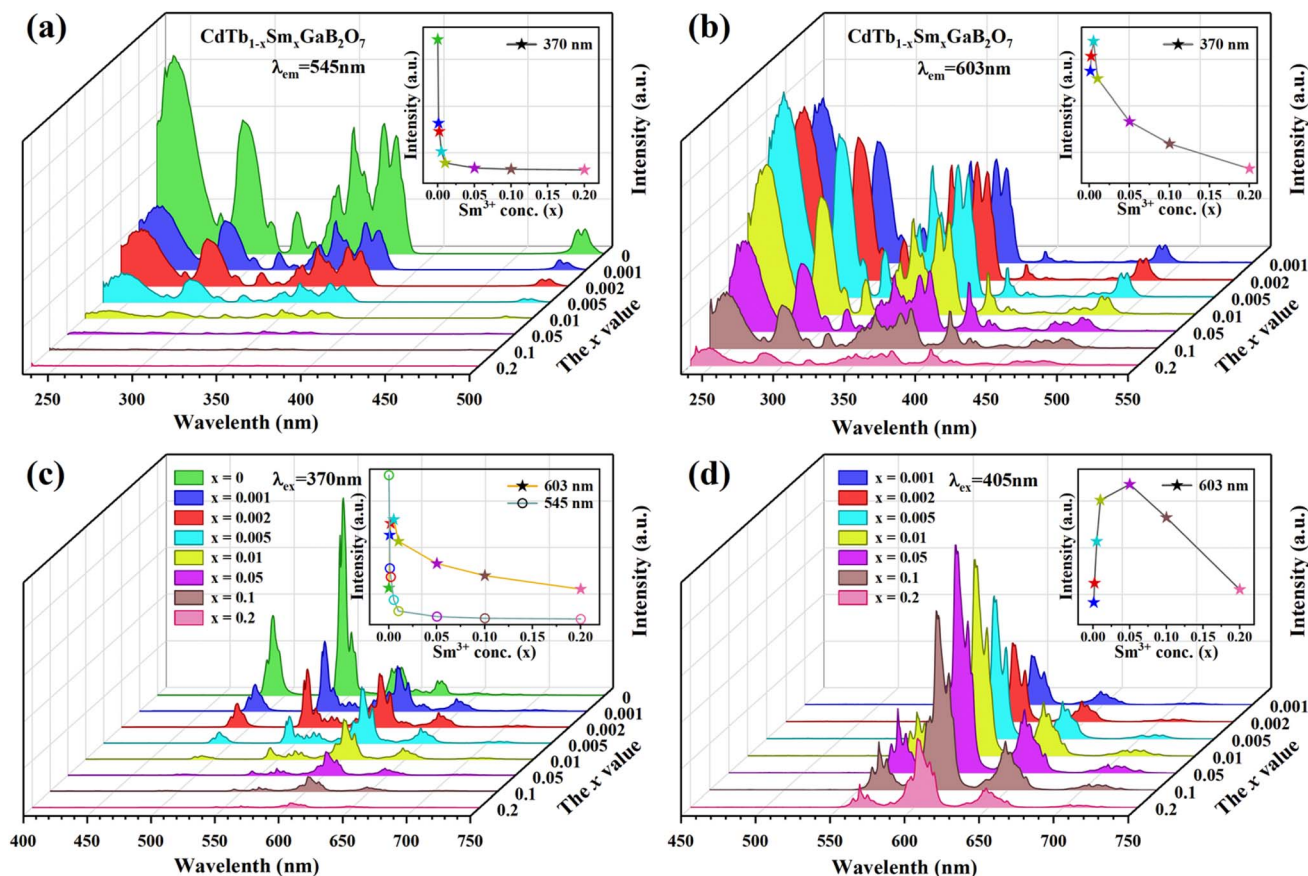


Fig. 5 The concentration dependent PLE [(a) $\lambda_{em} = 545$ nm; (b) $\lambda_{em} = 603$ nm] and PL [(c) $\lambda_{ex} = 370$ nm; (d) $\lambda_{ex} = 405$ nm] spectra of the $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ fluorescent powders.

3.7. Fluorescence lifetime and energy transfer mechanism

To further illustrate the $\text{Tb}^{3+} \rightarrow \text{Sm}^{3+}$ energy transfer process, the Tb^{3+} luminescence decay curves of the $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ phosphors ($\lambda_{ex} = 370$ nm, $\lambda_{em} = 545$ nm) were recorded, as shown in Fig. 6. All curves show a second-order exponential decay, which can be fitted by the following equation:

$$I_t = I_0 + B_1 \exp\left(-\frac{t}{\tau_1}\right) + B_2 \exp\left(-\frac{t}{\tau_2}\right)$$

where I_0 and I_t are the luminescence intensities corresponding to time 0 and t , B_1 and B_2 are fitting parameters, and τ_1 and τ_2 are lifetimes for rapid and slow decays, respectively. The double-exponential behavior indicates a heterogeneous distribution of Tb^{3+} ions in the $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ phosphors. In fact, when the excitation energy is transferred from the donor (Tb^{3+}) to acceptor (Sm^{3+}), a double-exponential decay behavior of the activator is usually observed.¹⁷ The decay process is characterized by an average lifetime (τ_{avg}), which can be calculated as follows:

$$\tau_{avg} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2}$$

The τ_{avg} values determined for different Sm^{3+} concentrations are also shown in Fig. 6. Apparently, the luminescence lifetime

of Tb^{3+} in $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ decreases successively with the increase of Sm^{3+} concentration, which offers clear evidence for the energy transfer from Tb^{3+} to Sm^{3+} . The energy transfer efficiency (η) from sensitizer to activator can be evaluated with the following expression:

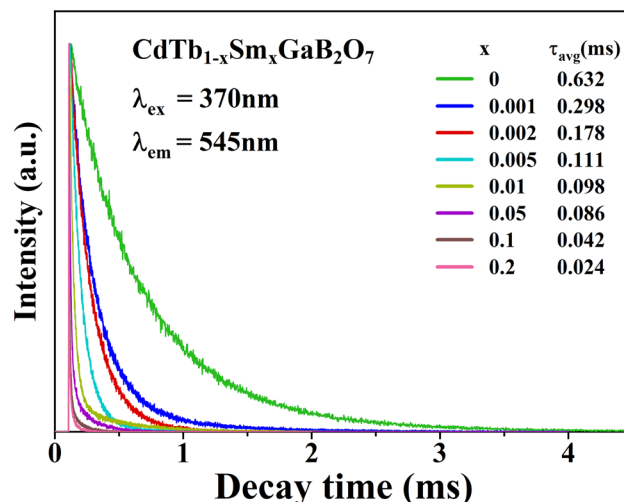


Fig. 6 Tb^{3+} decay curves of the $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ ($0 \leq x \leq 0.2$) phosphors monitoring 545 nm emission.

Table 2 CIE chromaticity coordinates, CCT values and energy transfer efficiencies (η) of the CdTb_{1-x}Sm_xGaB₂O₇ ($0 \leq x \leq 0.2$) phosphors

CdTb _{1-x} Sm _x GaB ₂ O ₇	λ_{ex} (nm)	CIE (x, y)	CCT (K)	η (%)
1 $x = 0$	370	(0.3134, 0.5750)	5854	—
2 $x = 0.001$	370	(0.4384, 0.4957)	3574	52.85
3 $x = 0.002$	370	(0.4656, 0.4779)	3093	71.84
4 $x = 0.005$	370	(0.5213, 0.4430)	2227	82.44
5 $x = 0.01$	370	(0.5539, 0.4202)	1838	84.49
6 $x = 0.05$	370	(0.5739, 0.4044)	1677	86.39
7 $x = 0.1$	370	(0.5746, 0.3979)	1655	93.35
8 $x = 0.2$	370	(0.5391, 0.3798)	1706	96.20

$$\eta = 1 - \left(\frac{\tau}{\tau_0} \right)$$

where τ and τ_0 are the decay times of Tb³⁺ (⁵D₄ → ⁷F₅) with and without Sm³⁺ co-doping. The calculated η values are provided in Table 2. It is found that the energy transfer efficiency increases monotonously from 52.85% to 96.20% with the raising Sm³⁺ concentration from $x = 0.001$ to 0.2.

Fig. 7 shows the energy level diagrams of Tb³⁺ and Sm³⁺ ions illustrating the energy migration processes in CdTb_{1-x}Sm_xGaB₂O₇. Upon excitation at 370 nm, the electrons on Tb³⁺ ions can jump from the ⁷F₆ ground state to the ⁵L₁₀ excited state. Afterwards, the nonradiative transition (NR) took place, leading to the population of the ⁵D₄ level. While some of the excited electrons return to the ⁷F_{6,5,4,3} ground state level in a radiative

manner, generating the typical Tb³⁺ emissions. The remaining electrons at the ⁵D₄ level of Tb³⁺ can move to the ⁴G_{7/2} excited level of Sm³⁺ due to energy level matching, followed by non-radiative relaxation to the ⁴G_{5/2} excited state and then radiative relaxation to the ⁶H_{*J*} (*J* = 5/2, 7/2, 9/2, 11/2) ground states to produce the observed Sm³⁺ emissions. This process enhances the characteristic emission of Sm³⁺ and simultaneously reduces the fluorescence emission intensity of Tb³⁺. In addition, it can be seen from Fig. 4(a) and (b) that there is a significant spectral overlap between the emission band of Tb³⁺ and the excitation band of Sm³⁺ in the range of 475–525 nm, which indicates that the energy transfer from Tb³⁺ to Sm³⁺ can be anticipated in CdTb_{1-x}Sm_xGaB₂O₇ via ⁵D₄ channel: ⁵D₄ (Tb³⁺) + ⁶H_{5/2} (Sm³⁺) → ⁷F₆ (Tb³⁺) + ⁴I_{11/2} (Sm³⁺).⁶² The Tb³⁺ → Sm³⁺ energy transfer is almost irreversible because the ⁵D₄ level of Tb³⁺ is slightly higher than the ⁴G_{7/2} level of Sm³⁺, which also explains the observation that Tb³⁺ cannot be excited by 405 nm (Sm³⁺:⁶H_{5/2} → ⁴K_{11/2} transition) in this system.

3.8. Emitting light color analysis

The CIE coordinates and CIE chromaticity diagram for the samples CdTb_{1-x}Sm_xGaB₂O₇ ($0 \leq x \leq 0.2$) were measured, as shown in Table 2 and Fig. 8. The inset of Fig. 8 also shows the digital photos of the selected phosphors under a 370 nm UV lamp. One can see that the CdTbGaB₂O₇ host emits green light when excited at 370 nm. Once Sm³⁺ ions were doped into this host and the Sm³⁺ content changed from $x = 0$ to 0.1, the CIE coordinates of CdTb_{1-x}Sm_xGaB₂O₇ would vary almost linearly

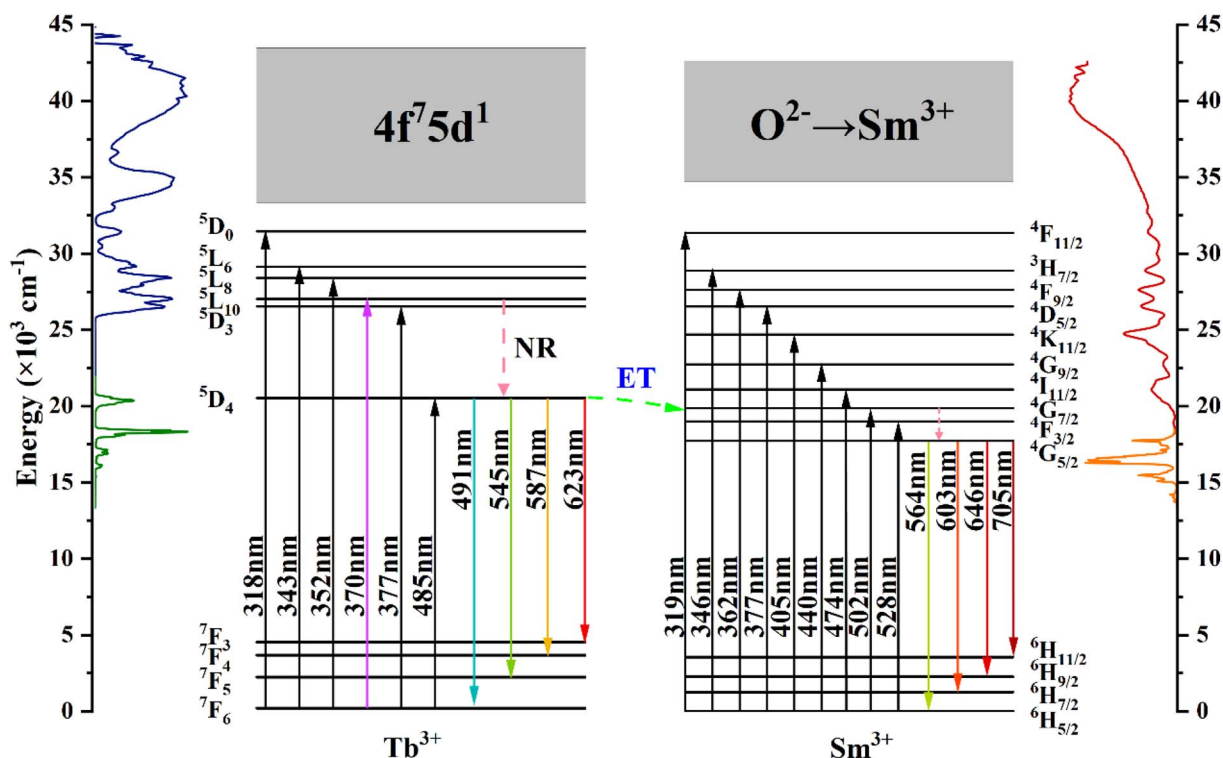


Fig. 7 Schematic energy-level diagrams of Tb³⁺ and Sm³⁺ in CdTb_{1-x}Sm_xGaB₂O₇, showing energy-transfer process (ET: energy transfer; NR: nonradiative).



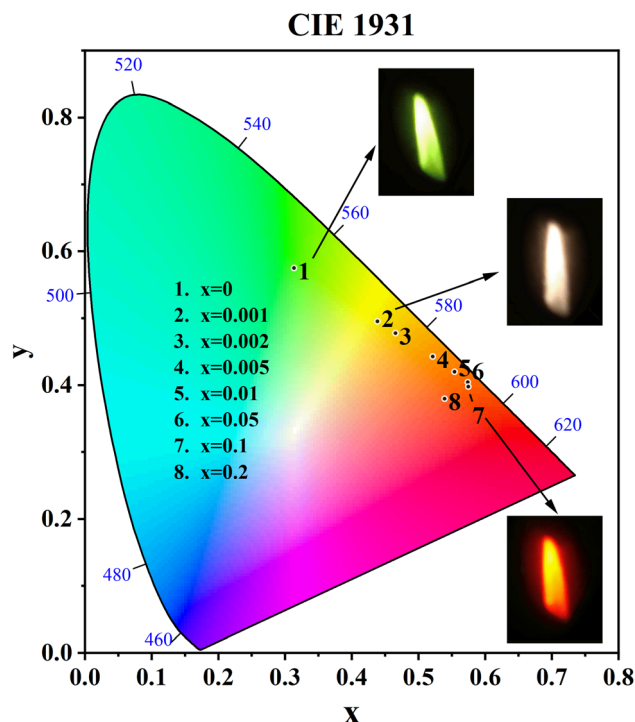


Fig. 8 CIE chromaticity coordinates of the $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ ($x = 0, 0.001, 0.002, 0.005, 0.01, 0.05, 0.1, 0.2$) phosphors and digital photographs of the selected samples ($x = 0, 0.001$ and 0.1) ($\lambda_{\text{ex}} = 370$ nm).

from (0.3134, 0.5750) to (0.5746, 0.3979), which means that the emitting color changes continuously from green to orange-red. In addition, as seen from Fig. 5(c), when the Sm^{3+} content was further increased from $x = 0.1$ to 0.2 , the characteristic blue and green emissions of Tb^{3+} remained basically unchanged, while the orange and red emissions of Sm^{3+} were significantly reduced due to the concentration quenching effect. Therefore, the chromaticity coordinates of the $x = 0.2$ sample are shifted toward the blue direction with respect to the $x = 0.1$ sample. A similar phenomenon was found in some previously reported Tb^{3+} and Sm^{3+} codoped phosphors, such as $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12} : 0.5\text{Tb}^{3+}, y\text{Sm}^{3+}$, $\text{Na}_3\text{Bi}(\text{PO}_4)_2 : 0.1\text{Tb}^{3+}, x\text{Sm}^{3+}$ and $\text{LaAl}_2.03\text{B}_4\text{O}_{10.54} : 0.1\text{Tb}^{3+}, y\text{Sm}^{3+}$.^{62–64} Next is the CCT (the Correlated Color Temperature), which is a measure of how cool or warm the appearance of a light source will be.⁶⁵ The CCT can be calculated by the analytical equation proposed by McCamy:⁶⁶

$$\text{CCT} = -449n^3 + 3525n^2 - 6823.3n + 5520.33$$

where $n = (x - x_e)/(y - y_e)$ and ($x_e = 0.332, y_e = 0.186$). The obtained CCT values for the $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ ($0.001 \leq x \leq 0.2$) phosphors decrease with the enhancement of Sm^{3+} concentration and are in the range of 1655–3574 K (Table 2), which means that the prepared phosphors have the “neutral to warm” colors. The above results indicate that multicolor photoluminescence can be realized in $\text{CdTb}_{1-x}\text{Sm}_x\text{GaB}_2\text{O}_7$ by controlling Sm^{3+} doping amount and choosing the appropriate excitation wavelength, and this material has potential application prospects as a color-tunable phosphor for w-LEDs.

3.9. Quantum yield and thermal stability

Quantum yield (QY) serves as a critical parameter to evaluate the luminescence properties of phosphors, which can be measured based on the following equation:

$$\text{QY} = \frac{\int L_S}{\int E_R - \int E_S}$$

where $\int L_S$ is the integrated emission profile of the sample, $\int E_R$ and $\int E_S$ represent the integrated excitation profile without and with the sample in the integrating sphere, respectively. The excitation and emission spectra of the phosphor $\text{CdTb}_{0.995}\text{Sm}_{0.005}\text{GaB}_2\text{O}_7$ and the reference sample collected in an integrating sphere ($\lambda_{\text{ex}} = 370$ nm) are displayed in Fig. S6,[†] which shows a QY of $\sim 13.22\%$. The relatively low QY may be due to the severe aggregation of phosphor particles. We believe that higher QY could be obtained by controlling the particle size, size distribution, morphology and crystalline defects *via* optimization of the preparation conditions or exploration of alternative synthetic routes. This will be investigated in our future work.

Thermal stability is one of the most important prerequisites for the synthesized phosphor to be used in a LED, as temperature greatly affects the brightness and color output. Fig. 9(a) exhibits the temperature-dependent PL spectra of the $\text{CdTb}_{0.995}\text{Sm}_{0.005}\text{GaB}_2\text{O}_7$ sample upon 370 nm excitation. Obviously, the position and shape of emission peaks remain almost unchanged, while the emission intensity diminishes with increasing temperature due to thermal quenching caused by non-radiative transitions. Furthermore, the emission intensities are integrated over the spectral range of 450–750 nm, and are normalized as compared to the case of 303 K. The results in the inset of Fig. 9(a) show that the relative emission intensity of $\text{CdTb}_{0.995}\text{Sm}_{0.005}\text{GaB}_2\text{O}_7$ at 423 K (the temperature at which LEDs typically operate) remains about 94% of that at 303 K. Compared with some previously reported phosphors, such as $\text{Ba}_3\text{BiPbEuO}(\text{BO}_3)_4$ (37%), $\text{Ba}_2\text{Lu}_{4.48}\text{Eu}_{0.5}\text{La}_{0.02}\text{B}_5\text{O}_{17}$ (38.2%) and $\text{LaMgAl}_{11}\text{O}_{19} : 0.05\text{Sm}^{3+}, 0.2\text{Eu}^{3+}$ (<60%),^{59,67,68} the thermal stability of $\text{CdTb}_{0.995}\text{Sm}_{0.005}\text{GaB}_2\text{O}_7$ seems to be better. For further understanding the influence of temperature on luminescence, the activation energy of thermal quenching (ΔE) was measured on the basis of the modified Arrhenius equation⁶⁹:

$$I = \frac{I_0}{1 + A \exp\left(-\frac{\Delta E}{kT}\right)}$$

where I and I_0 are related to the PL intensity at a given temperature T and initial temperature, respectively, A is a constant for the host, and k stands for the Boltzmann coefficient (8.62×10^{-5} eV K^{-1}). Upon specific rearrangement, the above equation can be rewritten as:

$$\ln\left(\frac{I_0}{I} - 1\right) = -\frac{\Delta E}{kT} + \ln A$$

Fig. 9(b) shows the relationship between $\ln[(I_0/I) - 1]$ and $1/kT$ of the phosphor. It can be seen that the plot can be well fitted to a straight line with the correlation coefficient $R^2 = 0.972$ and



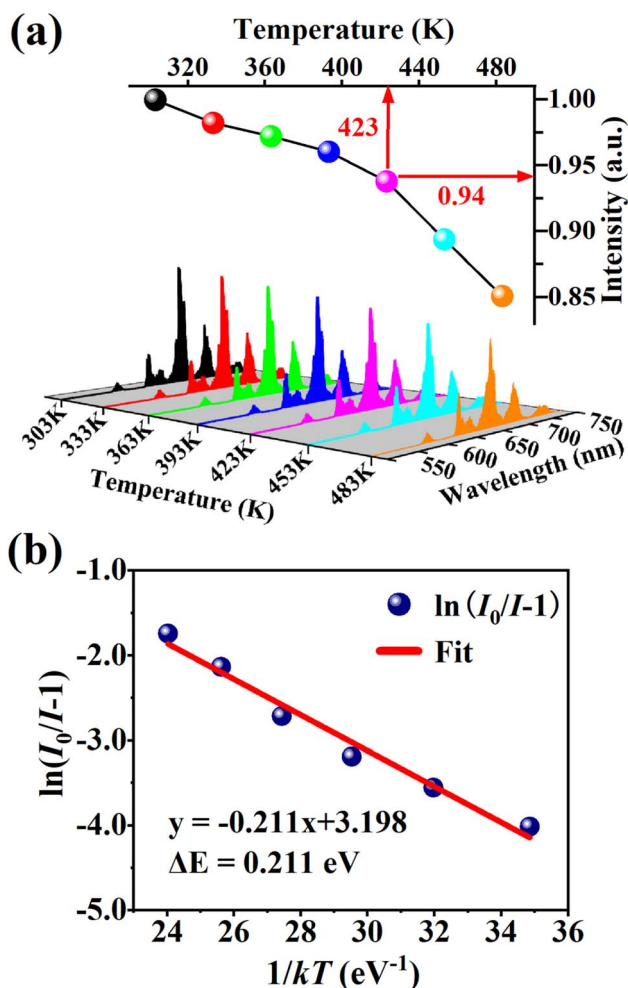


Fig. 9 (a) PL spectra and normalized PL intensities of CdTb_{0.995}Sm_{0.005}GaB₂O₇ under different temperatures within 303–483 K ($\lambda_{\text{ex}} = 370$ nm). (b) Relationship of $\ln(I_0/I - 1)$ versus $1/kT$ for this phosphor.

the slope of -0.211 , so the activation energy ΔE is 0.211 eV. The relatively high activation energy obtained in this work indicates that this phosphor possesses good color thermal stability and can be recommended as a suitable candidate for high-power LED applications.

4. Conclusions

CdTbGaB₂O₇ is the first quaternary compound found in the CdO–Ln₂O₃–Ga₂O₃–B₂O₃ (Ln = rare-earth metals) system. It has a melilite-type structure, in which [B₂O₇]⁶⁻ tetrahedral dimers and [GaO₄]³⁻ tetrahedra share corners to generate 2D [Ga(B₂O₇)_n]⁵ⁿ⁻ layers that are further bridged by 8-coordinated (Cd²⁺/Tb³⁺) cations giving rise to a 3D framework. The IR and Raman studies supported the presence of B₂O₇ tetrahedral dimers and GaO₄ groups. The UV-vis absorption measurement of CdTbGaB₂O₇ showed the typical Tb³⁺ absorption peaks and the band gaps of 4.10 and 4.33 eV for indirect and direct transitions, respectively. Furthermore, a series of CdTb_{1-x}Sm_xGaB₂O₇ ($0 \leq x \leq 0.2$) phosphors was synthesized at 800 °C. Under the irradiation of 370 nm, the emission lines of Tb³⁺: ⁵D₄ → ⁷F_{6,5,4,3} and

Sm³⁺: ⁴G_{5/2} → ⁶H_{5/2,7/2,9/2,11/2} appeared simultaneously in the PL spectra of CdTb_{1-x}Sm_xGaB₂O₇. The emission intensity of Tb³⁺ at 545 nm decreased monotonously, while that of Sm³⁺ at 603 nm first increased and then declined with increasing Sm³⁺ content, showing the Tb³⁺ → Eu³⁺ energy transfer and the concentration quenching between Sm³⁺ ions. The optimized CdTb_{0.995}Sm_{0.005}GaB₂O₇ phosphor exhibited a QY of 13.22% and good thermal stability with ΔE of 0.211 eV. The luminescence color can be tuned from green to orange-red by changing the Sm³⁺ doping concentration, and these types of materials have potential as tunable luminescence materials to meet the application requirements for n-UV LEDs.

Conflicts of interest

There are no conflicts to declare.

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