Luminescence, energy transfer, and up-conversion mechanisms of Yb³⁺ and Tb³⁺ co-doped LaNbO₄

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Abstract

Novel green-emitting Yb^{3+} and Tb^{3+} co-doped LaNbO_4 particles were prepared through a facile sol-gel and combustion method. X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), thermogravimetric and differential thermal analysis (TG-DTA), up-conversion luminescence (UCL) with different powers and varied concentrations, and luminescent lifetimes were employed to test the prepared samples. The XRD data exhibit that a sample with high crystallinity can be acquired at 1000 °C. FE-SEM images show homogeneous and spherical grains after Yb^{3+} and Tb^{3+} are co-doped in the LaNbO_4 samples. TG-DTA reveals that the LaNbO_4 synthetic process is accompanied by a temperature increase. In our work, we utilize a 980 nm laser to excite Yb^{3+} ions to achieve the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition, and the $\text{LaNbO}_4:\text{Yb}^{3+}, \text{Tb}^{3+}$ sample exhibits intense green emission. Luminescent spectra at different powers demonstrated the two-photon absorption process; meanwhile, the corresponding energy transfer mechanism from Yb^{3+} to Tb^{3+} and the emission of Tb^{3+} under 980 nm laser excitation was described via an energy level diagram. Moreover, concentration-dependent up-conversion luminescent properties were systematically explored, and it was confirmed that $\text{LaNbO}_4:0.15\text{Yb}^{3+}, 0.02\text{Tb}^{3+}$ exhibits the strongest luminescent properties. In particular, as the content of Yb^{3+} ions increases, the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition quickly becomes stronger, resulting in the emitted color shifting from green to blue. Therefore, the emitted color can be tuned by adjusting the content of Yb^{3+} ions. The excellent up-conversion emission properties of the obtained samples allow for their potential application in the fields of 3D display technologies and

solid-state lasers.

Keywords: Optical materials; Sol-gel processes; Optical properties; Luminescence

1. Introduction

Up-conversion is an anti-Stokes process to convert near infrared light to visible light. The process is characterized by the continuous absorption of two or more low-energy photons via an intermediate long-lived energy state to finally emit one high-energy photon. Recently, generation of various colors of light has been widely researched in different Lanthanide (Ln)-doped up-conversion materials, and which have attracted increasing attention for their wide prospective applications in many fields, such as clean energy, 3D displays, fluorescence labeling, background lighting, solid-state lasers, infrared detection, etc. [1-7]. Typically, up-conversion materials consist of dopant lanthanide ions and a host matrix. For up-conversion luminescence, it is vital to select a host material with low phonon energy and a close lattice match with dopant ions to achieve high up-conversion luminescence efficiency. Fluorides with low phonon energy can be generally employed as hosts for up-conversion materials to achieve high up-conversion (UC) efficiency [8-11]. Therefore, enormous efforts have been focused on the fluorides doped with different kinds of rare earth ions, such as Er^{3+} , Ho^{3+} , and Tm^{3+} as activator and Yb^{3+} as sensitizer. However, fluorides generally exhibit relatively poor stability, and in comparison, oxides exhibit higher thermal and chemical stability in high-temperature environments, which play a key role in its application. From this point of view, oxide phosphors possess

congenital advantages. Therefore, seeking out an appropriate oxide host with low phonon energy is essential [12]. Examples of inorganic oxides include molybdate, tungstate, vanadate, titanate, ferrite, niobate and other oxides. Among these materials, niobate exhibits a lower phonon energy than other oxides [13-16]. Meanwhile, niobates show outstanding physical properties and are usually used in photocatalysis [17-19] and photoluminescence [20-21]. LaNbO_4 has been reported to be a wonderful host in down-conversion and up-conversion phosphors for its self-activating properties [22-23]. As of now, J. P. C. do Nascimento et al have report the investigation of the up-conversion properties of LaNbO_4 with $\text{Yb}^{3+}/\text{Er}^{3+}$ [24]. Yb^{3+} possesses an extremely simple energy level scheme and strong $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition absorption for 950 nm to 1000 nm lasers. In addition, the excited state of Yb^{3+} is higher than the metastable states of some activators. It follows that Yb^{3+} is a great sensitizer to enhance the pump efficiency in up-conversion luminescence. In recent years, after the study of activators such as Er^{3+} , Ho^{3+} , and Tm^{3+} , the up-conversion luminescence of $\text{Yb}^{3+}\text{-Tb}^{3+}$ co-doped in various samples has gained increasing attention due to the high energy-transfer efficiency from Yb^{3+} to Tb^{3+} and green luminescence (~ 543 nm) from $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition in Tb [25-28]. However, for the $\text{Yb}^{3+}/\text{Tb}^{3+}$ dopants, the mechanism of up-conversion is cooperative energy transfer (CET) which differs from remaining. In the process, more than two Yb^{3+} ions simultaneously transfer energy to one Tb^{3+} ion. CET derives from the too large energy gap between the ground state and the first excited state of Ln^{3+} . Only some host compounds are suitable to support the relatively rare process [26]. In the present paper,

green-emitting LaNbO_4 co-doped with Yb^{3+} and Tb^{3+} was prepared by a facile sol-gel and combustion method. We present, in detail, an array of up-conversion luminescent properties, including the up-conversion mechanism, power-dependent spectra, concentration-dependent spectra, lifetimes and CIE chromaticity coordinates. In addition, XRD, structural analysis, FE-SEM and TG-DTA were employed to characterize the LaNbO_4 matrix. The excellent properties suggest that LaNbO_4 co-doped with Yb^{3+} and Tb^{3+} is a promising material.

2. Experimental

2.1. Preparation

The samples were prepared through a facile sol-gel and combustion method. First, a series of rare earth oxides, including lanthanum oxide (La_2O_3 , 99.9%), ytterbium oxide (Yb_2O_3 , 99.9%), and terbium oxide (Tb_4O_7 , 99.9%), were dissolved in stoichiometric amounts in diluted nitric acid to obtain the corresponding nitrates. All the raw materials in the experimental process were purchased from Aladdin (Shanghai, China). Residual nitric acid was eliminated via heating at 100 °C and evaporation. Second, excess hydrofluoric acid (HF, 40%) was employed to dissolve niobium oxide (Nb_2O_5 , 99.9%) at 90 °C. Then, aqueous ammonia solution was added to adjust the pH up to 9.0, and a white precipitate was obtained. Later, the precipitate was washed with deionized water and centrifugated repeatedly to guarantee the removal of all residual F^- ions. Third, three portions of citric acid and five portions of ammonium nitrate were used to dissolve the precipitate, where citric acid and

ammonium nitrate play the roles of complexant and fuel. Fourth, the rare earth nitrates ($\text{La}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$) were dissolved in the prepared mixed solution with continuous stirring at a constant temperature of 85 °C. During this process, along with the evaporation of water, the homogeneous sol gradually turned into a white gel with high viscosity. Afterwards, the gel was dried for 12 h at 110 °C, and the xerogel was obtained as the precursor. The precursor was directly annealed at 1000 °C for 3 h in a furnace and cooled naturally to room temperature. The annealed products were thoroughly ground into powder in an agate mortar for characterization.

2.2. Characterization

The X-ray diffraction (XRD) patterns of our samples are characterized by a Germany Bruker Axs D8-Focus diffractometer with graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) at a scanning rate of 0.04 sec per step over the 2θ range from 10° to 80°. The microstructures are carried out on a field emission scanning electron microscope (FE-SEM, Hitachi, S-4800). Thermal analysis of the precursor was obtained on a thermogravimetric-differential thermal analyser (TG-DTA) (Perkin Elmer Corporation, Diamond TG-DTA) The data are collected in the range from 30 °C to 1100 °C with a constant heating rate of 20 °C min⁻¹. The up-conversion luminescent spectra and lifetimes are observed through a fluorescence spectrometer (Edinburgh FLS 980-S2S2-STM) with a tuneable 980 nm semiconductor (1 W Laser) as the excitation source.

3. Results and discussion

3.1. Structural and morphological analysis

Fig. 1 shows the crystal phase determined from the XRD patterns of the samples, including the LaNbO_4 host annealed at 600 °C, 800 °C, and 1000 °C and the Yb^{3+} and Tb^{3+} co-doped LaNbO_4 annealed at 1000 °C. It can be found that all of the diffraction peaks of the samples are perfectly assigned to the standard reference, JCPDS Card No. 81-1973, and it demonstrates that the monoclinic phase of LaNbO_4 can be obtained via the facile sol-gel and combustion method. As the annealing temperature increases from 600 °C to 1000 °C, the diffraction peaks become obviously stronger and sharper, implying that the high annealing temperature contributes to the high crystallinity of the samples. LaNbO_4 begin to crystallize at 600 °C, and single-phase LaNbO_4 is obtained after annealing at 1000 °C. No redundant diffraction peaks or phases of other impurities are observed upon introducing Yb^{3+} and Tb^{3+} ions, which indicates that the samples crystallize in a single phase of LaNbO_4 and that Ln^{3+} doped in the host did not cause any significant impact on the phase structure. This may be because the La^{3+} ions are exactly replaced by Yb^{3+} and Tb^{3+} ions due to their similar ionic radii and coordination numbers ($r(\text{La}^{3+})=1.061 \text{ \AA}$, CN=8; $r(\text{Yb}^{3+})=0.858 \text{ \AA}$, CN=8; $r(\text{Tb}^{3+})=0.923 \text{ \AA}$, CN=8), and it is easy for the smaller-sized Yb^{3+} and Tb^{3+} ions to displace the larger-sized La^{3+} sites. However, this ionic replacement leads to a slight lattice distortion effect, which indicates that the crystallinity is relatively poor compared with that of undoped LaNbO_4 .

Fig. 1 XRD patterns of LaNbO_4 host samples annealed at 600 °C, 800 °C, 1000 °C for 3 h, $\text{LaNbO}_4: 0.15\text{Yb}^{3+}, 0.02\text{Tb}^{3+}$ annealed at 1000 °C for 3 h as well as the reference for standard card of LaNbO_4 (JCPDS no. 81-1973).

Fig. 2 indicates that the LaNbO_4 phase crystallizes in a monoclinic structure in the space group I112/b (15) with cell parameters $a=5.5634(3) \text{ \AA}$, $b=5.2030(2) \text{ \AA}$, $c=11.5227(7) \text{ \AA}$, $V=332.69(3) \text{ \AA}^3$, and $z=4$ [29]. The data above indicates that the monoclinic structure of the LaNbO_4 phase possesses a low-symmetry crystal structure. As is known, variations in the crystal structure of the host material can noticeably influence the optical properties of nanocrystals. This is because the crystal field around Ln^{3+} ions in a matrix can exhibit various symmetries. Generally, compared to high-symmetry crystal structures, low-symmetry crystal structures contain a more uneven distribution of components around the dopant ions, and the uneven component distribution can generate increased electronic coupling to enhance the f-f transition probability of the dopant ions. Furthermore, it can be found from Fig. 2 that La ions are located at the center of the polyhedral and are surrounded by eight oxygen ions, while Nb ions are surrounded by four oxygen ions.

Fig. 2 Scheme of crystal structure of the monoclinic LaNbO_4 phase.

To further identify the effects of Ln^{3+} doping in LaNbO_4 , FE-SEM images are used to examine the morphology and size of the undoped LaNbO_4 and Ln^{3+} -doped LaNbO_4 samples. It can be clearly observed in Fig. 3 that the samples present as aggregated particles with clear grain boundaries, and the aggregation is ascribed to the molten state in the high-temperatures reaction process. However, the spheroidal structures show grain sizes ranging from 300 to 800 nm, which is obviously smaller than those synthesized by the high-temperature solid-state reaction method in previous literature [22]. The samples annealed at 1000 °C for 3 h are vastly different from the irregular precursors, which were not treated at high temperature (in Fig. S1). By contrast, in Fig. 3(a) and Fig. 3(b), we can clearly see that the Ln^{3+} -doped LaNbO_4 samples are relatively more homogeneous and less agglomerated than undoped LaNbO_4 , which is due to the speed of nucleation being faster than the crystal growth upon doping Ln^{3+} into LaNbO_4 . In the LaNbO_4 matrix, Ln^{3+} ions are impurities, which lead to many defects in the crystal nuclei and consequently generate active sites for growth of the crystal nuclei. Meanwhile, the impurity ions reduce the critical

nucleus size and accordingly promote the growth of the crystal nuclei. However, beyond that, the dopants do not cause any considerable change in the surface of the grains (in Fig. S2), which indicates that the dopant does not influence the structure of the phosphor powders, which is consistent with the XRD patterns in Fig. 1. The SEM images of the other dopant phosphors are not shown because of the similar morphology.

Fig. 3 The FE-SEM micrographs of the host LaNbO_4 (a) and $\text{LaNbO}_4: 0.15\text{Yb}^{3+}, 0.02\text{Tb}^{3+}$ (b) samples annealed at $1000\text{ }^\circ\text{C}$ for 3 h.

Fig. 4 exhibits the LaNbO_4 xerogel dried for 12 h at $110\text{ }^\circ\text{C}$ in a drying oven. As shown in Fig. 4, there are three main weight loss periods between $30\text{ }^\circ\text{C}$ and $1100\text{ }^\circ\text{C}$. The first period occurs from $30\text{ }^\circ\text{C}$ to $235\text{ }^\circ\text{C}$. In this period, the evaporation of water, the combustion of organic phases and the thermal decomposition of NO_3^- collectively

leads to weight loss (approximately 40.36%), showing an endothermic peak (at approximately 62 °C) and a strong exothermic peak (at approximately 216 °C). In the second period, over which the temperature increases from 235 °C to 509 °C, the weight decreases by approximately 36.18%, and a strong exothermic peak occurs at 489 °C, which can be attributed to further combustion of the remaining organic materials. The third period represents phase transformation from the tetragonal phase to the monoclinic phase [30], which occurs between 509 °C and 642 °C, and the weight loss is low (only approximately 3.12%), corresponding to a faint exothermic peak at 631 °C. No obvious weight loss is observed above 631 °C, which demonstrates the complete decomposition of all organic compounds below 631 °C and the formation of the crystallized inorganic phase.

Fig. 4 TG-DTA curves of undoped LaNO_4 precursor xerogel powder with temperature the ranging from 30 °C to 1100 °C.

3.2. Upconversion properties and mechanism

To explore the populating mechanism, the up-conversion luminescent properties are compared at different powers. Fig. 5(a) exhibits the up-conversion spectra of $\text{LaNbO}_4:0.15\text{Yb}^{3+},0.02\text{Tb}^{3+}$ under the excitation of a 980 nm laser with powers

ranging from 18 mW to 46 mW. From the spectra, five emission peaks are present at approximately 477 nm, 543 nm, 587 nm, 620 nm and 658 nm, corresponding to the $^5D_4 \rightarrow ^7F_J$ ($J=6,5,4,3,2-0$) transitions of the Tb^{3+} ions. The up-conversion bands possess sharp splits, which are derived from the crystal-field splitting of the respective transitions due to the high crystallinity and successful substitution of Yb^{3+} and Tb^{3+} ions in the La^{3+} sites of the host lattice. In addition, the emission intensities increase with enhanced pump power. For an anti-Stokes up-conversion luminescent process, it is well known that the visible-light intensity I and according pump power P can be expressed by the following formula:

$$I \propto P^n$$

where n is the number of photons involved in the up-conversion mechanism. Fig. 5(b) shows the Ln-Ln plots of up-conversion intensity I versus pump power P of $LaNbO_4:0.15Yb^{3+},0.02Tb^{3+}$, corresponding to Fig. 5(a). The slopes of these curves (n) give the number of photons involved in the particular UC processes of the different bands. The slopes for 477 nm ($^5D_4 \rightarrow ^7F_6$), 543 nm ($^5D_4 \rightarrow ^7F_5$) and 658 nm ($^5D_4 \rightarrow ^7F_{0,1,2}$) are 1.66, 1.28 and 1.36, respectively. That is, a two-photon absorption process occurs in these emissions. However, as the photons enter the crystals, the loss of energy and nonluminous relaxation cause the emitted energy to be less than the absorbed energy, and thus the slope is less than 2.

Fig. 5 Up-conversion spectra of LaNbO₄: 0.15Yb³⁺, 0.02Tb³⁺ under excitation of a 980 nm laser at the different power (a) and the LnI (intensity of UC emission) versus LnP (power density) plot. (b)

Fig. 6 shows the simplified energy transfer mechanism from Yb³⁺ ions to Tb³⁺ ions and the emission of Tb³⁺ under 980 nm laser excitation. In the Yb³⁺ and Tb³⁺ co-doped LaNbO₄ sample, Yb³⁺ ions absorb energy from the 980 nm laser excitation, as it has a larger absorption, and carries the energy to Tb³⁺ to generate visible light. Generally, the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition is usually resonant with the f-f transition of Tb³⁺ ions, which accelerates the efficient energy transfer from Yb³⁺ to Tb³⁺ ions. According to our test results, the cooperative energy transfer occurs between two Yb³⁺

ions and one Tb^{3+} ion in the up-conversion process. Initially, the ground $^2\text{F}_{7/2}$ states of two Yb^{3+} ions are promoted to excited $^2\text{F}_{5/2}$ states by absorbing the laser emission, and meanwhile, the first photon excites one Tb^{3+} ion from the ground $^7\text{F}_6$ state to the excited $^5\text{D}_4$ state by a pair of Yb^{3+} ions via cooperative energy transfer. The energy transfer processes and mechanism are expressed as follows: $^7\text{F}_6 (\text{Tb}) + ^2\text{F}_{5/2} (\text{Yb}) + ^2\text{F}_{5/2} (\text{Yb}) \rightarrow ^5\text{D}_4 (\text{Tb}) + ^2\text{F}_{7/2} (\text{Yb}) + ^2\text{F}_{7/2} (\text{Yb})$. Further up-conversion emissions at 477 nm, 543 nm, 587 nm, 620 nm, and 658 nm are obtained, accompanied by the emission from $^5\text{D}_4$ to $^7\text{F}_J$ ($J=6-0$). In some host materials, a three-photon process usually exists. The excited $^5\text{D}_4$ state of the Tb^{3+} ions could also be promoted to the excited $^5\text{D}_1$ state by absorbing energy from another excited Yb^{3+} ion. Then, the Tb^{3+} ions in the excited $^5\text{D}_1$ state relax nonradiatively to the $^5\text{D}_3$ state, which radiatively decays to $^7\text{F}_J$ ($J=6-0$), resulting short-wavelength emissions [31-33]. However, in the Yb^{3+} and Tb^{3+} co-doped LaNbO_4 sample, short-wavelength emissions are not observed (in Fig. S3), and this fact demonstrates that there are no three-photon processes or that Tb^{3+} ions in the excited $^5\text{D}_3$ state relax nonradiatively to the $^5\text{D}_4$ state through phonons, but not radiative decays, to $^7\text{F}_J$ ($J=6-0$).

Fig. 6 Energy level diagrams of Yb³⁺ and Tb³⁺ ions, and possible energy transfer in the up-conversion processes under 980 nm laser excitation.

Fig. 7 displays the up-conversion spectra of the as-prepared LaNbO₄:yYb³⁺,tTb³⁺ (y=0.02–0.2, t=0.005–0.04) samples under 980 nm laser excitation at room temperature. All the samples have a similar spectral shape, indicating that the crystal field surrounding the Tb³⁺ ions is not really changed with variations in doping concentration. However, the different concentrations of Yb³⁺ and Tb³⁺, which can be attributed to the relative amount of Yb³⁺ and Tb³⁺ in the samples and the average distance in adjacent doping ions, have a strong influence on the optical properties of the materials. It is well known that the behavior of up-conversion spectra for oxides co-doped by Yb³⁺ ions are significantly dependent on the cationic coordination of the Yb³⁺ and Tb³⁺ ions. Generally, at high dopant concentration, substantial energy transfer occurs between ions because the energy transfer rate primarily depends on the distance between the ions. At lower concentrations, ions are usually randomly distributed in the host, and there is less chance for energy transfer than at higher

concentrations. In addition, it is important to achieve cationic coordination of the Yb^{3+} ions (donors) and Tb^{3+} ions (acceptors) to acquire outstanding up-conversion luminescent intensity [34]. Whether donors or acceptors, any kind of excessive ions can cause a decrease in the up-conversion luminescent intensity. The spectra of Tb^{3+} at different concentrations are shown in Fig. 7(a). We can observe that the up-conversion luminescent intensities continue to increase with the ever-increasing concentration of Tb^{3+} , which can be attributed to the induced energy transition. The phenomenon is derived from the shorter distance between the sensitizers and activators, which promotes the energy due to sensitizer enhancement. Generally, the content of activators is relatively small in the presence of Yb^{3+} , and this is because the large absorption cross-section of Yb^{3+} in the NIR region decreases the cross-relaxation energy loss. The experimental results indicate that the optimal content of Tb^{3+} is 0.02 for the up-conversion emission intensity. The intensities decrease when the content exceeds 0.02, due to energy migration and concentration quenching. Fig. 7(b) shows the trend in the variation of the up-conversion intensity due to the influence of the Yb^{3+} concentration. The intensity increases first and then decreases with increasing concentration of Yb^{3+} . First, more Yb^{3+} ions can promote more energy absorbed from the 980 nm laser source and transfer it to the Tb^{3+} ions, leading to an increase in the up-conversion emission intensity [35]. Second, concentration quenching occurs when the Yb^{3+} ion content surpasses 0.15, which is attributed to the quenching effect resulting from the pairing or aggregation of Yb^{3+} ions. This behavior is also due to the redundant Yb^{3+} ions becoming an energy

migration bridge for defects, wasting the non-radiative energy from Yb^{3+} ions [36]. In particular, as the content of Yb^{3+} ions increases, the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition quickly becomes stronger relative to the other transitions. It is possible that more energy from the Yb^{3+} ions is being used to emit a blue color. In any case, however, the green emission of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition is obviously predominant at room temperature, which can be explained by the large values of the reduced matrix elements at $J=5$ and the Judd-Ofelt theory [24,37,38]. In addition, the maximum concentration is restricted by the clustering of Ln^{3+} ions and energy migration between pairs of Yb^{3+} ions. In essence, the dopant concentration of Yb^{3+} ions and Tb^{3+} ions determines the average distance between the donors and acceptors and consequently strongly influences the up-conversion efficiency of the energy transfer process, finally changing the luminescent phenomenon.

Fig. 7 Up-conversion spectra of the $\text{LaNbO}_4: 0.05\text{Yb}^{3+}, \text{tTb}^{3+}$ (a) $\text{LaNbO}_4: \text{yYb}^{3+}, 0.02\text{Tb}^{3+}$ (b) samples under 980 nm laser excitation at room temperature.

To further research the luminescent properties of the Yb^{3+} and Tb^{3+} co-doped LaNbO_4 samples, decay curves of the characteristic emissions are measured under the excitation of a 980 nm laser. Generally, for samples with double doping, double-exponential decay behavior of the activators is usually observed. Decay times of all the samples can be determined with the double-exponential formula as follows:

$$I(\tau) = I_1 \exp(-\tau / \tau_1) + I_2 \exp(-\tau / \tau_2)$$

where $I(\tau)$ is the luminescent intensity, I_1 and I_2 are constants, τ_1 and τ_2 are fitted

decay times. In addition, the average decay time can be calculated by the equation

$$t = (I_1 \tau_1^2 + I_2 \tau_2^2) / (I_1 \tau_1 + I_2 \tau_2)$$

The decay times of all the samples were calculated, as shown in Table 1. For the $\text{LaNbO}_4:0.15\text{Yb}^{3+},0.02\text{Tb}^{3+}$ sample, the decay curves (monitored at 477 nm, 543 nm and 658 nm) are exhibited in Fig. 8, and the decay times are 133.63 μs , 186.56 μs , and 229.72 μs , respectively.

Fig. 8 Decay curves for $\text{LaNbO}_4: 0.15\text{Yb}^{3+}, 0.02\text{Tb}^{3+}$ samples (monitored at 477 nm, 543 nm, 658 nm, respectively) under 980 nm excitation laser.

Table 1 Decay lifetimes of the LaNbO_4 : $y\text{Yb}^{3+}$, $t\text{Tb}^{3+}$ samples at 543 nm and 658 nm.

LaNbO_4 : $y\text{Yb}^{3+}$, $t\text{Tb}^{3+}$		543 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$)			658 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_{0-2}$)		
		τ_1	τ_2	τ	τ_1	τ_2	τ
$y=0.05$	$t=0.005$	152.88	538.44	206.50	208.4	452.91	268.11
	$t=0.01$	236.62	1066.43	284.87	329.34	1270.09	350.14
	$t=0.02$	210.17	680.39	274.77	283.42	1169.82	303.27
	$t=0.03$	266.18	740.47	559.35	332.68	867.35	386.97
	$t=0.04$	292.52	777.29	400.52	217.14	741.82	693.51
$t=0.02$	$y=0.02$	91.58	499.12	163.30	112.27	438.09	230.94
	$y=0.05$	237.55	777.47	412.88	343.83	790.76	389.89
	$y=0.10$	201.74	747.77	292.52	301.94	935.96	323.78
	$y=0.15$	163.88	837.33	186.56	217.22	819.79	229.72
	$y=0.20$	118.87	729.57	251.85	141.27	453.36	166.63

The variation of the dopant ion concentration can significantly influence not only the up-conversion emission intensity but also the up-conversion emission color. The output color can be controlled by changing the amount of Yb^{3+} ions and Tb^{3+} ions, and this is attributed to the relative amount of dopant ions and the average distance between neighboring dopant ions. The corresponding CIE (Commission Internationale de l'Eclairage 1931 chromaticity) coordinates for the as-prepared LaNbO_4 : $y\text{Yb}^{3+}$, $t\text{Tb}^{3+}$ samples are shown in Fig. 9, accompanied by the chromaticity coordinates shown in Table 2, under 980 nm laser excitation. All the sites are located in the green region, except for T9 (0.22723, 0.47608) and T10 (0.22985, 0.46607), which correspond to LaNbO_4 :0.15 Yb^{3+} ,0.02 Tb^{3+} and LaNbO_4 :0.2 Yb^{3+} ,0.02 Tb^{3+} . This is because the blue transition, $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (477 nm), rapidly grows stronger and is only associated with the concentration spectra in Fig. 7(b).

Fig. 9 The variety of CIE chromaticity coordinates of the $\text{LaNbO}_4: \text{yYb}^{3+}, \text{tTb}^{3+}$ ($\text{y}=0.02\text{-}0.2, \text{t}=0.005\text{-}0.04$) samples excited at 980 nm laser.

Table 2 Variations of CIE Chromaticity Coordinate for $\text{LaNbO}_4: \text{yYb}^{3+}, \text{tTb}^{3+}$ ($\text{y}=0.02\text{-}0.2, \text{t}=0.005\text{-}0.04$) samples under 980 nm excitation laser.

no. of points	LNO: $\text{yYb}^{3+}, \text{tTb}^{3+}$		CIE(x, y)
T1	y=0.05	t=0.005	(0.28757,0.67070)
T2	y=0.05	t=0.01	(0.30441,0.67757)
T3	y=0.05	t=0.02	(0.26970,0.67486)
T4	y=0.05	t=0.03	(0.29248,0.64658)
T5	y=0.05	t=0.04	(0.31067,0.61909)
T6	y=0.02	t=0.02	(0.28303,0.67903)
T7	y=0.05	t=0.02	(0.28383,0.67425)
T8	y=0.10	t=0.02	(0.27923,0.66093)
T9	y=0.15	t=0.02	(0.22723,0.47608)
T10	y=0.20	t=0.02	(0.22985,0.46607)

4. Conclusions

In summary, a facile sol-gel and combustion method has been used to synthesize Yb^{3+} and Tb^{3+} co-doped LaNbO_4 samples, and the up-conversion results are presented.

The results of XRD, FE-SEM, and TG-DTA analyses indicate that the samples annealed at 1000 °C present as the monoclinic phase of LaNbO_4 with no additional phases and exhibit homogeneous and spherical grains. We obtained intense up-conversion green emission in a series of Yb^{3+} and Tb^{3+} co-doped LaNbO_4 samples. A two-photon absorption process has been demonstrated by power-dependent up-conversion luminescent analysis. The corresponding mechanism, including energy transfer between Yb^{3+} and Tb^{3+} and emission of Tb^{3+} under the excitation of a 980 nm laser, was discussed in detail. Furthermore, the effect of doping concentration on the up-conversion emissions was studied, and the $\text{LaNbO}_4:0.15\text{Yb}^{3+},0.02\text{Tb}^{3+}$ sample reaches the optimal luminescent intensity. In addition, multiple colors can be acquired by adjusting the concentrations of Yb^{3+} and Tb^{3+} . In sum, it can be concluded that we have found a perfect matrix, which exhibits relatively low phonon energy and high thermal and chemical stability in high-temperature environments. All the results indicate that the Yb^{3+} and Tb^{3+} co-doped LaNbO_4 samples are undoubtedly outstanding materials for up-conversion luminescence in the UV-Vis-NIR region with NIR excitation, indicating that these materials would also be great candidates in LEDs for producing green emission under the excitation of an IR source.

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Graphical Abstract