

Enhancement of orange-red emission and thermal stability of double perovskite $\text{Cd}_2\text{CaTeO}_6\text{:Sm}^{3+}$ phosphors via charge compensation

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ABSTRACT

A novel orange-red tellurate phosphor, $\text{Cd}_2\text{CaTeO}_6\text{:Sm}^{3+}$ (CCTO:Sm³⁺), was synthesized via a high-temperature solid-state method. The phase purity, luminescent properties and thermostability of the produced phosphors were assessed. The CCTO:Sm³⁺ phosphors emit orange-red light (600 nm) upon 406 nm excitation due to the ⁴G_{5/2} → ⁶H_{7/2} transition. The optimal Sm³⁺ doping concentration was 5 mol%. The chromaticity coordinates for CCTO:5 mol%Sm³⁺ were (0.622, 0.378), achieving 100% color purity. CCTO:2 mol%Sm³⁺ exhibited anomalous thermal quenching, where the luminescence intensity increasing by 5.9% as the temperature rises from 300 K to 320 K. The Na⁺ co-doped phosphor exhibited an emission intensity 1.9 times that of CCTO:5 mol%Sm³⁺, and its residual luminescent intensity at 420 K reached 99.7%. The temperature sensor sensitivities *FIR* of *I*₅₆₈/*I*₆₀₃ reached their maximum values at 480 K, with 0.0014 K⁻¹ (*S_a*) and 0.44% K⁻¹ (*S_r*). It was incorporated into a white light-emitting diode (WLED), demonstrating a high color rendering index of 87, an appropriate correlated color temperature of 5886 K, and Commission International de L' Eclairage (CIE) color coordinates of (0.324, 0.337). These characteristics suggest that CCTO:Sm³⁺ can serve as a potential candidate for specialized optoelectronic applications based on NUV-driven WLEDs and possesses potential feasibility for optical temperature sensing.

1. Introduction

WLEDs have emerged as critical energy-saving devices, experiencing extensive deployment across various applications due to their numerous advantages. These benefits include environmental sustainability, minimal energy usage, elevated luminescent efficacy, as well as safety and eco-friendliness [1,2]. In the conventional production of WLEDs, commercial yellow phosphor in conjunction with gallium nitride (GaN) blue-emitting chips are typically employed. This approach, while demonstrating efficiency and simplicity, results in the absence of red emission within the fabricated WLEDs. Consequently, this deficiency leads to suboptimal color rendering index (CRI, *R_a*) values and elevated correlated color temperature (CCT) values [3,4]. A new approach was introduced to address this issue, entailing the utilization of a red-emitting phosphor with green/blue-emitting phosphors in

combination with an NUV chip, as documented in Refs. [5–7]. Commercially available nitride-based red phosphors have been synthesized under rigorous conditions, involving high temperatures and the necessity for an inert atmosphere, which increases the cost in practical applications [8–10]. Therefore, the development of new red-emitting phosphors that can be synthesized via low stringent methods is of paramount importance.

Rare earth ions, such as Sm³⁺, Dy³⁺, and Eu³⁺, are essential in the domain of photoluminescent materials due to their outstanding luminescent properties. Typically, Sm³⁺-doped red phosphors exhibit four prominent emission peaks, corresponding to the 4*f*-4*f* transition from the ⁴G_{5/2} state to the ⁶H_{*J*} states (*J* = 5/2, 7/2, 9/2, 11/2). This behavior is attributed to the minimal interaction between the Sm³⁺ ions and the host lattice, enabling efficient activation of a wide range of inorganic matrices. Publications have emerged detailing the activation of red

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phosphors via Sm^{3+} , including $\text{LiMgPO}_4\text{:Sm}^{3+}$, $\text{BaYAlZn}_3\text{O}_7\text{:Sm}^{3+}$, $\text{KBaScSi}_3\text{O}_9\text{:Sm}^{3+}$, and $\text{Bi}_4\text{Si}_3\text{O}_{12}\text{:Sm}^{3+}$ [11–14]. The typical double-perovskite structure has become an excellent matrix for doping rare earth ions due to its high tolerance to rare earth ions and good crystal field environment [15–19]. The low phonon energy range ($800\text{--}900\text{ cm}^{-1}$) of tellurate represents a significant advantage within the domain of phosphors. This property effectively suppresses non-radiative transitions in doped rare earth ions, thereby enhancing the luminous efficiency [20].

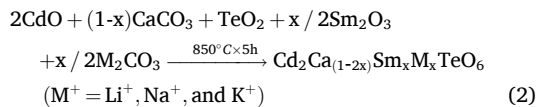
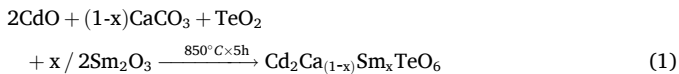
Optical non-contact thermometry has been widely implemented using thermographic phosphors (TGPs) as functional optical sensing materials [21]. Compared with conventional detection techniques, thermographic phosphors exhibit remarkable merits including rapid response speed, non-invasive measurement, and excellent detection accuracy [22,23]. Among various luminescence-based thermometric methods, the fluorescence intensity ratio (FIR) technique has become one of the most used approaches for phosphor-based temperature detection. This method possesses prominent superiorities such as fast response, high spatial and thermal resolution, small measurement deviation, and strong immunity to external interference [24]. Accordingly, phosphor thermometry based on the FIR strategy demonstrates enormous application potential in the field of optical temperature sensing.

In this work, a series of Sm^{3+} -doped double perovskite CCTO:xSm^{3+} ($0.5\text{ mol}\% \leq x \leq 35\text{ mol}\%$) phosphors were synthesized via a solid-state reaction method. Furthermore, a comprehensive analysis was conducted on the morphology, phase purity, luminescence properties and crystal structure of CCTO:Sm^{3+} . The CRI and CCT of the fabricated WLED by CCTO:Sm^{3+} phosphor were the focus of further discussion. The CRI and CCT of the WLED fabricated using CCTO:Sm^{3+} phosphor were further discussed, and the temperature sensing properties of the phosphor were also investigated.

2. Experiment section

2.1. Synthesis of $\text{Cd}_2\text{CaTeO}_6\text{:Sm}^{3+}$ phosphor

The Sm^{3+} -doped CCTO phosphors were synthesized using the conventional high-temperature solid-state reaction method. CdO (A.R.), CaCO_3 (A.R.), TeO_2 (A.R.), Sm_2O_3 (A.R.), Li_2CO_3 (A.R.), Na_2CO_3 (A.R.), and K_2CO_3 (A.R.) were utilized as the initial materials. Taking $\text{Cd}_2\text{CaTeO}_6\text{:}0.05\text{Sm}^{3+}$ as a representative example, 0.4226 g CdO , 0.1565 g CaCO_3 , 0.2626 g TeO_2 , and 0.0143 g Sm_2O_3 were weighed accurately using an electronic balance [9]. The raw materials were accurately measured according to a specified ratio and meticulously ground in an agate mortar for 20 min at room temperature. Once the mixture was fully combined, it was transferred to a crucible and heated in a muffle furnace at 850°C for 5 h. The experimental reaction can be represented by the following equations (1) and (2):



2.2. Measurements and characterization

The crystal structure of the prepared phosphors was thoroughly described using Diamond software. A Bruker D2 PHASER X-ray diffractometer was operated with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405\text{ nm}$) at 40 kV and 40 mA. The morphology of $\text{CCTO:5 mol}\% \text{Sm}^{3+}$ was examined using a scanning electron microscope Nova Nano SEM-450, and its elemental composition was determined using an energy dispersive spectrometer (EDS). The particle size distribution was assessed using a

Malvern MS 2000 laser particle size analyser. Photoluminescence (PL), photoluminescence excitation (PLE) properties and internal quantum efficiency (IQE) were investigated using an FLS 980 spectrometer (Edinburgh Instruments, UK), which was equipped with a 450 W xenon lamp and a BaSO_4 integrating sphere. The thermal quenching (TQ) test was conducted using an F-4600 spectrometer fitted with a TAP-02 temperature controller. Meanwhile, the lumen efficiency of the packaged WLED was determined using a light meter (TES-133, TES Electrical Electronic Corp., Taiwan) integrated with a BaSO_4 -coated integrating sphere.

2.3. Fabrication of the LED

The red LED was prepared using a 406 nm NUV chip and 0.1 g of $\text{CCTO:5 mol}\% \text{Sm}^{3+}, \text{Na}^+$. The WLED was assembled by combining orange-red phosphor $\text{CCTO:Sm}^{3+}, \text{Na}^+$, green phosphor $(\text{Ba}, \text{Sr})_2\text{SiO}_4\text{:Eu}^{2+}$, blue phosphor $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}^{2+}$ and a 406 nm InGaN chip. The assembled LED devices' electroluminescence characteristics were analyzed and tested using the Ocean Optics USB 4000 fibre optic spectrometer.

3. Results and discussion

Fig. 1(a) illustrates the structural model of CCTO, which crystallizes in the monoclinic crystal structure and falls into the $P2_1/n$ space group. CCTO is a double perovskite-structured material belonging to the $\text{A}_2\text{BB}'\text{O}_6$ type. The crystal parameters are as follows: $a = 5.527\text{ \AA}$, $b = 5.687\text{ \AA}$, $c = 7.997\text{ \AA}$, with cell angles $\alpha = \gamma = 90.00^\circ$ and $\beta = 90.90^\circ$, yielding a unit cell volume of $251.40\text{ \AA}^3$ (Table 1). In the crystal structure, Cd^{2+} ions occupy the A-site, while Ca^{2+} and Te^{6+} reside at the B and B'-sites, respectively. The Te^{6+} coordinated oxygen octahedra are labeled in pink, whereas the Ca^{2+} coordinated oxygen octahedra are designated in green. The percentage difference (D_r) can be determined utilizing formula (3), which serves as a metric for validating the occupancy within the CCTO host matrix [25].

$$D_r = \frac{R_s(\text{CN}) - R_d(\text{CN})}{R_s(\text{CN})} \times 100\% \quad (3)$$

The coordination number is represented by CN, while R_s and R_d denote the radii of the doped ions and potential substituted ions, respectively. Similar to Ca^{2+} ($r = 1.00\text{ \AA}$ when $\text{CN} = 6$), Sm^{3+} ($r = 0.96\text{ \AA}$) has a similar radius [26]. The calculated value of the D_r parameter between Sm^{3+} and Ca^{2+} stood at 4%, which is less than 30%. The experimental results demonstrate that Sm^{3+} can partially substitute for Ca^{2+} in the CCTO lattice [27], leading to a moderate decrease in the material's D_r value.

The tolerance factor (T_f), first proposed by Goldschmidt, serves as a key parameter to assess the geometric stability and phase transition behavior of perovskite structures. In perovskite crystals, the ionic radius distribution adheres to a specific mathematical relationship, typically computed using formula (4) [28].

$$T_f = \frac{R_{\text{Cd}} + R_{\text{O}}}{\sqrt{2} \left(\frac{R_{\text{Ca}} + R_{\text{Te}}}{2} + R_{\text{O}} \right)} \quad (4)$$

Different elements have different atomic radii in a specific coordination environment. Take, for instance, the ionic radii of Ca, O, Cd and Te, which are $1.00\text{ \AA}$, $1.40\text{ \AA}$, $1.31\text{ \AA}$, and $0.56\text{ \AA}$, respectively. According to Goldschmidt's theory, when the tolerance factor (T_f) is greater than 1, the crystal tends to form a cubic structure; when T_f is equal to 1, the lattice has the highest symmetry. If T_f is less than 1, lattice distortion may occur, resulting in the transformation of the crystal structure from cubic to orthorhombic or monoclinic [29]. Calculations show that T_f is 0.63, which is less than 1, so it is speculated that the structure type is monoclinic.

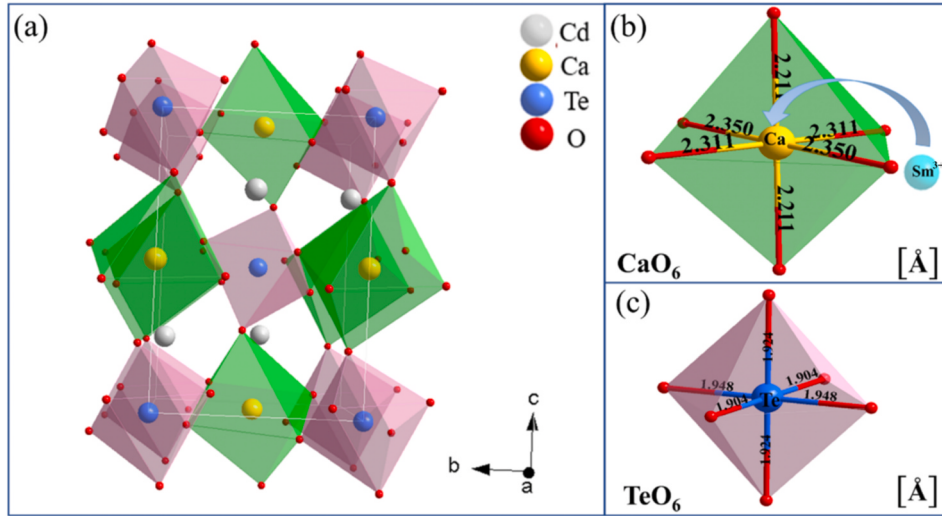


Fig. 1. (a) The structural model for CCTO. (b) The process of Sm^{3+} substituting Ca^{2+} . (c) Crystal structure of TeO_6 polyhedron.

Table 1

The cell parameters of the $\text{Cd}_2\text{CaTeO}_6$.

Formula	$\text{Cd}_2\text{CaTeO}_6$
Space group	$P2_1/n$
Structural type	Monoclinic structure
a (Å)	5.527
b (Å)	5.687
c (Å)	7.997
$\alpha = \gamma$ (degree)	90°
β (degree)	90.90°
Cell volume ($\text{\AA}^3$)	251.40

XRD patterns in Fig. 2(a) was utilized to assess the phase purity of $\text{CCTO}:x\text{Sm}^{3+}$ ($0.5 \text{ mol}\% \leq x \leq 35 \text{ mol}\%$) phosphors. The diffraction pattern matches well with the standard spectrum (PDF # 00-054-1059), confirming the successful preparation of single-phase samples. Importantly, the introduction of Sm^{3+} -doping did not induce any phase changes. Following the Bragg equation [30], $2d\sin\theta = n\lambda$, Fig. 2(b)

illustrates diffraction peaks gradually shift to a high angle as the concentration of Sm^{3+} ions increases. This is explained by the smaller Sm^{3+} ions (0.96 Å ionic radius) replacing Ca^{2+} ions (1.00 Å ionic radius) in the matrix, and lattice volume contraction occurs. Consequently, the diffraction peak shifts towards the high angle [31,32].

When evaluating the application prospects of phosphors, the physical morphology and particle size distribution are crucial factors that cannot be overlooked. As a case in point, Fig. 3(a) shows the representative scanning electron microscope (SEM) image of the $\text{CCTO}:5 \text{ mol}\% \text{Sm}^{3+}$ phosphor at $5000 \times$ magnification, which reveals its microstructure characteristics. It can be observed that partial agglomeration occurs in the specimen, a phenomenon arising from the high-temperature reaction and further indicative of the intrinsic aggregation characteristics of grains during synthesis. This phenomenon may be attributed to the Ostwald ripening and directional attachment mechanism, where the decrease in grain surface energy under high-temperature conditions promotes their approach and aggregation [33,34]. The phenomenon of Ostwald ripening is explained by the stability of larger particles with respect to their energy. The orientation attachment process arises

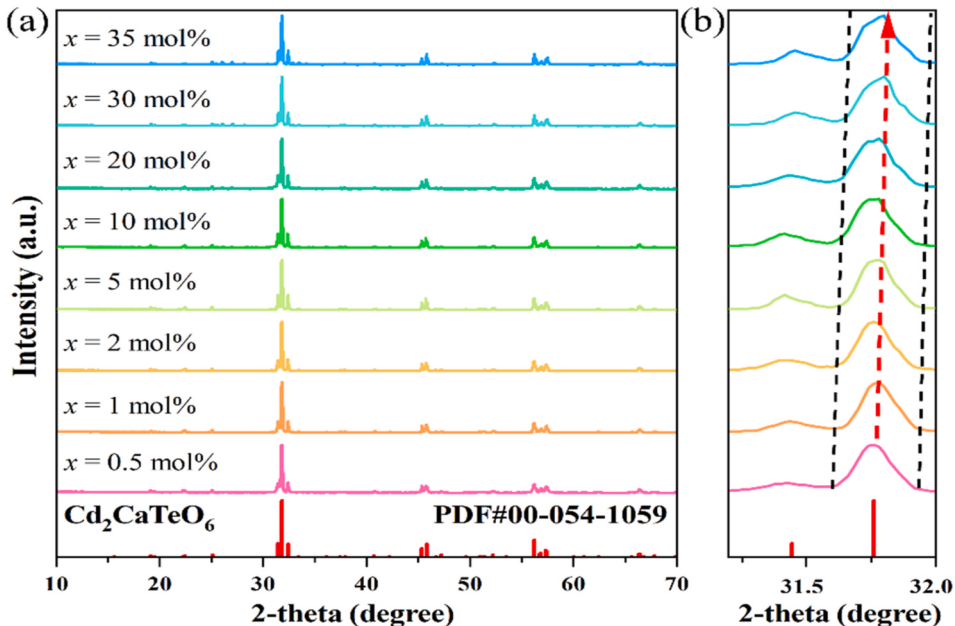


Fig. 2. (a) The XRD patterns of the $\text{CCTO}:x\text{Sm}^{3+}$ ($0.5 \text{ mol}\% \leq x \leq 35 \text{ mol}\%$) phosphors. (b) Enlarged 2θ angles of $\text{CCTO}:\text{Sm}^{3+}$ from 31.2° to 32.0° .

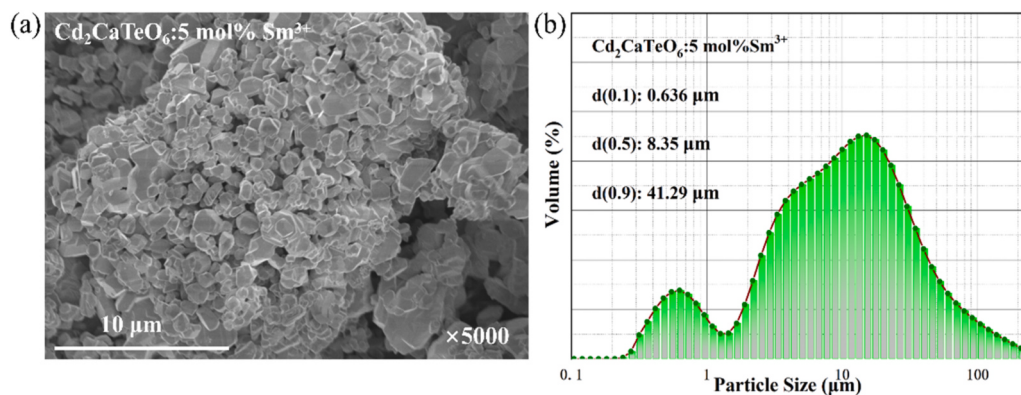


Fig. 3. (a, b) The SEM micrograph and the particle size distribution histogram of CCTO:5 mol%Sm³⁺.

because aggregation diminishes the interface boundary and decreases the overall surface energy of the sample. Consequently, in the case of synthesized phosphors, smaller particles coalesce into larger ones at elevated temperatures, leading to a reduction in the surface energy of the particles.

The distribution of particle sizes for the phosphor was illustrated in Fig. 3(b). Specifically, $d(0.1)$ is 0.636 μm , denoting that 10% of the particles have diameters smaller than this value; $d(0.5)$, as the median particle size, serves as a critical parameter to characterize the central tendency of the particle size distribution; while $d(0.9)$ is 41.29 μm , indicating that 90% of the particles are smaller than this diameter. The particle size analysis indicates that further grinding and sieving of the phosphor are necessary for practical WLED applications.

EDS analysis of CCTO:5 mol% Sm³⁺ phosphors revealed the following elemental compositions: Cd, Ca, Te, O, and Sm. As demonstrated in Fig. 4(a), the characteristic peaks of these elements substantiated their presence in the sample. Furthermore, as illustrated in Fig. 4 (b–g), the uniform distribution of these elements was demonstrated through distinct colour coding, which also indicated homogeneous Sm³⁺ ion doping within the CCTO matrix. The table shows that the measured atomic ratios are basically consistent with the theoretical stoichiometry of the target phase $\text{Cd}_2\text{Ca}_{0.95}\text{Sm}_{0.05}\text{TeO}_6$ within the instrumental error range. Furthermore, the actual phase composition has been further verified by XRD results, which confirm the formation of the pure target phase.

As shown in Fig. 5, due to the 4f–4f transitions of the Sm³⁺ ion, the CCTO:2 mol% Sm³⁺ phosphor exhibits an excitation spectrum in the 360–500 nm range when monitored at emission wavelengths of 566, 600, and 646 nm. The positions were 378 ($^6\text{H}_{5/2} \rightarrow ^4\text{D}_{1/2}$), 406 ($^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$), 420 ($^6\text{H}_{5/2} \rightarrow ^4\text{M}_{19/2}$), 473 ($^6\text{H}_{5/2} \rightarrow ^4\text{I}_{11/2}$), 481 ($^6\text{H}_{5/2} \rightarrow ^4\text{M}_{15/2}$).

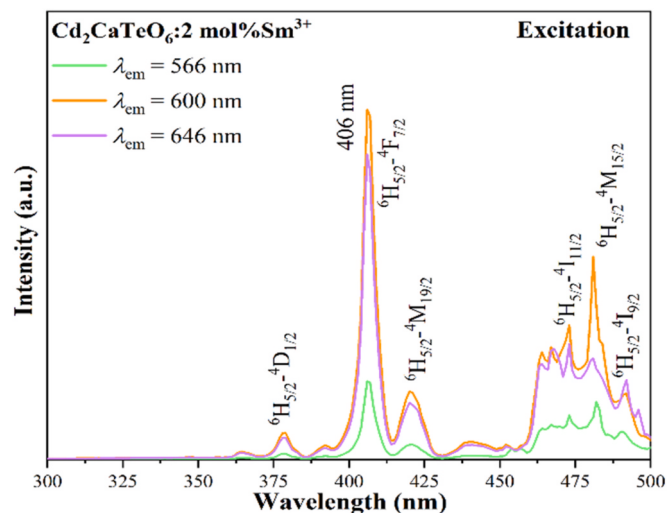


Fig. 5. The excitation spectra of CCTO doped with 2 mol% Sm³⁺ were monitored at various wavelengths (566, 600, and 646 nm).

2), and 491 nm ($^6\text{H}_{5/2} \rightarrow ^4\text{I}_{9/2}$) in that order. The strongest peak was close to the near ultraviolet region. It can therefore be concluded that the CCTO:Sm³⁺ phosphor can serve as a potential candidate for specialized optoelectronic applications based on NUV-driven WLEDs.

As shown in Fig. 6(a), the emission spectra of CCTO:2 mol%Sm³⁺ phosphors exhibited similar characteristic peaks under excitation at 378, 406, 420, and 481 nm. The main luminescent characteristic of the

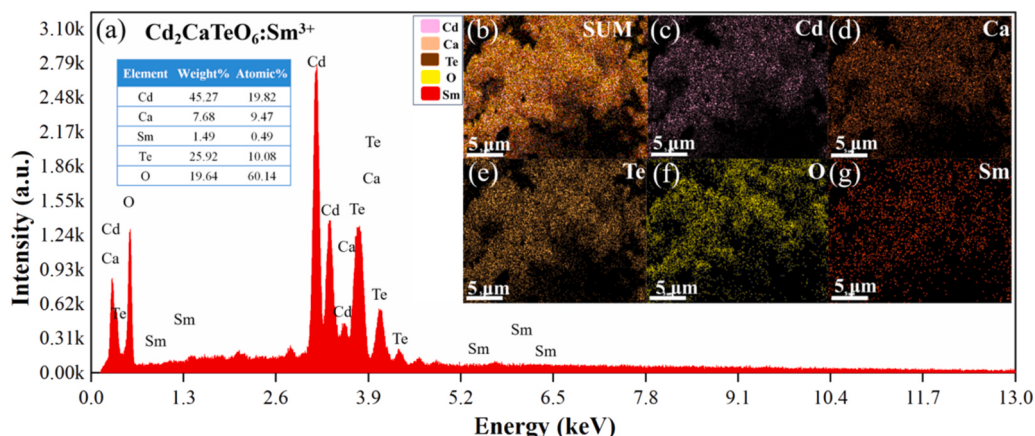


Fig. 4. (a) The EDS spectrum of CCTO:5 mol%Sm³⁺ phosphor. (b–g) The elemental mapping patterns of CCTO:5 mol%Sm³⁺ phosphor.

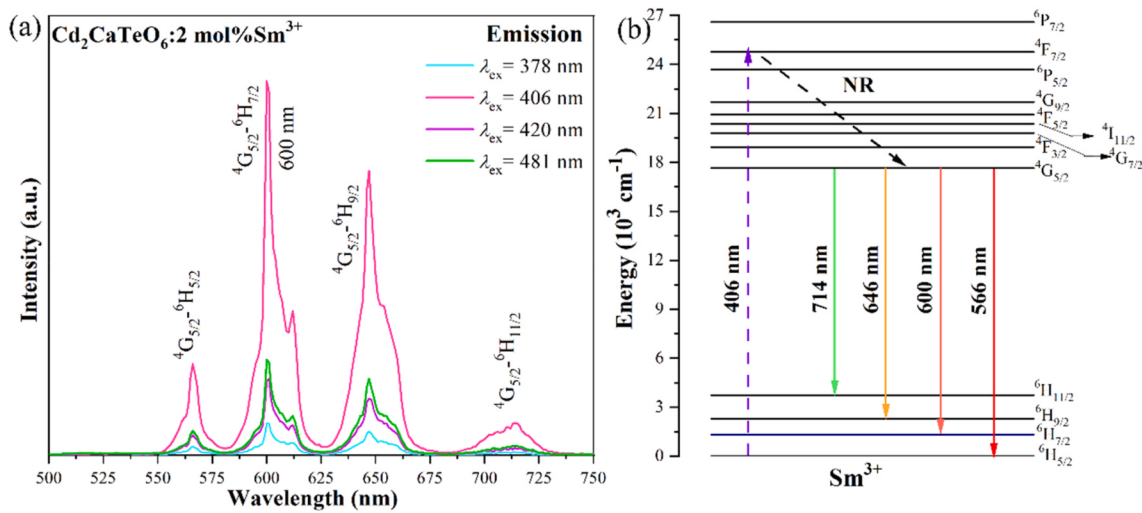


Fig. 6. (a) Emission spectra of CCTO:2 mol%Sm³⁺ phosphor (λ_{ex} = 378, 406, 420, and 481 nm). (b) The energy level diagram of Sm³⁺ ions.

phosphor was the emission of orange-red light, with the strongest emission peak at 600 nm being particularly significant. Furthermore, four distinct emission peaks at 566, 600, 646, and 714 nm were observed, corresponding to the 4f-4f transitions of Sm³⁺. Specifically, these peaks originated from the transitions of the ⁴G_{5/2} state to the ⁶H_{5/2}, ⁶H_{7/2}, ⁶H_{9/2}, and ⁶H_{11/2} states, respectively [35]. The emission peaks observed at 566 nm and 646 nm are attributed to the magnetic dipole (MD) and electric dipole (ED) transitions, respectively. The transition from ⁴G_{5/2} to ⁶H_{7/2} at 600 nm is mainly ascribed to both ED and MD transitions. The transitions of electric dipoles adhere to the selection rule that the change in the total angular momentum quantum number, denoted as ΔJ , must be less than or equal to 6. However, when the total angular momentum quantum number J or J^1 equals zero, the allowed changes in ΔJ are restricted to 2, 3, and 6. In contrast, MD transitions are governed by the selection rule that the change in the total angular momentum quantum number, ΔJ , is restricted to 0 and ± 1 . In the emission spectrum, the red light emission is observed at 566 nm, the transition type is ⁴G_{5/2} → ⁶H_{5/2}, and the calculated $\Delta J = 0$, which is caused by the allowed MD transition. Similarly, the transition type at 646 nm is ⁴G_{5/2} → ⁶H_{9/2}, and the calculated $\Delta J = 2$, which is the allowed ED transition. The emission peak at 600 nm corresponds to the ⁴G_{5/2} → ⁶H_{7/2} transition, which has MD properties as it involves a J value change ($\Delta J = 1$) conforming to the magnetic dipole transition selection rule [36].

As illustrated in Fig. 6(b), the luminescence mechanism of Sm³⁺ is elucidated under 406 nm excitation. In the ground state ⁶H_{5/2}, Sm³⁺ electrons absorb energy, transitioning to the excited state ⁴F_{7/2}. Thereafter, these excited electrons relax to lower-energy states via non-radiative (NR) transitions, ultimately emitting visible light at distinct wavelengths. These emissions correspond to transitions from the ⁴G_{5/2} state to the ⁶H_{5/2}, ⁶H_{7/2}, ⁶H_{9/2}, and ⁶H_{11/2} states, respectively, with corresponding wavelengths of 566, 600, 646, and 714 nm.

The emission asymmetry ratio is employed to characterize the positional symmetry of doped cations in crystal structures, defined as the ratio of the ED transition area to the MD transition area. According to the Judd-Ofelt theory, ED transitions dominate the spectral behavior of CCTO crystals, resulting in a higher transition intensity at 646 nm than at 566 nm. The root cause of this intensity difference lies in the fact that ED transitions are more sensitive to the local symmetry environment, whereas MD transitions are mainly regulated by magnetic dipole interactions [37]. Fig. 7 shows the normalized integral intensities and the asymmetry ratios for ED and MD at different doping concentrations. As tabulated in Table 2, the asymmetry ratio R/O of CCTO: x Sm³⁺ phosphors ranges from 5.283 (at 0.5 mol%) to 6.075 (at 5 mol%), all exceeding unity. These values surpass comparable ratios reported for red phosphors such as La₂HfO₇:Sm³⁺, Zn₂P₂O₇:Sm³⁺, NaY(MoO₄)₂:Sm³⁺ [38–40]. This observation indicates that Sm³⁺ ions reside in asymmetric coordination environments within the CCTO crystal structure.

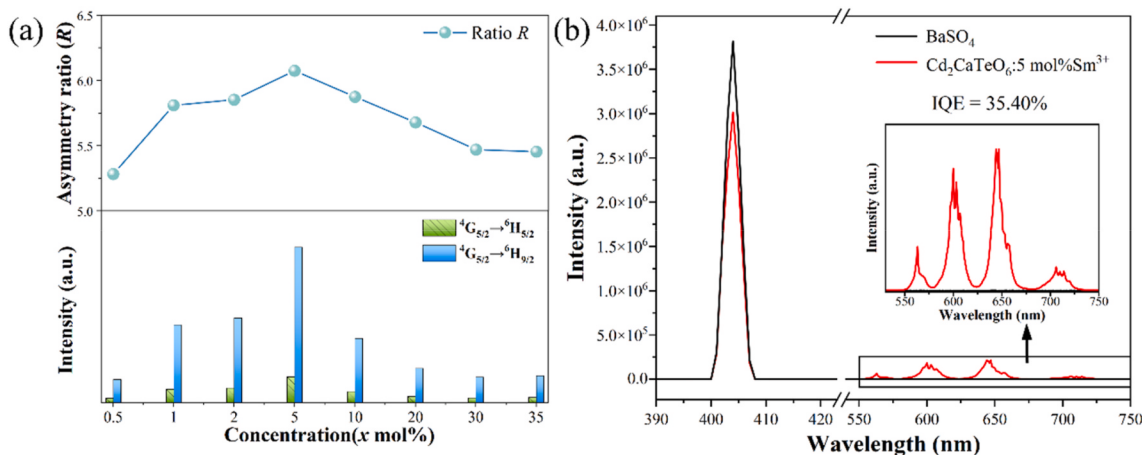


Fig. 7. (a) Comparison of ED, MD intensity, and asymmetry ratio line chart across different doping concentrations. (b) IQE of CCTO:5 mol%Sm³⁺.

Table 2

The asymmetry ratio R/O of the prepared CCTO: $x\text{Sm}^{3+}$ phosphors ($0.5 \text{ mol}\% \leq x \leq 35 \text{ mol}\%$).

Concentration(mol%)	R/O
0.5	5.283
1	5.810
2	5.853
5	6.075
10	5.874
20	5.679
30	5.470
35	5.454

IQE serves as a key performance indicator for phosphors. As shown in Fig. 7 (b), for the CCTO: Sm^{3+} phosphor system, the concentration quenching effect can significantly impair its internal quantum efficiency through dipole-dipole interactions, a rule that can be directly visualized via the calculation formula for IQE:

$$\eta_{\text{int}} = \frac{\int L_s}{\int E_R - E_S} \quad (5)$$

In the above quantitative calculation expression, L_s and E_S correspond to the photoluminescence emission spectrum and photoluminescence excitation spectrum of the CCTO:5 mol% Sm^{3+} sample, respectively, while E_R represents the excitation spectrum of BaSO_4 powder used as the reference standard. Figure presents the measured IQE result of this system at the optimal doping concentration (5 mol% Sm^{3+}), with an IQE value of 35.4%.

The emission spectra of CCTO: $x\text{Sm}^{3+}$ phosphors with the dopant concentration varying from 0.5 mol% to 35 mol% displayed similar characteristic peaks, as depicted in Fig. 8(a). The inset illustrates the graphical representation of the normalized emission intensity in relation to the Sm^{3+} doping concentration within CCTO phosphors. An observed increase in luminescent intensity correlates with the rising concentration of luminescent centers, and the trend is obvious in a specific doping concentration range. The maximum luminescence intensity was recorded at a doping concentration of 5 mol%. The luminescent intensity of the phosphors was noted to diminish progressively as their concentration rose from 5 to 35 mol%. Such a decrease is indicative of the emergence of a concentration quenching phenomenon [41]. As the Sm^{3+} ion concentration increases, the distance between their luminescent centers decreases, facilitating the prevalence of NR energy transfer. This process causes the energy originally destined for radiative transitions to dissipate via NR pathways, ultimately leading to a reduction in luminescence intensity.

Blasse determined the optimal concentration (x_c) and critical energy transfer distance (R_c) for interactions between Sm^{3+} ions, as defined by

formula (6) [42]:

$$R_c \approx 2 \left(\frac{3V}{4\pi x_c N} \right)^{1/3} \quad (6)$$

In this context, V denotes the unit cell volume, x_c represents the critical concentration threshold, and N signifies the number of exchangeable cations per unit cell. In accordance with Blasse's theoretical framework [43], when the critical radius (R_c) exceeds 5 Å, the occurrence of concentration quenching is attributed to multipolar interactions. In the CCTO host, with $N = 2$, $x_c = 0.05$ and $V = 251.40 \text{ Å}^3$, the calculated R_c was found to be 25.3 Å. This value is significantly larger than the typical threshold of 5 Å, which is generally associated with energy transfer mechanisms.

The observed concentration quenching phenomenon is attributed to multipole interactions. The application of formula (7), derived from Dexter's theory, further verifies the characteristics of these interactions [44].

$$\frac{I}{x} = K \left[1 + \beta(x) Q^3 \right]^{-1} \quad (7)$$

Q is defined as the multipole interaction constant, taking on values of 3, 6, 8, or 10. The constants K and β remain invariant under uniform excitation conditions. Fig. 8(b) illustrates the correlation between $\lg I/x$ and $\lg x$ for CCTO: Sm^{3+} phosphors. The regression analysis conducted revealed that the slope of the curve derived from the fitting process equaled -1.97 . Utilizing equation (7), the θ parameter was determined to be 5.91. The findings indicated that the specific multipolar interaction under investigation was identified as dipole-dipole interaction. This quenching mechanism is in agreement with results observed in other Sm^{3+} -doped phosphors, such as $\text{Ca}_3\text{Al}_2\text{O}_6:\text{Sm}^{3+}$, $\text{NaLaMgTeO}_6:\text{Sm}^{3+}$, $\text{KBaScSi}_3\text{O}_9:\text{Sm}^{3+}$ [13,45,46].

The CIE chromaticity coordinates and color purity are widely acknowledged as pivotal parameters for evaluating phosphor performance. Fig. 9(a) depicts the CIE chromaticity diagram of CCTO phosphors, with all samples' CIE coordinates falling within the orange-red region. Notably, the CCTO:5 mol% Sm^{3+} sample exhibits CIE coordinates of (0.622, 0.378), and its standard deviation can be computed using formula (8).

$$\Delta x = \sqrt{\frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (8-1)$$

$$\Delta y = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \bar{y})^2} \quad (8-2)$$

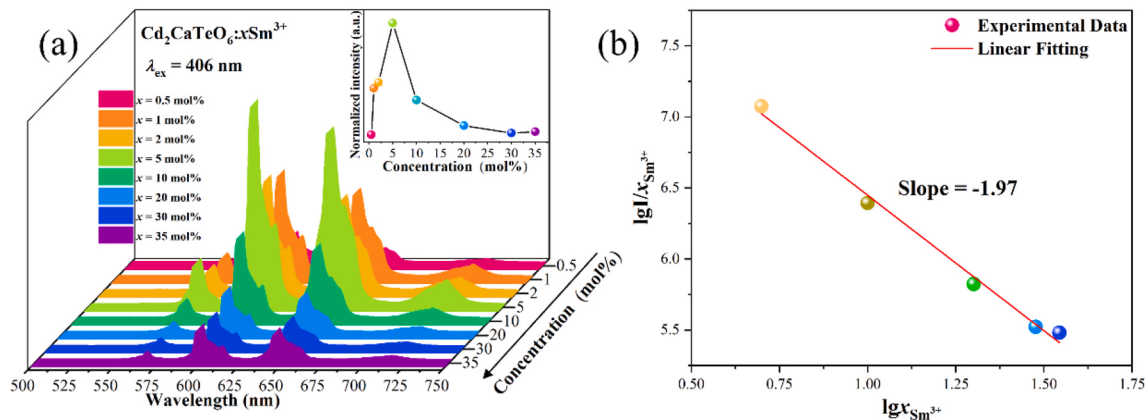


Fig. 8. (a) The emission spectra of CCTO: $x\text{Sm}^{3+}$ ($0.5 \text{ mol}\% \leq x \leq 35 \text{ mol}\%$) phosphors ($\lambda_{\text{ex}} = 406 \text{ nm}$). Inset: The normalized luminescence intensity curve for CCTO doped with varying concentrations of Sm^{3+} mol%. (b) The linear correlation between $\lg x$ and $\lg(I/x)$ for CCTO: Sm^{3+} phosphors.

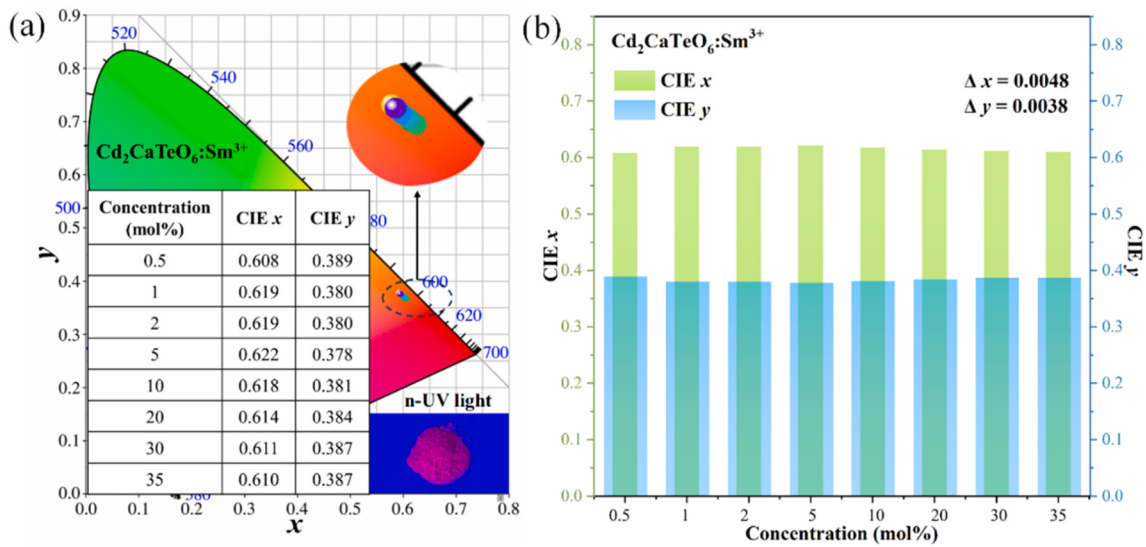


Fig. 9. (a) Chromaticity coordinates chart of the CCTO: $x\text{Sm}^{3+}$ ($0.5 \text{ mol}\% \leq x \leq 35 \text{ mol}\%$) samples; (b) The Δx and Δy of the CCTO: Sm^{3+} phosphors.

In Fig. 9(b), x_i and y_i denote the CIE chromaticity coordinates measured at varying Sm^{3+} concentrations, while Δx and Δy represent the standard deviations. The mean values of the CIE chromaticity coordinates are denoted by x and y . As shown in the figure, the mean CIE Δx and Δy values are 0.0048 and 0.0038, respectively. This minor difference indicates that doping with Sm^{3+} ions has a minimal impact on the CIE color rendering. In addition, color purity is essential for evaluating the chromatic stability of phosphors, and it can be calculated using equation (9) presented below:

$$\text{Color purity} = \frac{\sqrt{(x_s - x_i)^2 + (y_s - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\% \quad (9)$$

While (x_s, y_s) represent the CIE coordinates, which are associated with various doping concentrations, the coordinates (x_i, y_i) in the given mathematical expression correspond to the values (0.333, 0.333). In the chromaticity diagram, the line connecting the points (x_s, y_s) and (x_i, y_i) intersects the boundary at (x_d, y_d) . Table 3 lists the color purity and CIE coordinate data for CCTO: $x\text{Sm}^{3+}$ samples, with doping concentrations ranging from 0.5 to 35 mol%. Experimental results demonstrate that the material exhibits high color purity, spanning 99.2–100%. These results highlight the stable characteristics and excellent orange-red fluorescence of the synthesized phosphors. As a result, the CCTO: $x\text{Sm}^{3+}$ phosphors have the potential to be an exceptional red-emitting substance in WLEDs.

As shown in Fig. 10(a and b), the PL spectra of CCTO: $x\text{Sm}^{3+}$ samples ($x = 5 \text{ mol}\%$ and $2 \text{ mol}\%$) exhibit consistent emission properties across the temperature range of 300–480 K. Emission profiles derived from these spectra show uniform shapes for all samples, with luminescence intensity at 300 K normalized to 100% as a reference. When the

Table 3

CIE (x, y), CCT, and Color purity of CCTO: $x\text{Sm}^{3+}$ ($0.5 \text{ mol}\% \leq x \leq 35 \text{ mol}\%$) phosphors at different concentrations.

Concentration (mol%)	CIE (x, y)	CCT (K)	Color purity
0.5	(0.608, 0.389)	1370	99.3%
1	(0.619, 0.380)	1280	99.8%
2	(0.619, 0.380)	1280	99.8%
5	(0.622, 0.378)	1258	100%
10	(0.618, 0.381)	1289	99.8%
20	(0.614, 0.384)	1320	99.5%
30	(0.611, 0.387)	1347	99.5%
35	(0.610, 0.387)	1351	99.2%

temperature exceeds 320 K, the intensity gradually decreases, demonstrating TQ. Between 300 and 320 K, a brief anomalous enhancement occurs, with intensity increases of 5.92% (2 mol%) and 3.75% (5 mol%), respectively. Notably, in Fig. 10(c and d), at 420 K, the luminescence intensities of the two samples remain at 68.3% and 57.2% of their initial values, indicating that their $T_{0.5}$ (the temperature at which intensity drops to 50% of the initial value) exceeds 420 K. This exceeds the typical operating temperature of LEDs, confirming excellent thermal stability.

As shown in Fig. 11(a and b), within the temperature range of 300 to 440 K, it was apparent that with an increase in temperature, the CIE x value decreased, whereas the CIE y value increased. The variances of CCTO:5 mol% Sm^{3+} was $S_x = 1.45 \times 10^{-4}$, $S_y = 1.14 \times 10^{-4}$, and that of CCTO:2 mol% Sm^{3+} are $S_x = 2.61 \times 10^{-4}$, $S_y = 2.01 \times 10^{-4}$. The small variation in CIE coordinates suggests that the phosphor exhibits stable luminescent properties, supporting its potential use in WLED applications.

Alkali metal ions act as charge compensators to reduce the NR transition. At the same time, they can also unbalance the charge in the main lattice [47]. In Fig. 12(a), the XRD patterns of CCTO:5 mol% Sm^{3+} , 5 mol% M^+ , and CCTO:5 mol% Sm^{3+} phosphors was tested, and they fitted well with the standard pattern of PDF#00-054-1059. The 5s and 5p electrons of Sm^{3+} have a shielding effect on the 4f orbital. Therefore, the influence of the doping charge compensator on the energy level structure of Sm^{3+} in the main lattice is limited. Hence, the emission spectra of CCTO:5 mol% Sm^{3+} , 5 mol% M^+ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{and K}^+$) and CCTO:5 mol% Sm^{3+} phosphors have similar shapes and positions in Fig. 12(b). The emission intensities of Li^+ , Na^+ , and K^+ co-doped phosphors at 600 nm were 1.61, 1.90, and 1.53 times that of CCTO:5 mol% Sm^{3+} phosphors, respectively. Obviously, the charge compensators greatly improved the emission intensity of CCTO:5 mol% Sm^{3+} .

Further, in Fig. 12(c), the relationship between temperature and emission intensity of CCTO:5 mol% Sm^{3+} , 5 mol% M^+ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{and K}^+$), CCTO:5 mol% Sm^{3+} and commercial $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors was displayed. The TQ curves of CCTO:5 mol% Sm^{3+} , 5 mol% M^+ differed from CCTO:5 mol% Sm^{3+} phosphors, the $T_{0.5}$ values of the former were improved to varying degrees, among which the enhancement of CCTO:5 mol% Sm^{3+} , 5 mol% Na^+ is the most significant [48]. Among the three co-doped alkali metal ions, Ca^{2+} ions have the closest radius to Na^+ ions. Thus, Na^+ ions can easily co-doped into the main lattice. The thermal stability of CCTO:5 mol% Sm^{3+} , 5 mol% Na^+ is better than that of commercial powder $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. Its $T_{0.5}$ exceeded 480 K and the residual at 420 K intensity remained at 99.7% of the initial value. Therefore, the introduction of Na^+ as a charge compensator not only

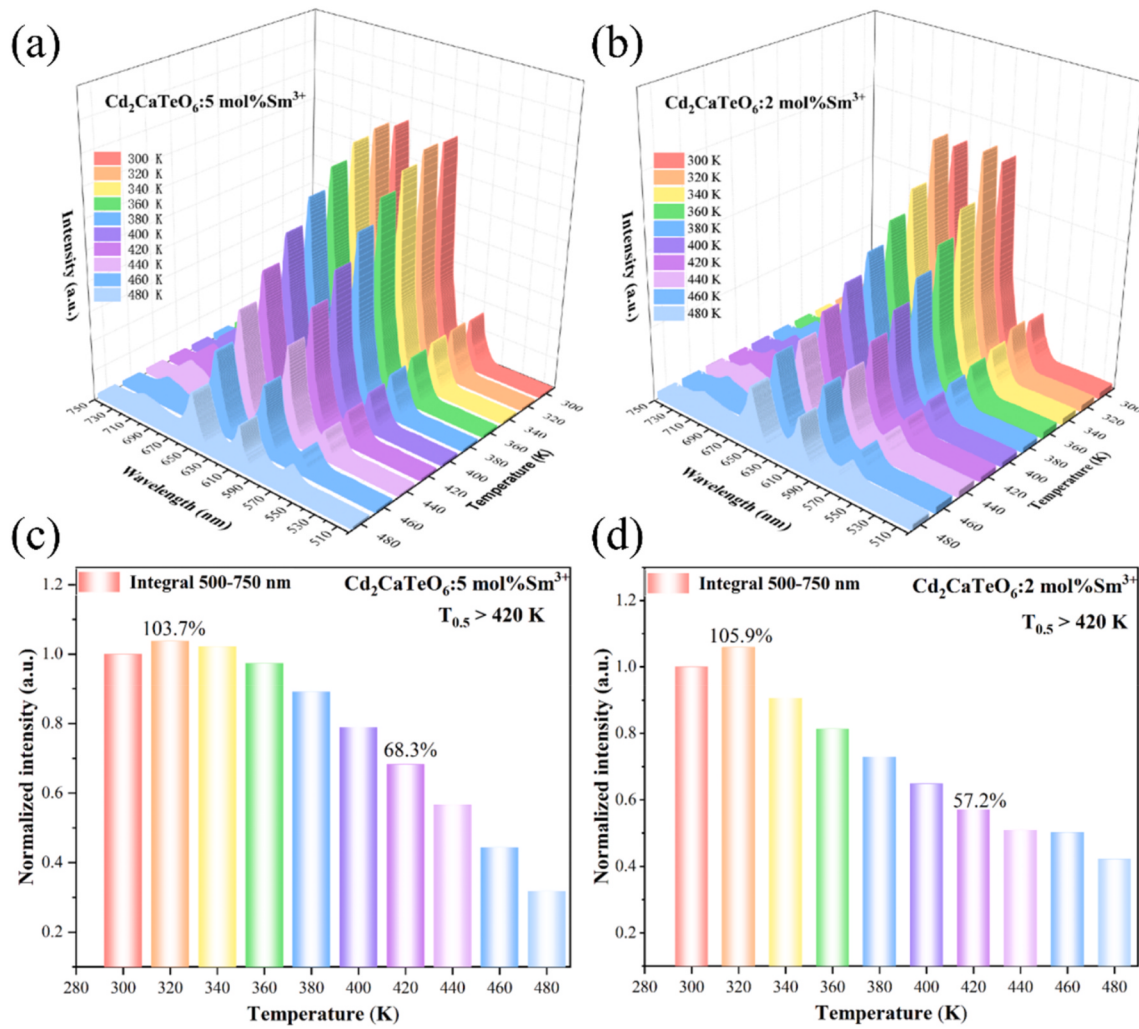


Fig. 10. (a, b) Temperature-dependent PL spectra of CCTO: $x \text{ mol\%Sm}^{3+}$. (c, d) Normalized integral intensity under various temperatures of CCTO:5 mol% Sm^{3+} and CCTO:2 mol% Sm^{3+} .

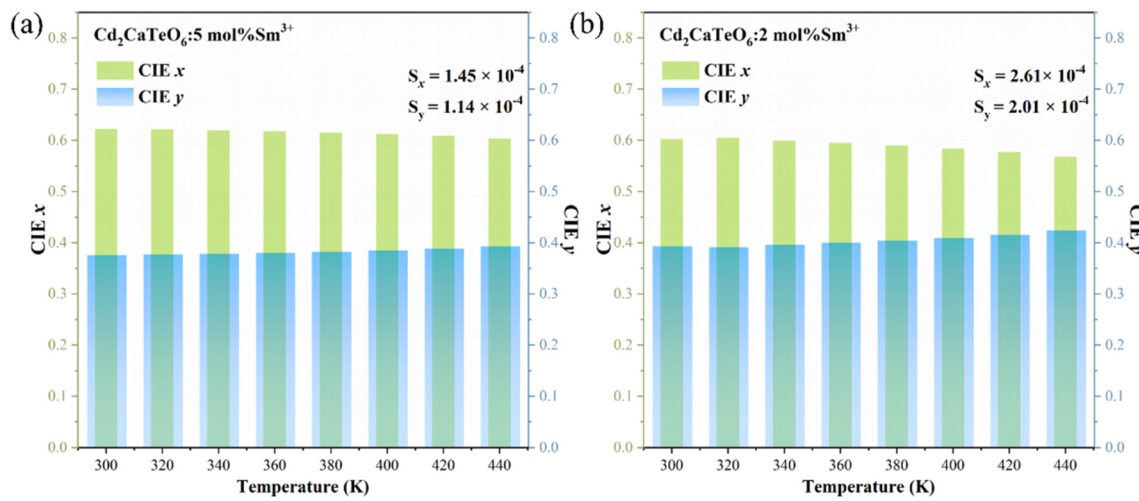


Fig. 11. (a, b) Relationship between the temperature and CIE x , CIE y of the CCTO:5 mol% Sm^{3+} and CCTO:2 mol% Sm^{3+} phosphor.

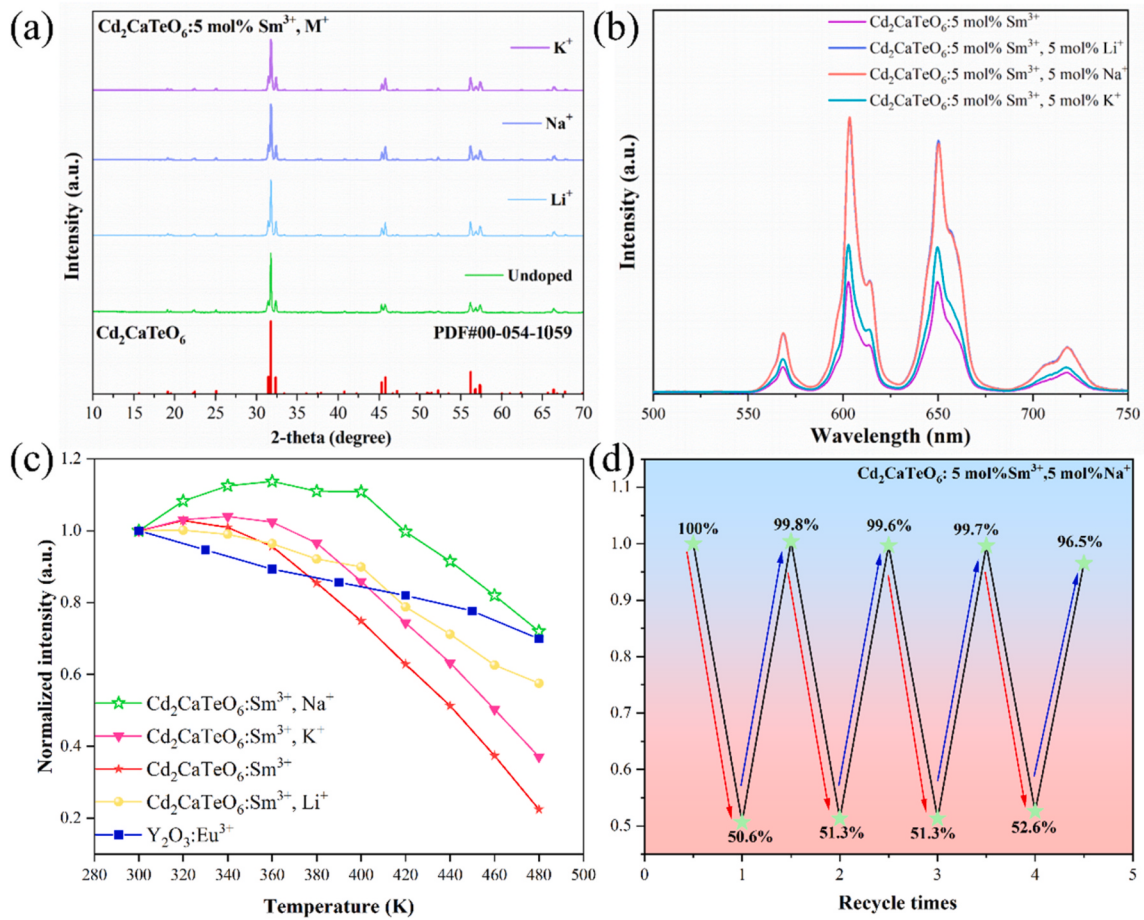


Fig. 12. (a) XRD patterns of CCTO:5 mol% Sm^{3+} , 5 mol% M^+ ($\text{M}^+ = \text{Li}^+$, Na^+ , and K^+). (b) Emission spectra of CCTO:5 mol% Sm^{3+} , 5 mol% M^+ phosphor. (c) Normalized integral plot of PL spectra of CCTO:5 mol% Sm^{3+} , 5 mol% M^+ phosphor at different temperatures. (d) CCTO:5 mol% Sm^{3+} , 5 mol% Na^+ heating and cooling cycle (300 K-480 K) results.

mitigates TQ at elevated temperatures by suppressing NR transitions but also significantly improves the overall thermal stability of CCTO:5 mol% Sm^{3+} . Furthermore, a continuous heating-cooling cycle examination was conducted on CCTO:5 mol% Sm^{3+} , 5 mol% Na^+ . As depicted in Fig. 12 (d), the material retains 96.5% of its initial intensity even after being heated to 480 K on four heating-cooling cycles, thereby reaffirming its excellent thermal stability.

Upon heating, it is necessary for electrons to acquire sufficient energy to surmount the specified energy barrier denoted as activation energy (E_a). For in-depth investigation into product stability, E_a serves as

a valuable parameter for consideration. According to the Arrhenius equation, the calculation E_a is consistent with equation (10) [49].

$$I(T) = \frac{I_0}{1 + c \exp(-E_a/kT)} \quad (10)$$

In this equation, c denotes a constant, k is the Boltzmann constant ($8.629 \times 10^{-5} \text{ eV/K}$), $I(T)$ represents the emission intensity at temperature T , and I_0 signifies the peak emission intensity. Equation (10) can be transformed into equation (11) via linear fitting.

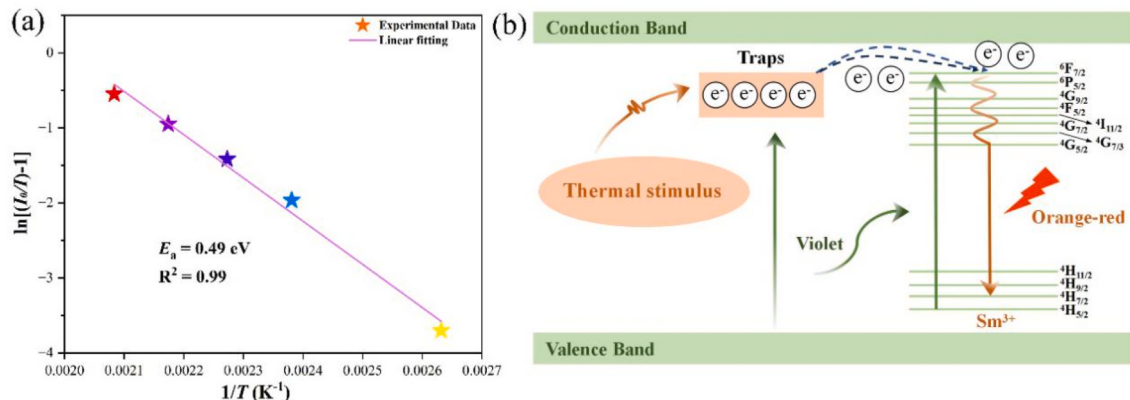


Fig. 13. (a) The fitting of $\ln[(I_0/I)-1]$ against $1/T$ for the CCTO:5 mol% Sm^{3+} , 5 mol% Na^+ phosphor. (b) The ATQ of the CCTO:5 mol% Sm^{3+} and its mechanism.

$$\ln\left(\frac{I_0}{I_T} - 1\right) = -\frac{E_a}{T} + \ln M \quad (11)$$

E_a for thermal quenching, quantified by linearly fitting the $\ln[(I_0/I) - 1]$ and $1/T$ plot in Fig. 13(a), is 0.49 eV for CCTO:5 mol%Sm³⁺, 5 mol% Na⁺. This value is higher than those reported for Sm³⁺-doped phosphors such as KBaScSi₃O₉:Eu²⁺, Tb³⁺, Sm³⁺ (0.226 eV), La₃Mg₂NbO₉:Sm³⁺ (0.279 eV), Na₅Y(MoO₄)₄:Sm³⁺ (0.289 eV) [13,50,51]. Since higher E_a correlates with stronger thermal stability, this phosphor has lower TQ risk at elevated temperatures, showing a bright promise for solid-state lighting.

The energy level diagram in Fig. 13(b) elucidates the anomalous thermal quenching (ATQ) behavior. Under NUV excitation, electrons are promoted from the valence band to the conduction band; some are captured by metastable traps (lattice defects) in the forbidden gap. Within 300–320 K, thermal stimulation releases trapped electrons back to the conduction band. These electrons then undergo radiative recombination, resulting in orange-red emission from Sm³⁺. This radiative pathway is more efficient than NR energy dissipation, leading to a significant enhancement in luminescence intensity. When temperature reaches 320 K, trap states are depleted, and the probability of NR transitions rises. The competition between trap-assisted radiative recombination, NR decay, and conventional TQ shifts: TQ dominates after trap exhaustion, causing luminescence intensity to decline [52].

WLEDs were constructed using 406 nm chips along with BaMgAl₁₀O₁₇:Eu²⁺, (Ba, Sr)₂SiO₄:Eu²⁺, and the CCTO:5 mol%Sm³⁺, 5 mol% Na⁺ phosphors. In the spectrum shown in Fig. 14(a), the distinct peaks at 566, 600, 646, and 714 nm align with the emission spectrum of the CCTO:5 mol%Sm³⁺ phosphors, demonstrating that the phosphor functions normally to emit light in the device. The measured CIE coordinates (0.324, 0.337) of the fabricated WLED device, being in excellent agreement with the isoenergetic point (0.333, 0.333), demonstrate a highly balanced white light emission. The CRI is a metric that assesses a light source's capability to reproduce colors relative to natural sunlight. Fig. 14(b) compares the CRI of this WLED with the commercial WLEDs. Table 4 presents a comprehensive set of color index values, ranging from R₁ to R₁₄. The fabricated WLED exhibits superior performance with a high CRI ($R_a = 87$) and an R₉ value 4.7 times greater than commercial counterparts. The 406 nm chip-based WLED exhibited a high CRI and a relatively low CCT of 5886 K, outperforming other reported results. For instance, Sr₃Ga₂Sn_{1.5}Si_{2.5}O₁₄:Sm³⁺ ($R_a = 72.8$, CCT = 8849 K), CaAlSi₃N₃:Eu²⁺ ($R_a = 80.4$, CCT = 6560 K) and Ca(Mg_{0.8}Al_{0.2})(Si_{1.8}Al_{0.2})O₆:Ce³⁺, Tb³⁺ ($R_a = 80.5$, CCT = 6137 K) [53–55]. Additionally, the lumen

efficiency of the packaged WLED was determined to be 6.92 lm/W, which could be further improved by optimizing the packaging structure and phosphor preparation concentration in future work.

To explore the potential application of the CCTO:5 mol% Sm³⁺ phosphor in temperature sensing, the temperature-dependent PL emission spectra were systematically analyzed over the temperature range of 300–480 K. As illustrated in Fig. 15(a), the temperature-dependent PL emission spectra of the CCTO:5 mol% Sm³⁺ phosphor are presented at various temperatures. It is clearly observed that the peak positions and profiles of the characteristic Sm³⁺ emissions remain nearly unchanged with increasing temperature, confirming the excellent structural and energy-level stability of the material. As the temperature rises, the overall PL emission intensity of the sample first increases and then decreases, which is attributed to the anomalous thermal quenching behavior induced by lattice defects arising from the substitution of Sm³⁺ for Ca²⁺. Notably, the decrease rates of PL intensities vary among different emission bands, offering the possibility of temperature measurement by analyzing the correlation between changes in the FIR and temperature.

As can be observed from the results presented in Fig. 15(b), during the variation of temperature, the emission peak corresponding to the ⁴G_{5/2} - ⁶H_{5/2} transition exhibits a relatively gentle decay in intensity, whereas the emission peak associated with the ⁴G_{5/2} - ⁶H_{7/2} transition shows a much more significant variation trend. In view of the distinct differences in the temperature-dependent response behaviors between the two characteristic emission peaks of ⁴G_{5/2} - ⁶H_{5/2} (I_{568}) and ⁴G_{5/2} - ⁶H_{7/2} (I_{603}), FIR of I_{568}/I_{603} is adopted as the research objective to explore its intrinsic relationship with temperature. The FIR of I_{568}/I_{603} can be deduced, and its specific expression is defined as follows [56]:

$$FIR = \frac{I_{568}}{I_{603}} \approx B + C \exp\left(-\frac{E}{kT}\right) \quad (12)$$

where the values of constants B , C , and E depend on those of the constants A , ΔE , and I_0 of I_{568}/I_{603} . As shown in Fig. 15(c), the calculated FIR values as a function of temperature can be perfectly fitted by equation (12). The values of B , C , and E/k are determined to be 0.191, 31.137, and 2683.908, respectively. On the basis of previous literature, the temperature of the studied sample corresponding to each experimentally observed FIR value can be deduced from the following expression:

$$T = \left[\frac{1}{\ln C - \ln(FIR - B)} \right] \frac{E}{k} \quad (13)$$

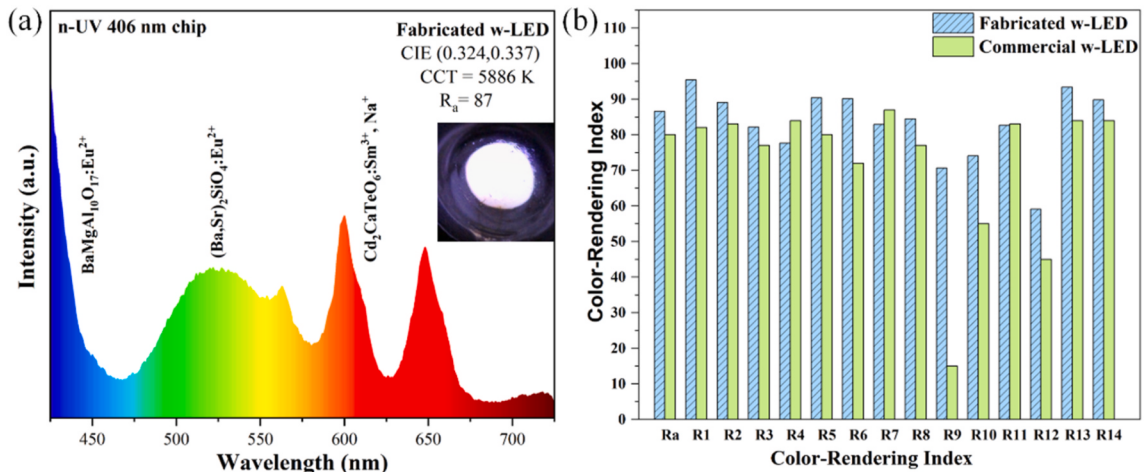


Fig. 14. (a) The EL spectrum of fabricated WLED. Inset: The photo of the fabricated WLED (b) The CRI comparison diagram of the prepared WLED and the commercial WLED.

Table 4The R_a and R_{1-14} of the fabricated and commercial WLED.

WLED	R_a	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}
Fabricated	87	95	89	82	78	90	90	83	85	71	74	83	59	93	90
commercial	80	82	83	77	84	80	72	87	77	15	55	83	45	84	84

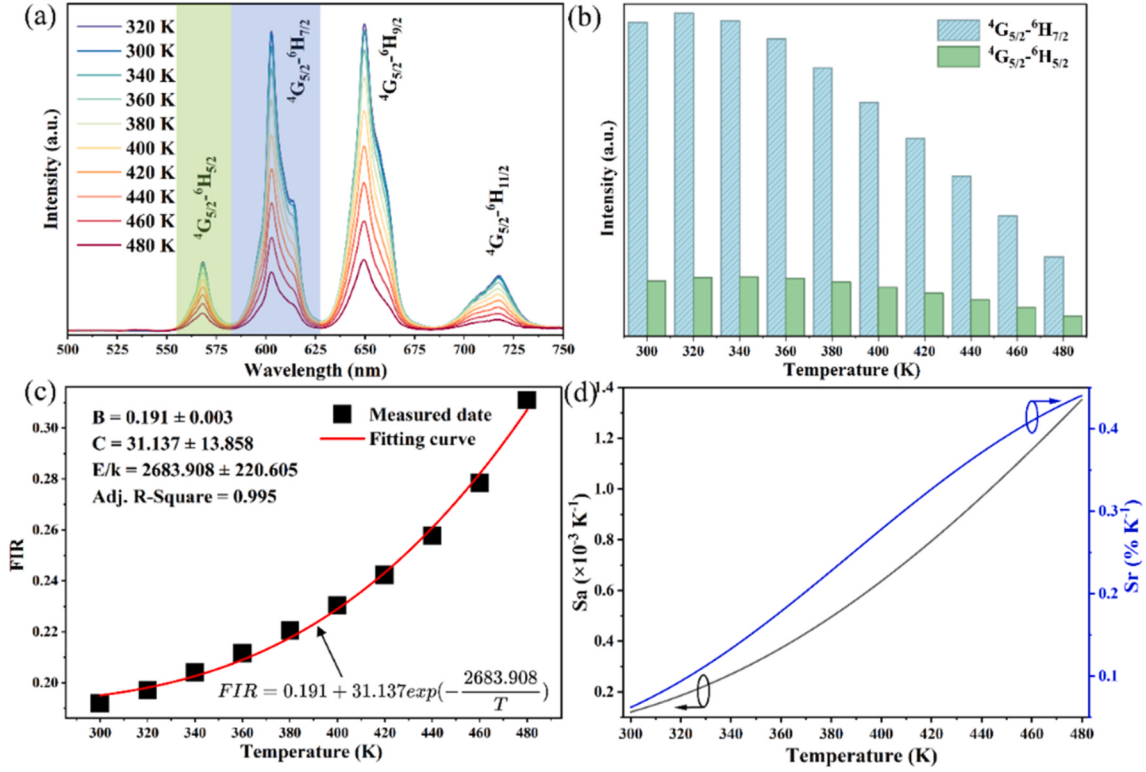


Fig. 15. (a) Temperature-dependent PL emission spectra of the CCTO:5 mol%Sm³⁺ phosphor. (b) Variation of the integrated PL emission intensities corresponding to the ${}^4G_{5/2} - {}^6H_{5/2}$ and ${}^4G_{5/2} - {}^6H_{7/2}$ transitions as a function of temperature. (c) FIR values at various temperatures. (d) The sensor sensitivities S_a and S_r of the FIR of I_{568}/I_{603} for the tested phosphor.

Herein, the parameters in the above formula have the same definitions as those mentioned above. Consequently, the average deviation between the calculated and measured temperatures is determined to be approximately ± 3.93 K within the temperature range of 320–480 K.

In the practical application of temperature sensing, sensitivity serves as a key parameter for evaluating sensor performance. According to previous reports, the absolute sensitivity S_a and relative sensitivity S_r can be defined to describe the absolute and relative change rates of FIR with temperature, respectively, which can be derived from the following expressions [57]:

$$S_a = \frac{d(FIR)}{dT} \quad (14)$$

$$S_r = 100\% \times \frac{1}{FIR} \frac{d(FIR)}{dT} \quad (15)$$

In these formulas, the parameters including B, C, and E share the same meanings as those mentioned above. Based on equations (14) and (15) together with the fitting results shown in Fig. 15(c), the values of S_a and S_r as functions of temperature were calculated and plotted in Fig. 15(d). The results reveal that both S_a and S_r increase gradually with rising temperature and reach their maximum values of 0.0014 K^{-1} and $0.44\% \text{ K}^{-1}$ at 480 K, respectively. This phenomenon indicates that the as-prepared sample possesses superior temperature-sensing performance in the medium–high temperature region. It indicates that the CCTO:5

mol% Sm³⁺ phosphor exhibits potential feasibility for application in temperature sensing.

4. Conclusions

This work presents a series of orange-red CCTO: $x\text{Sm}^{3+}$ phosphors ($0.5 \text{ mol}\% \leq x \leq 35 \text{ mol}\%$) synthesized by solid-state reaction. The samples (space group $P2_1/n$) enabled strong Sm³⁺ emission at 600 nm (${}^4G_{5/2} \rightarrow {}^6H_{7/2}$) under 406 nm excitation, with optimal performance at 5 mol% Sm³⁺ beyond which dipole-dipole quenching prevailed. The optimal sample showed high color purity emission at (0.622, 0.378). Codoping with Na⁺ ions drastically improved thermal stability, yielding a material that maintains 99.7% intensity at 420 K and has a $T_{0.5}$ above 480 K. A prototype WLED fabricated with the optimized phosphor achieved excellent performance metrics, a CCT of 5886 K, R_a of 87, and CIE coordinates of (0.324, 0.337), confirming that the CCTO:Sm³⁺ phosphor can serve as a potential candidate for specialized optoelectronic applications based on NUV-driven WLEDs. The temperature sensor sensitivities FIR of I_{568}/I_{603} reach their maximum values at 480 K, with 0.0014 K^{-1} (S_a) and $0.44\% \text{ K}^{-1}$ (S_r). These findings indicate that the CCTO:5 mol%Sm³⁺ phosphor possesses promising potential for temperature sensing.

CRediT authorship contribution statement

Fei Li: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Chaoyue Wang:** Writing – original draft, Visualization, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jingyue Yan:** Visualization, Methodology, Investigation, Data curation. **Junjie Feng:** Visualization, Methodology, Formal analysis, Data curation. **Daixin Hu:** Visualization, Formal analysis, Data curation. **Anyu Cheng:** Visualization, Data curation. **Dan Zhang:** Validation, Supervision, Resources, Methodology, Funding acquisition. **Yi Qu:** Validation, Supervision, Resources. **Ruijin Yu:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Compliance with ethical standards

This article does not contain any studies with human participants or animals performed by any of the authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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