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Tunable color, optical properties, and energy transfer of Tb³⁺-Sm³⁺-Yb³⁺ tri-doped lithium-niobium-tellurite glass for applications in color display devices and WLEDs†

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A $TeO_2-Nb_2O_5-LiO_2-CaO$ (TNLC) lithium-niobium-tellurite glass single-doped and co-doped with Tb^{3+} , Sm^{3+} , and Yb^{3+} ions was synthesized *via* a conventional melt-quenching method. The $Tb^{3+}-Sm^{3+}$ co-doped TNLC glass could be tuned to emit white light effectively by controlling the ratio of Tb^{3+} and Sm^{3+} in the glass. The fluorescence lifetime of the $Tb^{3+}-Sm^{3+}$ co-doped TNLC glass indicated the existence of multiple energy transfer channels, including from Tb^{3+} to Sm^{3+} ions and the reverse energy transfer from Sm^{3+} to Tb^{3+} ions. Taking advantage of these energy transfer channels, the color coordinates of the material could be changed from yellowish-pink and yellowish-green emissions to white emission by controlling the ratio of ions doped in TNLC glasses. The optimal molar concentration ratio between Tb^{3+} and Sm^{3+} ions for the best white light emission was 0.83 for the TNLC-0.5Tb0.6Sm sample. Changing the ratio of these rare-earth (RE) ions allowed tuning the color temperature of the material from 5616 to 7699 K. Thus, $Tb^{3+}-Sm^{3+}$ co-doped and $Tb^{3+}-Sm^{3+}-Yb^{3+}$ tri-doped TNLC glasses are promising materials for color display applications and white light-emitting diodes (WLEDs).

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1. Introduction

In recent years, with the rapid development and high demand of optoelectronic materials for color display technologies and devices, ^{1,2} light-emitting diodes (LEDs)^{3,4} that emit in the visible region, display full colors and are color-tunable are in high demand, promoting extensive research on rare-earth (RE)-ion

doping in various host matrices,5-7 such as phosphors, glasses, and glass-ceramic containing nanocrystals. Among various host matrices, tellurite-based glasses have emerged as promising candidates owing to their unique physicochemical and optical properties.^{5,6} Tellurite-based glasses have a relatively low melting point, high thermal stability, good RE ion solubility, a wide transmission window (covering the visible (VIS) to near-infrared (NIR) region), and low phonon energy (which minimizes non-radiative (NR) losses and enhances emission efficiency).^{7,8} Co-doping RE ions in tellurite glasses facilitates sharp, well-defined intra-4f electronic transitions that result in highly stable and efficient luminescence. The incorporation of RE ions in tellurite glasses further opens up pathways for energy transfer (ET) interactions, enabling the tuning of emission intensity and chromaticity of color in the visible wavelength range. 9,10 The combination of Sm3+, Tb3+, and Yb3+ ions produces a cooperative, energy-transferring, and tunable emission intensity and colorimetry for visible and upconversion (UC) emissions when excited at different wavelengths. 11 Sm³⁺ ions exhibit prominent orange-red emission around 600-650 nm, corresponding to ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ and ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ transitions;12,13 Tb3+ ions produce strong green emission near 546 nm, corresponding to ${}^5D_4 \rightarrow {}^7F_5$ transition, 14,15 and Yb^{3+} ions exhibit only one ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and acts as a sensitizer owing to their strong absorption at ~980 nm and the ability to participate in UC and cross-relaxation (CR)

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mechanisms. 16,17 Some works have explored the color tunability, luminescence properties, and ET mechanisms in RE ion codoped glasses/glass ceramics to develop materials suitable for color display and LED applications. 18-20 F. Nawaz et al. 21 investigated and reported the influence of Yb3+ co-doping on the optical properties of Sm³⁺-doped sodium tellurite glasses. They found that Yb3+ co-doping affected the absorption and emission characteristics of Sm3+ ions, indicating ET between the Sm3+ and Yb3+ ions.21 J. Li et al.22 reported a multi-color afterglow in Tb³⁺-Sm³⁺ co-doped gallo-silicate glass ceramics. By adjusting the concentrations of Tb³⁺ and Sm³⁺ ions, the afterglow emission could be tuned from green to orange and then to yellow.22 This study highlighted ET and trap-sharing mechanisms between the dopants, which are significant for optical anticounterfeiting applications. In general, these studies collectively enhance our understanding of ET dynamics and luminescence tuning in RE co-doped tellurite glass systems, contributing to the development of materials for color displays, LEDs, and other photonic applications.21,22

Lithium–niobium–tellurite (Li–Nb–Te) glass is particularly advantageous as a host because the incorporation of lithium and niobium oxides enhances the structural network,²³ improves RE ion dispersion, and increases the optical bandgap and nonlinear optical properties. The presence of Nb⁵⁺ ions, which act as a glass modifier, can influence local field symmetry and aid the creation of non-centrosymmetric sites that are beneficial for RE ion emission.^{23,24} Furthermore, the addition of Li₂O serves to improve glass formability and optical clarity while also aiding ET dynamics by modifying the local coordination environment of the RE ions.²⁵ Although several studies have explored tellurite glasses single-doped and co-doped with Tb³⁺, Sm³⁺, and Yb³⁺ ions, as well as other optical materials containing these RE ions, most of them have focused on ET mechanisms from Tb³⁺ to Sm³⁺ ions. However, reverse ET

mechanisms, such as from Sm3+ to Tb3+ ions or from Yb3+ to both Tb3+ and Sm3+ ions, have not been reported. These mechanisms are crucial for enabling strong visible emission under 980 nm infrared excitation, corresponding to the transition of Yb³⁺ from the ²F_{7/2} to ²F_{5/2} state. In this study, TeO₂-Nb₂O₅-Li₂O-CaO (TNLC) glasses with various doping schemes, including Tb3+-doped, Sm3+-doped, Tb3+-Sm3+ co-doped, and Tb³⁺-Sm³⁺-Yb³⁺ tri-doped glasses, were synthesized via meltquenching. We investigated the effect of varying the concentrations of these ions on the emission color. A detailed analysis of the ET processes from Tb³⁺ to Sm³⁺, Sm³⁺ to Tb³⁺, and Yb³⁺ to both Tb³⁺ and Sm³⁺ ions was conducted. By adjusting the ion ratios, white-light emission was achieved. These findings suggest that TNLC glasses co-doped with Tb3+, Sm3+, and Yb3+ ions are promising candidates for color display technologies and white light-emitting diodes (LEDs).

2. Experimental details

The lithium–niobium–tellurite glasses used in this work were synthesized using a conventional melt-quenching technique. High-purity laboratory-grade reagents (99.99%), including ${\rm TeO_2}$, ${\rm Nb_2O_5}$, ${\rm Li_2O}$, ${\rm CaO}$, ${\rm TbF_3}$, ${\rm Sm_2O_3}$, and ${\rm Yb_2O_3}$, were used as raw materials. Specific compositions, molar ratios, and corresponding sample abbreviations are summarized in Table 1.

Approximately 12 grams of each glass batch was prepared by accurately weighing the required mixtures of raw materials using an electronic analytical balance. After finely grinding them using an onyx mortar and agate pestle, the mixtures were compacted, placed in a platinum crucible and then heated in a Nabertherm electric furnace (Germany) at 1150 °C for 45 minutes under an air atmosphere. Following the melting process, the molten materials were cast into molds and rapidly cooled on a stainless-steel plate to form the initial glass

 $\textbf{Table 1} \quad \textbf{Specific glass compositions and molar concentration ratios of the as-synthesized } \textbf{TeO}_2-\textbf{Nb}_2\textbf{O}_5-\textbf{LiO}_2-\textbf{CaO}-\textbf{TbF}_3-\textbf{Sm}_2\textbf{O}_3-\textbf{Yb}_2\textbf{O}_3\\ \textbf{lithium-niobium-tellurite glasses}$

	Molar cond	centration ratio of	the components									
Glass sample	${ m TeO_2}$	$\mathrm{Nb_2O_5}$	${ m LiO_2}$	CaO	TbF_3	$\mathrm{Sm_2O_3}$	Yb_2O_3					
TNLC-0.5Tb	60	18	12	9.5	0.5	0	0					
TNLC-0.5Sm	60	18	12	9.5	0	0.5	0					
TNLC-0.5Tb0.5Sm	60	18	12	9.0	0.5	0.5	0					
TNLC-0.6Tb0.5Sm	60	18	12	8.9	0.6	0.5	0					
TNLC-0.7Tb0.5Sm	60	18	12	8.8	0.7	0.5	0					
TNLC-0.8Tb0.5Sm	60	18	12	8.7	0.8	0.5	0					
TNLC-0.9Tb0.5Sm	60	18	12	8.6	0.9	0.5	0					
TNLC-1.0Tb0.5Sm	60	18	12	8.5	1.0	0.5	0					
TNLC-0.5Tb0.6Sm	60	18	12	8.9	0.5	0.6	0					
TNLC-0.5Tb0.7Sm	60	18	12	8.8	0.5	0.7	0					
TNLC-0.5Tb0.8Sm	60	18	12	8.7	0.5	0.8	0					
TNLC-0.5Tb0.9Sm	60	18	12	8.6	0.5	0.9	0					
TNLC-0.5Tb1.0Sm	60	18	12	8.5	0.5	1.0	0					
TNLC-0.5Tb0.5Sm2Yb	60	18	12	7.0	0.5	0.5	2					
TNLC-0.6Tb0.5Sm2Yb	60	18	12	6.9	0.6	0.5	2					
TNLC-0.7Tb0.5Sm2Yb	60	18	12	6.8	0.7	0.5	2					
TNLC-0.8Tb0.5Sm2Yb	60	18	12	6.7	0.8	0.5	2					
TNLC-1.0Tb0.5Sm2Yb	60	18	12	6.5	1.0	0.5	2					

samples. To enhance the mechanical strength and eliminate residual thermal stresses, the glass samples were annealed at approximately 342 °C for 10 hours.26,27 The TNLC glass materials used for optical measurements were cut into samples with approximate dimensions of 10 mm \times 10 mm \times 2 mm. These TNLC glass samples were then thoroughly polished on the edges and surfaces. Differential thermal analysis (DTA) was performed on a Shimadzu DTG-60H TG/DTA. The absorption spectra of the TNLC glasses in the wavelength range of 350-2000 nm were recorded using a Hitachi U-4100 UV/VIS/NIR spectrophotometer. The excitation, visible, and UC emission spectra of the Tb³⁺-doped, Sm³⁺-doped, Tb³⁺-Sm³⁺ co-doped, Tb³⁺-Sm³⁺-Yb³⁺ tri-doped TNLC glasses were measured in the wavelength range of 200 to 750 nm using an Edinburgh Instruments FLS-1000 photoluminescence spectrometer. All the absorption, excitation, visible, and UC emission spectral measurements, and decay lifetime analyses of the TNLC glass samples were performed at ambient temperature. 26,27

3. Results and discussion

DTA was conducted to investigate the thermal stability and glass-forming ability of the lithium-niobium-tellurite glass using the TNLC-0.5Tb0.5Sm2Yb glass sample. The DTA curve was recorded in the 100 to 1000 °C temperature range at a constant heating rate (typically 10 °C min⁻¹) under a nitrogen atmosphere. The DTA curve revealed typical thermal parameters. The onset of endothermic deviation in the DTA curve corresponded with the glass transition temperature (T_g) , which was observed at approximately 342 °C. This T_g value indicates the temperature at which the amorphous glass matrix transitions from a rigid, glassy state to a more flexible, rubbery state. A relatively low $T_{\rm g}$ is characteristic of tellurite-based glasses and is attributed to the weak Te-O bonds and the open network structure of the tellurite matrix. An exothermic peak was observed at around 493 °C, corresponding to the onset of crystallization (T_x) . This temperature indicates the initiation of

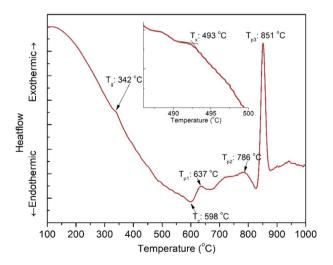


Fig. 1 DTA analysis of the TNLC-0.5Tb0.5Sm2Yb lithium-niobium-tellurite glass sample.

structural reorganization and phase separation within the glass matrix, leading to the formation of crystalline phases. 16,28,29 The difference between $T_{\rm x}$ and $T_{\rm g}$ was $\Delta T = T_{\rm x} - T_{\rm g} = (493 - 342)^{\circ}{\rm C} = 151$ °C; often referred to as the thermal stability window, it is an important parameter to evaluate glass stability against devitrification. 16,29,30 For the TNLC-0.5Tb0.5Sm2Yb sample, the ΔT of approximately 151 °C indicates reasonably good thermal stability and suggests that the material is suitable for optical applications that require thermal processing. 16 Besides, the values of crystallization temperature ($T_{\rm c}$) and crystallization peak temperatures $T_{\rm p}$ (including $T_{\rm p1}$, $T_{\rm p2}$, and $T_{\rm p3}$ temperatures) 16 were also determined to be \sim 598, 637, 786, and 851 °C, respectively, as depicted in Fig. 1.

The absorption spectra of TNLC-0.5Tb, TNLC-0.5Sm, TNLC-0.5Tb0.5Sm, and TNLC-0.5Tb0.5Sm2Yb lithium-niobium-tellurite glass samples are shown in Fig. 2. The absorption spectra characterize the Tb³⁺ ions due to f-f transitions. These transitions typically occur in the ultraviolet (UV) and visible wavelength regions, primarily at \sim 398 and 480 nm, corresponding to the ${}^{7}F_{6} \rightarrow {}^{5}D_{3}$ and ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ transitions of Tb $^{3+}$ ions. 18,31 Sm $^{3+}$ has different absorption characteristics from Tb3+, primarily because of the 4f states. The absorption peaks of Sm³⁺ are typically broader than those of the Tb³⁺ ions due to the nature of its electronic transitions. The absorption spectrum of Sm³⁺ in the wavelength range of 350-2000 nm includes peaks at \sim 360, 374, 402, 473, 939, 1076, 1224, 1369, 1472, and 1536 nm attributed to the ${}^{6}H_{5/2} \rightarrow -{}^{6}P_{7/2}, -{}^{4}F_{5/2}, -{}^{4}F_{7/2}, -{}^{4}I_{11/2}, -{}^{6}F_{11/2},$ $-{}^{6}F_{9/2}$, $-{}^{6}F_{7/2}$, $-{}^{6}F_{5/2}$, $-{}^{6}F_{3/2}$ and ${}^{6}H_{15/2}$ transitions, respectively. 4,22,32 The absorption spectrum of the Tb3+-Sm3+ co-doped TNLC-0.5Tb0.5Sm glass sample in the wavelength range of 350-2000 nm contains all the absorption peaks of Tb³⁺ and Sm³⁺ ions. 4,22,32-34 The absorption spectrum of the Tb3+-Sm3+-Yb3+ tridoped TNLC-0.5Tb0.5Sm2Yb glass sample in the wavelength range of 350-2000 nm includes all the absorption peaks of Tb³⁺, Sm³⁺ ions and the absorption peak of Yb³⁺ ions at ~975 nm $(^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}).$

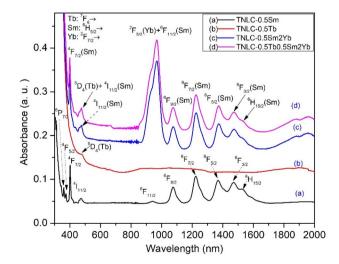


Fig. 2 Absorption spectra of TNLC-0.5Tb, TNLC-0.5Sm, TNLC-0.5Tb0.5Sm, and TNLC-0.5Tb0.5Sm2Yb lithium-niobium-tellurite glass samples.

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TNLC-0.5Sm TNLC-0.5Tb TNLC-0.5Sm2Yb TNLC-0.5Tb0.5Sm2Yb 60 50 $(\alpha h v)^2$ 40 30 20 2.0 2.2 2.6 2.8 3.0 32 hv (eV)

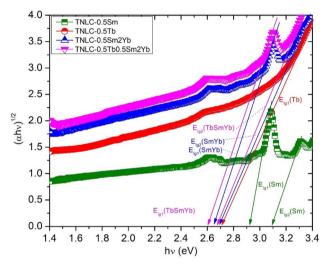


Fig. 3 (a) Direct optical bandgaps of the TNLC-0.5Sm, TNLC-0.5Tb, TNLC-0.5Sm2Yb, and TNLC-0.5Tb0.5Sm2Yb glass samples. (b) Indirect optical bandgaps of the TNLC-0.5Sm, TNLC-0.5Tb, TNLC-0.5Sm2Yb, and TNLC-0.5Tb0.5Sm2Yb glass samples.

The direct optical bandgaps (DOB) and indirect optical bandgaps (IOB) of the TNLC-0.5Sm, TNLC-0.5Tb, TNLC-0.5Sm2Yb, and TNLC-0.5Tb0.5Sm2Yb glass samples were calculated and analyzed based on their absorption spectra using the Tauc formula:19,35,36

$$\alpha(\lambda) = B \frac{\left(h\nu - E_{\rm g}\right)^{\gamma}}{h\nu} \tag{1}$$

Here, $\alpha(\lambda)$ is the absorption coefficient; λ is the wavelength; ν is the frequency; h is the Planck constant; B is the energyindependent constant; 19,35,36 $E_{\rm g}$ is the energy gap of the glass samples; $\gamma = 2$ for DOB; $\gamma = \frac{1}{2}$ for IOB. 19,35,36 The calculated direct optical bandgaps (DOB) of the TNLC-0.5Sm, TNLC-0.5Tb, TNLC-0.5Sm2Yb, and TNLC-0.5Tb0.5Sm2Yb glass samples are shown in Fig. 3(a).

Similarly, the indirect optical bandgaps of the TNLC-0.5Sm, TNLC-0.5Tb, TNLC-0.5Sm2Yb, and TNLC-0.5Tb0.5Sm2Yb glass samples were calculated based on their absorption spectra using the Tauc formula, as shown in Fig. 3(b). A summary of the energy indirect/direct bandgap values of the TNLC-0.5Tb, TNLC-0.5Sm, TNLC-0.5Tb0.5Sm, and TNLC-0.5Tb0.5Sm2Yb glass samples is presented in Table 2.

As shown in Table 2, all the glass samples exhibited significantly smaller bandgaps than pure TeO2 glass. The incorporation of Nb₂O₅, CaO, and Li₂O introduces electronic states within the TeO₂ bandgap, resulting in a notable reduction in the band gap. Among the samples, the TNLC-0.5Sm glass sample had a larger bandgap than the TNLC-0.5Tb glass sample, though both remain smaller than that of pure TeO2. This reduction is attributed to the addition of RE ions, which alter the glass network by modifying oxygen bonding, increasing non-bridging oxygen content, and affecting light absorption. Furthermore, the TNLC-0.5Sm2Yb and TNLC-0.5Tb0.5Sm2Yb glass samples showed even lower bandgaps owing to the higher RE ion concentrations, which introduced additional intermediate energy levels and further enhanced non-bridging oxygen states. The increasing concentration of RE ions in the glass matrix also increases the non-bridging oxygen bonding state, causing the band gap of the glass to decrease.

The excitation spectra of the TNLC-0.5Tb, TNLC-0.5Sm, and TNLC-0.5Tb0.5Sm glass samples were obtained, as shown in Fig. 4, to determine the excitation wavelengths for the TNLC glass samples containing both Tb³⁺ and Sm³⁺ ions. Based on the spectral data, we chose 374 nm as the excitation wavelength for the Tb³⁺-Sm³⁺ co-doped TNLC glass sample.^{37,38}

The visible emission spectra of the TNLC-0.5Tb, TNLC-0.5Sm, and TNLC-0.5Tb0.5Sm lithium-niobium-tellurite glass samples under 374 nm are shown in Fig. 5. For the TNLC-0.5Tb glass sample, the visible emission of Tb3+ under 374 nm excitation revealed weaker peaks at around 415 and 438 nm due to the ${}^{3}D_{5} \rightarrow {}^{7}F_{5}$ and ${}^{3}D_{5} \rightarrow {}^{7}F_{4}$ transitions. 4,16,32 This result is intriguing because these emission peaks have not been reported in most previous works. For the TNLC-0.5Sm glass sample, the

Table 2 Indirect/direct energy bandgap values of the TNLC-0.5Tb, TNLC-0.5Tb, TNLC-0.5Tb0.5Sm, and TNLC-0.5Tb0.5Sm2Yb glass samples

	Direct bandgap values		Indirect bandgap values			
Glass sample	E_{Dg1} (eV)	E_{Dg2} (eV)	$\Delta E_{\rm D} = E_{\rm Dg2} - E_{\rm Dg1} (\rm eV)$	E_{Ig1} (eV)	E_{Ig2} (eV)	$\Delta E_{\rm I} = E_{\rm Ig2} - E_{\rm Ig1} (\rm eV)$
TNLC-0.5Sm	3.02	3.23	0.21	2.98	3.19	0.21
TNLC-0.5Tb	2.34	2.95	0.61	2.84	_	_
TNLC-0.5Sm2Yb	2.36	2.74	0.38	2.75	2.82	0.07
TNLC-0.5Tb0.5Sm2Yb	2.28	2.59	0.31	2.72	2.79	0.07

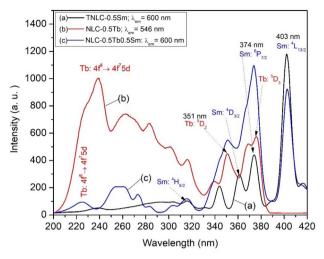


Fig. 4 Excitation spectra of the TNLC-0.5Tb, TNLC-0.5Sm, and TNLC-0.5Tb0.5Sm lithium-niobium-tellurite glass samples.

visible emission peaks of Sm³+ under 374 nm excitation at around 440, 564, 601, and 645 nm could be attributed to the $^4G_{7/2} \rightarrow ^6H_{9/2}, ^4G_{5/2} \rightarrow ^6H_{5/2}, ^4G_{5/2} \rightarrow ^6H_{7/2},$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions, respectively.³2-34 For the TNLC-0.5Tb0.5Sm glass sample, the visible emission of peaks co-doped Tb³+ and Sm³+ under 374 nm excitation were found at around 415, 438, 490, 546, 587, 622, and 645 nm due to transitions from Tb³+, Sm³+ ions or the combination of transitions from both Tb³+ and Sm³+ions corresponding to (Tb³+: ³D₅ \rightarrow ⁷F₅), (Tb³+: ³D₅ \rightarrow ⁷F₄ + Sm³+: $^4G_{7/2} \rightarrow ^6H_{9/2}$), (Tb³+: ³D₄ \rightarrow ⁷F_{f(f=6, 5, 4, and 3)}) and (Sm³+: $^4G_{5/2} \rightarrow ^6H_{9/2}$) transitions, respectively.⁴4,32-34

The Commission Internationale de L'Eclairage (CIE) 1931 (x; y) chromaticity coordinates^{19,39} for the visible emission spectra of the TNLC-0.5Tb, TNLC-0.5Sm, and TNLC-0.5Tb0.5Sm glass samples were determined to be P_{Tb} (0.2840; 0.5303), P_{Tb-Sm} (0.2901; 0.3728), and P_{Sm} (0.4906; 0.3537) located in the

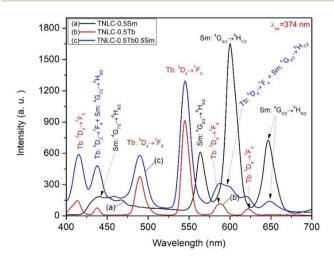


Fig. 5 Visible emission spectra of the TNLC-0.5Tb, TNLC-0.5Sm, and TNLC-0.5Tb0.5Sm lithium-niobium-tellurite glass samples under 374 nm excitation.

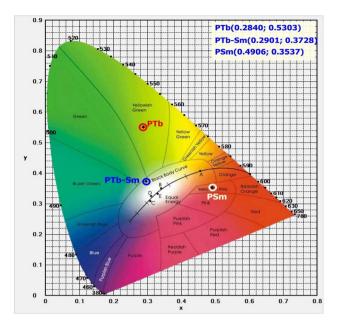


Fig. 6 CIE 1931 (x; y) color coordinates for the visible emission spectra of the TNLC-0.5Tb, TNLC-0.5Sm, and TNLC-0.5Tb0.5Sm glass samples under 374 nm excitation.

yellow-pink, yellowish-green and black body curve regions, respectively, as shown in Fig. 6.

The visible emission spectra of the TNLC-pTb0.5Sm (p=0.6, 0.7, 0.8, 0.9, and 1.0 mol%) lithium–niobium–tellurite glass samples under 374 nm are shown in Fig. 7. With the increase in molar concentration of Tb³⁺ from 0.6 to 1.0 mol%, the visible emission intensity of the peaks of Tb³⁺ ions at \sim 415, 438, 490, 546, and 622 nm increased significantly. ^{32,33} Similarly, the visible emission intensity of the Sm³⁺ ion peaks at around 645 nm, which is attributed to the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition, was also increased. These findings confirm that energy from the neighboring states of Tb³⁺ ions were transferred to the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition of Sm³⁺ ions. ^{33,34,37-40}

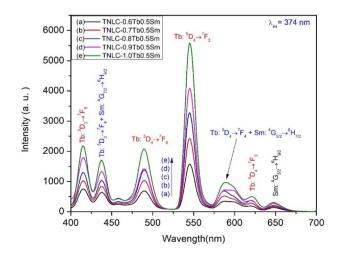


Fig. 7 Visible emission spectra of the TNLC-pTb0.5Sm (p=0.6, 0.7, 0.8, 0.9, and 1.0 mol%) glass samples under 374 nm excitation.

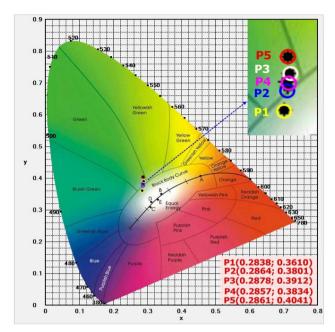


Fig. 8 CIE 1931 (x; y) color coordinates for the visible emission spectra of the TNLC-pTb0.5Sm ($p=0.6,\ 0.7,\ 0.8,\ 0.9,\ and\ 1.0\ mol\%$) glass samples under 374 nm excitation.

Fig. 8 shows the CIE1931 (x; y) color coordinates for the visible emission spectra of the TNLC-pTb0.5Sm (p = 0.6, 0.7, 0.8, 0.9, and 1.0 mol%) lithium-niobium-tellurite glass samples under excitation at 374 nm. With the increase in the molar concentration of Tb³+ ions from 0.6 to 1.0 mol%, the color points of the visible emission spectra of the Tb³+-Sm³+ codoped glass shifted in the order of P1 <math>(0.2838; 0.3610), P2 (0.2864; 0.3801), P3 (0.2878; 0.3912), P4 (0.2857; 0.3834) and P5 (0.2861; 0.4041) in the CIE1931 (x; y) color coordinate chart, respectively, 19,33,34 as shown in Fig. 8. From the results in Fig. 8, we can see that the TNLC-0.6Tb0.5Sm sample corresponding to the Tb³+/Sm³+ concentration ratio of 1.2 has the color point closest to the white light region. 33,34

To further investigate the optimal concentration ratio between ${\rm Tb}^{3+}$ and ${\rm Sm}^{3+}$ ions for the color point to move closer to the white light region, which is necessary for application to WLEDs, the ${\rm Sm}^{3+}$ concentration was changed while keeping the ${\rm Tb}^{3+}$ concentration constant to investigate the emission of the ${\rm Tb}^{3+}$ – ${\rm Sm}^{3+}$ co-doped glass sample. The visible emission spectra of the TNLC-0.5TbqSm (q=0.6,0.7,0.8,0.9, and 1.0 mol%) lithium–niobium–tellurite glass samples under 374 nm are shown in Fig. 9.

When excited at 374 nm, with an increase in $\rm Sm^{3+}$ concentration from 0.6 to 1.0 mol%, most of the emission peaks of both $\rm Sm^{3+}$ and $\rm Tb^{3+}$ ions increased in intensity. This result affirms that energy from the neighboring states of $\rm Sm^{3+}$ ions is transferred to the $\rm Tb^{3+}$ ions. Simultaneously, with the increase in molar concentration of $\rm Sm^{3+}$ ions from 0.6 to 1.0 mol%, the tunable color for the visible emission spectra of the $\rm Tb^{3+}{-}Sm^{3+}$ co-doped glass samples shifted to color points 1 (0.3118; 0.3821), 2 (0.3093; 0.3827), 3 (0.3095; 0.3875), 4 (0.3169; 0.3937) and 5 (0.3263; 0.4049) on the CIE 1931 (x; y) coordinate

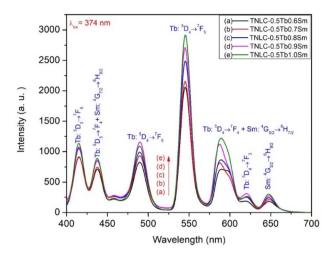


Fig. 9 Visible emission spectra of the TNLC-0.5TbqSm ($q=0.6,\,0.7,\,0.8,\,0.9,\,$ and 1.0 mol%) glass samples under 374 nm excitation.

diagram, ^{19,33,34} as shown in Fig. 10. From the visible emission spectra results of the Tb³⁺–Sm³⁺ co-doped glass samples under 374 nm excitation (Fig. 7 and 9), as well as the color coordinates for their visible emission spectra (Fig. 8 and 10), we determined the optimal concentration ratio of Tb³⁺ and Sm³⁺ ions to be 0.83 for the color point to move the closest to the white light region, corresponding to the TNLC-0.5Tb0.6Sm glass sample.

During the analysis of the absorption capacity of the materials in the infrared region, we observed that the material strongly absorbed in the range from 940 to 1070 nm, with a maximum peak at about 980 nm. We surveyed the UC emission process of the Tb³⁺–Sm³⁺–Yb³⁺ co-doped material samples to investigate the ET process between Yb³⁺ ions and Tb³⁺/Sm³⁺

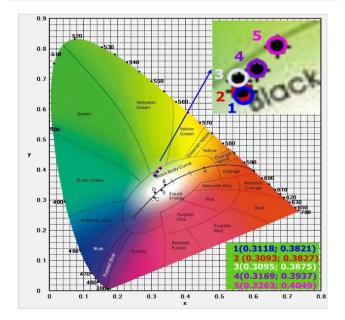


Fig. 10 CIE1931 (x; y) color coordinates for the visible emission spectra of the TNLC-0.5TbqSm (q=0.6,0.7,0.8,0.9, and 1.0 mol%) glass samples under 374 nm excitation.

ions. In addition to investigating the VIS emission spectra of ${\rm Tb}^{3+}{\rm -Sm}^{3+}$ co-doped glass samples, we conducted further investigations using the UC emission spectra of these samples. Fig. 11 shows the UC emission spectra of the TNLC- $p{\rm Tb0.5Sm2Yb}$ ($p=0.5,~0.6,~0.7,~0.8,~{\rm and}~1.0~{\rm mol\%}$) lithiumniobium–tellurite glass samples under a 980 nm laser diode (LD). With the increase in molar concentration of ${\rm Tb}^{3+}$ from 0.5 to 1.0 mol%, the UC emission intensity of the ${\rm Tb}^{3+}$ ion peaks at around 415, 438, 490, 546, and 622 nm increased for the ${\rm Tb}^{3+}{\rm -Sm}^{3+}{\rm -Yb}^{3+}$ co-doped glass samples. Meanwhile, the UC emission intensity of the peaks at around 645 nm, attributed to the ${}^4{\rm G}_{5/2} \rightarrow {}^6{\rm H}_{9/2}$ transition of Sm $^{3+}$ ions, was also increased. This result confirms that energy from the neighboring states of ${\rm Tb}^{3+}$ ions was transferred to the ${}^4{\rm G}_{5/2} \rightarrow {}^6{\rm H}_{9/2}$ transition of Sm $^{3+}$ ions was transferred to the ${}^4{\rm G}_{5/2} \rightarrow {}^6{\rm H}_{9/2}$ transition of Sm $^{3+}$ ions.

Fig. 12 shows the CIE 1931 (x; y) color coordinates for the UC emission spectra of the TNLC-pTb0.5Sm (p = 0.5, 0.6, 0.7, 0.8, and 1.0 mol%) lithium-niobium-tellurite glass samples under a 980 nm LD. With the increase in molar concentration of Tb³⁺ ions from 0.5 to 1.0 mol%, the color points shifted from in the order of points A <math>(0.3277; 0.4847), B (0.2974; 0.5169), C (0.2997; 0.5441), D (0.3050; 0.5676), and E (0.3167; 0.5782) on the CIE 1931 (x; y) color coordinate diagram and were mainly located in the yellowish-green region.

To further determine the roles of excitation wavelength and the molar concentration of the doped RE ions on the CIE 1931 (x; y) color coordinates and color region, we compared the results obtained in this study with previously published reports, as listed in Table 3.

Investigation and calculation of correlated color temperature (CCT) are essential for optimizing the output light quality. From the CIE 1931 (x; y) results, the CCT of the TNLC glass samples was calculated using the McCamy formula (often called McCamy's approximation):^{50,52}

$$CCT = an^{3} + bn^{2} + cn + d \approx -449n^{3} + 3525n^{2} -6823.3n + 5520.33$$
(3)

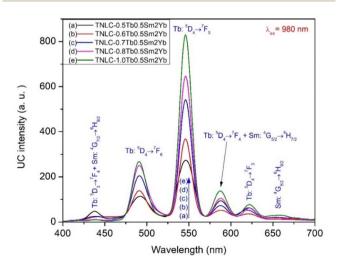


Fig. 11 UC emission spectra of the TNLC-pTb0.5Sm2Yb (p=0.5, 0.6, 0.7, 0.8,and 1.0 mol%) glass samples under 980 nm LD excitation.

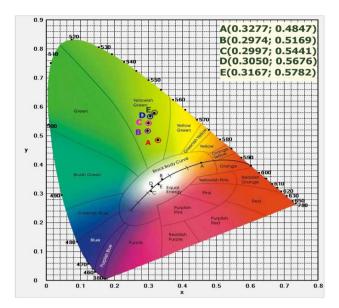


Fig. 12 CIE 1931 (x; y) color coordinates for the UC emission spectra of the TNLC-pTb0.5Sm2Yb (p=0.5, 0.6, 0.7, 0.8, and 1.0 mol%) glass samples excited under a 980 nm LD.

where:

$$n = \frac{x - x_{\rm e}}{y - y_{\rm e}},\tag{4}$$

Here, x and y are the CIE 1931 (x; y) chromaticity coordinates of the light source; $x_{\rm e}=0.3320$ and $y_{\rm e}=0.1858$ are the chromaticity coordinates of the Planckian locus.^{50,52} The CCT calculation results of the as-prepared glass samples are described in detail in Table 4.

The energy level diagram of the visible and UC emissions corresponding to the transitions of the Tb³+-Sm³+ and Tb³+-Sm³+-Yb³+ co-doped glass materials under excitation wavelengths of 374 nm and 980 nm is shown in Fig. 13. The Tb³+ ions are excited from the ground state $^3\mathrm{H}_6$ to the higher-energy state $^3\mathrm{D}_5$. These ions show characteristic emission in the visible region due to $^3\mathrm{D}_5$ and $_4$ \rightarrow $^5\mathrm{F}_{J\ (J=3,\ 4,\ 5,\ and\ 6)}$ transitions. 39 Under 374 nm excitation, the visible emission of Tb³+ peaks at around 490, 546, 587, and 622 nm, which can be attributed to the $^3\mathrm{D}_4$ \rightarrow $^5\mathrm{F}_{J\ (J=6,\ 5,\ 4,\ and\ 3)}$ transitions. The Sm³+ ions, when excited at 374 nm, move from the $^6\mathrm{H}_{5/2}$ ground state to a higher-energy $^6\mathrm{P}_{7/2}$ state. 40 From this $^6\mathrm{P}_{7/2}$ state, energy is transferred to $^4\mathrm{G}_{5/2}$ lower-energy states through non-radiative and ET processes. The ET1, ET2, CET1, and CET2 processes shown in Fig. 13 can be described in detail as follows: 41,51,53

$$\begin{split} &ET1:\, ^5D_4(Tb^{3+}) + \, ^4G_{7/2}(Sm^{3+}) \, \to \, ^5F_6(Tb^{3+}) + \, ^6H_{5/2}(Sm^{3+}). \\ &ET2:\, ^4G_{5/2}(Sm^{3+}) + \, ^5D_4(Tb^{3+}) \, \to \, ^6H_{7/2}(Sm^{3+}) + \, ^7F_6(Tb^{3+}). \\ &CET1:\, 2^2F_{5/2}(Yb^{3+}) + \, ^7F_6(Tb^{3+}) \, \to \, 2^2F_{7/2}(Yb^{3+}) + \, ^5D_4(Tb^{3+}). \\ &CET2:\, 2^2F_{5/2}(Yb^{3+}) + \, ^6H_{5/2}(Sm^{3+}) \, \to \, \\ & 2^2F_{7/2}(Yb^{3+}) + \, ^4I_{11/2}(Sm^{3+}). \end{split}$$

Table 3 Compare the energy transfer processes, color coordinates, and excitation wavelengths of RE ions in this study with those reported in previously published papers

Host material	RE co-doping ratio	λ _{ex} (nm)	Energy transfer	CIE 1931 coordinates $(x; y)$	Color region	References
Tellurite glass	1Ce^{3^+} -1Tb^{3^+} -1Sm^{3^+}	350	$Ce^{3+} \rightarrow Tb^{3+}$	0.3750; 0.3245	Pure white	T. T. Hong et al. 42
LiYF ₄ single crystals	1.24 Tb $^{3+}$ - 1.63 Sm $^{3+}$ - 0.25 Ce $^{3+}$	374	1	0.3084; 0.3612	Yellowish-green	Y. Z. Jiang et al. 43
Ba ₃ MgSi ₂ O ₈ :phosphors	$0.12 \mathrm{Tb}^{3+} - 0.05 \mathrm{Sm}^{3+}$	233	$Tb^{3+} \rightarrow Sm^{3+}$	0.555; 0.425	Orange yellow	X. K. Sun et al. 44
Phosphate glasses	$0.5 \mathrm{Sm}^{3+} - 0.1 \mathrm{Tb}^{3+}$	374	$\mathrm{Tb}^{3+} \rightarrow \mathrm{Sm}^{3+}$	0.541; 0.300	Reddish-orange	K. A. Kumar et al. ³⁷
	$1.0 \mathrm{Sm}^{3+} - 0.1 \mathrm{Tb}^{3+}$			0.551; 0.312		
Zinc phosphate glasses	$0.5 \mathrm{Sm}^{3+} - 1.0 \mathrm{Tb}^{3+}$	361	$Tb^{3+} \rightarrow Sm^{3+}$	0.448; 0.459	Greenish-yellow	A. N. Meza-Rocha et al. 45
		374		0.407; 0.485	Yellow	
CaWO ₄ nanoparticles	$0.5 \mathrm{Sm}^{3+} - 0.5 \mathrm{Tb}^{3+}$	355	I	0.3098; 0.4033	White	N. F. Andrade Neto et al. 46
	$1.0 \mathrm{Sm}^{3+} - 1.0 \mathrm{Tb}^{3+}$	355		0.3002; 0.3997	Blue	
$Ca_2La_3(SiO_4)_3F$ phosphor	$0.15 \mathrm{Tb}^{3+}, 0.04 \mathrm{Sm}^{3+}$	377	$Tb^{3+} \rightarrow Sm^{3+}$	0.4175; 0.5658	Yellow-green	K. Nie <i>et al.</i> ⁴⁷
	$0.15 \mathrm{Tb}^{3+} - 0.18 \mathrm{Sm}^{3+}$	377		0.4691; 0.5160	Greenish-yellow	
$CaLa_4(SiO_4)_3O$:phosphors	$9\% \mathrm{Tb^{3^+}} - 11\% \mathrm{Sm^{3^+}}$	377	$Tb^{3+} \rightarrow Sm^{3+}$	0.393; 0.387	Bright white	B. Yuan <i>et al.</i> ⁴⁸
$K_3Gd(PO_4)_2$ crystalline	$0.3\% \text{Tb}^{3+}$ $-0.4\% \text{Sm}^{3+}$	376	$Tb^{3+} \rightarrow Sm^{3+}$	0.3201; 0.3297	White	Y. N. Guo et al. 49
glass ceramics						
$\overline{\mathrm{K}_2\mathrm{Y}(\mathrm{WO}_4)(\mathrm{PO}_4)}$ phosphors	$2\% \text{Sm}^{3+} - 5\% \text{Tb}^{3+}$	377	$\text{Sm}^{3+} \rightarrow \text{Tb}^{3+}$	0.37; 0.57	Yellow-green	E. J. Ansari et al. ⁵⁰
Potassium-zinc phosphate	$1.0 \mathrm{Sm}^{3+} - 1.0 \mathrm{Tb}^{3+}$	344	$Tb^{3+} \rightarrow Sm^{3+}$	0.529; 0.447	Orange	O. Soriano-Romero et al. ⁵¹
glasses	$1.0 \mathrm{Sm}^{3+} - 1.0 \mathrm{Tb}^{3+}$	360	$Tb^{3+} \rightarrow Sm^{3+}$	0.534; 0.442	Yellow	
	$1.0 \mathrm{Sm}^{3^+} - 1.0 \mathrm{Tb}^{3^+}$	377	$Tb^{3+} \rightarrow Sm^{3+}$	0.442; 0.507	Yellow	
Lithium-niobium-tellurite	$0.5 \mathrm{Tb}^{3+} - 0.6 \mathrm{Sm}^{3+}$	374	$Tb^{3+} \leftrightarrow Sm^{3+}$	0.3118; 0.3821	White	This study
glass					(near black body curve)	
	$0.5 \mathrm{Tb}^{3+} - 0.5 \mathrm{Sm}^{3+} - 2 \mathrm{Yb}^{3+}$	086	$Yb^{3+} \rightarrow Tb^{3+}$ $Yb^{3+} \rightarrow Sm^{3+}$	0.3277; 0.4847	Yellowish-green	

Table 4 CCT values and CIE 1931 (x; y) chromaticity coordinates of the TNLC glass samples

Glass samples	λ_{ex}	Color point	CIE 1931 <i>x</i>	CIE 1931 y	CCT (K)	Color region
TNLC-0.5Tb	374 nm	P_{Tb}	0.2840	0.5303	6544	Yellowish green
TNLC-0.5Tb0.5Sm	374 nm	P_{Tb-Sm}	0.2901	0.3728	7208	White
TNLC-0.5Sm	374 nm	P_{Sm}	0.4906	0.3537	15 489	Yellowish pink
TNLC-0.6Tb0.5Sm	374 nm	P1	0.2838	0.3601	7662	Green
TNLC-0.7Tb0.5Sm	374 nm	P2	0.2864	0.3801	7294	Green
TNLC-0.8Tb0.5Sm	374 nm	P3	0.2878	0.3912	7129	Green
TNLC-0.9Tb0.5Sm	374 nm	P4	0.2857	0.3834	7290	Green
TNLC-1.0Tb0.5Sm	374 nm	P5	0.2861	0.4041	7085	Green
TNLC-0.5Tb0.6Sm	374 nm	1	0.3118	0.3821	6254	White
TNLC-0.5Tb0.7Sm	374 nm	2	0.3093	0.3827	6347	White
TNLC-0.5Tb0.8Sm	374 nm	3	0.3095	0.3875	6318	White
TNLC-0.5Tb0.9Sm	374 nm	4	0.3169	0.3937	6033	White
TNLC-0.5Tb1.0Sm	374 nm	5	0.3263	0.4049	5706	White
TNLC-0.5Tb0.5Sm2Yb	980 nm	A	0.3277	0.4847	5616	Yellowish green
TNLC-0.6Tb0.5Sm2Yb	980 nm	В	0.2974	0.5169	6274	Yellowish green
TNLC-0.7Tb0.5Sm2Yb	980 nm	C	0.2997	0.5441	6165	Yellowish green
TNLC-0.8Tb0.5Sm2Yb	980 nm	D	0.3050	0.5676	6020	Yellow
TNLC-1.0Tb0.5Sm2Yb	980 nm	E	0.3167	0.5782	5790	Yellowish green

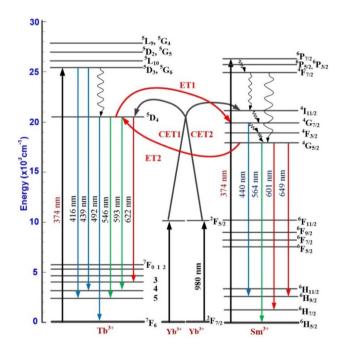


Fig. 13 Energy levels of the ${\rm Tb}^{3+}$, ${\rm Sm}^{3+}$, and ${\rm Yb}^{3+}$ ions and the mechanisms of visible and UC emissions via CET1, CET2, ET1, and ET2 processes in the TNLC glass system.

The charge transfer process between the Tb³+ and Sm³+ ions depends on the concentration of optical centers in the material. To further investigate the influence of Tb³+ ion concentration on the ET process, we analyzed the decay lifetimes of Tb³+ and Sm³+ ions in the synthesized TNLC glass materials. We measured the time-resolved fluorescence spectra of TNLC-0.5TbqSm ($q=0,\ 0.6,\ 0.7,\ 0.8,\ 0.9,\ and\ 1.0\ mol%)$ lithium-niobium-tellurite glass samples using an excitation wavelength of 374 nm and emission at 546 nm corresponding to the $^5\mathrm{D}_4 \rightarrow ^5\mathrm{F}_6$ transition of Tb³+;4,32-34 the obtained results are presented in

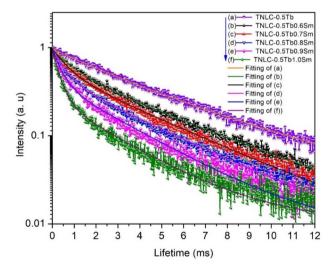


Fig. 14 Decay lifetimes of Tb³⁺ at the $^5D_4 \rightarrow ^5F_6$ transition in TNLC-0.5TbqSm ($q=0,\,0.6,\,0.7,\,0.8,\,0.9,$ and 1.0 mol%) glass samples under 374 nm excitation.

Fig. 14. Through the fitting process, we observed that the time-resolved fluorescence spectra of the materials followed the equation:^{16,50}

$$I_t = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right),\tag{5}$$

where τ_1 and τ_2 are the decay lifetime components, and A_1 and A_2 are constants. The average decay lifetime τ was calculated as follows: $^{\mathbf{16},51,54,55}$

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}.$$
(6)

The decay lifetimes of TNLC-0.5TbqSm (q = 0, 0.6, 0.7, 0.8, 0.9,and 1.0 mol%) lithium–niobium–tellurite glass samples

Table 5 Decay lifetimes of Tb $^{3+}$ ions at 546 nm ($^5D_4 \rightarrow ^5F_6$) and Sm $^{3+}$ ions at 564 nm ($^4G_{5/2} \rightarrow ^6H_{5/2}$) under 374 nm excitation

Glass sample	Decay lifetime (ms)
TNLC-0.5Tb	4.62
TNLC-0.5Tb0.6Sm	3.97
TNLC-0.5Tb0.7Sm	3.48
TNLC-0.5Tb0.8Sm	3.13
TNLC-0.5Tb0.9Sm	2.63
TNLC-0.5Tb1.0Sm	2.21
TNLC-0.5Sm	7.86
TNLC-0.6Tb0.5Sm	6.91
TNLC-0.7Tb0.5Sm	5.63
TNLC-0.8Tb0.5Sm	4.24
TNLC-0.9Tb0.5Sm	3.18
TNLC-1.0Tb0.5Sm	2.56

calculated according to formula (6) are listed in Table 5. The decay lifetimes at 546 nm, corresponding to the ${}^5D_4 \rightarrow {}^5F_6$ transition of Tb^{3+} ions in the TNLC-0.5TbqSm (q = 0, 0.6, 0.7,0.8, 0.9, and 1.0 mol%) lithium-niobium-tellurite glass samples, were found to decrease with increasing Sm³⁺ concentration. This is strong evidence for ET from Tb3+ to Sm3+ ions. 4,32-34,44 Similarly, the decay lifetimes of Sm3+ ions at 601 nm, corresponding to the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm³⁺ ions^{4,32-34} in the TNLC-pTb0.5Sm (p = 0, 0.6, 0.7, 0.8, 0.9, and1.0 mol%) lithium-niobium-tellurite glass samples, were measured under 374 nm excitation, as shown in Fig. 15. The average decay lifetimes of TNLC-pTb0.5Sm (p = 0, 0.6, 0.7, 0.8,0.9, and 1.0 mol%) lithium-niobium-tellurite glass samples were calculated, as presented in Table 5. The decay lifetimes of ${\rm Sm^{3+}}$ at 601 nm, corresponding to ${}^4{\rm G}_{5/2} \rightarrow {}^6{\rm H}_{7/2}$ transition of Sm³⁺ ions^{32,33} in these glass samples under 374 nm excitation were found to decrease with increasing Tb3+ concentration in the glass samples, further proving ET from Sm³⁺ to Tb³⁺ ions.33,34,39,40

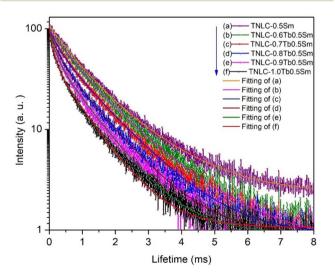


Fig. 15 Decay lifetimes of Sm $^{3+}$ at the $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition in TNLC-pTb0.5Sm ($p=0,\,0.6,\,0.7,\,0.8,\,0.9,\,$ and 1.0 mol%) glass samples under 374 nm excitation.

To evaluate the energy transfer efficiency (ETE) between Tb³⁺ and Sm³⁺ ions, we carried out ETE calculations for these ET processes. The ETE from Tb³⁺ to Sm³⁺ ions is denoted as $\eta_{\text{ET(Tb} \rightarrow \text{Sm)}}$ and was estimated using the luminescence lifetimes of the donor (Tb³⁺) in the presence and absence of the acceptor (Sm³⁺), according to the following equation:

$$\eta_{\text{ET(Tb}\to\text{Sm)}} = 1 - \frac{\tau_{\text{Tb}-\text{Sm}}}{\tau_{\text{Tb}}},\tag{7}$$

where τ_{Tb} is the luminescence lifetime of Tb^{3+} ions in the absence of Sm^{3+} ions, and $\tau_{\text{Tb-Sm}}$ is the luminescence lifetime of Tb^{3+} ions in the presence of Sm^{3+} ions (*i.e.* when energy transfer occurs).

Similarly, the ETE from Sm^{3+} to Tb^{3+} ions is denoted as $\eta_{\text{ET(Sm} \to \text{Tb)}}$ and was estimated using the luminescence lifetimes of the donor (Sm^{3+}) in the presence and absence of the acceptor (Tb^{3+}), according to the following equation:

$$\eta_{\text{ET(Sm}\to\text{Tb)}} = 1 - \frac{\tau_{\text{Sm}-\text{Tb}}}{\tau_{\text{Sm}}},\tag{8}$$

where τ_{Sm} is the luminescence lifetime of Sm³⁺ ions in the absence of Tb³⁺ ions, and τ_{Sm-Tb} is the luminescence lifetime of Sm³⁺ ions in the presence of Tb³⁺ ions. Based on the results presented in Table 5, we calculated ETE values to be 52.26% and 67.43% for the ET processes from Tb³⁺ to Sm³⁺ ions and from Sm³⁺ to Tb³⁺ ions, respectively.

4. Conclusions

In this study, a series of Tb³⁺-doped, Sm³⁺-doped, Tb³⁺-Sm³⁺ codoped, and Tb³⁺-Sm³⁺-Yb³⁺ tri-doped lithium-niobium-tellurite TeO2-Nb2O5-LiO2-CaO glasses were synthesized via conventional melt-quenching. These glasses exhibited tunable multicolor emissions under excitation at 374 nm and 980 nm, which could be attributed to Sm3+ (yellow-pink), Tb3+ (yellowish-green), and Yb³⁺-sensitized UC emissions of Tb³⁺-Sm³⁺-Yb³⁺ tri-doped glass materials. The DTA analysis showed the high thermal stability of the tri-doped glass, with $\Delta T = 151$ °C, suitable for heat treatment and mechanical durability. The emission color could be effectively controlled by varying the Sm³⁺-Tb³⁺ concentrations and excitation wavelengths. The optimal Tb³⁺/Sm³⁺ molar ratio was 0.83 in the TNLC-0.5Tb0.6Sm sample for achieving CIE coordinates closest to white light emission. Spectral and lifetime measurements confirmed ETE between Tb³⁺ and Sm³⁺ ions. The combination of low phonon energy, high stability, emission tunability, and efficient ET highlights the potential of Tb³⁺-Sm³⁺ co-doped and Tb3+-Sm3+-Yb3+ tri-doped TNLC glasses for application in advanced color display and solid-state lighting devices, including WLEDs.

Data availability

The authors confirm that the data supporting the findings of this study are available from the corresponding author upon request.

Conflicts of interest

There are no conflicts of interest to declare.

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References

- 1 G. J. Li, M.-C. Tseng, Y. Chen, F. S.-Y. Yeung, H. Y. He, Y. C. Cheng, J. H. Cai and E. G. Chen, Color-conversion displays: current status and future outlook, *Light:Sci. Appl.*, 2024, 13, 301, DOI: 10.1038/s41377-024-01618-8.
- 2 J. C. Chen, Q. L. Zhao, B. H. Yu and U. Lemmer, A review on quantum dot-based color conversion layers for mini/micro-LED displays: Packaging, light management, and pixelation, *Adv. Opt. Mater.*, 2024, 12, 2300873, DOI: 10.1002/adom.202300873.
- 3 M. Vasilopoulou, A. R. B. M. Yusoff, M. Daboczi, J. Conforto, A. E. X. Gavim, W. J. D. Silva, A. G. Macedo, A. Soultati, G. Pistolis, F. K. Schneider, Y. F. Dong, P. Jacoutot, G. Rotas and J. Jang, High efficiency blue organic light-emitting diodes with below-bandgap electroluminescence, *Nat. Commun.*, 2021, 12, 4868, DOI: 10.1038/s41467-021-25135-z.
- 4 T. Q. Sheng, Z. L. Fu, X. J. Wang, S. H. Zhou, S. Y. Zhang and Z. W. Dai, Solvothermal synthesis and luminescence properties of BaCeF₅, and BaCeF₅: Tb³⁺, Sm³⁺ Nanocrystals: An approach for white light emission, *J. Phys. Chem. C*, 2012, 36(116), 19597–19603, DOI: 10.1021/jp306935k.
- 5 J. S. Alzahrani, Z. A. Alrowaili, A. V. Lebedev, I. O. Olarinoye, A. Hammoud, L. V. Vasileva and M. S. Al-Buriahi, Optical properties and radiation shielding performance of tellurite glassy composites: role of rare earth oxides, *Radiat. Phys. Chem.*, 2023, 212, 111168, DOI: 10.1016/j.radphyschem.2023.111168.
- 6 J. E. Stanworth, Tellurite glasses, *Nature*, 1952, 169, 581–582,
 DOI: 10.1038/169581b0.
- 7 R. El-Mallawany, The optical properties of tellurite glasses, *J. Appl. Phys.*, 1992, 72, 1774–1777, DOI: **10.106**3/**1.351649**.
- 8 J. Lousteau, D. Milanese, S. Abrate, N. Boetti, M. Pittarelli, S. Barbero and M. Ferrari, Exploring the influence of ZnF₂ on zinc-tellurite glass: unveiling changes in OH content, structure, and optical properties, *ACS Omega*, 2023, 8(38), 35266–35274, DOI: 10.1021/acsomega.3c05010.
- 9 J. Biswas, S. Jana and S. Ghosh, Investigation on luminescence characteristics of Dy³⁺–Tb³⁺ co-doped phospho-tellurite glasses for tunable green/white LED applications, *Spectrochim. Acta, Part A*, 2025, **331**, 125756, DOI: **10.1016/j.saa.2025.125756**.
- 10 V. K. Rai, S. B. Rai and D. K. Rai, Optical properties of Tb³⁺ doped tellurite glass, *J. Mater. Sci.*, 2004, **39**, 4971–4975, DOI: **10.1023/B:JMSC.0000035348.82074.0a**.
- 11 K. S. Rudramamba, S. K. Taherunnisa, D. V. K. Reddy, N. Veeraiah and M. R. Reddy, The structural and warm light emission properties of Sm³⁺/Tb³⁺ doubly doped strontium bismuth borosilicate glasses for LED applications, *Spectrochim. Acta, Part A*, 2019, **220**, 117097, DOI: **10.1016/j.saa.2019.05.002**.

- 12 M. Vijayakumar and K. Marimuthu, Effect of Tb³⁺ concentration on Sm³⁺ doped leadfluoro-borophosphate glasses for WLED applications, *J. Non-Cryst. Solids*, 2016, 447, 45–54, DOI: 10.1016/j.jnoncrysol.2016.05.028.
- 13 G. Lakshminarayana, A. N. Meza-Rocha, O. Soriano-Romero, E. F. Huerta, U. Caldiño, A. Lira, D.-E. Lee, J. H. Yoon and T. J. Park, Analysis of fluorescence characteristics of Sm³⁺doped B₂O₃-rich glasses for Orange-light-emitting diodes, J. Alloys Compd., 2021, 884, 161076, DOI: 10.1016/ j.jallcom.2021.161076.
- 14 A. U. Trápala-Ramírez, J. L. N. Gálvez-Sandoval, A. Lira, I. Camarillo, E. Alvarez-Ramos, A. N. Meza-Rocha and U. Caldiño, Calcium-zinc phosphate glasses activated with Tb³⁺/Eu³⁺ for laser and white LED applications, *J. Lumin.*, 2019, 215, 116621, DOI: 10.1016/j.jlumin.2019.116621.
- 15 H. K. Dan, D. C. Zhou, R. F. Wang, Q. Jiao, Z. W. Yang, Z. G. Song, X. Yu and J. B. Qiu, Effect of Mn²⁺ ions on the enhancement upconversion emission and energy transfer of Mn²⁺/Tb³⁺/Yb³⁺ tri-doped transparent glass-ceramics, *Mater. Lett.*, 2015, 150, 76–80, DOI: 10.1016/j.matlet.2015.03.005.
- 16 P. X. Le, N. M. Ty, J. B. Qiu, D. C. Zhou and H. K. Dan, Enhanced upconversion and near-infrared emissions of codoped Ho³⁺/Yb³⁺ in TeO₂-ZnO-Na₂CO₃-La₂O₃ tellurite glasses, *Opt. Mater. Express*, 2019, 9, 3998–4008, DOI: 10.1364/OME.9.003998.
- 17 A. Roy, A. Dwivedi, H. Mishra, A. K. Rai and S. B. Rai, Generation of color tunable emissions from Ho³⁺/Tm³⁺/Yb³⁺ co-doped YTaO₄ phosphors through NIR excitation under different conditions (variation of concentration, excitation pump power and the external temperature), *J. Alloys Compd.*, 2021, 865, 158938, DOI: 10.1016/j.jallcom.2021.158938.
- 18 P. Dharmaiah, C. S. Dwaraka Viswanath, C. Basavapoornima, K. V. Krishnaiah, C. K. Jayasankar and S.-J. Hong, Luminescence and energy transfer in Dy³⁺/Tb³⁺ co-doped transparent oxyfluorosilicate glass-ceramics for green emitting applications, *Mater. Res. Bull.*, 2016, 83, 507–514, DOI: 10.1016/j.materresbull.2016.06.044.
- 19 H. K. Dan, N. D. Trung, T. H. Le, N. L. Thai, N. M. Ty, D. C. Zhou and J. B. Qiu, Influence of F⁻ on the reduction process of Eu³⁺ to Eu²⁺ and optical properties of Eu³⁺/Eu²⁺-Er³⁺-Yb³⁺ co-doped niobate silicate glasses, *J. Non-Cryst. Solids*, 2022, 581, 121417, DOI: 10.1016/j.jnoncrysol.2022.121417.
- 20 J. Dahiya, A. Hooda, A. Agarwal and S. Khasa, Effect of Dysprosium and Samarium RE ion co-doping on photoluminescence behaviour of novel alkali fluoride bismuth borate glasses: A white LED material, *Opt. Mater.*, 2022, **134**, 113162, DOI: **10.1016/j.optmat.2022.113162**.
- 21 F. Nawaz, M. R. Sahar and S. K. Ghoshal, The influence of Yb co-doping on optical properties of Sm-doped sodium tellurite glasses, *Adv. Mater. Res.*, 2014, 895, 359–362, DOI: 10.4028/www.scientific.net/AMR.895.
- 22 J. Li, D. Zhang, Y. X. Wu, L. L. Li, X. L. Zhang, S. Q. Xu and J. J. Zhang, Multi-color afterglow of the $LiGa_5O_8$: Tb^{3+}/Sm^{3+} co-doped gallosilicate glass *via* energy transfer and trap

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sharing for optical anti-counterfeiting, *J. Mater. Chem. C*, 2024, **12**, 15733–15738, DOI: **10.1039/D4TC03171G**.

- 23 N. Elkhoshkhany, R. Essam and E. Sayed Yousef, Influence of La₂O₃ on the structural, optical and thermal properties of TeO₂–ZnO–Li₂O–Nb₂O₅ glass, *J. Non-Cryst. Solids*, 2020, 536, 119994, DOI: 10.1016/j.jnoncrysol.2020.119994.
- 24 N. Elkhoshkhany, S. Y. Marzouk, N. Moataz and S. H. Kandil, Structural and optical properties of TeO₂–Li₂O–ZnO–Nb₂O₅–Er₂O₃ glass system, *J. Non-Cryst. Solids*, 2018, **500**, 289–301, DOI: **10.1016/j.jnoncrysol.2018.08.011**.
- 25 H. Benrejeb, K. Soler-Carracedo, A. D. Lozano-Gorrín, S. Hraiech and I. R. Martin, Energy transfer studies in Tb³⁺-Yb³⁺ co-doped phosphate glasses, *Mater.*, 2021, 14(22), 6782, DOI: 10.3390/ma14226782.
- 26 H. K. Dan, N. M. Ty, V. H. Nga, D. T. Phuc, A.-L. Phan, D. C. Zhou and J. B. Qiu, Broadband flat near-infrared emission and energy transfer of Pr³⁺-Er³⁺-Yb³⁺ tri-doped niobate tellurite glasses, *J. Non-Cryst. Solids*, 2020, 549, 120335, DOI: 10.1016/j.jnoncrysol.2020.120335.
- 27 D. C. Zhou, R. F. Wang, Z. W. Yang, Z. G. Song, Z. Y. Yin and J. B. Qiu, Spectroscopic properties of Tm³⁺ doped TeO₂-R₂O-La₂O₃ glasses for 1.47 μm optical amplifiers, *J. Non-Cryst. Solids*, 2011, 357, 2409–2412, DOI: 10.1016/j.jnoncrysol.2010.12.027.
- 28 R. El-Mallawany, Tellurite glasses Part 2. Anelastic, phase separation, Debye temperature and thermal properties, *Mater. Chem. Phys.*, 1999, **60**, 103–131, DOI: **10.1016/S0254-0584(99)00082-6**.
- 29 G. V. Prakash, D. N. Rao and A. K. Bhatnagar, Linear optical properties of niobium-based tellurite glass, *Solid State Commun.*, 2001, 119(1), 39–44, DOI: 10.1016/S0038-1098(01)00195-8.
- 30 H. K. Dan, N. M. Ty, T. D. Tap, D.-N. Le, L. T. Vinh, D. C. Zhou and J. B. Qiu, Energy transfer and spectroscopic properties of Cr³⁺/Yb³⁺ co-doped TeO₂–ZnO–La₂O₃ tellurite glasses under different wavelength excitation lights, *Opt. Mater.*, 2020, **100**, 109662, DOI: **10.1016/j.optmat.2020.109662**.
- 31 H. K. Dan, D. C. Zhou, R. F. Wang, T. M. Hau, Q. Jiao, Z. W. Yang, Z. G. Song, X. Yu and J. B. Qiu, Energy transfer and upconversion emission of Tm³⁺/Tb³⁺/Yb³⁺ co-doped transparent glass-ceramics containing Ba2LaF7 nanocrystals, *J. Non-Cryst. Solids*, 2013, 378, 181–185, DOI: 10.1016/j.jnoncrysol.2013.07.006.
- 32 C. Jin, J. Zhang, W. D. Lu and Y. T. Fei, Tunable luminescence of $LiY_9(SiO_4)_6O_2$: $Ce^{3+}-Tb^{3+}-Sm^{3+}$ phosphors for LED and temperature-sensing applications, *J. Lumin.*, 2019, 214, 116581, DOI: 10.1016/j.jlumin.2019.116581.
- 33 Y. N. Guo, Q. W. Wang, X. Y. Zhao, L. P. Wang, Y. Wan, H. Zhang and C. Su, Preparation and luminescence properties of Tb³⁺-Sm³⁺ co-doped K₃Gd(PO₄)₂ crystalline glass ceramics, *Opt. Mater.*, 2024, **148**, 114830, DOI: **10.1016/j.optmat.2024.114830**.
- 34 Le-Q. Yao, G.-H. Chen, T. Yang, Y. Luo and Y. Yang, Optical properties and energy transfer in Tb³⁺/Sm³⁺ co-doped Na₂O-CaO-P₂O₅-B₂O₃-ZrO₂ glasses, *J. Alloys Compd.*, 2017, **692**, 346–350, DOI: **10.1016/j.jallcom.2016.09.053**.

- 35 H. K. Dan, A. L. Phan, N. M. Ty, D. C. Zhou and J. B. Qiu, Optical bandgaps and visible/near-infrared emissions of Biⁿ⁺-doped (n=1, 2, and 3) fluoroaluminosilicate glasses via Ag^+ - K^+ ions exchange process, *Opt. Mater.*, 2021, 112, 110762, DOI: 10.1016/j.optmat.2020.110762.
- 36 P. T. Phong, P. H. Nam, N. X. Phuc, B. T. Huy, L. T. Lu, D. H. Manh and I.-J. Lee, Effect of zinc concentration on the structural, optical, and magnetic properties of mixed Co–Zn ferrites nanoparticles synthesized by low-temperature hydrothermal method, *Metall. Mater. Trans. A*, 2019, 50, 1571–1581, DOI: 10.1007/s11661-018-5096-z.
- 37 K. A. Kumar, S. Babu, V. R. Prasad, S. Damodaraiah and Y. C. Ratnakaram, Optical response and luminescence characteristics of Sm³⁺ and Tb³⁺/Sm³⁺ co-doped potassium-fluoro-phosphate glasses for reddish-orange lighting applications, *Mater. Res. Bull.*, 2017, **90**, 31–40, DOI: **10.1016/j.materresbull.2017.01.046**.
- 38 V. Lakkamraju, K. N. Kumar and H. Pyung, Unravelling the process of energy transfer and color tuning from warm to cool white light emission in (Tb/Sm): lithium borate glasses, *Opt. Lett.*, 2019, 44(20), 5029–5032, DOI: 10.1364/OL.44.005029.
- 39 C. G. Pérez-Hernández, R. Sánchez-Zeferino, U. Salazar-Kuri and M. E. Álvarez-Ramos, Fabrication, structural properties, and tunable light emission of Sm³⁺, Tb³⁺ co-doped SrSnO₃ perovskite nanoparticles, *Chem. Phys.*, 2021, **551**, 111324, DOI: **10.1016/j.chemphys.2021.111324**.
- 40 A. Bahadur, R. S. Yadav, R. V. Yadav and S. B. Rai, Multimodal emissions from Tb³⁺/Yb³⁺ co-doped lithium borate glass: upconversion, downshifting and quantum cutting, *J. Solid State Chem.*, 2017, **246**, 81–86, DOI: **10.1016/j.jssc.2016.11.004**.
- 41 S. Pandey, A. Pandey and V. K. Rai, Synthesis and Characterization of Sm³⁺–Yb³⁺ codoped Y₂O₃ Phosphor, *J. Disp. Technol.*, 2013, **9**(12), 989–994. https://doi:10.1016/s0038-1098(01)00195-8.
- 42 T. T. Hong, P. D. H. Yen, V. X. Quang and P. T. Dung, Luminescence properties of Ce/Tb/Sm co-doped tellurite glass for white LEDS application, *Mater. Trans.*, 2015, 56(9), 1419–1421, DOI: 10.2320/matertrans.MA201509.
- 43 Y. Z. Jiang, H. P. Xia, L. Fu, J. Z. Zhang, S. Yang, X. M. Gu, J. L. Zhang, Y. P. Zhang, D. J. Wang, H. C. Jiang and B. J. Chen, Growth and Optical Spectra of Tb³⁺/Sm³⁺/Ce³⁺ Triply doped LiYF₄ single crystals for White-Light LEDs, *Nanosci. Nanotechnol.*, 2016, 16, 1532–1536, DOI: 10.1166/jnn.2016.10803.
- 44 X. K. Sun, Z. Z. Huang, Y. H. Guo, S. H. Zhou and K. L. Liu, $Tb^{3+} \rightarrow Sm^{3+}$ energy transfer induced tunable luminescence in $Ba_3MgSi_2O_8:Tb^{3+}/Sm^{3+}$ phosphors, *J. Lumin.*, 2020, 219, 116925, DOI: 10.1016/j.jlumin.2019.116925.
- 45 A. N. Meza-Rocha, G. Muñoz H, A. Speghini, M. Bettinelli and U. Caldiño, Neutral and warm white light emission in Tb³⁺/Sm³⁺ zinc phosphate glasses, *Opt. Mater.*, 2015, 47, 537–542, DOI: 10.1016/j.optmat.2015.06.035.
- 46 N. F. Andrade Neto, J. M. P. Silva, R. L. Tranquilin, E. Longo, J. F. M. Domenegueti, M. R. D. Bomio and F. V. Motta, Photoluminescent properties of Sm³⁺ and Tb³⁺ codoped

- CaWO₄ nanoparticles obtained by a one-step sonochemical method, *J. Mater. Sci.: Mater. Electron.*, 2020, **31**, 13261–13272, DOI: **10.1007/s10854-020-03878-7**.
- 47 K. Nie, R. R. Zhou, C.-A. Cheng, X. Q. Duan, Z. Y. Hu, L. F. Mei, H. K. Liu, L. X. Wang, H. Wang and X. X. Ma, Tb³⁺ and Sm³⁺ co-doped Ca₂La₃(SiO₄)₃F phosphor: Synthesis, color regulation, and luminescence properties, *RSC Adv.*, 2022, 12, 33200–33206, DOI: 10.1039/D2RA06648C.
- 48 B. Yuan, J. X. Gou, C. C. Qi, L. Kong, M. Y. Qu, G. Y. Luan and X. T. Zhang, Energy transfer for Ce³⁺/Tb³⁺/Sm³⁺ induced bright white emission in single-phase CaLa₄(SiO₄)₃O: Ce³⁺, Tb³⁺, Sm³⁺ phosphors and their application in white-light-emitting diodes, *RSC Adv.*, 2024, **14**, 7061–7072, DOI: **10.1039**/D4RA00443D.
- 49 Y. N. Guo, Q. W. Wang, X. Y. Zhao, L. P. Wang, Y. C. Wan, H. B. Zhang and C. H. Su, Preparation and luminescence properties of Tb³⁺-Sm³⁺ co-doped K₃Gd(PO₄)₂ crystalline glass ceramics, *Opt. Mater.*, 2024, **148**, 114830, DOI: **10.1016/j.optmat.2024.114830**.
- 50 E. J. Ansari, S. Patle, A. R. Pusdekar, N. S. Ugemuge and A. Selokar, Structural and spectroscopic analysis of K₂Y(WO₄)(PO₄): Sm³⁺, Tb³⁺ phosphors for optical applications, *Spectrochim. Acta Part A Mol. Spectrosc.*, 2025, 126269, DOI: 10.1016/j.saa.2025.126269,https://www.sciencedirect.com/journal/spectrochimica-acta-part-a-

molecular-and-biomolecular-spectroscopy/vol/339/suppl/C339.

- 51 O. Soriano-Romero, E. F. Huerta, A. N. Meza-Rocha and U. Caldiño, Orange and yellow emissions through Sm³⁺ and Tb³⁺/Sm³⁺ doped potassium-zinc phosphate glasses for WLED applications, *Ceram. Interfaces*, 2023, **49**, 36353–36359, DOI: **10.1016**/j.ceramint.2023.08.319.
- 52 J. Hernández-Andrés, R. L. Lee and J. Romero, Calculating correlated color temperatures across the entire gamut of daylight and skylight chromaticities, *Appl. Opt.*, 1999, 38(27), 5703–5709, DOI: 10.1364/AO.38.005703.
- 53 M. E. Alvarez-Ramos, J. Alvarado-Rivera, M. E. Zayas, U. Caldiño and J. Hernández-Paredes, Yellow to orange-reddish glass phosphors: Sm³⁺, Tb³⁺ and Sm³⁺/Tb³⁺ in zinc tellurite-germanate glasses, *Opt. Mater.*, 2018, **112**, 88–93, DOI: **10.1016/j.optmat.2017.09.033**.
- 54 X. S. Qiao, X. P. Fan, Z. Xue and X. H. Xu, Short-wavelength upconversion luminescence of Yb³⁺/Tm³⁺ co-doped glass ceramic containing SrF₂ nanocrystals, *J. Non-Cryst. Solids*, 2011, 357(1), 83–87, DOI: 10.1016/j.jnoncrysol.2010.09.008.
- 55 D. T. Khan, N. T. Dang, S. H. Jabarov, T. G. Naghiyev, R. M. Rzayev, T. Q. Nguyen, H. V. Tuyen, N. T. Thanh and L. V. T. Son, Study on luminescent properties of Tb³⁺ and Sm³⁺ co-doped CaSiO3 phosphors for white light emitting diodes, *Mater. Res. Express*, 2020, 7, 016507, DOI: 10.1088/ 2053-1591/ab5ab8.