

Enhanced luminescence and ultra-stability of WLEDs combined with urchin-like $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4:\text{Ln}^{3+}$ with hierarchical structure through charge self-compensation combined with 3D printing

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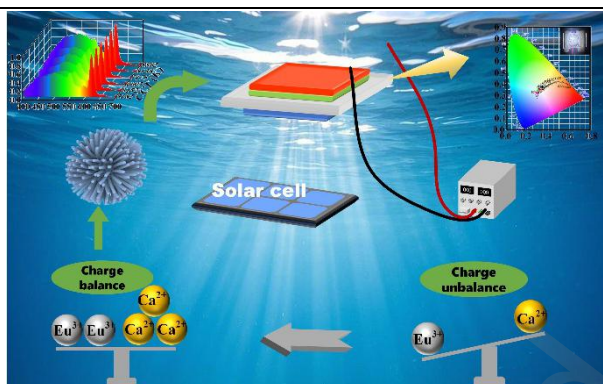
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In order to improve the luminescent properties of tungstate phosphors, a new charge self-compensation strategy was proposed to solve the problem of charge imbalance in rare earth doping. The integrated emission peak areas is enhanced by up to 2.96-fold after charge compensation. Combined with 3D printing technology, the resulting phosphor-resin composites exhibit excellent long-term ambient-storage stability and retain their characteristic luminescence. This approach provides a promising strategy for developing durable luminescent materials and color-tunable optoelectronic components.

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ABSTRACT: Although rare-earth tungstates exhibit significant advantages in luminescence, the common problem of charge imbalance in traditional Ln^{3+} doping systems poses a serious challenge for further improving luminescence intensity and color purity. Based on this, a charge self-compensation strategy is proposed by optimizing the charge balance state within the crystal lattice at the atomic scale, which effectively suppresses lattice defects and significantly reduces non-radiative transition processes, thereby greatly improving the luminescence intensity and stability. Detailed calculations and analysis based on density functional theory (DFT) were conducted on the crystal structure, band structure, density of states (DOS), and charge density distribution by constructing different doping structure models. The luminescence efficiency and stability have been improved by enhancing the hybridization of material orbitals. Compared with the corresponding uncompensated samples, the integrated emission peak areas of $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4\text{:Ln}^{3+}$ is enhanced by up to 2.96-fold after charge compensation. In addition, the 3D-printed phosphor-resin composites exhibit robust storage stability, with their integrated emission peak areas remaining above 95% of the initial values after six months of storage. Finally, white light-emitting diodes (WLEDs) manufactured using optimized phosphors achieved better color quality with a color rendering index (CRI) of 95, highlighting their potential in high-quality solid-state lighting and indoor photovoltaic applications.

KEYWORDS: charge self-compensation, luminescence enhancement, stability, three-dimensional (3D) printing, density functional theory (DFT), energy transfer

1 Introduction

As efficient, environmentally friendly, and long-lifetime light sources, white light-emitting diodes (WLEDs) have gradually replaced traditional incandescent and fluorescent lamps and have been widely used in lighting and display applications^[1,2]. Commercial WLEDs typically adopt either a blue LED chip combined with a yellow phosphor or an ultraviolet (UV) LED chip combined with tricolor phosphors^[3-6]. However, the standard “blue + yellow” configuration suffers from insufficient red spectral components^[7], resulting in a low color rendering index (CRI) and limited correlated color temperature (CCT) tunability^[8-10], which cannot satisfy the stringent requirements of high-fidelity color reproduction in specialized lighting and high-end displays^[11]. In contrast, UV LED-pumped tricolor phosphor-converted WLEDs can provide broader visible-spectrum coverage, improved color rendering, and flexible CCT tuning^[12,13]. It is well known that the overall device performance critically depends on the luminescence properties of each individual phosphor component. Therefore, designing efficient tricolor luminescent phosphors, especially by manipulating the local lattice environment at the atomic level to achieve high luminescence efficiency and robust thermal stability, is crucial for improving the service life and color consistency of next-generation WLEDs^[14-16].

Rare-earth (RE) ions have been extensively employed as luminescent activators due to their characteristic intra-4f electronic transitions^[17-19], which yield sharp emission peaks with long excited-state lifetimes and high color purity^[20,21]. So far, RE-doped phosphors have become indispensable for realizing high-performance WLEDs and advanced displays^[22,23]. It is well established that while the emission wavelengths of trivalent RE ions remain relatively insensitive to the host lattice, their luminescence efficiency and thermal stability are critically influenced by the host matrix^[24]. Among various host candidates, perovskite-type composite oxides have attracted considerable attention due to their excellent structural robustness, strong UV absorption, and outstanding thermal stability^[25-27]. As a typical representative, tungstates stand out as promising luminescent hosts^[28]. They not only exhibit an efficient host-sensitization effect to efficiently transfer absorbed energy to RE ions, but also possess a highly flexible and adjustable crystal structure^[29]. This structural versatility allows for precise lattice tuning, thereby significantly enhancing the luminescence efficiency and stability of the RE activators^[30,31]. Recent studies further demonstrate the importance of host-lattice and local-environment engineering in regulating RE luminescence. For example, Du et al. reported a Eu^{3+} -activated tungstate phosphor with broadband UV excitation and demonstrated that the highly symmetric local coordination environment of Eu^{3+} plays a crucial role in its characteristic orange-red emission^[32]. In addition, Li et al.

developed an $\text{Eu}^{2+}/\text{Nd}^{3+}$ co-doped phosphor capable of UV-visible-to-NIR photon down-conversion, highlighting the effectiveness of RE co-doping and energy-transfer regulation for spectral conversion and photovoltaic applications. Leveraging these structural advantages, researchers have recently explored various strategies for modifying tungstate-based materials, successfully improving luminescence intensity, tunable emission, and reversible photochromism^[33,34]. So far, RE-doped tungstates hold significant potential for applications in anti-counterfeiting, information storage, high-performance LEDs, bio-imaging and photovoltaics^[35].

For transition metal tungstate matrix materials, the valence states of rare earth ions and transition metal ions are different. In RE^{3+} -doped tungstate phosphors, heterovalent substitution of trivalent rare-earth ions for divalent alkaline-earth-metal sites can introduce local charge imbalance and associated lattice defects, which may adversely affect luminescence performance and stability^[35]. However, it is precisely this charge imbalance phenomenon that provides opportunities and challenges for further modification of rare earth luminescent materials. Charge self-compensation has been shown to be an effective strategy to reduce crystal defects and improve the quantum efficiency, luminescence intensity and stability of luminescent materials^[36,37].

In this work, RE-doped $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4$ phosphors were designed by combining density functional theory (DFT) calculations with compositional control of aliovalent substitution and A-site vacancies. The charge-compensated RE-doped $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4$ phosphors exhibit enhanced

luminescence and improved thermal stability compared with their corresponding uncompensated counterparts. Incorporation into photocurable resin by 3D printing provides structurally customizable composites with long-term ambient-storage stability. When integrated into WLEDs, the devices achieved a high CRI of 95 and a widely tunable CCT. Furthermore, the spectral coupling between these phosphors and silicon solar cells led to a marked enhancement in output photocurrent. The atomically regulated phosphors provide a promising platform for high-quality solid-state lighting and advanced photovoltaic applications.

2 Results and Discussion

In this work, a novel 3D urchin-like hierarchical architecture, self-assembled by 1D nanowires, is successfully synthesized. The detailed synthesis process, conditions, and sample abbreviation are provided in Figure 3a and Tables S8-S11. Our research focused on regulating at the atomic level through the adjustment of specific atomic sites to achieve charge self-compensation, thereby obtaining phosphors with enhanced luminescence performance and stability. This study aims to develop promising luminescent materials for use in WLEDs and indoor photovoltaic systems. The performance of WLEDs fabricated with the synthesized phosphors is evaluated, and the underlying applications are discussed in the subsequent sections.

2.1 DFT calculation and discussion

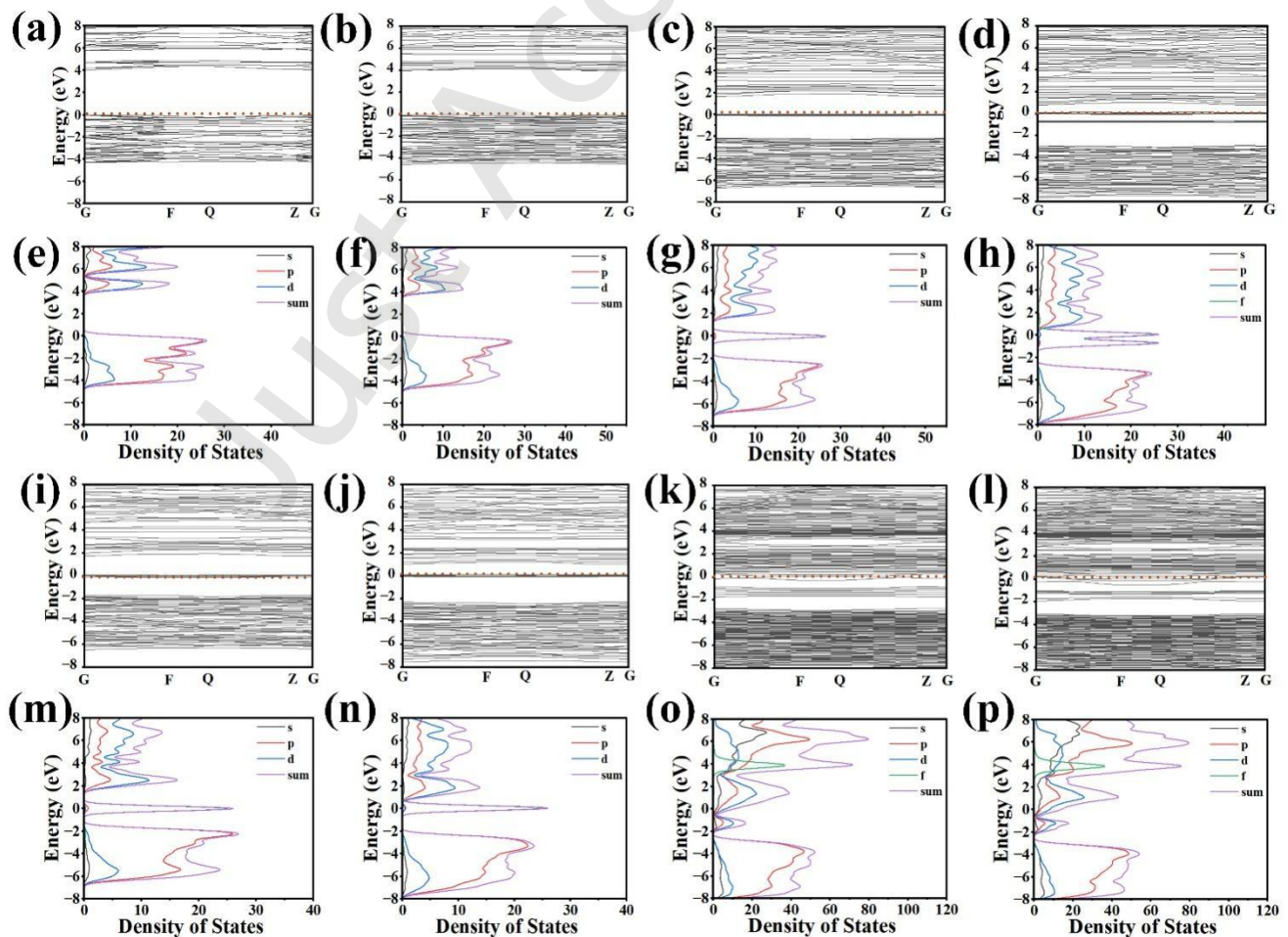


Figure 1. Energy band structure and DOS of (a,e) $\text{Ca}_4\text{W}_4\text{O}_{16}$, (b,f) $\text{Ca}_3\text{SrW}_4\text{O}_{16}$, (c,g) $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$ and (d,h) $\text{CaSrTbEuW}_4\text{O}_{16}$, (i,m) $\text{CaSrTbW}_4\text{O}_{16}$, (j,n) $\text{CaSrEuW}_4\text{O}_{16}$, (k,o) $\text{Ca}_{2.6}\text{Sr}_{2.4}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$, and (l,p) $\text{Ca}_{3.6}\text{Sr}_{2.4}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$.

The charge-compensation mechanism in this system is associated with rare-earth doping rather than Sr substitution. Because the substitution of Sr^{2+} for Ca^{2+} is isovalent, it does not directly affect the charge balance. In contrast, the substitution of $\text{Tb}^{3+}/\text{Eu}^{3+}$ for Ca^{2+} introduces excess positive effective charges, which are balanced by A-site cation vacancies in the charge-compensated compositions. In Kröger-Vink defect reaction, Ln^{3+} occupying a Ca^{2+} site is represented as $\text{Ln}_{\text{Ca}}^{\bullet}$, whereas the corresponding Ca-site vacancy is represented as V_{Ca}'' . The charge-neutrality relationship can therefore be expressed as: $2\text{Ln}_{\text{Ca}}^{\bullet} + V_{\text{Ca}}'' = 0$. Thus, one divalent cation vacancy is required for every two Ln^{3+} ions incorporated at Ca^{2+} sites.

Here, crystal structure models of $\text{Ca}_4\text{W}_4\text{O}_{16}$, $\text{Ca}_3\text{SrW}_4\text{O}_{16}$, $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$, and $\text{CaSrTbEuW}_4\text{O}_{16}$ were initially constructed based on the tungstate framework (Figure S1a-d) to evaluate their electronic properties. The pristine host consists of stable $[\text{WO}_4]^{2-}$ tetrahedra with Ca^{2+} ions occupying the interstitial sites. Cationic substitution was performed by replacing Ca^{2+} with Sr^{2+} , and subsequently doping with Tb^{3+} and Eu^{3+} activators. Figure 1(a-h) shows the calculated band structures and density of states (DOS) of the $\text{Ca}_4\text{W}_4\text{O}_{16}$, $\text{Ca}_3\text{SrW}_4\text{O}_{16}$, $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$, and $\text{CaSrTbEuW}_4\text{O}_{16}$ series. The characteristic of the host's electronic skeleton is hybridization between O 2p and W 5d orbitals. The original $\text{Ca}_4\text{W}_4\text{O}_{16}$ exhibits a wide band gap of 3.80 eV. When Ca^{2+} is partially replaced by Sr^{2+} , the band gap slightly narrows to 3.60 eV, indicating that alkaline earth metal substitution maintains the insulating properties of the host. However, the introduction of a small amount of rare earth ions significantly regulates the electronic environment. For $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$, the band gap decreases to 1.80 eV due to the appearance of localized Tb 4f states above the valence band maximum (VBM). In the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped system, the band gap further narrows to 0.80 eV.

The vacancy-containing models were also constructed to serve as direct comparisons with the corresponding vacancy-free configurations, thereby enabling a direct evaluation of the electronic-structure effect of the charge-compensation strategy (Figure 1i-p and Figure S1e-h). Specifically, $\text{CaSrTbW}_4\text{O}_{16}$ and $\text{CaSrEuW}_4\text{O}_{16}$ were constructed to examine the influence of A-site cation vacancies on the local electronic environment of the Tb^{3+} - and Eu^{3+} -doped systems, respectively. Furthermore, a larger $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped supercell was constructed according to the experimentally optimized composition, and the charge-compensated configuration containing an A-site cation vacancy was directly compared with its corresponding uncompensated configuration. In the charge-compensated $\text{Ca}_{2.6}\text{Sr}_{2.4}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$ model, one Ca-site vacancy compensates for the excess positive charge introduced by the trivalent RE ions, whereas the uncompensated $\text{Ca}_{3.6}\text{Sr}_{2.4}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$ model retains all eight A-site positions. These additional models provide direct theoretical controls for evaluating the microscopic role of cation-vacancy-mediated charge-compensation and improve the correspondence between the DFT models and the experimentally investigated phosphors. Of course, details of the model construction and the limitations of the adopted occupation-statistical approach are provided in the Supporting Information. The results indicate that the $\text{CaSrTbW}_4\text{O}_{16}$ and $\text{CaSrEuW}_4\text{O}_{16}$ models exhibit localized electronic states near the Fermi level. A direct comparison between the charge-compensated $\text{Ca}_{2.6}\text{Sr}_{2.4}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$ model (Figures 1k and 1o) and the uncompensated $\text{Ca}_{3.6}\text{Sr}_{2.4}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$ model (Figures 1l and 1p) reveals a distinct redistribution of the electronic bands and DOS near the Fermi level. These results suggest that the compensating cation vacancy is electronically active rather than serving merely as a stoichiometric charge-balancing component.

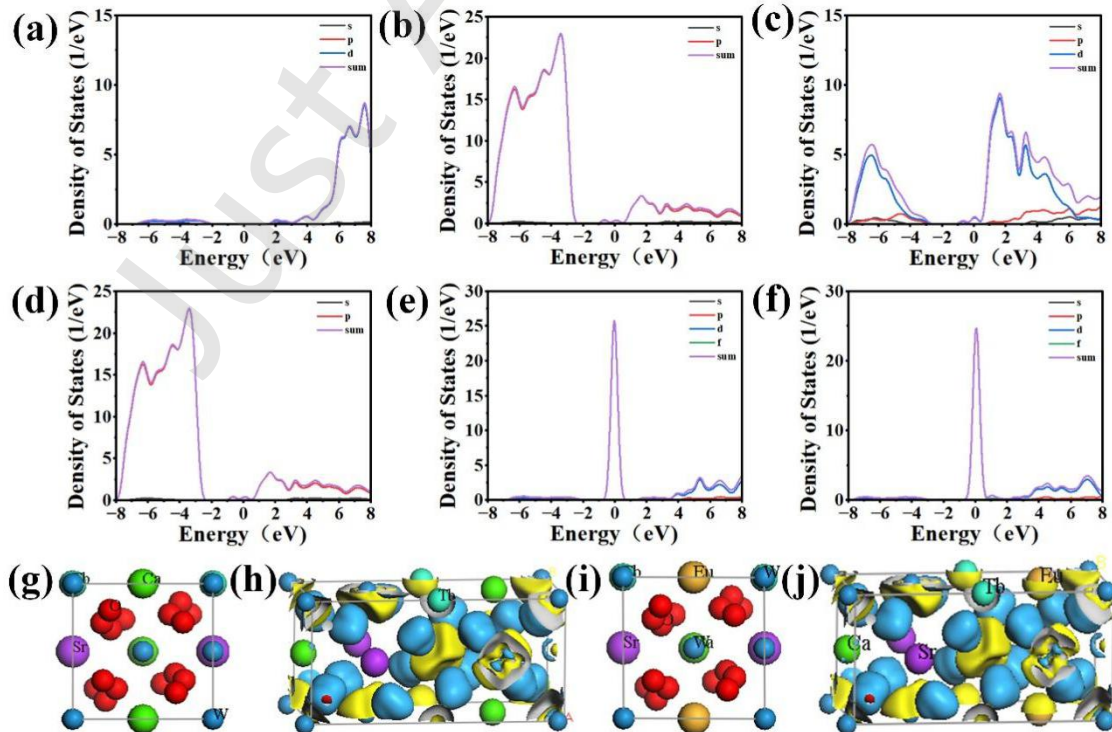


Figure 2. Partial DOS for $\text{CaSrTbEuW}_4\text{O}_{16}$. (a) Ca, (b) Sr, (c) W, (d) O, (e) Tb, and (f) Eu. Charge density distribution of (g,h) $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$ and (i,j) $\text{CaSrTbEuW}_4\text{O}_{16}$.

Then, the step-by-step component regulation processes of $\text{Ca}_4\text{W}_4\text{O}_{16}$, $\text{Ca}_3\text{SrW}_4\text{O}_{16}$ and $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$ were compared

(Figures S2-S4). As shown in the partial DOS spectra, all three compounds exhibit similar host-lattice characteristics, in which the VBM is mainly composed of O 2p states, while the conduction band minimum is primarily dominated by W 5d orbitals. This indicates that the fundamental optical transition originates from charge transfer within the WO_4^{2-} groups. After partial substitution of Ca^{2+} by Sr^{2+} (Figure S3), slight redistribution of the electronic states near the band edges is observed, which can be attributed to the modified crystal-field environment and lattice distortion around the $[\text{WO}_4]$ tetrahedra. With further Tb^{3+} incorporation, additional localized states emerge near the forbidden-gap region, originating from Tb 4f orbitals (Figure S4). These impurity levels can serve as intermediate energy states, facilitating energy migration from the host lattice to activator centers and thereby improving luminescence efficiency. Further insight into the optimized luminescence behavior was obtained from a detailed analysis of the electronic structure of $\text{CaSrTbEuW}_4\text{O}_{16}$ (Figure 2). The valence band remains dominated by O 2p states, whereas the conduction band is mainly contributed by W 5d orbitals, demonstrating preservation of the tungstate host electronic framework after co-doping. In addition, local impurity levels related to Tb 4f and Eu 4f states were introduced near the Fermi level, which align well with the increased electron density transfer observed in the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped matrix (Table S4). This transformation facilitates carrier transport and energy-transfer (ET) from the host lattice to $\text{Tb}^{3+}/\text{Eu}^{3+}$ activators, thereby improving luminescence efficiency.

The spatial distribution of electrons in the crystal was analyzed, and the charge density of the system was calculated. As shown in Figure 2(g-j), electrons are mainly concentrated in the bonding region between W atoms and O atoms, indicating that the W-O bond has a relatively obvious covalent characteristic. Meanwhile, the electron distribution around Ca and Sr atoms is relatively small, indicating that these atoms mainly exhibit ionic interactions in the crystal structure. When Tb^{3+} and Eu^{3+} ions are doped into the crystal lattice, the charge density distribution in the surrounding area changes to some extent, indicating that the introduction of rare earth ions has a certain impact on the local electronic structure. In addition, Hirshfeld charge analysis was performed on the $\text{Ca}_4\text{W}_4\text{O}_{16}$, $\text{Ca}_3\text{SrW}_4\text{O}_{16}$, $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$, and $\text{CaSrTbEuW}_4\text{O}_{16}$ systems. The results are presented in Tables S1 to S4. Based on the Hirshfeld charges, indicating a strong covalent nature of the W-O bonds, while metal ions such as Ca and Sr exhibit a certain degree of ionic character. As Sr^{2+} , Tb^{3+} , and Eu^{3+} are gradually introduced, the shift of electrons towards O atoms intensifies, leading to an increase in local charge polarization, which plays a significant role in the electronic properties of the material. This change in charge distribution not only affects the electronic structure of the material but may also have a certain impact on its optical properties and luminescence performance. Further insight into the effect of cation-vacancy-mediated charge-compensation was obtained from the Hirshfeld charge analysis of the vacancy-containing Tb^{3+} - and Eu^{3+} -doped models (Tables S5 and S6). In the $\text{CaSrTbW}_4\text{O}_{16}$ and $\text{CaSrEuW}_4\text{O}_{16}$ configurations, the calculated Hirshfeld charges of Tb and Eu are +0.58 e and +0.53 e, respectively. Meanwhile, the surrounding O and W sites exhibit nonuniform charge distributions, indicating that the introduction of an A-site cation vacancy induces local charge redistribution within the RE-doped tungstate framework. Combined with the corresponding DOS results in Figure 1, these calculations demonstrate that the

compensating cation vacancy not only maintains charge neutrality but also modifies the local electronic environment around the RE^{3+} activators. Such vacancy-induced charge redistribution provides microscopic electronic-structure support for the proposed charge self-compensation mechanism.

Calculated optical functions for the simplified models are shown in Figures S5-S8. The simulated optical properties of the systems were analyzed (Figure S5-S8). Since the first-principles optical calculation is fundamentally rooted in the determination of the dielectric function, other parameters including reflectivity, absorption, and conductivity were derived accordingly. The results show that $\text{CaSrTbEuW}_4\text{O}_{16}$ exhibits its primary optical response in the UV region. Specifically, the absorption spectrum reflects a major peak in the short-wavelength region, consistent with the high-energy transitions enabled by the RE 4f states. The refractive index and the dielectric function both show peak intensities in the UV range, indicating strong electronic polarization and light-matter interaction under high-energy photon excitation. The energy loss function peak further identifies the collective electronic oscillation frequency, which is crucial for understanding the non-radiative dissipation in these phosphors.

Comparative analysis shows that the optical functions of $\text{CaSrTbEuW}_4\text{O}_{16}$ differ significantly from the host $\text{Ca}_4\text{W}_4\text{O}_{16}$ and the Sr-substituted $\text{Ca}_3\text{SrW}_4\text{O}_{16}$ due to the introduction of multi-channel excitation pathways. Therefore, by precisely adjusting the doping ratios of Sr^{2+} , Tb^{3+} , and Eu^{3+} , the electronic environment and optical band gap can be reasonably tuned. This simulation-based insight provides a theoretical foundation for constructing high-quality optoelectronic devices, including WLEDs and indoor photovoltaics, and offers a strategic approach to optimizing the stability in practical applications.

2.2 Structural and morphological characterizations

The X-ray diffraction (XRD) patterns of the synthesized phosphors are presented in Figure S9. The investigated compositions include $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{WO}_4$, $\text{Ca}_{0.7-x}\text{Sr}_{0.3}\text{Tb}_x\text{WO}_4$, $\text{Ca}_{0.7-y}\text{Sr}_{0.3}\text{Eu}_y\text{WO}_4$, and $\text{Ca}_{0.7-x-y}\text{Sr}_{0.3}\text{Tb}_x\text{Eu}_y\text{WO}_4$. Owing to the unavailability of standard diffraction data for the $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{WO}_4$ solid solution, the JCPDS card for CaWO_4 (NO.85-0443) was accordingly employed as the reference compound for phase identification. As shown in Figure S9a, the diffraction peaks of all samples match well with the standard card, and no impurity peaks are observed, indicating successful synthesis of phase-pure materials. All samples crystallize in the body-centred tetragonal scheelite structure, and the doping of rare-earth ions did not alter the host structure. Table S7 summarizes the (112) peak positions, apparent FWHM values, interplanar spacings, and integrated emission areas for the compensated and uncompensated samples; Figure S9b enlarges the 27° - 30° region. For the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped pair with $\text{Eu}^{3+} = 0.05$, charge compensation shifts the (112) reflection from 28.435° to 28.537° ($\Delta 2\theta = +0.102^\circ$) and decreases d from 3.1363 to 3.1254 Å. The other compensated samples show the same overall shift to higher 2θ , although the FWHM changes are small and non-monotonic. Under eightfold coordination, Tb^{3+} (1.04 Å) and Eu^{3+} (1.066 Å) are smaller than Ca^{2+} (1.12 Å) and Sr^{2+} (1.26 Å). Therefore, the combined effects of RE^{3+} substitution, Ca-site vacancy formation, and associated lattice relaxation lead to a slight contraction of the local lattice. According to Bragg's law, this

contraction is consistent with the observed shift toward higher diffraction angles. Meanwhile, the integrated emission peak areas increase after charge compensation, indicating

that the observed lattice regulation is accompanied by enhanced luminescence performance and reduced defect-associated non-radiative relaxation.

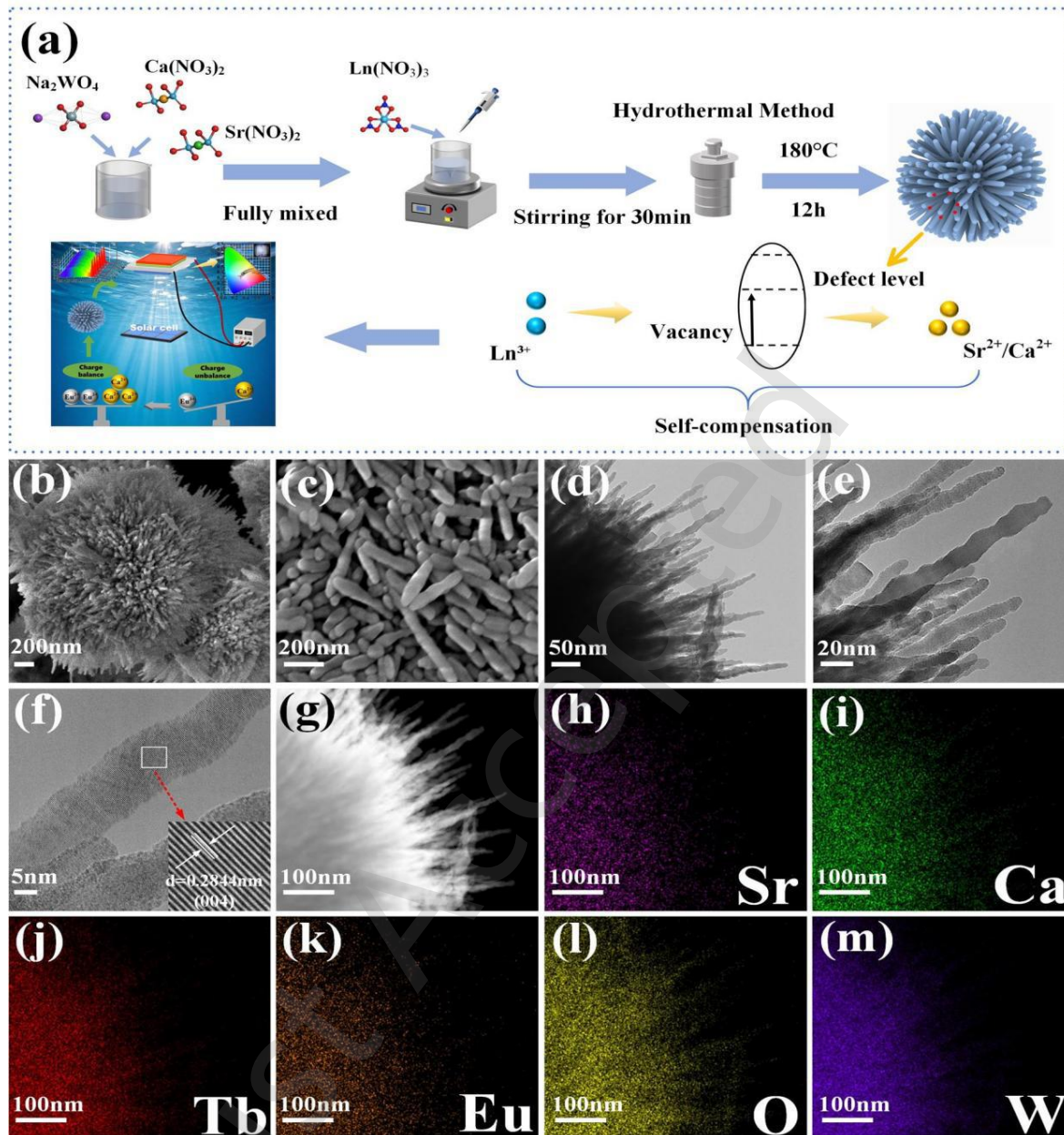


Figure 3. (a) Synthesis process of the material. (b,c) SEM images of $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$. (d-f) TEM and HRTEM images of $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$. (g-m) STEM-HAADF image and the corresponding EDS elemental mapping images of Tb, Ca, Sr, Eu, O, and W in $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$.

The morphology of the $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ phosphor was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in the SEM images in Figure (3b,c), the synthesized phosphors exhibit a well-defined 3D sea-urchin-like hierarchical morphology with a uniform diameter. High-magnification observations reveal that these micro-urchins are densely constructed by numerous 1D nanowires radiating from the core to the surface. The TEM images Figure 3 (d-f) further confirm the radial assembly of the nanowires. The HRTEM image Figure 3f displays clear lattice fringes with an interplanar spacing of 0.284 nm, corresponding to the (004) plane, indicating the highly crystalline nature of the individual nanowire building blocks. Furthermore, elemental mapping Figures 3h-3m confirms the uniform spatial distribution of Sr, Ca, W, O, Tb, and Eu throughout the nanowires, verifying the successful incorporation of rare-earth ions into the Sr/CaWO_4 host

lattice. The energy-dispersive X-ray (EDX) spectrum (Figure S10) reveals characteristic peaks for Tb and Eu, thereby demonstrating the successful incorporation of these RE ions.

X-ray photoelectron spectroscopy (XPS) was used to examine the elemental composition and surface chemical states. As shown in Figure S11, the characteristic photoelectron peaks of Ca, Sr, W, O, and doping rare-earth elements are clearly identified, with no foreign impurity elements detected, confirming the high chemical purity of the synthesized phosphors. Subsequently, high-resolution XPS spectra of Ca 2p, Sr 3d, and W 4f were investigated in detail to analyze local binding energy variations. For the O 1s spectra (Figure 4a), the broad asymmetric peak can be deconvoluted into three distinct components, which are assigned to lattice oxygen (Lattice O, $\sim 529.6 \text{ eV}$), defect oxygen/oxygen vacancies (Defect O, $\sim 530.3 \text{ eV}$), and surface adsorbed oxygen (Adsorbed O, $\sim 532.5 \text{ eV}$)^[38]. Comparing the spectra before and after doping, the peak area of the

adsorbed oxygen significantly decreases, and its position shifts toward a higher binding energy (to 532.98 eV). This indicates a decrease in the surrounding electron cloud density, suggesting an electron-loss state. Conversely, the peaks corresponding to lattice oxygen and defect oxygen on the right side generally shift toward lower binding energies. For the W 4f spectra (Figure 4d), the curves exhibit the characteristic spin-orbit split doublet of W 4f_{7/2} and W 4f_{5/2}. It should be noted that the multiple fitted peaks here primarily originate from the different local coordination environments or slight lattice distortions of W⁶⁺ in the complex solid solution^[39]. After doping, all characteristic peaks of W 4f exhibit a noticeable shift toward lower binding energies as the main peak shifts from 34.76 eV to 34.74 eV, and the relative area of the peaks on the high-binding-energy side decreases. This confirms an increase in electron density around the W atoms, indicating an electron-gain state. Regarding the alkaline-earth metals Ca 2p (Figure 4b) and Sr 3d (Figure 4c) spectra, both can be fitted into multiple pairs

of doublets. This is typically attributed to the Ca and Sr ions occupying different crystallographic sites or existing in distinct coordination polyhedra within the scheelite structure^[40]. A comparative analysis reveals that the main peaks of Ca 2p generally shift toward higher binding energies, indicating an overall tendency for Ca to lose electrons. However, the main peaks on the right side of the Sr 3d spectra shift toward lower binding energies, representing an electron gain for Sr, accompanied by a decrease in the area of the left-side peaks. This complex dynamic of electron gain and loss reflects intricate site substitutions and charge redistribution. For the rare-earth dopants, the Eu 3d spectrum in Figure 4e displays peaks at ~1134.5 eV and ~1165.0 eV, which should be accurately assigned to the 3d_{5/2} and 3d_{3/2} energy levels of Eu³⁺^[41], confirming the successful incorporation of Eu into the host lattice in the +3 oxidation state. Furthermore, Figure 4f shows the typical core-level characteristic peak of Tb 4d at ~151.36 eV^[42].

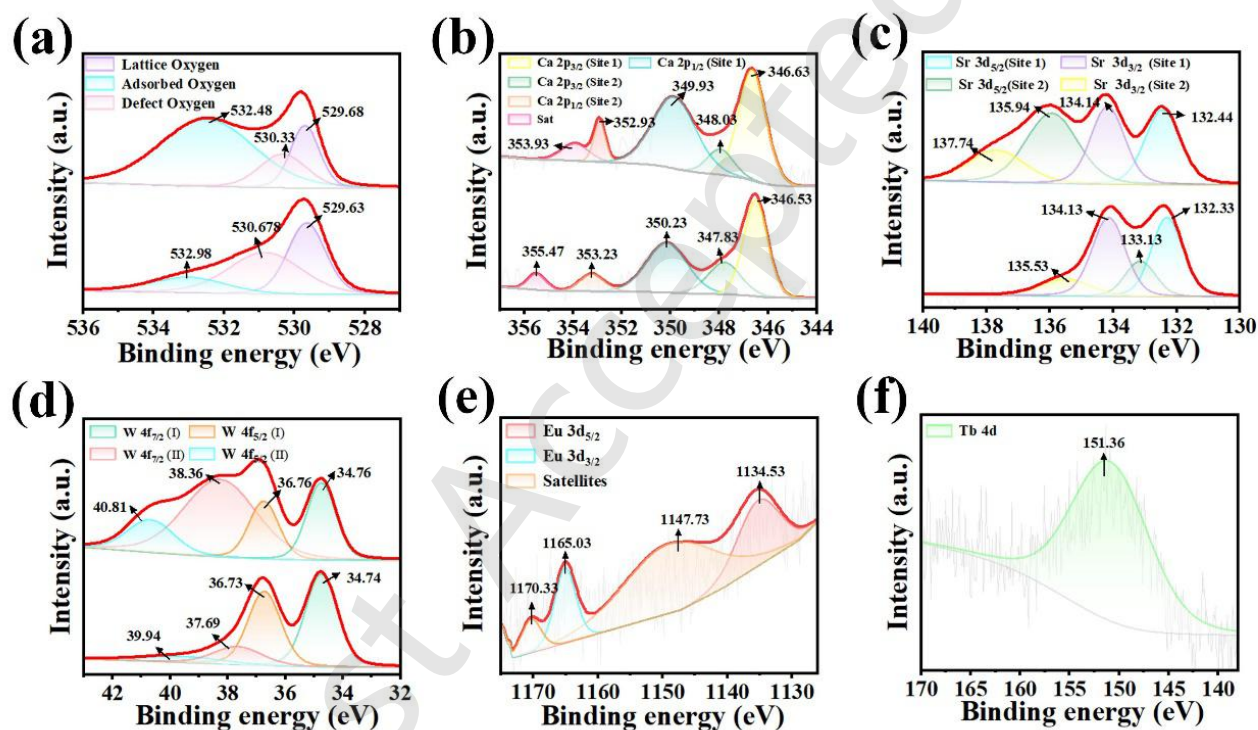


Figure 4. High-resolution XPS spectra of Ca_{0.5}Sr_{0.5}WO₄ (top curves) and Ca_{0.45}Sr_{0.3}Tb_{0.2}Eu_{0.05}WO₄ (bottom curves). (a) O 1s, (b) Ca 2p, (c) Sr 3d, (d) W 4f, (e) Eu 3d, and (f) Tb 4d.

The UV-vis absorption spectra of the prepared phosphors are presented in Figure S12. All samples exhibit a broad absorption band in the UV region, which is mainly associated with the O 2p → W 5d charge-transfer transition within the [WO₄]²⁻ groups. The charge-compensated and uncompensated samples exhibit similar overall absorption profiles, with only modest differences in absorption intensity in the main absorption region. Therefore, the relatively limited changes in the absorption spectra compared with the substantial enhancement in emission intensity suggest that charge-compensation predominantly influences the subsequent excitation-energy relaxation processes^[43].

The Fourier-transform infrared (FT-IR) spectra of the samples are shown in Figure S13 (4000–500 cm⁻¹). The spectra of several samples exhibit similar band profiles. Notably, the characteristic band near 800 cm⁻¹ corresponds to the antisymmetric stretching vibration of W–O bonds, while the peak around 1500 cm⁻¹ is attributed to the stretching vibrations of C=O and C=C groups. The spectral

features observed near 2900 cm⁻¹ and at 3400 cm⁻¹ arise from C–H vibrations and surface O–H stretching (from adsorbed H₂O), respectively.

2.3 Luminescence Properties and Stability Analysis

Figure S14 illustrates the photoluminescence (PL) properties of Ca_{1-x}Tb_xWO₄ with different Tb³⁺ concentrations (x) (Table S8). As observed in Figure S14a, the emission intensity of the characteristic green transition at 545 nm (⁵D₄ → ⁷F₅) gradually increases with increasing Tb³⁺ concentration and reaches a maximum at x = 0.20. Further increasing the Tb³⁺ concentration results in a decrease in emission intensity, which can be attributed to concentration quenching caused by enhanced non-radiative energy migration between adjacent Tb³⁺ ions. Therefore, Tb³⁺ concentration of 0.20 was selected as the optimal activator concentration for subsequent studies.

The local environment of Tb³⁺ was next adjusted by

replacing Ca^{2+} with Sr^{2+} in $\text{CaWO}_4:0.2\text{Tb}^{3+}$ host lattice to regulate the local crystal environment. A series of compositions based on $\text{Ca}_{0.8-y}\text{Sr}_y\text{Tb}_{0.2}\text{WO}_4$ with different Sr^{2+} concentrations (Sr/Ca ratios of 1/7, 2/6, 3/5, 4/4, 5/3, 6/2, and 7/1) were synthesized (Table S9). The dependence of the 545 nm emission intensity on the Sr^{2+} concentration is shown in Figure S15. The emission intensity gradually increases with increasing Sr^{2+} content and reaches a maximum at an Sr content of 0.30, indicating that the optimized Sr^{2+} concentration effectively modifies the local lattice environment and promotes Tb^{3+} luminescence. Therefore, $\text{Ca}_{0.5}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{WO}_4$ was selected as the optimized host composition for further charge-compensation studies. Figure S16a shows the emission spectrum of $\text{Ca}_{0.7-y}\text{Sr}_{0.3}\text{Eu}_y\text{WO}_4$ at 396 nm ($y = 0.03, 0.04, 0.05, 0.06, 0.07$) (Table S10). The emission spectra of Eu^{3+} , featuring multiple peaks from 545 to 750 nm, are dominated by the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. Luminescence intensity shows a nonlinear

dependence on doping concentration (y), enhancing with y until reaching a maximum at $y = 0.05$. Further increase leads to quenching due to enhanced non-radiative ET. Consequently, the strongest emission peak at 618 nm is observed at this optimal 5% doping level. Figure S16b presents the excitation spectra (monitored at 618 nm) of the $\text{Ca}_{0.7-y}\text{Sr}_{0.3}\text{Eu}_y\text{WO}_4$ series ($y = 0.03, 0.04, 0.05, 0.06, 0.07$). The broad absorption band centered around 273 nm is attributed to the superposition of two charge transfer transitions: from O^{2-} to W^{6+} (LMCT) within the WO_4^{2-} group and from O^{2-} to Eu^{3+} (CT). This synergistic overlap of the LMCT and CT bands leads to significant spectral broadening, thereby enhancing the light-harvesting capability within this energy range. The spectral profile in the long-wavelength region is characterized by sharp excitation peaks arising from the $\text{Eu}^{3+} 4f \rightarrow 4f$ transitions, the strongest of which (at 396 nm) is assigned to $^7\text{F}_0 \rightarrow ^5\text{L}_6$.

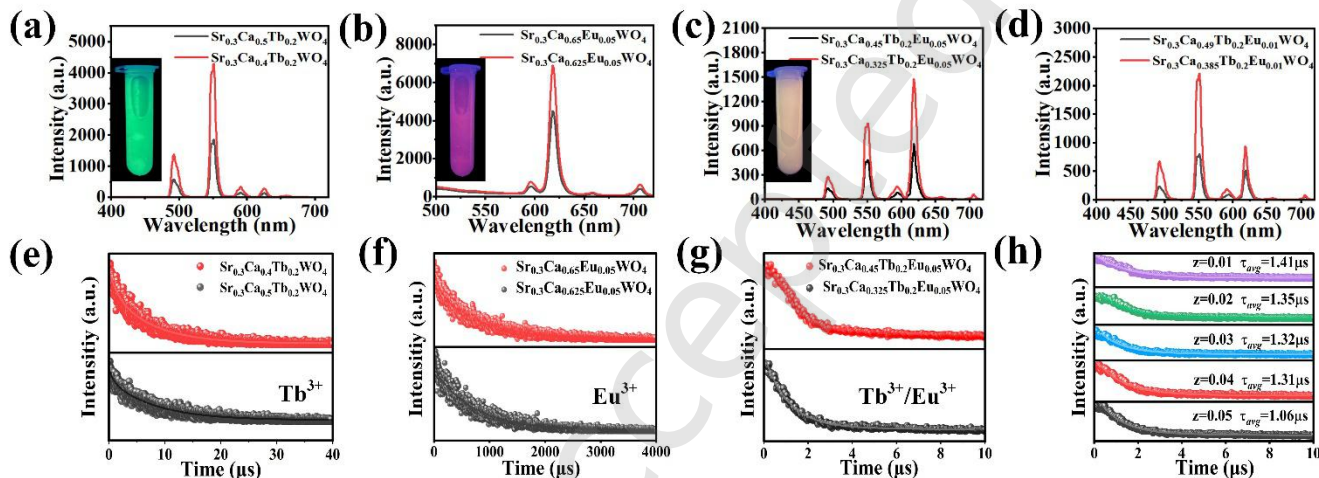


Figure 5. The influence of charge-compensation on luminescence properties. (a-d) Emission spectra and digital photos (insets) of Tb^{3+} , Eu^{3+} , and $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped charge-compensated (colored lines) and uncompensated (black lines) samples. The insets in (a-c) show digital photographs of the corresponding samples under UV irradiation. (e-g) PL decay curves of (e) Tb^{3+} -doped, (f) Eu^{3+} -doped, and (g) $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped samples. (h) Tb^{3+} decay curves monitored at 545 nm for the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped samples with different Eu^{3+} concentrations.

Figure S17 presents the concentration-dependent emission and excitation spectra of the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped phosphors. Here, z represents the Eu^{3+} concentration in $\text{Ca}_{0.5-z}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_z\text{WO}_4$ and varies from 0.01 to 0.05. The corresponding sample compositions and amounts of the starting materials are summarized in Table S11. As shown in Figure S17a, with increasing Eu^{3+} concentration, the characteristic Tb^{3+} emission at 545 nm gradually decreases, whereas the relative contribution of the Eu^{3+} emission at 618 nm becomes increasingly prominent. Figure S17b shows the corresponding excitation spectra monitored at the Eu^{3+} emission wavelength of 618 nm. The main excitation band in the UV region generally increases in intensity with increasing Eu^{3+} concentration. Therefore, the energy-transfer process is supported by the concentration-dependent redistribution of Tb^{3+} and Eu^{3+} emissions together with the shortening of the Tb^{3+} donor lifetime upon increasing Eu^{3+} concentration.

Compensated and uncompensated phosphors were measured under identical conditions to quantify the effect of charge regulation. Figure 5(a-d) compares the characteristic emission behaviors of the Tb^{3+} -doped, Eu^{3+} -doped, and $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped phosphors before and after introducing the charge self-compensation strategy. The corresponding digital photographs under UV irradiation are also presented as insets. For the Tb^{3+} -doped phosphors, the integrated emission peak areas is enhanced by approximately 2.45-fold after charge-compensation. For the Eu^{3+} -doped phosphors

measured under 396 nm integrated emission peak areas gives an enhancement factor of approximately 1.43. For the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped systems under 250 nm excitation, the integrated emission peak areas of the charge-compensated samples are approximately 2.96 and 2.30 times those of their corresponding uncompensated counterparts at Eu^{3+} concentrations of 0.01 and 0.05, respectively. Meanwhile, the ratios of the characteristic emission peak values of the charge-compensated samples to those of the corresponding uncompensated samples are approximately 2.30, 1.52, 2.17, and 2.74 for the samples shown in Figure 5a-d, respectively. The consistent enhancement of the integrated emission intensity in the Tb^{3+} -doped, Eu^{3+} -doped, and $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped systems demonstrates that the beneficial effect of charge-compensation is not limited to an individual emission line or a specific activator but is reflected in the overall emission output. This enhancement can be reasonably associated with regulation of the local charge environment introduced by heterovalent Ln^{3+} substitution and the consequent reduction of defect-associated non-radiative energy-loss pathways.

The excited-state dynamics and energy-relaxation processes of Ln^{3+} in the investigated phosphors were examined by recording the PL decay curves and fitting them with a bi-exponential decay model. The average lifetimes were calculated from the corresponding fitting parameters. Details of the fitting model and average-lifetime calculation are provided in the Supporting Information, and the

calculated energy-transfer efficiencies are summarized in Tables S12 and S13. Figures 5e-g present the decay curves of the single- and co-doped phosphors before and after charge compensation. Specifically, Figures 5e and 5f correspond to the Tb^{3+} - and Eu^{3+} -single-doped systems, respectively, whereas Figure 5g shows the corresponding comparison for the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped system. In the single-doped systems, the charge-compensated samples exhibit moderately prolonged decay behavior. The average lifetime of Tb^{3+} increases from 13.39 to 14.07 μs , while that of Eu^{3+} increases from 705.78 to 762.50 μs after charge compensation. These lifetime increases, together with the enhanced steady-state emission intensities, indicate that charge regulation suppresses defect-associated non-radiative relaxation and improves the local luminescent environment of the Ln^{3+} activators^[44].

The concentration-dependent $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy-transfer behavior was further examined using the Tb^{3+} decay curves of the $\text{Ca}_{0.5-z}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_z\text{WO}_4$ series shown in Figure 5h. The Eu^{3+} -free $\text{Sr}_{0.3}\text{Ca}_{0.5}\text{Tb}_{0.2}\text{WO}_4$ phosphor, with a Tb^{3+} average lifetime of 13.39 μs , was used as the reference donor sample. After Eu^{3+} incorporation, the progressive shortening of the Tb^{3+} donor lifetime indicates that Eu^{3+} incorporation introduces an additional depopulation pathway for the Tb^{3+} ($^5\text{D}_4$) excited state. This lifetime evolution is consistent with the steady-state emission spectra in Figure S17a, in which the Tb^{3+} emission at approximately 545 nm gradually decreases, whereas the Eu^{3+} emission at approximately 618 nm becomes increasingly prominent as the Eu^{3+} concentration increases. The resulting η_{ET} values are 89.48%, 89.92%, 90.17%, 90.24%, and 92.10% for $z = 0.01, 0.02,$

0.03, 0.04, and 0.05, respectively. The simultaneous shortening of the Tb^{3+} donor lifetime, redistribution of the characteristic emission intensities, and high η_{ET} values collectively confirm efficient $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer.

Based on the aforementioned luminescence enhancement in both single-doped and co-doped systems, the ET process between Tb^{3+} and Eu^{3+} ions was further investigated. The comparison of the PL and photoluminescence excitation (PLE) spectra of $\text{Ca}_{0.65}\text{Sr}_{0.3}\text{Eu}_{0.05}\text{WO}_4$, $\text{Ca}_{0.5}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{WO}_4$, and $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ under identical conditions is shown in Figure S18. Experimentally, characteristic emissions from both Tb^{3+} and Eu^{3+} are observed in the co-doped phosphor under 250 nm excitation. In particular, the appearance of the characteristic Eu^{3+} red emission centered at approximately 618 nm under excitation in the Tb^{3+} -related absorption region indicates that excitation energy can be delivered to the Eu^{3+} emitting states in the co-doped system. Under UV excitation, the excitation energy absorbed by the host lattice and Tb^{3+} sensitizer populates the excited states of Tb^{3+} , followed by non-radiative relaxation to the ($^5\text{D}_4$) level. The excitation energy can subsequently be released through the characteristic ($^5\text{D}_4 \rightarrow ^7\text{F}_j$) transitions of Tb^{3+} or transferred non-radiatively to neighboring Eu^{3+} acceptors. The transferred energy ultimately populates the Eu^{3+} ($^5\text{D}_0$) emitting state, from which the characteristic ($^5\text{D}_0 \rightarrow ^7\text{F}_j$) emissions occur. Together with the spectral evolution of the Tb^{3+} and Eu^{3+} emissions, these observations support the presence of an ET pathway between Tb^{3+} and Eu^{3+} . The proposed $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ ET pathway is illustrated in Figure S19.

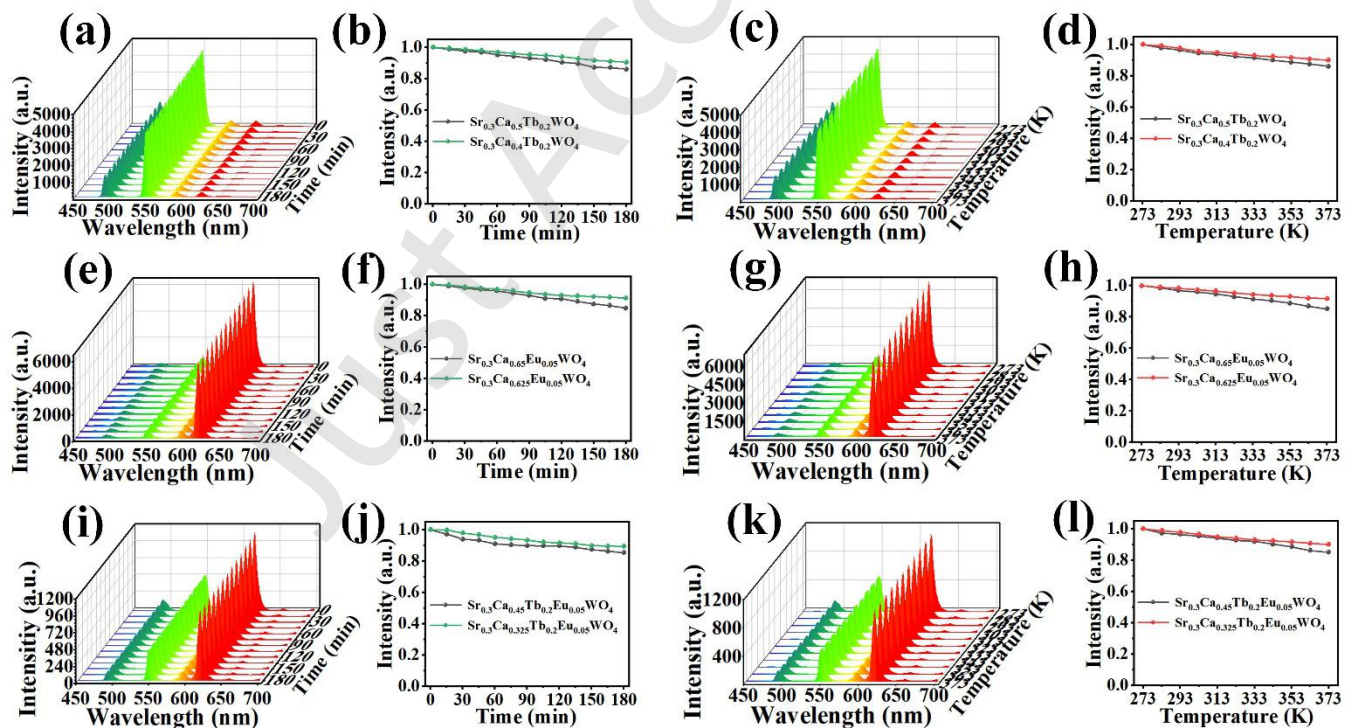


Figure 6. Stability spectra and line charts of charge-compensated samples. Photostability (left) and thermal stability (right) characterization of (a-d) Tb^{3+} -doped, (e-h) Eu^{3+} -doped, and (i-l) $\text{Tb}^{3+}/\text{Eu}^{3+}$ -doped charge-compensated (colored lines) and uncompensated (black lines) samples.

The Commission Internationale de l'Éclairage (CIE) 1931 chromaticity coordinates and corresponding emission spectra of charge-compensated and uncompensated phosphor systems were compared (Figure S20). Charge-compensation engineering effectively optimizes the emission spectrum, shifting the chromaticity coordinates from the

magenta region (Point A: CIE [0.38, 0.26]) to the red region (Point B: CIE [0.46, 0.27]). This shift positions the emission much closer to the requirements for warm-white lighting devices. The charge-compensated phosphor exhibits significantly enhanced color purity and saturation, making it highly suitable for use as a red-light source or a red

component in white phosphor converters. This advancement paves the way for its application in next-generation WLEDs.

The operational stability of phosphors, including resistance to continuous irradiation and thermal quenching, is critical for their application in WLEDs. The photostability and thermal stability of uncompensated and charge-compensated samples in Tb^{3+} -doped, Eu^{3+} -doped, and $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped systems were systematically compared. Figure S21(a-c) illustrates the changes in emission spectra of uncompensated phosphors over time during continuous excitation for 180 minutes. Figures 6(a,e,i) illustrate the time-dependent emission spectra of charge-compensated phosphors under continuous excitation for 180 minutes. As shown in the normalized intensity curves Figures 6(b,f,j), all samples exhibit a slight degradation in luminescence intensity over time. However, the charge-compensated samples (colored lines) consistently demonstrate superior photostability compared to their uncompensated counterparts (black lines). Specifically, for the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped system (Figure 6j), the charge-compensated $\text{Ca}_{0.325}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ retains a much higher percentage of its initial intensity after 180 min, whereas the uncompensated sample shows a more pronounced decay. This enhanced resistance to optical degradation suggests that charge-compensation strategy effectively reduces surface defects that often act as quenching centers under continuous photon bombardment. Furthermore, the thermal quenching behavior was investigated from 273 K to 373 K, as shown in Figure S21 (e-g) and Figure 6(c,g,k). The thermal stability profiles (Figure 6d,h,l) reveal that the emission intensity decreases with increasing temperature due to the intensified non-radiative transitions. Notably, the charge-compensated samples exhibit a slower decay rate. For instance, in the co-doped system (Figure 6l), the charge-compensated phosphor maintains a higher relative intensity at 373 K compared to the uncompensated one. The charge-compensated phosphor demonstrates superior thermal stability, retaining over 90% of its initial intensity at 373 K, compared to only 85% for the uncompensated system. The improved thermal stability demonstrates the success of

charge-compensation in mitigating thermal quenching, a key factor in phosphor performance degradation at elevated temperatures. The simultaneous improvement in both photostability and thermal stability can be attributed to the charge self-compensation strategy. By balancing the valence charges in the crystal lattice, the formation of uncontrolled defects and defect-associated non-radiative centers is suppressed. This leads to a more rigid crystal lattice and fewer non-radiative relaxation channels, thereby ensuring stable luminescence output under harsh operating conditions.

2.4 High-Performance WLEDs and Their Application in Indoor Photovoltaics

As mentioned above, $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ and $\text{Ca}_{0.325}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ were employed as orange-emitting phosphors for WLED fabrication. The phosphors were combined with the blue-emitting CsBr component and integrated with a 275 nm UV LED chip. By adjusting the relative proportions of the two luminescent components, white-light emission with a CRI above 90 and tunable CCT was obtained, enabling a continuous shift from cool to warm white light (Figure 7a,b). Under identical experimental conditions, WLEDs were fabricated separately using the uncompensated and charge-compensated phosphors for direct comparison. The corresponding CRI, CCT, and calculated luminous efficacy of radiation (LER) values are summarized in Tables S14 and S15. The charge-compensated WLEDs exhibited favorable CRI and CCT characteristics. By optimizing the operating voltage between 4.4 V and 4.7 V, the spectral output was further fine-tuned, yielding an LED source with chromaticity coordinates closer to the standard white-light locus, as shown in Figure 7c,d. Tuning the operating voltage (4.4-4.7 V) enabled precise adjustment of the WLED spectral characteristics and CIE coordinates (Tables S16, S17). This spectral tuning enables adjustable white-light emission while maintaining a high color-rendering quality and favorable LER.

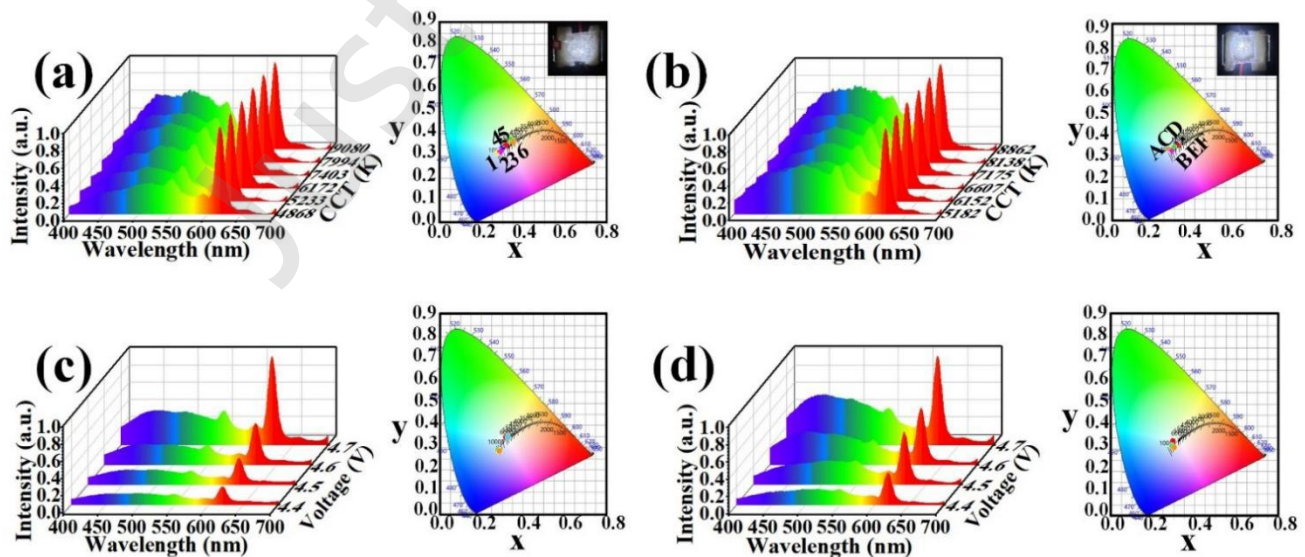


Figure 7. Emission spectra and corresponding CIE chromaticity coordinates of WLEDs fabricated using (a, c) uncompensated and (b, d) charge-compensated $\text{Tb}^{3+}/\text{Eu}^{3+}$ -doped phosphors.

The fabricated WLEDs were tested under continuous irradiation and at elevated temperature. Figure 8a and 8c illustrate the variation of luminous intensity under continuous UV irradiation (365 nm) for 8 hours. For the

uncompensated device (LED-4, Figure 8a), the luminous intensity shows a slight degradation over time. In contrast, the charge-compensated device (LED-E, Figure 8c) exhibits superior aging resistance, retaining nearly 90% of its initial

intensity after 8 h of continuous UV irradiation. This suggests that the optimized phosphor possesses excellent structural stability against UV radiation. Figure 8b and 8d present the temperature-dependent luminescence properties from 273 K to 373 K. Thermal stability is a critical parameter for high-power LEDs, as the junction temperature inevitably rises during operation. As the temperature increases to 373 K (100 °C), the luminous intensity of LED-E (Figure 8d) decreases more slowly than that of LED-4 (Figure 8b). The LED-E device maintains a high emission

intensity at elevated temperatures, indicating a low thermal quenching rate. The enhanced stability of LED-E can be attributed to the charge self-compensation strategy. The introduction of cation vacancies to balance the charge regulates the defect environment and suppresses competing non-radiative relaxation pathways induced by thermal vibration or UV irradiation. These results confirm that the optimized phosphor is a robust candidate for long-term, high-quality WLED applications.

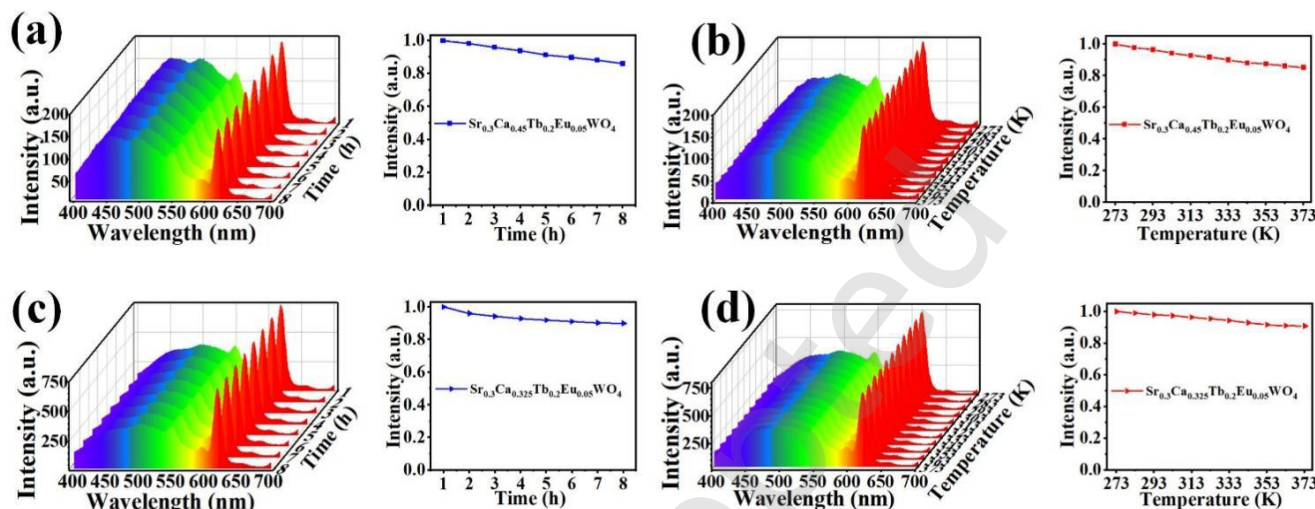


Figure 8. (a,c) Photostability and (b,d) thermal stability characterization of (a,b) LED-4 and (c,d) LED-E.

As discussed previously, WLEDs fabricated using $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped phosphors not only deliver high-quality white light with a CRI exceeding 90, but also maintain more consistent LER and CCT characteristics, while exhibiting excellent luminescence stability. These results highlight the considerable potential of the fabricated WLEDs for indoor photovoltaic applications. Specifically, the LED-4 device achieved chromaticity coordinates of (0.2959, 0.3331), with a CRI of 95, a CCT of 7403 K, a gamut index (R_g) of 100, and a fidelity index (R_f) of 91. Notably, the charge-compensated device (LED-E) demonstrated a similarly high CRI of 93 and a CCT of 6150 K, along with an R_g of 101 and an R_f of 91 (Figure S22). Overall, the charge self-compensation strategy represents an efficient and versatile approach to enhancing phosphor performance, as it directly addresses the fundamental limitations of luminescence efficiency and thermal stability through defect engineering. The feasibility of the WLEDs for indoor light-energy harvesting was subsequently evaluated by coupling them with silicon solar cells. Similar phosphor-based spectral-conversion strategies have also been reported for crystalline-silicon solar cells, demonstrating the potential of luminescent materials for improving spectral utilization in photovoltaic applications^[45].

Figures S23-S25 show the current-voltage, transient-photocurrent, and impedance responses as the LED drive voltage increases from 2.9 to 3.2 V. At 3.2 V, illumination by LED-E increases J_{sc} from 27.75 to 61.57 $\mu\text{A cm}^{-2}$ and the conversion efficiency (η) from 3.25% to 7.49% relative to LED-4. The generated photocurrent exhibits a positive correlation with the WLED driving voltage, resulting from the increased excitation intensity. The corresponding photovoltaic parameters, including short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and conversion efficiency (η), are summarized in Tables S18 and S19. Under identical LED operating voltages, the silicon solar

cell illuminated by the charge-compensated LED-E device generally exhibits higher photovoltaic output than that illuminated by LED-4. Additionally, the transient photocurrent measurements demonstrate a stable and reproducible photoresponse under repeated LED illumination, making them suitable candidates for indoor photovoltaic (IPV) applications.

2.5 3D-printed phosphor-resin composites and long-term ambient-storage stability

In recent years, the field of 3D printing and photovoltaic materials has gradually become a research hotspot in the field of photochemistry^[46]. In this study, composite materials were prepared by dispersing the phosphors within a photopolymerizable resin (Figure 9a-d). The detailed preparation and printing procedures are provided in the Supporting Information. As a proof of structural customizability, a representative printed sample featuring the characters “Heilongjiang University” is shown in the inset of Figure 9f. The resulting composites exhibit vivid green, red, and orange emissions under UV excitation, demonstrating that the characteristic luminescence of the phosphors is retained after incorporation into the photocurable resin matrix.

The long-term ambient-storage stability of the 3D-printed resin composites was evaluated by monitoring their PL spectra under 250 nm excitation. As shown in Figures 9c and 9d, the phosphor-resin composites retain their characteristic emission profiles after 6 months of ambient storage. The characteristic Eu^{3+} (618 nm) and Tb^{3+} (545 nm) integrated emission peak areas above 95% of their initial values, corresponding to an intensity loss of less than 5%. These results demonstrate the excellent long-term ambient-storage stability of the 3D-printed resin composites under

the investigated conditions. A comparative analysis of the thermal stability for resin-embedded phosphors 3D-printed materials is presented in Figure 9e. The materials incorporating charge-compensated phosphors retained

93.8% of their initial performance, compared to 91.3% for their non-compensated counterparts, confirming the beneficial effect of charge-compensation.

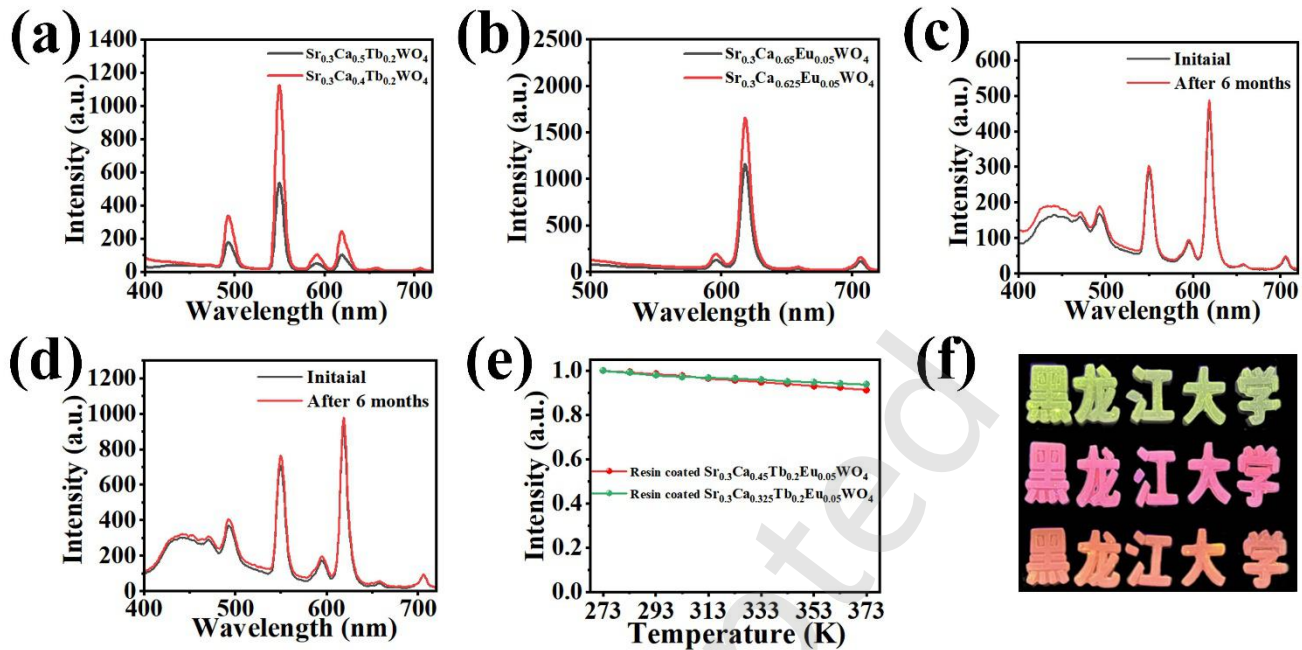


Figure 9. (a,b) Emission spectra of phosphor-resin composites Tb^{3+} - and Eu^{3+} -doped charge-compensated (colored lines) and uncompensated (black lines) samples. (c,d) Emission spectra of $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped uncompensated and charge-compensated samples coated with resin, measured at 6 months intervals. (e) Thermal-stability characterization of $\text{Tb}^{3+}/\text{Eu}^{3+}$ -doped compensated (green line) and uncompensated (red line) samples. (f) Photographs of printed "Heilongjiang University" under UV light.

At the microscopic level, charge-compensation regulates the local charge environment associated with Ln^{3+} incorporation and modifies defect-associated non-radiative relaxation pathways, thereby improving the luminescence properties of the phosphor. At the macroscopic level, the photocured resin matrix physically confines the phosphor particles within the printed architecture and helps maintain the structural integrity of the composite during long-term storage. This strategy translates the performance advantages of the phosphor-resin composites phosphor system into a novel paradigm for smart LEDs, enabling customizable architectures and enhanced durability. It thus paves the way for innovative applications in areas such as flexible electronics and advanced anti-counterfeiting.

3 Conclusion

In this work, $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4:\text{Ln}^{3+}$ microspheres composed of highly crystalline, radially aligned nanowires were successfully synthesized. The material design was guided by DFT calculations and implemented through a charge self-compensation strategy. By regulating the local lattice and charge environment through aliovalent Ln^{3+} substitution and A-site vacancy compensation, defect-associated non-radiative relaxation pathways were reduced, resulting in enhanced luminescence and improved thermal stability. Structural and spectroscopic analyses further revealed a consistent relationship between lattice regulation and optical performance. Concentration-dependent emission spectra and fluorescence decay analyses support the $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ ET process. When incorporated into WLED prototypes, the optimized phosphors provided a high CRI of up to 95 and tunable CCT. In addition, coupling the phosphor-converted WLEDs with silicon solar cells resulted in enhanced photocurrent output. Embedding the phosphors in

photocurable resin also yields 3D-printed composites that retain more than 95% of their characteristic emission intensity after six months of ambient storage. Overall, the charge-compensated tungstate phosphors provide a promising platform for high-quality solid-state lighting and optical conversion applications.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Electronic Supplementary Material: Supplementary material (experimental section, detailed characterization, spectral optimization, and computational details)

Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

Ao Xu: Data curation, project administration, validation, writing manuscript, experimental design. Yuxin Liu: Data curation, project administration, validation, experimental design. Wenshu Yuan: Experimental design. Zhangong Bai: Data curation. Guofeng Wang: Project administration,

funding acquisition. All the authors have approved the final manuscript.

References

- [1] Mehare, M. D.; Mehare, C. M.; Swart, H. C.; Dhoble, S. J. Recent development in color tunable phosphors: A review. *Progress in Materials Science* **2023**, *133*, 101067.
- [2] Feng, W.; Chen, X.; Cui, Y.; Chen, J.; Hou, E.; Xu, J.; Wei, Z.; Ma, D. Intermediate stabilization enables antisolvent-free crystallization of perovskites for high-performance light-emitting diodes. *Nano Research* **2026**, *19*, 94908503.
- [3] Haider, G.; Usman, M.; Chen, T.-P.; Perumal, P.; Lu, K.-L.; Chen, Y.-F. Electrically Driven White Light Emission from Intrinsic Metal-Organic Framework. *ACS Nano* **2016**, *10*, 8366-8375.
- [4] Chen, X.; Han, X.; Zhang, C.; Ou, X.; Liu, X.; Zhang, J.; Liu, W.; Ragauskas, A. J.; Song, X.; Zhang, Z. Synthesis of Red, Green, and Blue Carbon Quantum Dots and Construction of Multicolor Cellulose-Based Light-Emitting Diodes. *Small Structures* **2024**, *5*, 2300449.
- [5] Ai, D.; Zhang, W.; Wu, J.; Jin, J.; Jiang, H.; Xie, Z. Constructing White Fluorescence Supramolecular-Carbon Dots Hybrids with Room Temperature Phosphorescence for Efficient Light-Emitting Diodes. *Small* **2026**, *22*, e73278.
- [6] Sharma, G.; Khurana, S.; Sapra, S.; Santra, P. K. Vacancy Passivation and ALD Alumina Encapsulation Strategies for Stable Multilayered All-Inorganic Halide Perovskite Pc-WLEDs. *Small* **2026**, *22*, e12820.
- [7] He, C.; Takeda, T.; Huang, Z.; Xu, J.; Chen, J.; Yi, W.; Xie, R.; Hirosaki, N. Powder synthesis and luminescence of a novel yellow-emitting $\text{Ba}_5\text{Si}_{11}\text{Al}_7\text{N}_{25}:\text{Eu}^{2+}$ phosphor discovered by a single-particle-diagnosis approach for warm WLEDs. *Chemical Engineering Journal* **2023**, *455*, 140932.
- [8] Han, L.; Liu, P.; Li, B.; Zhang, Y.; Liu, Z.; Liu, X.; Xu, Y. Lattice-Matched BaClF/CsPbBr_3 Heterostructure with Enhanced and Stable Cyan Emission to Overcome Blue Overshoot and Cyan Gap of White Light-Emitting Diodes. *Laser & Photonics Reviews* **2025**, *19*, 2401596.
- [9] Dang, P.; Li, G.; Yun, X.; Zhang, Q.; Liu, D.; Lian, H.; Shang, M.; Lin, J. Thermally stable and highly efficient red-emitting Eu^{3+} -doped $\text{Cs}_3\text{GdGe}_3\text{O}_9$ phosphors for WLEDs: non-concentration quenching and negative thermal expansion. *Light: Science & Applications* **2021**, *10*, 29.
- [10] Xiang, R.; Liang, X.; Li, P.; Di, X.; Xiang, W. A thermally stable warm WLED obtained by screen-printing a red phosphor layer on the LuAG:Ce^{3+} PiG substrate. *Chemical Engineering Journal* **2016**, *306*, 858-865.
- [11] Li, K.; Ye, Y.; Zhang, W.; Zhou, Y.; Zhang, Y.; Lin, S.; Lin, H.; Ruan, J.; Liu, C. Ultra-stable and color-tunable manganese ions doped lead-free cesium zinc halides nanocrystals in glasses for light-emitting applications. *Nano Research* **2022**, *15*, 9368-9376.
- [12] Huang, S.; Shang, M.; Yan, Y.; Wang, Y.; Dang, P.; Lin, J. Ultra-Broadband Green-Emitting Phosphors without Cyan Gap Based on Double-Heterovalent Substitution Strategy for Full-Spectrum WLED Lighting. *Laser & Photonics Reviews* **2022**, *16*, 2200473.
- [13] Huang, X.; Liang, J.; Rtimi, S.; Devakumar, B.; Zhang, Z. Ultra-high color rendering warm-white light-emitting diodes based on an efficient green-emitting garnet phosphor for solid-state lighting. *Chemical Engineering Journal* **2021**, *405*, 126950.
- [14] Sun, Y.; Li, Y.; Zhang, W.; Zhu, P.; Zhu, H.; Qin, W.; Wang, G. Simultaneous Synthesis, Modification, and DFT Calculation of Three-Color Lead Halide Perovskite Phosphors for Improving Stability and Luminous Efficiency of WLEDs. *Advanced Optical Materials* **2022**, *10*, 2101765.
- [15] Huang, L.; Ye, R.; Hua, Y.; Qi, Y.; Jiang, G.; Tan, R.; Jiang, T.; Jin, C.; Zhao, J.; Cai, M.; Li, B.; Huang, F.; Bai, G.; Zhao, S.; Zhang, J.; Xu, S. A full-spectrum color converter based on tricolor phosphor-in-glass films for laser-driven white lighting. *Journal of Materials Chemistry C* **2025**, *13*, 7402-7410.
- [16] Sohn, K.-S.; Park, D. H.; Cho, S. H.; Kwak, J. S.; Kim, J. S. Computational Evolutionary Optimization of Red Phosphor for Use in Tricolor White LEDs. *Chemistry of Materials* **2006**, *18*, 1768-1772.
- [17] Jin, S.; Zhang, M.; Zeng, L.; Chen, D. Lanthanide-Doped Lead-Free Halide Double Perovskites: Optical Synergy, Performance Engineering, and Multifunctional Optoelectronics. *Advanced Functional Materials* **2026**, *36*, e32102.
- [18] Zhang, J.-W.; Liang, Y.; Zhang, X.-Y.; Yang, Y.; Dong, H.; Sun, L.-D.; Yan, C.-H. Tailoring Upconversion Emissions through Core-Shell and Local Structure Engineering. *Accounts of Chemical Research* **2026**, *59*, 1401-1413.
- [19] Jin, R.; Zhang, X.-D. Light up the 'Dark'-Near-Infrared II. *Accounts of Chemical Research* **2026**, *59*, 815-816.
- [20] Zhang, Q.; Liu, Y.; Liu, K.; Zhang, H. Lanthanide-based microlasers: Synthesis, structures, and biomedical applications. *Nano Research* **2024**, *17*, 97-111.
- [21] Jia, M.; Chen, X.; Sun, R.; Wu, D.; Li, X.; Shi, Z.; Chen, G.; Shan, C. Lanthanide-based ratiometric luminescence nanothermometry. *Nano Research* **2023**, *16*, 2949-2967.
- [22] Zhang, H.; Zhang, H. Special Issue: Rare earth luminescent materials. *Light: Science & Applications* **2022**, *11*, 260.
- [23] Du, P.; Lei, P.; Liang, Y.; An, R.; Zhang, H. New Strategy: Molten Salt-Assisted Synthesis to Enhance Lanthanide Upconversion Luminescence. *Small* **2023**, *19*, 2302465.
- [24] Ansari, A. A.; Muthumareeswaran, M. R.; Lv, R. Coordination chemistry of the host matrices with dopant luminescent Ln^{3+} ion and their impact on luminescent properties. *Coordination Chemistry Reviews* **2022**, *466*, 214584.
- [25] Cheng, M.; Robinson, B.; Shah, M.; Badrudeen, E. O.; Mondragon, A. H.; Rodriguez, R. G.; Cui, J.; Lin, Y.; Kaul, A. B.; Watanabe, F.; Wangila, G.; Mortazavi, M.; Yan, C.; Guo, Z.; Jiang, Q. Halide perovskite-polymer composite film for bright and stable light-emitting devices. *Advanced Composites and Hybrid Materials* **2025**, *8*, 213.
- [26] Zhou, R.; Cheng, C.-A.; Wang, X.; Nie, K.; Wu, J.; Wu, M.; Duan, X.; Hu, Z.; Huq, I. U.; Wang, H.; Wang, L.; Mei, L.; Liu, H.; Ma, X. Metal halide perovskite nanocrystals with enhanced photoluminescence and stability toward anti-counterfeiting high-performance flexible fibers. *Nano Research* **2023**, *16*, 3542-3551.
- [27] Ran, C.; Huang, C.; Wang, Y.; Wu, F.; Zhang, Q.; Teng, Y.; Dong, H.; Wen, H.; Mu, Z. Mn^{4+} and Ni^{2+} -based near infrared emitting phosphors for temperature sensing in the biological windows. *Journal of Molecular Structure* **2026**, *1363*, 145776.
- [28] Feng, K.; Sun, Z.; Liu, Y.; Tao, F.; Ma, J.; Qian, H.; Yu, R.; Pan, K.; Wang, G.; Wei, S.; Zhang, Q. Shining light on transition metal tungstate-based nanomaterials for electrochemical applications: Structures, progress, and perspectives. *Nano Research* **2022**, *15*, 6924-6960.
- [29] Gong, T.; Chen, Y.; Wang, S.; Wang, M.; Zhao, J. Rigid-flexible-ligand-ornamented lanthanide-incorporated selenotungstates and photoluminescence properties. *Chinese Journal of Structural Chemistry* **2024**, *43*, 100370.
- [30] Kröger, F. A. Fluorescence of Tungstates and Molybdates. *Nature* **1947**, *159*, 674-675.
- [31] Cheng, M.; Wang, H.; Liu, Y.; Shi, J.; Zhou, M.; Du, W.; Zhang, D.; Yang, G. Bouquet-like uranium-containing selenotungstate consisting of two different Keggin-/Anderson-type units with excellent photoluminescence quantum yield. *Chinese Chemical Letters* **2023**, *34*, 107209.
- [32] Du, H.; Zhu, G.; Li, Z.; Li, S.; He, M.; Bi, Z.; Xin, S. Highly symmetric lattice environment induced orange-red emitting of Eu^{3+} in a novel tungstate phosphor with broad-band ultraviolet excitation. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2023**, *302*, 123134.
- [33] Zakrzewski, J. J.; Jankowski, R.; Romanowska, M.; Wang, J.; Pinkowicz, D.; Sieklucka, B.; Ohkoshi, S. i.; Chorazy, S. Luminescent Detection of Photomagnetic Effect in a Near-Infrared Emissive Neodymium(III)-Octacyanidotungstate(IV) Framework. *Angewandte Chemie International Edition* **2025**, *10.1002/anie.202424651*.
- [34] Zi, Y.; Huang, A.; Zhao, H.; Bai, X.; Liu, Y.; Cun, Y.; Song, Z.; Qiu, J.; Shen, Y.; Zhou, J.; Yang, Z. Force-light-heat stimulation-induced multicolor chromism and multifunctional applications of europium tungstate phosphor. *Nature Communications* **2025**, *16*, 6857.
- [35] Chauhan, N. S.; Ono, I.; Miyazaki, Y. Lattice anharmonicity in charge compensated higher manganese silicide single crystals. *Journal of Materials Chemistry A* **2023**, *11*, 19107-19117.
- [36] Huang, Y.; Zhao, X.; Huang, Z.; Quan, J.; Tang, Y.; Jia, C.; Jia, J.; Xie, J.; Shen, Y.; Zhu, J. Boosting photoluminescence of

- Ba₅P₆O₂₀:Dy³⁺ phosphor through facile alkali charge compensation. *Progress in Solid State Chemistry* **2025**, *78*, 100517.
- [37] Liu, M.; Lin, C.; Zhang, H.; Shi, X.; Zeng, R.; Pan, D. Tailored SnO₂ electron transport layer delivers over 27% external quantum efficiency in quantum dot light-emitting diodes compatible with multiple hole transport layers. *Nano Research* **2026**, 10.26599/nr.2026.94908720.
- [38] Li, Y.; Lv, Q.; Feng, S.; Ur Rehman, K. M.; Kan, X.; Liu, X. A comparative investigation of B-site ordering and structure, magnetic, magnetocaloric effect, critical behavior in double perovskite Nd₂BMnO₆ (B = Co and Ni). *Ceramics International* **2021**, *47*, 32599-32609.
- [39] Xiao, W.; Yin, L.; Zhou, J.; Lei, F.; Shi, Y.; Xie, J.; Zhang, L. Influence of reaction parameters on the luminescence properties of monodisperse NaGd_(1-x-y)(WO₄)₂: xEu³⁺, yTb³⁺ phosphor by molten salt synthesis. *Journal of Rare Earths* **2018**, *36*, 49-57.
- [40] Tian, B.; Chen, B.; Tian, Y.; Li, X.; Zhang, J.; Sun, J.; Zhong, H.; Cheng, L.; Fu, S.; Zhong, H.; Wang, Y.; Zhang, X.; Xia, H.; Hua, R. Excitation pathway and temperature dependent luminescence in color tunable Ba₅Gd₈Zn₄O₂₁:Eu³⁺ phosphors. *Journal of Materials Chemistry C* **2013**, *1*, 2338-2344.
- [41] Wang, J.; Lu, Q.; Zhao, S. Two-dimensional g-C₃N₄/α-AgAl_{0.4}Ga_{0.6}O₂ p-n heterostructure with improved visible-light-driven photocatalytic property. *Applied Surface Science* **2019**, *470*, 150-160.
- [42] Tranquilin, R. L.; Lovisa, L. X.; Almeida, C. R. R.; Paskocimas, C. A.; Li, M. S.; Oliveira, M. C.; Gracia, L.; Andres, J.; Longo, E.; Motta, F. V.; Bomio, M. R. D. Understanding the White-Emitting CaMoO₄ Co-Doped Eu³⁺, Tb³⁺, and Tm³⁺ Phosphor through Experiment and Computation. *The Journal of Physical Chemistry C* **2019**, *123*, 18536-18550.
- [43] Huang, C.; Ran, C.; Wei, J.; Chen, H.; Wu, F.; Zhang, Q.; Teng, Y.; Dong, H.; Wen, H.; Mu, Z. Enabling NIR emission of Fe³⁺ under NUV excitation in CaYGaO₄ via energy transfer from co-doped Bi³⁺. *Journal of Alloys and Compounds* **2026**, 1061, 187488.
- [44] Ouyang, T.; Ran, C.; Wu, F.; Zhang, Q.; Teng, Y.; Zhang, X.; Dong, H.; Xie, X.; Mu, Z. Synchronously broadening excitation range and enhancing NIR emission intensity of Er³⁺ in CaLaGaO₄ via energy transfer from Cr⁴⁺ for popularization of Er³⁺ lasers. *Journal of Rare Earths* **2026**, *44*, 1007-1014.
- [45] Li, Z.; Bian, Q.; Zhu, G.; Wang, Z.; Zhu, Q.; Cong, Y.; Bai, X.; Li, J.-G.; Dong, B. Full-spectrum driven UV-visible to NIR photon down-conversion phosphors toward crystalline silicon solar cell applications. *Journal of Colloid and Interface Science* **2025**, *695*, 137729.
- [46] Jeon, Y.; Park, C.; Seong, J.; Rho, J. Printable grayscale nano-template for full-colour organic light-emitting diode near-eye displays with 3D achromatic metalenses. *Nature Communications* **2026**, 10.1038/s41467-026-73940-1.

Electronic Supplementary Material

Enhanced luminescence and ultra-stability of WLEDs combined with urchin-like $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4:\text{Ln}^{3+}$ with hierarchical structure through charge self-compensation combined with 3D printing

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EXPERIMENTAL

Chemicals: All chemicals were used directly without further purification. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, with 99.999% purity, were purchased from Kermel Chemical Reagent. Na_2WO_4 (AR, 99.5%) and NaOH (AR, 99%) were purchased from Ron Chemical Reagent. $\text{Sr}(\text{NO}_3)_2$ was purchased from Sinopharm Chemical Reagent Co. Oleic acid was purchased from Xilong Chemical Co.

Synthesis of $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4:\text{Ln}^{3+}$: 1 mmol of Na_2WO_4 aqueous solution was added to a mixture of NaOH (1.1 g), ethanol (8 mL), deionized water (4 mL), and oleic acid (15 mL), and then a mixture of $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Tb}(\text{NO}_3)_3$, and $\text{Eu}(\text{NO}_3)_3$ was added to the above solution with thorough stirring for 30 min. Subsequently, the milky colloidal solution was transferred to an autoclave lined with polytetrafluoroethylene and heated at 180 °C for 12 h. After cooling to room temperature, the final product was collected by centrifugation, washed three times with cyclohexane, twice with ethanol, and dried at 80 °C.

Characterization. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The size and morphology of the final products were investigated by transmission electron microscopy (TEM; JEM-2100, Japan) and scanning electron microscopy (SEM; S-4800, Japan). The surface morphology/roughness was characterized by atomic force microscopy (AFM, SPA-400, Japan). UV-vis absorption spectra were obtained with the help of a UV-vis spectrophotometer (Shimadzu UV-2550, Japan). The elemental compositions were determined using X-ray photoelectron spectroscopy (XPS; Kratos-AXIS ULTRA DLD apparatus with Al (mono) X-ray source). Fourier-transform infrared (FT-IR) spectra of the samples were measured by using a Perkin-Elmer Spectrum One FTIR spectrometer employing the KBr pellet method. The Raman spectrum was measured using a Jobin Yvon HR 800 micro-Raman spectrometer. The PL spectra were measured using a Hitachi F-4600 fluorescence spectrophotometer. Luminescent lifetimes were obtained from an Edinburgh luminescence spectrophotometer (FLS 920).

Calculation of the average lifetime and energy-transfer efficiency. The PL decay curves were fitted using a bi-exponential decay model:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

where $I(t)$ is the luminescence intensity at time t , A_1 and A_2 are the pre-exponential factors, and τ_1 and τ_2 represent the corresponding decay components. The average lifetime τ_{avg} was calculated according to:

$$\tau_{\text{avg}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

The corresponding fitting parameters and calculated average lifetimes are summarized in Tables S12 and S13. The $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy-transfer efficiency (η_{ET}) was calculated from the Tb^{3+} donor lifetimes according to:

$$\eta_{\text{ET}} = 1 - \frac{\tau_s}{\tau_{s0}} \quad (3)$$

where (τ_{s0}) and (τ_s) are the average lifetimes of Tb^{3+} in the absence and presence of Eu^{3+} , respectively. The calculated energy-transfer efficiencies are summarized in Table S13.

Spectral optimization of white light emission: The optimized $\text{Tb}^{3+}/\text{Eu}^{3+}$ -co-doped $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4$ phosphors and CsBr were used as the green-red and blue-emitting components, respectively. CsBr and the $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped phosphor were mixed at an optimized mass ratio of 1:5. The resulting luminescent components were coated onto cleaned ITO-coated glass substrates and integrated with a 275 nm UV LED chip. The electroluminescence spectra and colorimetric parameters were measured at an operating voltage of 4.4 V and a current of 20 mA. For further application evaluation, the indoor photovoltaic response under illumination from the fabricated LED devices was investigated using a CHI 660 electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). The combined spectral power distribution (SPD) was calculated using the following

equation:

$$SPD(\lambda) = r_B \cdot I_B(\lambda) + r_G \cdot I_G(\lambda) + r_R \cdot I_R(\lambda) \quad (4)$$

where $I_B(\lambda)$, $I_G(\lambda)$, and $I_R(\lambda)$ represent the normalized emission spectra of CsBr blue emission, Tb³⁺-activated green-yellow emission, and Eu³⁺ red emission, respectively. The weighting factors r_B , r_G , and r_R were varied systematically in the range of 0-5 (step size 0.2) to simulate different mixing ratios, and the corresponding color ratios were defined as B:G:R = r_B : r_G : r_R . A large number of SPDs were generated by varying the relative intensities of the three emission components. For each SPD, key photometric and colorimetric parameters were calculated, including the Commission Internationale de l'Éclairage (CIE) chromaticity coordinates (x, y), (CCT), (CRI), distance from the Planckian locus (Duv), and LER. The LER was calculated from the spectral power distribution (SPD) according to:

$$LER = 683 \frac{\int_{\lambda_1}^{\lambda_2} P(\lambda) V(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} P(\lambda) d\lambda} \quad (5)$$

where $P(\lambda)$ is the spectral power distribution and $V(\lambda)$ is the photopic luminous-efficiency function. LER characterizes the spectral utilization efficiency of the emitted radiation and does not account for the electrical input power of the LED device. This approach enables systematic spectral engineering and optimization of white light quality based on multi-component phosphor blending.

Preparation of resin-based composites for 3D printing: First, 0.1 g of the phosphor powder was added to 10 mL of photosensitive resin and thoroughly mixed. The resulting mixture was then transferred to the resin vat of an Anycubic Photon Mono 2 3D printer for printing. After printing, the samples were removed and washed several times with ethanol to remove uncured resin.

Computational details: All structural and electronic-structure calculations, DOS, and partial density of states (PDOS) were simulated with the plane-wave ultrasoft (PWUS) pseudopotential method as implemented in the Cambridge Sequential Total Energy Package (CASTEP) code. The optical spectra were obtained with the PW91 functional in CASTEP. The generalized gradient approximation (GGA) with the PW91 exchange-correlation functional was used in the calculations. The cutoff energy for the plane-wave expansion was set to 900 eV. For geometry optimization, the convergence criterion of total energy was 2.0×10^{-5} eV/atom. The spin-polarized magnetic calculation was used to do geometry optimization, electronic structure, and optical property calculation. For CASTEP, if it is necessary to reflect the presence of multiple elements in a certain location, it must be achieved through supercell replacement modeling (ordered/disordered solid solutions) or occupation statistical description. If modeling with supercell, in order to match the experimental concentration, a super large supercell must be established. For example, the experimental sample $\text{Sr}_{0.3}\text{Ca}_{0.45}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ requires the establishment of $\text{Sr}_6\text{Ca}_9\text{Tb}_4\text{Eu}_{20}\text{W}_{20}\text{O}_{80}$ supercell, while the actual sample $\text{Sr}_{0.3}\text{Ca}_{0.325}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ requires the establishment of $\text{Sr}_{12}\text{Ca}_{13}\text{Tb}_8\text{Eu}_2\text{W}_{40}\text{O}_{160}$ supercell. It should be noted that the lower right corner of the actual sample name indicates the content of the element, while the lower right corner of the calculation model name indicates the number of elements. Such a massive supercell is difficult to accomplish with a regular server. Therefore, we adopted the second method to establish the $\text{Sr}_{2.4}\text{Ca}_{3.6}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$ supercell for the experimental sample $\text{Sr}_{0.3}\text{Ca}_{0.45}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$, while the actual sample $\text{Sr}_{0.3}\text{Ca}_{0.325}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$ established the $\text{Sr}_{2.4}\text{Ca}_{2.6}\text{Tb}_{1.6}\text{Eu}_{0.4}\text{W}_8\text{O}_{32}$ supercell. It should be noted that the second approach does not allow the calculation of either optical properties or the PDOS for every constituent element. For example, in $\text{Sr}_{0.3}\text{Ca}_{0.45}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$, the Eu content is too low for Eu to be selected as an independent element. Consequently, a complete comparison of the element-resolved PDOS among the different models cannot be performed.

Supplementary Tables and Figures

Table S1. Analysis results of Hirshfeld charges for $\text{Ca}_4\text{W}_4\text{O}_{16}$.

Species	Charge (e)	Species	Charge (e)	Species	Charge (e)	Species	Charge (e)
O ₁	-0.24	O ₇	-0.24	O ₁₃	-0.24	Ca ₃	0.27
O ₂	-0.24	O ₈	-0.24	O ₁₄	-0.24	Ca ₄	0.27
O ₃	-0.24	O ₉	-0.24	O ₁₅	-0.24	W ₁	0.71
O ₄	-0.24	O ₁₀	-0.24	O ₁₆	-0.24	W ₂	0.71

O ₅	-0.24	O ₁₁	-0.24	Ca ₁	0.27	W ₃	0.71
O ₆	-0.24	O ₁₂	-0.24	Ca ₂	0.27	W ₄	0.71

Table S2. Analysis results of Hirshfeld charges for Ca₃SrW₄O₁₆.

Species	Charge (e)	Species	Charge (e)	Species	Charge (e)	Species	Charge (e)
O ₁	-0.26	O ₇	-0.24	O ₁₃	-0.24	Ca ₃	0.27
O ₂	-0.26	O ₈	-0.24	O ₁₄	-0.24	Sr ₁	0.31
O ₃	-0.25	O ₉	-0.24	O ₁₅	-0.26	W ₁	0.73
O ₄	-0.25	O ₁₀	-0.24	O ₁₆	-0.26	W ₂	0.70
O ₅	-0.25	O ₁₁	-0.24	Ca ₁	0.27	W ₃	0.70
O ₆	-0.25	O ₁₂	-0.24	Ca ₂	0.24	W ₄	0.69

Table S3. Analysis results of Hirshfeld charges for Ca₂SrTbW₄O₁₆.

Species	Charge (e)	Species	Charge (e)	Species	Charge (e)	Species	Charge (e)
O ₁	-0.29	O ₇	-0.26	O ₁₃	-0.24	Sr ₁	0.30
O ₂	-0.29	O ₈	-0.26	O ₁₄	-0.24	Tb ₁	0.57
O ₃	-0.25	O ₉	-0.24	O ₁₅	-0.26	W ₁	0.73
O ₄	-0.25	O ₁₀	-0.24	O ₁₆	-0.26	W ₂	0.66
O ₅	-0.27	O ₁₁	-0.25	Ca ₁	0.24	W ₃	0.69
O ₆	-0.27	O ₁₂	-0.25	Ca ₂	0.27	W ₄	0.69

Table S4. Analysis results of Hirshfeld charges for CaSrTbEuW₄O₁₆.

Species	Charge (e)	Species	Charge (e)	Species	Charge (e)	Species	Charge (e)
O ₁	-0.31	O ₇	-0.27	O ₁₃	-0.27	Tb ₁	0.51
O ₂	-0.31	O ₈	-0.26	O ₁₄	-0.27	Eu ₁	0.56
O ₃	-0.25	O ₉	-0.24	O ₁₅	-0.28	W ₁	0.73
O ₄	-0.25	O ₁₀	-0.24	O ₁₆	-0.28	W ₂	0.65
O ₅	-0.28	O ₁₁	-0.27	Ca ₁	0.27	W ₃	0.66
O ₆	-0.28	O ₁₂	-0.27	Sr ₁	0.30	W ₄	0.67

Table S5. Hirshfeld charge analysis of the charge-compensated CaSrTb-vacancy-W₄O₁₆ model containing an A-site cation vacancy.

Species	Charge (e)	Species	Charge (e)	Species	Charge (e)	Species	Charge (e)
O ₁	-0.27	O ₇	-0.26	O ₁₃	-0.21	Tb ₁	0.58
O ₂	-0.27	O ₈	-0.26	O ₁₄	-0.21	W ₁	0.73
O ₃	-0.24	O ₉	-0.23	O ₁₅	-0.24	W ₂	0.66
O ₄	-0.24	O ₁₀	-0.23	O ₁₆	-0.24	W ₃	0.67
O ₅	-0.26	O ₁₁	-0.23	Ca ₁	0.27	W ₄	0.67
O ₆	-0.26	O ₁₂	-0.23	Sr ₁	0.31	---	---

Table S6. Hirshfeld charge analysis of the charge-compensated CaSrEu-vacancy-W₄O₁₆ model containing an A-site cation vacancy.

Species	Charge (e)	Species	Charge (e)	Species	Charge (e)	Species	Charge (e)
O ₁	-0.25	O ₇	-0.22	O ₁₃	-0.26	Eu ₁	0.53
O ₂	-0.25	O ₈	-0.22	O ₁₄	-0.26	W ₁	0.71
O ₃	-0.24	O ₉	-0.23	O ₁₅	-0.27	W ₂	0.67
O ₄	-0.24	O ₁₀	-0.23	O ₁₆	-0.27	W ₃	0.68
O ₅	-0.21	O ₁₁	-0.25	Ca ₁	0.28	W ₄	0.66
O ₆	-0.21	O ₁₂	-0.25	Sr ₁	0.32	---	---

Table S7. (112) diffraction peak positions, apparent FWHM values, interplanar spacings, and integrated emission peak areas of the uncompensated and charge-compensated phosphors.

Samples	2θ of (112) plane (°)	FWHM	d (Å)	Emission peak area (a.u.·nm)
Ca _{0.5} Sr _{0.3} Tb _{0.2} WO ₄	28.244°	0.506°	3.1571	1.1×10 ⁵
Ca _{0.4} Sr _{0.3} Tb _{0.2} WO ₄	28.429°	0.549°	3.1370	2.7×10 ⁵
Ca _{0.65} Sr _{0.3} Eu _{0.05} WO ₄	28.407°	0.434°	3.1394	3.5×10 ⁵
Ca _{0.625} Sr _{0.3} Eu _{0.05} WO ₄	28.478°	0.417°	3.1317	5.0×10 ⁵
Ca _{0.45} Sr _{0.3} Tb _{0.2} Eu _{0.05} WO ₄	28.435°	0.584°	3.1363	1.0×10 ⁵
Ca _{0.325} Sr _{0.3} Tb _{0.2} Eu _{0.05} WO ₄	28.537°	0.569°	3.1254	2.3×10 ⁵

Table S8. Control experiments to prepare Tb doped CaWO_4 with different $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ content as raw reaction material (corresponding to Figure S14).

Samples	$\text{Tb}(\text{NO}_3)_3$	Na_2WO_4	$\text{Ca}(\text{NO}_3)_2$
$\text{Ca}_{0.95}\text{WO}_4:0.05\text{Tb}^{3+}$	0.05 mmol	1 mmol	0.95 mmol
$\text{Ca}_{0.90}\text{WO}_4:0.1\text{Tb}^{3+}$	0.1 mmol	1 mmol	0.90 mmol
$\text{Ca}_{0.85}\text{WO}_4:0.15\text{Tb}^{3+}$	0.15 mmol	1 mmol	0.85 mmol
$\text{Ca}_{0.82}\text{WO}_4:0.18\text{Tb}^{3+}$	0.18 mmol	1 mmol	0.82 mmol
$\text{Ca}_{0.80}\text{WO}_4:0.20\text{Tb}^{3+}$	0.2 mmol	1 mmol	0.8 mmol
$\text{Ca}_{0.78}\text{WO}_4:0.22\text{Tb}^{3+}$	0.22 mmol	1 mmol	0.78 mmol
$\text{Ca}_{0.75}\text{WO}_4:0.25\text{Tb}^{3+}$	0.25 mmol	1 mmol	0.75 mmol

Table S9. For Sr^{2+} -doped $\text{CaWO}_4:0.2\text{Tb}^{3+}$ control experiments with different Sr/Ca ratios (corresponding to Figure S15).

Samples	$\text{Tb}(\text{NO}_3)_3$	Na_2WO_4	$\text{Ca}(\text{NO}_3)_2$	$\text{Sr}(\text{NO}_3)_2$
Sr/Ca=1/7	0.20 mmol	1 mmol	0.70 mmol	0.1 mmol
Sr/Ca=2/6	0.20 mmol	1 mmol	0.60 mmol	0.2 mmol
Sr/Ca=3/5	0.20 mmol	1 mmol	0.50 mmol	0.3 mmol
Sr/Ca=4/4	0.20 mmol	1 mmol	0.40 mmol	0.4 mmol
Sr/Ca=5/3	0.20 mmol	1 mmol	0.30 mmol	0.5 mmol
Sr/Ca=6/2	0.20 mmol	1 mmol	0.20 mmol	0.6 mmol
Sr/Ca=7/1	0.20 mmol	1 mmol	0.10 mmol	0.7 mmol

Table S10. Control experiments with $\text{Ca}_{0.7-y}\text{Sr}_{0.3}\text{Eu}_y\text{WO}_4$ prepared with different molar amounts of Eu^{3+} (corresponding to Figure S16).

Samples	$\text{Eu}(\text{NO}_3)_3$	Na_2WO_4	$\text{Ca}(\text{NO}_3)_2$	$\text{Sr}(\text{NO}_3)_2$
$\text{Ca}_{0.67}\text{Sr}_{0.3}\text{Eu}_{0.03}\text{WO}_4$	0.03 mmol	1 mmol	0.67 mmol	0.3 mmol
$\text{Ca}_{0.66}\text{Sr}_{0.3}\text{Eu}_{0.04}\text{WO}_4$	0.04 mmol	1 mmol	0.66 mmol	0.3 mmol
$\text{Ca}_{0.65}\text{Sr}_{0.3}\text{Eu}_{0.05}\text{WO}_4$	0.05 mmol	1 mmol	0.65 mmol	0.3 mmol
$\text{Ca}_{0.64}\text{Sr}_{0.3}\text{Eu}_{0.06}\text{WO}_4$	0.06 mmol	1 mmol	0.64 mmol	0.3 mmol
$\text{Ca}_{0.63}\text{Sr}_{0.3}\text{Eu}_{0.07}\text{WO}_4$	0.07 mmol	1 mmol	0.63 mmol	0.3 mmol

Table S11. Control experiments to prepare $\text{Ca}_{0.5-z}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_z\text{WO}_4$ with different Eu^{3+} concentrations (corresponding to Figure S17).

Samples	$\text{Eu}(\text{NO}_3)_3$	$\text{Tb}(\text{NO}_3)_3$	Na_2WO_4	$\text{Ca}(\text{NO}_3)_2$	$\text{Sr}(\text{NO}_3)_2$
$\text{Ca}_{0.49}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.01}\text{WO}_4$	0.01 mmol	0.2 mmol	1 mmol	0.49 mmol	0.3 mmol
$\text{Ca}_{0.48}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.02}\text{WO}_4$	0.02 mmol	0.2 mmol	1 mmol	0.48 mmol	0.3 mmol
$\text{Ca}_{0.47}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.03}\text{WO}_4$	0.03 mmol	0.2 mmol	1 mmol	0.47 mmol	0.3 mmol
$\text{Ca}_{0.46}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.04}\text{WO}_4$	0.04 mmol	0.2 mmol	1 mmol	0.46 mmol	0.3 mmol
$\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$	0.05 mmol	0.2 mmol	1 mmol	0.45 mmol	0.3 mmol

Table S12. Bi-exponential fitting parameters and average lifetimes of the charge-compensated and uncompensated Tb^{3+} -, Eu^{3+} -, and $\text{Tb}^{3+}/\text{Eu}^{3+}$ -doped phosphors.

Sample	A_1	τ_1 (μs)	A_2	τ_2 (μs)	τ_{avg} (μs)	R^2
$\text{Ca}_{0.5}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{WO}_4$	695.70	0.07	63.05	14.15	13.39	0.95
$\text{Ca}_{0.4}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{WO}_4$	732.71	0.09	70.97	14.92	14.07	0.96
$\text{Ca}_{0.65}\text{Sr}_{0.3}\text{Eu}_{0.05}\text{WO}_4$	19.63	17.13	68.64	710.53	705.78	0.95
$\text{Ca}_{0.625}\text{Sr}_{0.3}\text{Eu}_{0.05}\text{WO}_4$	23.11	76.690	60.00	788.20	762.50	0.95
$\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$	60.84	9.40	2072189.93	1.06	1.06	0.99
$\text{Ca}_{0.325}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$	58296.49	1.55	50082.59	1.55	1.55	0.98

Table S13. Bi-exponential fitting parameters, average Tb^{3+} lifetimes, and calculated $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy-transfer efficiencies for the $\text{Ca}_{0.5-z}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_z\text{WO}_4$ series.

Sample	A_1	τ_1 (μs)	A_2	τ_2 (μs)	τ_{avg} (μs)	R^2	η_{ET} (%)
$z=0$	695.70	0.07	63.05	14.15	13.39	0.95	—
$z=0.01$	131365.49	1.39	10.64	19.06	1.41	0.98	89.48
$z=0.02$	195352.58	1.34	17.18	15.64	1.35	0.98	89.92
$z=0.03$	18.06	14.41	240057.97	1.30	1.32	0.98	90.17
$z=0.04$	30.49	13.65	359797.88	1.30	1.31	0.98	90.24
$z=0.05$	60.84	9.40	2072189.93	1.06	1.06	0.98	92.10

Table S14. The emission spectra and corresponding color coordinates of WLEDs in Figure 7a with different CCTs constructed from uncompensated fluorescent powders.

WLEDs	CCT (K)	R _a	CIE-x	CIE-y	D _{uv}	LER(lm/W)	R _g
LED-1	9080	95	0.2772	0.3160	0.0160	270	97
LED-2	7986	92	0.2907	0.3194	0.0101	275	100
LED-3	6172	93	0.3170	0.3495	0.0113	296	98
LED-4	7403	95	0.2959	0.3331	0.0139	285	100
LED-5	5223	94	0.3402	0.3716	0.0117	312	98
LED-6	4868	90	0.3500	0.3639	0.0042	304	101

Table S15. The emission spectra and corresponding color coordinates of WLEDs in Figure 7b with different CCTs constructed using charge-compensated phosphors.

WLEDs	CCT (K)	R _a	CIE-x	CIE-y	D _{uv}	LER(lm/W)	R _g
LED-A	8862	93	0.2766	0.3241	0.0202	281	95
LED-B	8140	93	0.2888	0.3184	0.0106	274	100
LED-C	7173	95	0.2991	0.3364	0.0138	286	99
LED-D	6606	94	0.3076	0.3500	0.0160	298	98
LED-E	6150	93	0.3178	0.3460	0.0092	297	101
LED-F	5182	94	0.3416	0.3717	0.0111	312	98

Table S16. Color characteristics of the LED-4 devices in Figure 7c under different voltage.

Voltage (V)	CCT (K)	R _a	CIE-x	CIE-y	D _{uv}	LER(lm/W)
4.4	7403	95	0.2959	0.3331	0.0139	285
4.5	8091	90	0.2908	0.3143	0.0074	270
4.6	7873	86	0.2954	0.3096	0.0024	266
4.7	7403	81	0.3024	0.3063	0.0033	263

Table S17. Color characteristics of the LED-E devices in Figure 7d under different voltage.

Voltage (V)	CCT (K)	R _a	CIE-x	CIE-y	D _{uv}	LER(lm/W)
4.4	6150	93	0.3178	0.3460	0.0092	297
4.5	5715	89	0.3275	0.3455	0.0074	296
4.6	10025	85	0.2801	0.2888	0.0006	249
4.7	9523	79	0.2867	0.2874	-0.0058	245

Table S18. Photovoltaic parameters of the silicon solar cell under illumination from the LED-4 device at different operating voltages.

LED operating voltage	J _{sc} (μA cm ⁻²)	V _{oc} (V)	FF	η (%)
2.9 V	0.72	0.19	0.14	0.002
3.0 V	5.54	0.70	0.52	0.25
3.1 V	19.17	1.24	0.684	2.03
3.2 V	27.75	1.33	0.71	3.25

Table S19. Photovoltaic parameters of the silicon solar cell under illumination from the LED-E device at different operating voltages.

LED operating voltage	J _{sc} (μA cm ⁻²)	V _{oc} (V)	FF	η (%)
2.9 V	1.49	0.48	0.52	0.05
3.0 V	9.12	1.08	0.67	0.82
3.1 V	31.27	1.59	0.64	4.00
3.2 V	61.57	1.88	0.53	7.49

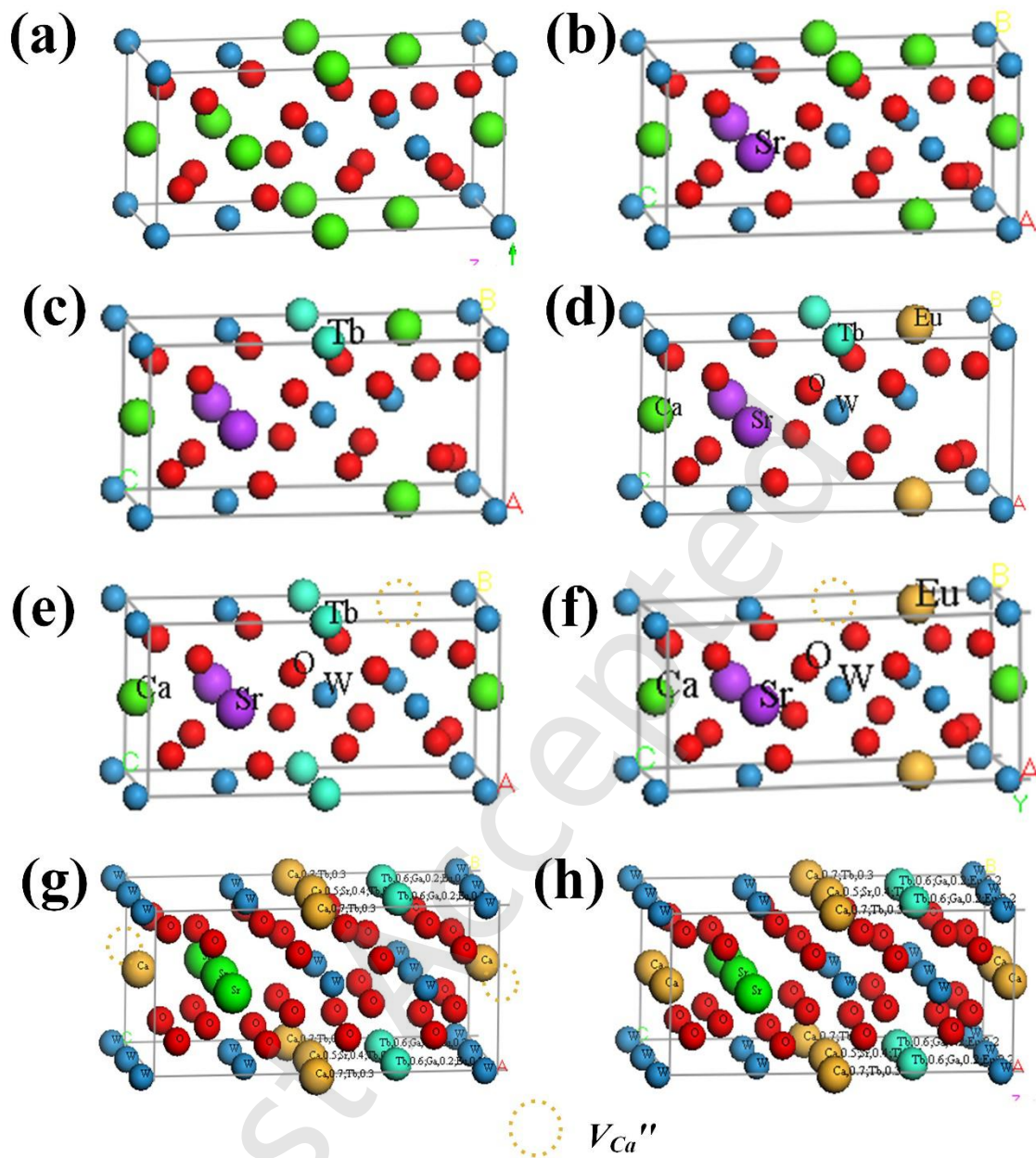


Figure S1. Crystal structure models of (a) $Ca_4W_4O_{16}$, (b) $Ca_3SrW_4O_{16}$, (c) $Ca_2SrTbW_4O_{16}$, and (d) $CaSrTbEuW_4O_{16}$, (e) $CaSrTbW_4O_{16}$, (f) $CaSrEuW_4O_{16}$, (g) $Ca_{2.6}Sr_{2.4}Tb_{1.6}Eu_{0.4}W_8O_{32}$, and (h) $Ca_{3.6}Sr_{2.4}Tb_{1.6}Eu_{0.4}W_8O_{32}$.

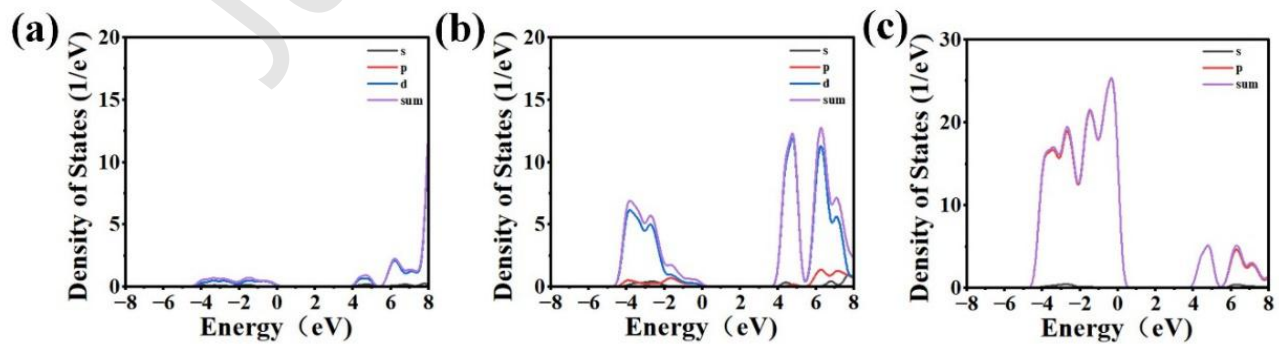


Figure S2. Partial DOS for $Ca_4W_4O_{16}$: (a) Ca, (b) W, and (c) O.

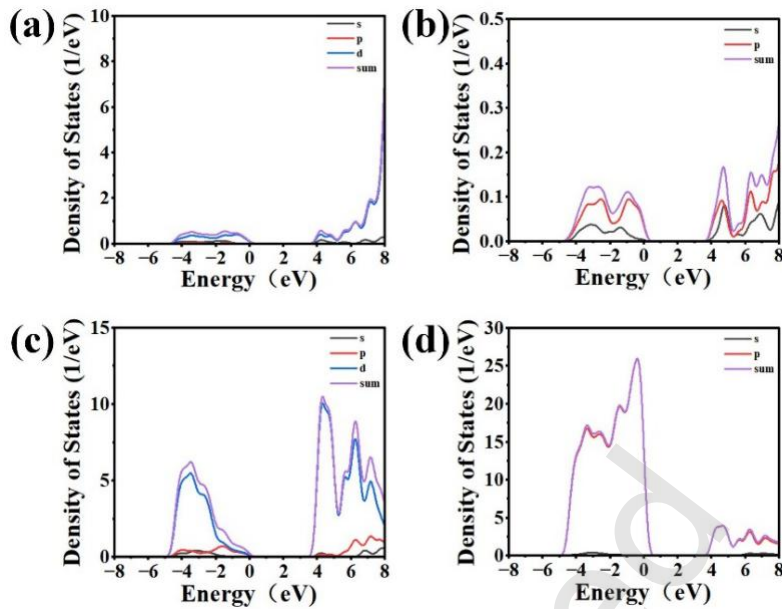


Figure S3. Partial DOS for $\text{Ca}_3\text{SrW}_4\text{O}_{16}$: (a) Ca, (b) Sr, (c) W, and (d) O.

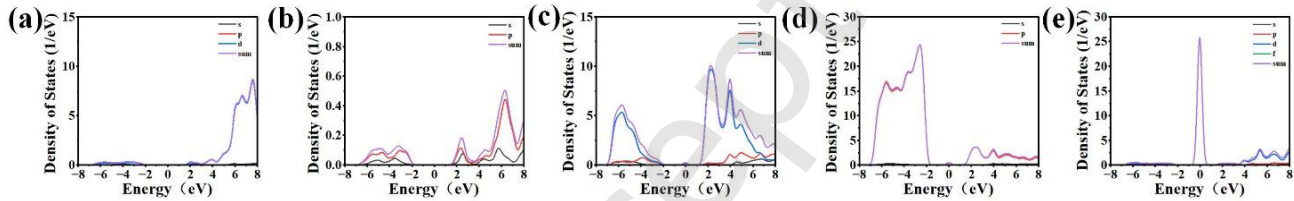


Figure S4. Partial DOS for $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$: (a) Ca, (b) Sr, (c) W, (d) O, and (e) Tb.

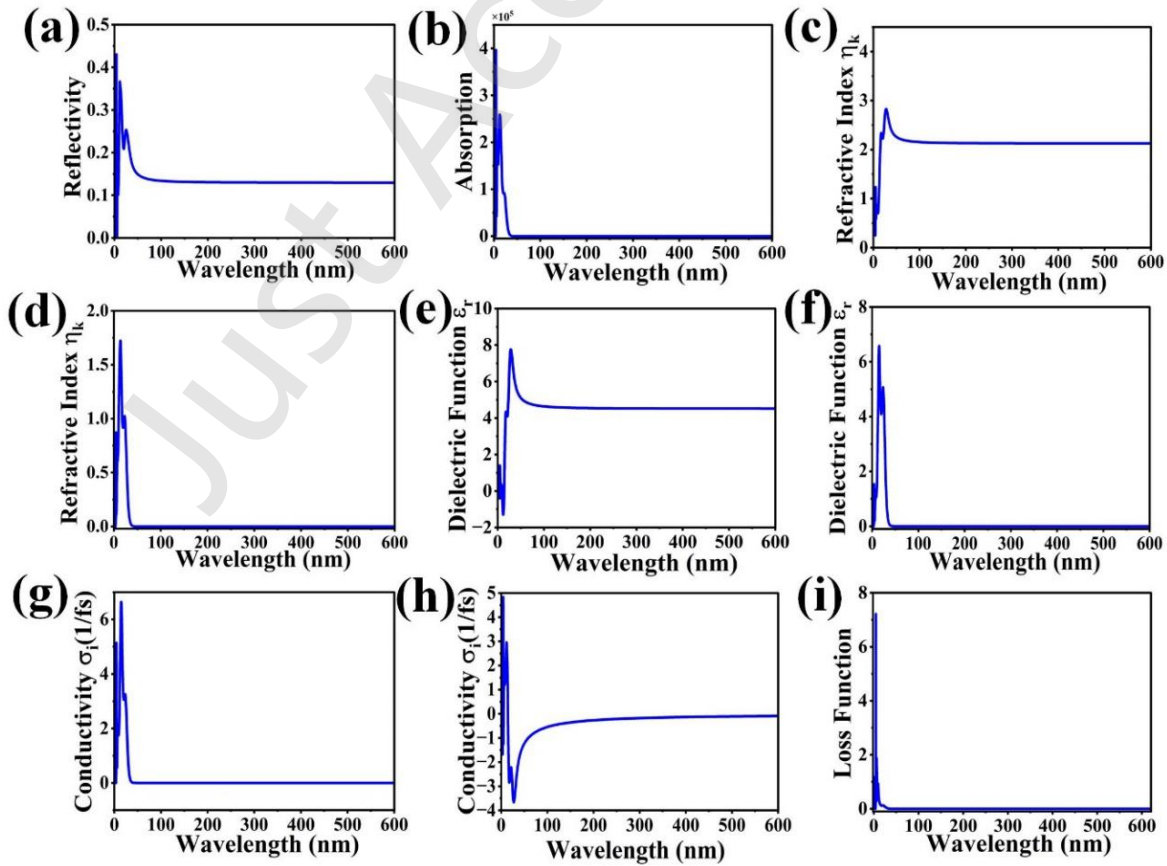


Figure S5. Calculated optical spectra of $\text{Ca}_4\text{W}_4\text{O}_{16}$.

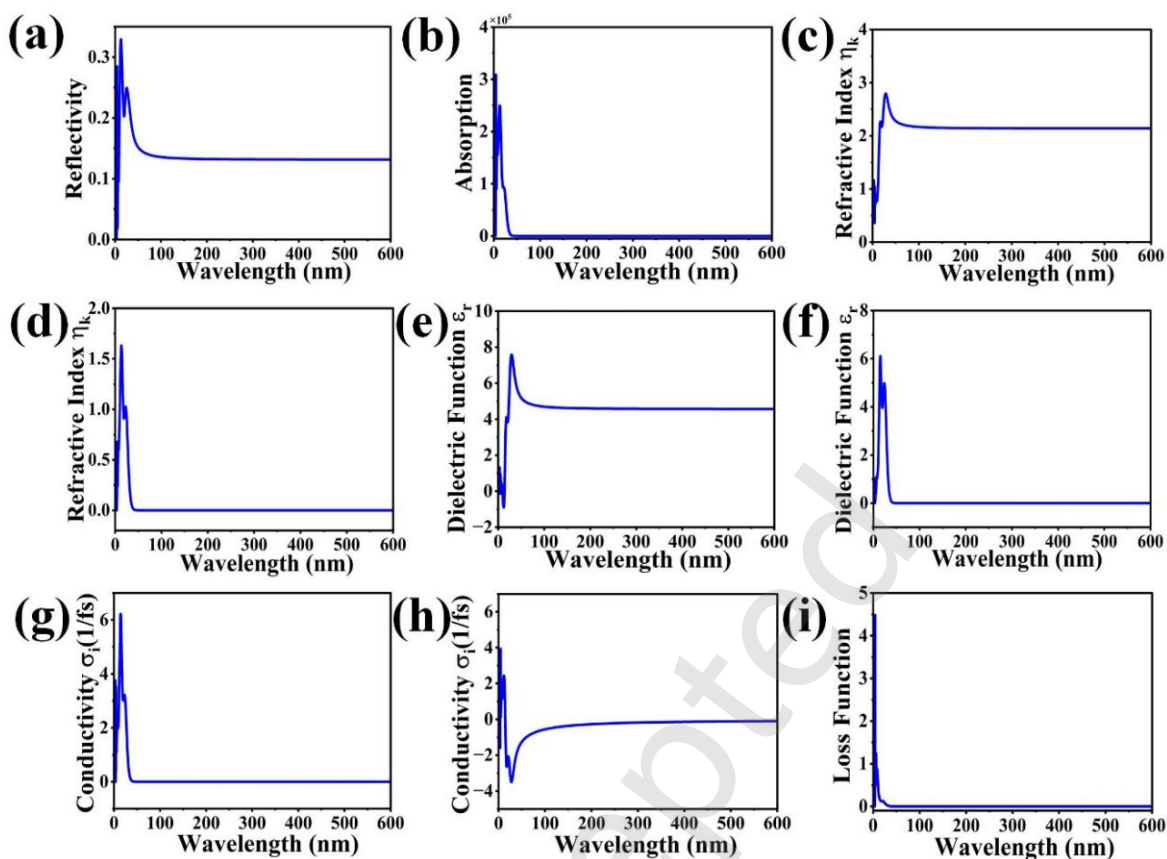


Figure S6. Calculated optical spectra of $\text{Ca}_3\text{SrW}_4\text{O}_{16}$.

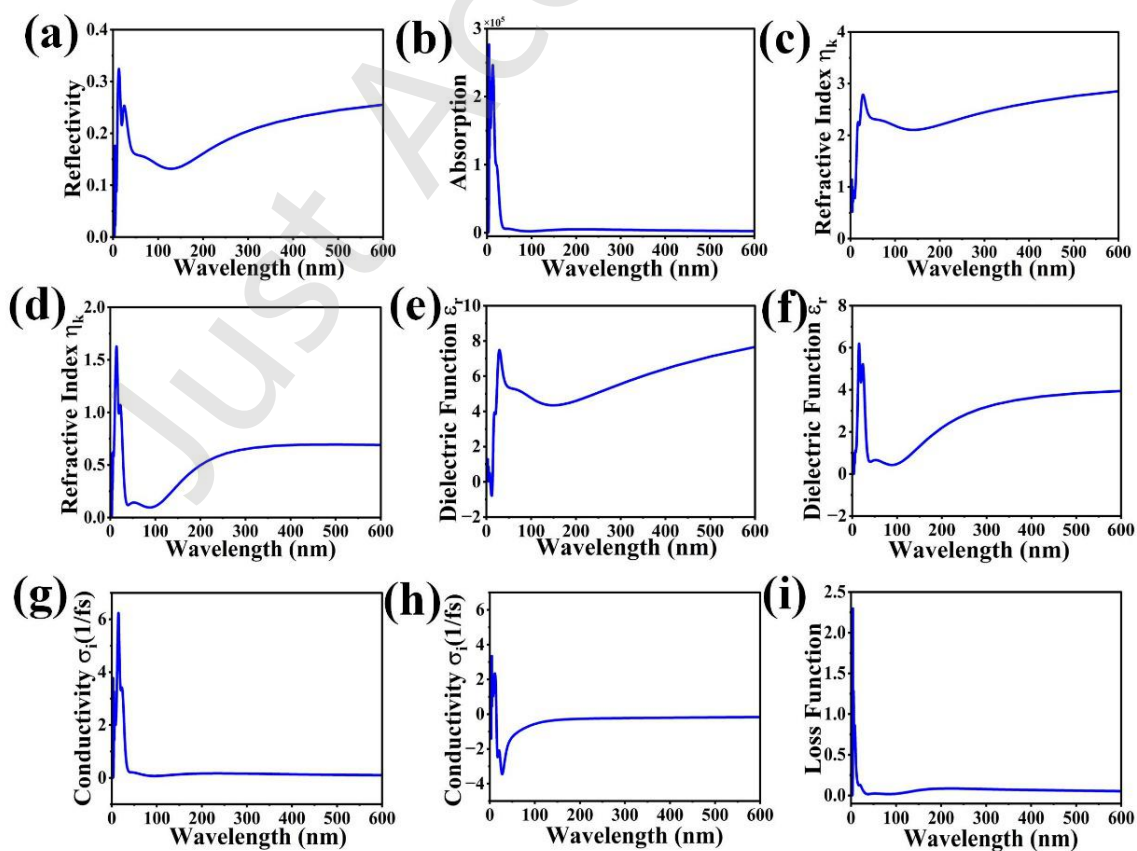


Figure S7. Calculated optical spectra of $\text{Ca}_2\text{SrTbW}_4\text{O}_{16}$.

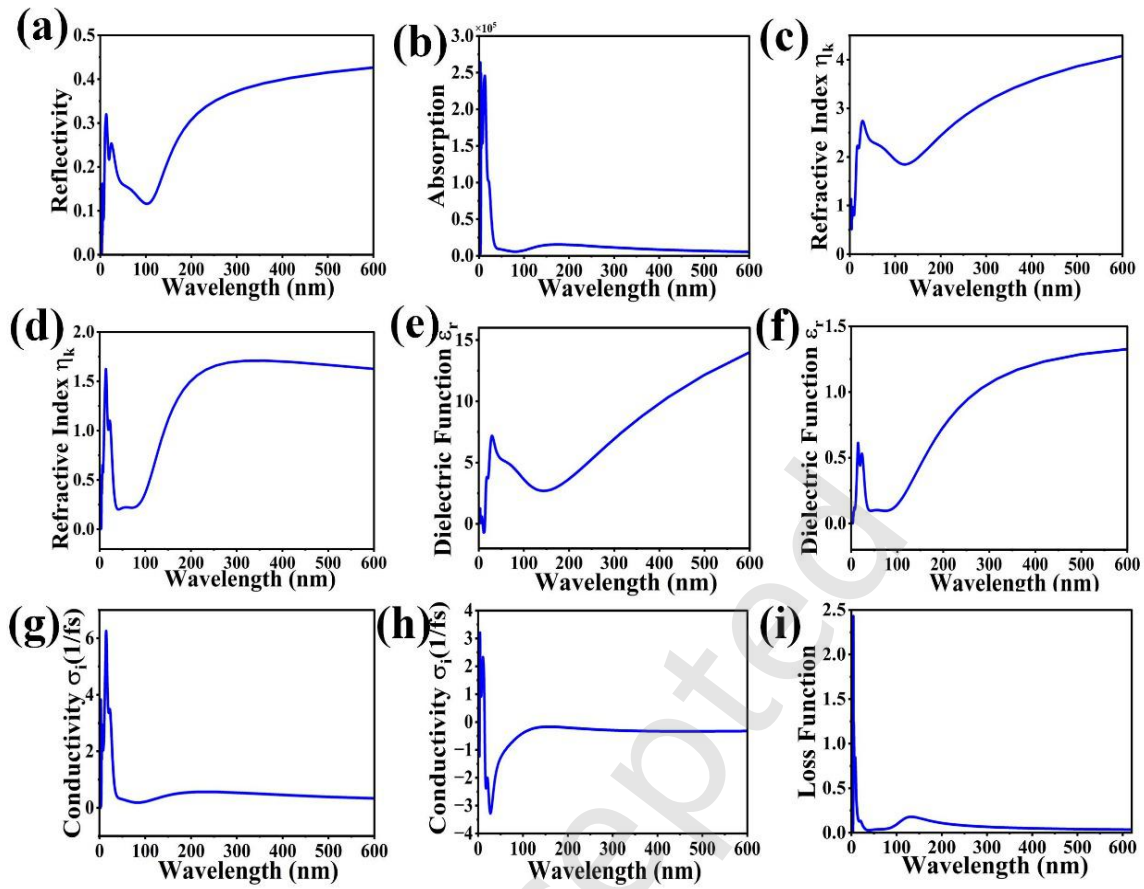


Figure S8. Calculated optical spectra of $\text{CaSrTbEuW}_4\text{O}_{16}$.

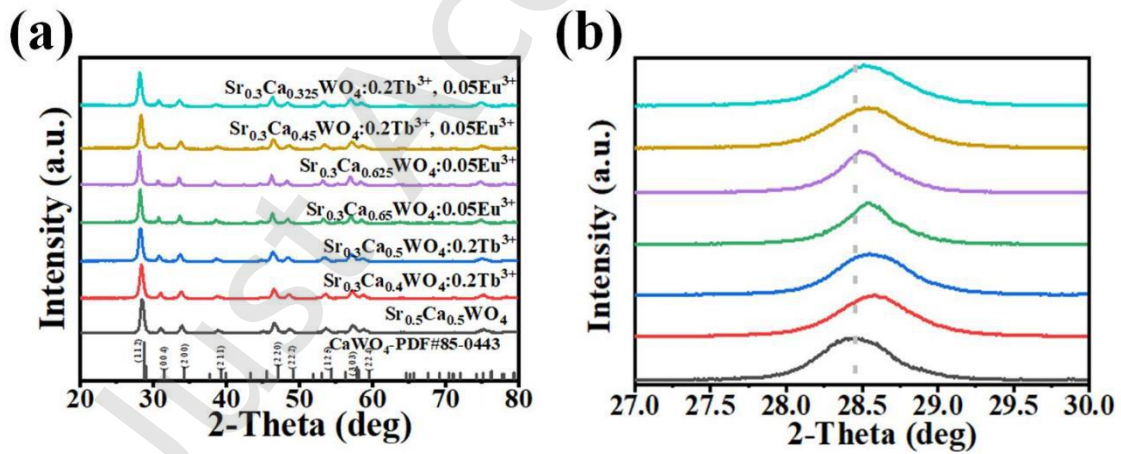


Figure S9. (a) XRD patterns of the investigated samples. (b) Enlarged XRD patterns in the 2θ range of 27° - 30° .

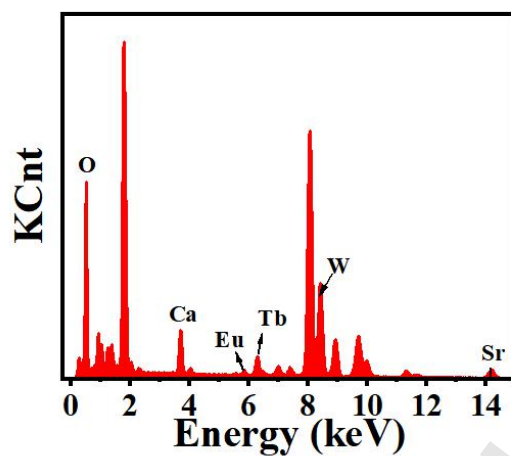


Figure S10. EDS spectrum of $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$.

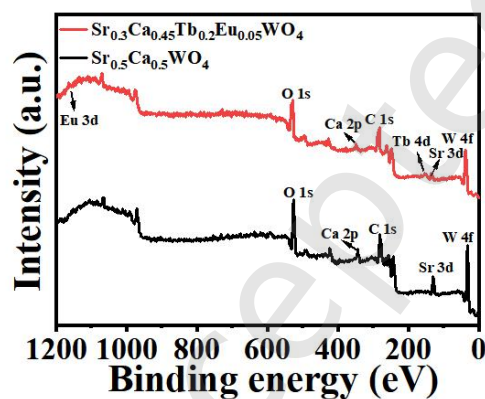


Figure S11. Full-survey XPS of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{WO}_4$ and $\text{Ca}_{0.45}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_{0.05}\text{WO}_4$.

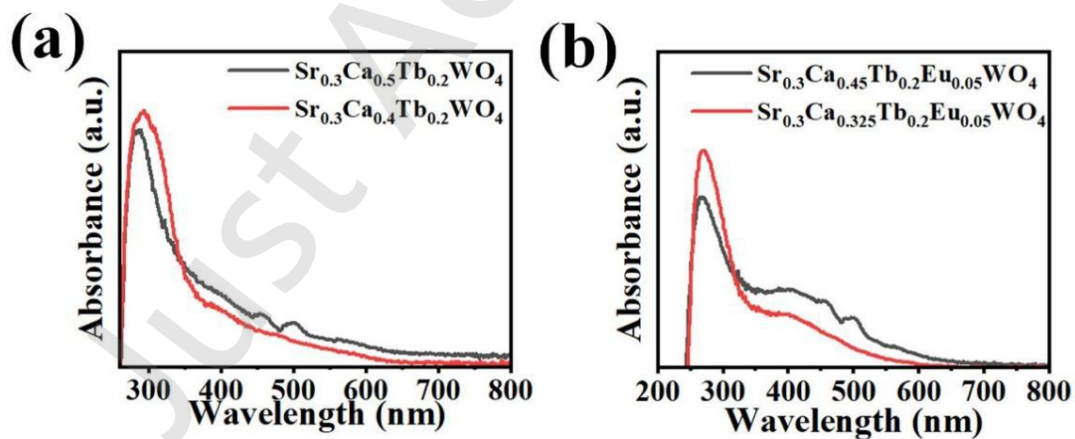


Figure S12. UV-vis absorption spectra of different samples.

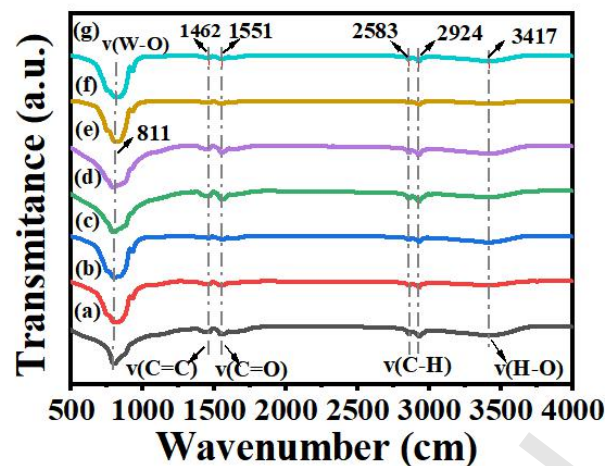


Figure S13. Fourier transform infrared (FT-IR) analysis: (a) $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{WO}_4$, (b) charge-compensated and (c) uncompensated $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{WO}_4:\text{Tb}^{3+}$, (d) charge-compensated and (e) uncompensated $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{WO}_4:\text{Eu}^{3+}$, and (f) charge-compensated and (g) uncompensated $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{WO}_4:\text{Tb}^{3+}/\text{Eu}^{3+}$.

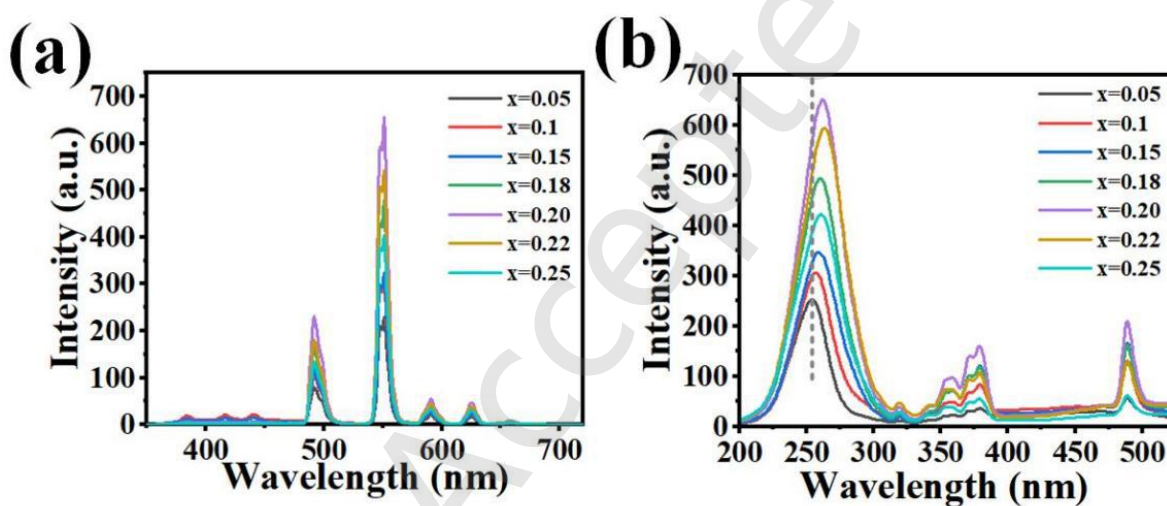


Figure S14. (a) Emission ($\lambda_{\text{ex}} = 250 \text{ nm}$) and (b) excitation ($\lambda_{\text{em}} = 545 \text{ nm}$) spectra of $\text{CaWO}_4:x\text{Tb}^{3+}$.

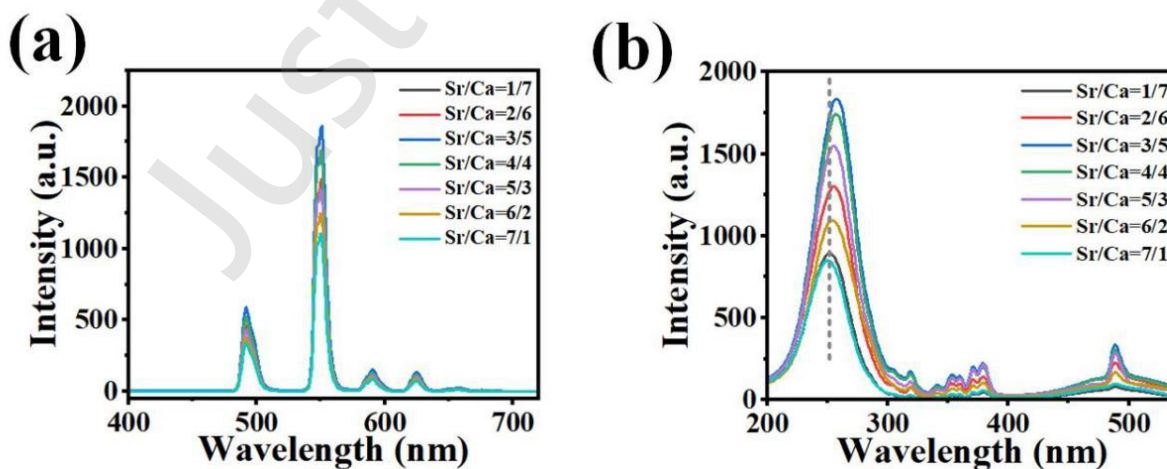


Figure S15. (a) Emission ($\lambda_{\text{ex}} = 250 \text{ nm}$) and (b) excitation ($\lambda_{\text{em}} = 545 \text{ nm}$) spectra of $\text{Ca}_{0.8-x}\text{Sr}_x\text{Tb}_{0.2}\text{WO}_4$ with different Sr/Ca ratios. The molar concentration of Tb is fixed at 20%.

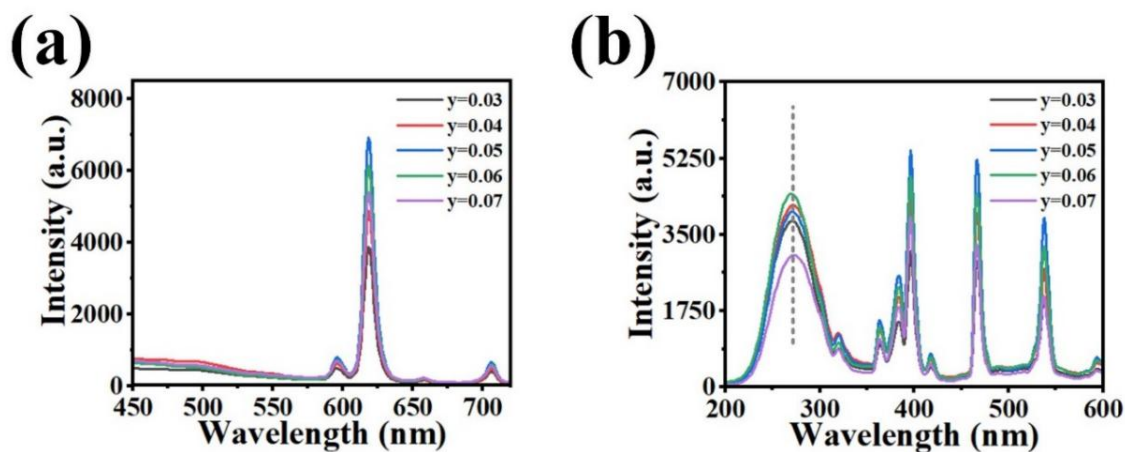


Figure S16. (a) Emission ($\lambda_{\text{ex}} = 396 \text{ nm}$) and (b) excitation ($\lambda_{\text{em}} = 618 \text{ nm}$) spectra of $\text{Ca}_{0.7-y}\text{Sr}_{0.3}\text{Eu}_y\text{WO}_4$ with different Eu^{3+} concentrations ($y=0.03$ - 0.07).

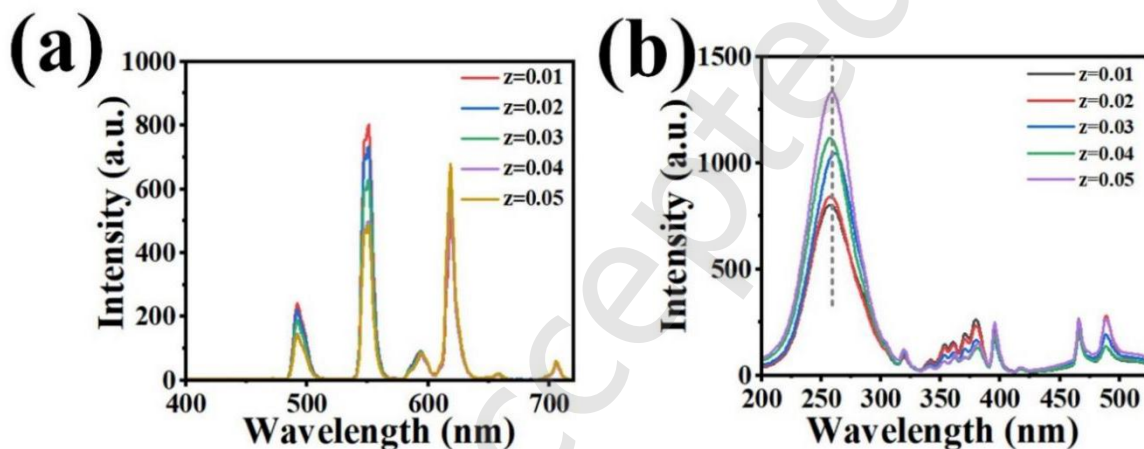


Figure S17. (a) Emission ($\lambda_{\text{ex}} = 250 \text{ nm}$) and (b) excitation ($\lambda_{\text{em}} = 618 \text{ nm}$) spectra of $\text{Ca}_{0.5-z}\text{Sr}_{0.3}\text{Tb}_{0.2}\text{Eu}_z\text{WO}_4$ with different Eu^{3+} concentrations ($z=0.01$ - 0.05).

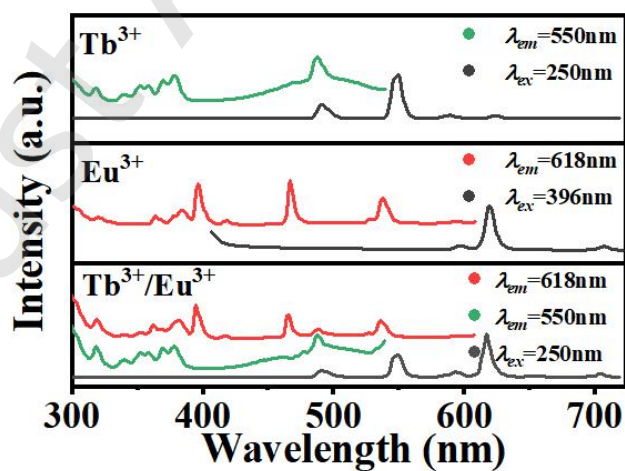


Figure S18. Excitation and emission spectra of Tb^{3+} -, Eu^{3+} -, and $\text{Tb}^{3+}/\text{Eu}^{3+}$ -doped $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4$ phosphors.

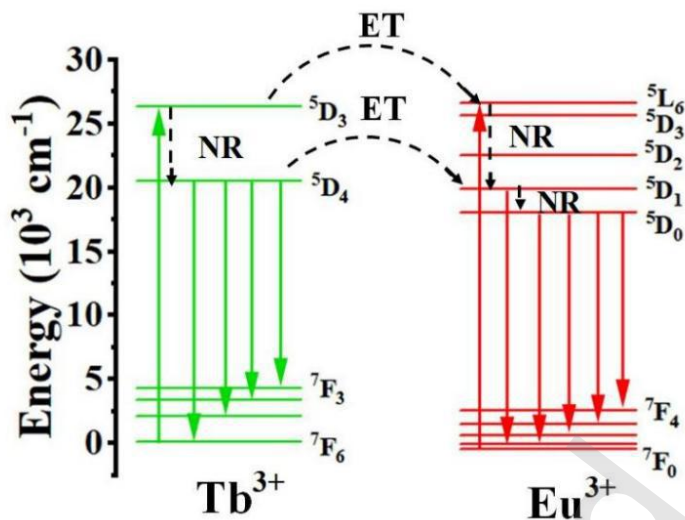


Figure S19. A graphical model for the energy transfer from Tb^{3+} to Eu^{3+} in $\text{Ca}_{0.8-x-y}\text{Sr}_{0.3}\text{Tb}_x\text{Eu}_y\text{WO}_4$.

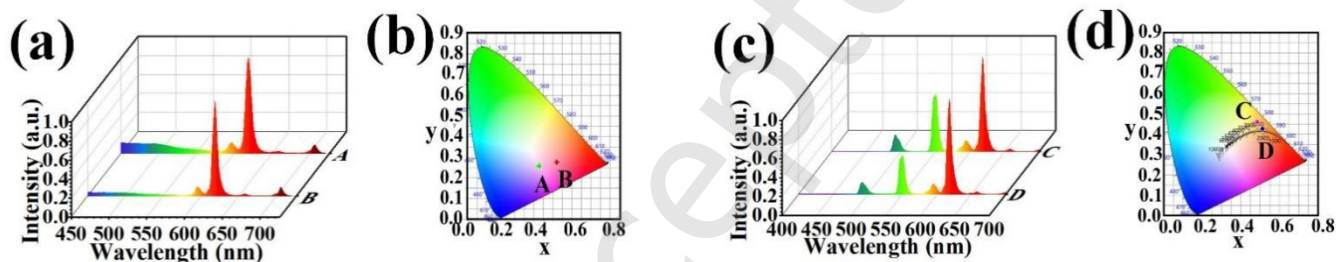


Figure S20. Three-dimensional emission spectra and corresponding CIE chromaticity diagrams of (a, b) Eu^{3+} -doped and (c, d) $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4$ phosphors with and without charge-compensation.

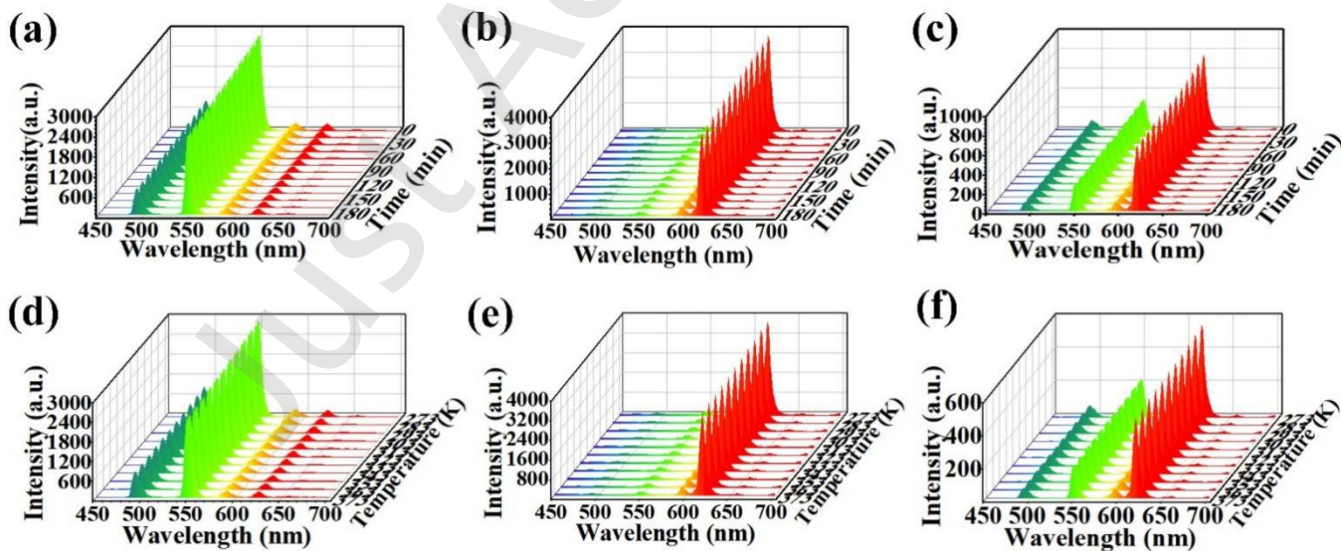
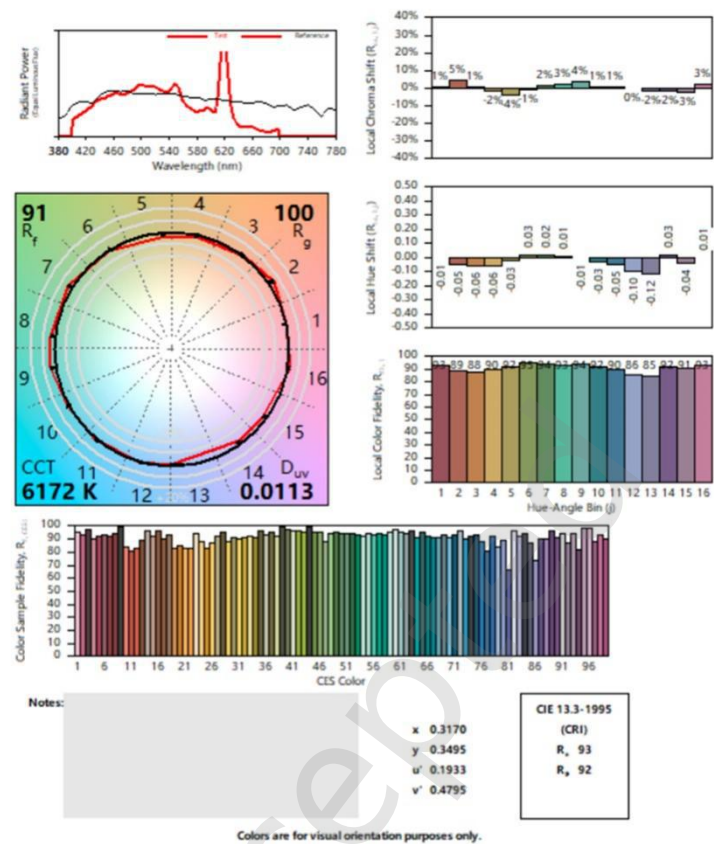


Figure S21. Photostability (a-c) and thermal stability (d-f) of uncompensated samples doped with (a, d) Tb^{3+} , (b, e) Eu^{3+} , and (c, f) $\text{Tb}^{3+}/\text{Eu}^{3+}$.

(a)



(b)

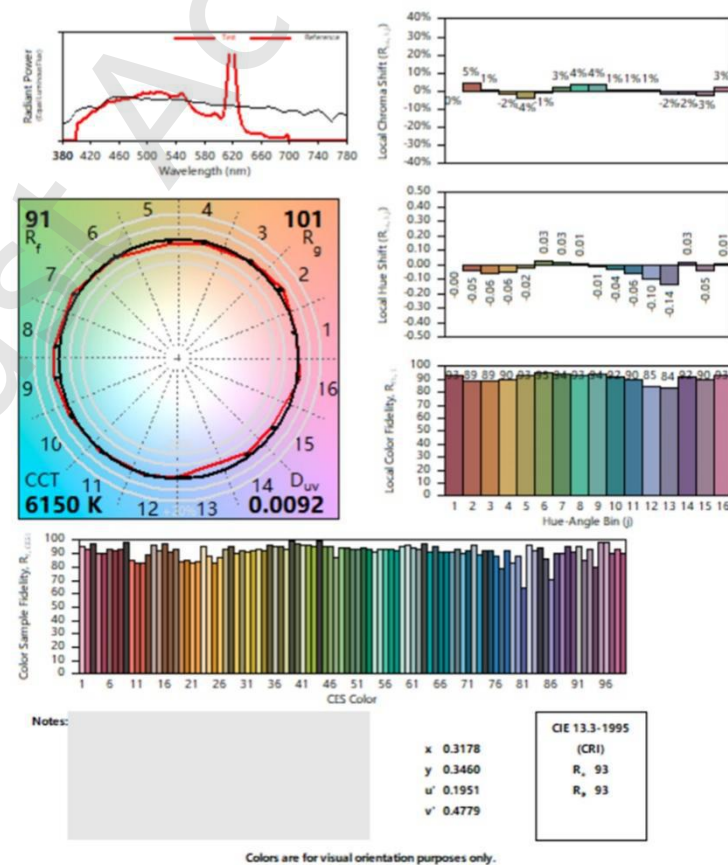


Figure S22. The optimized LED-4 (a) in Figure 7a and LED-E (b) in Figure 7b were characterized by using the IES TM-30-18 gamut index.

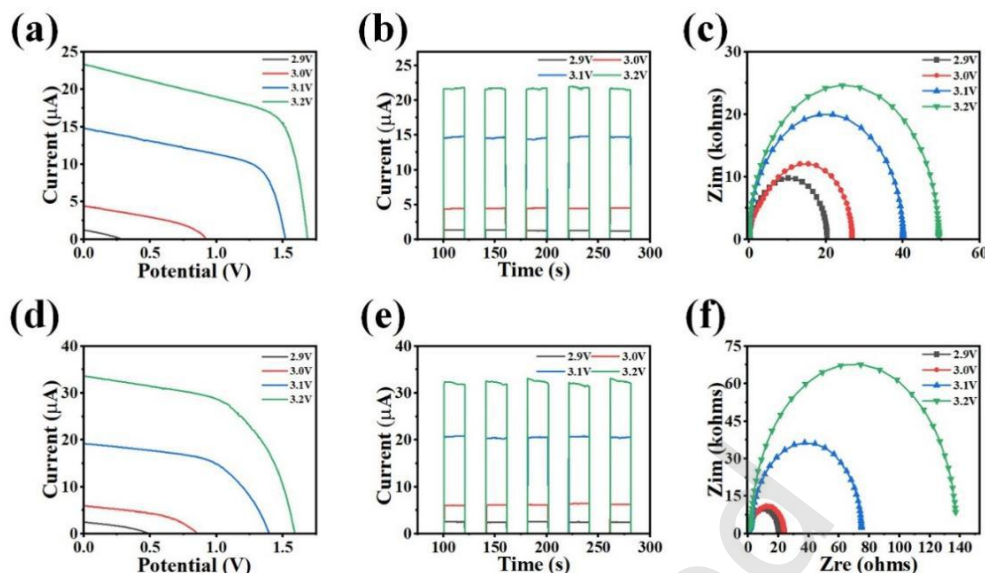


Figure S23. The photocurrent-voltage (I-V) curves, transient photocurrent curves, and Nyquist diagrams of silicon solar cells under illumination from LEDs composed of (a-c) uncompensated and (d-f) charge-compensated Tb³⁺ doped phosphors.

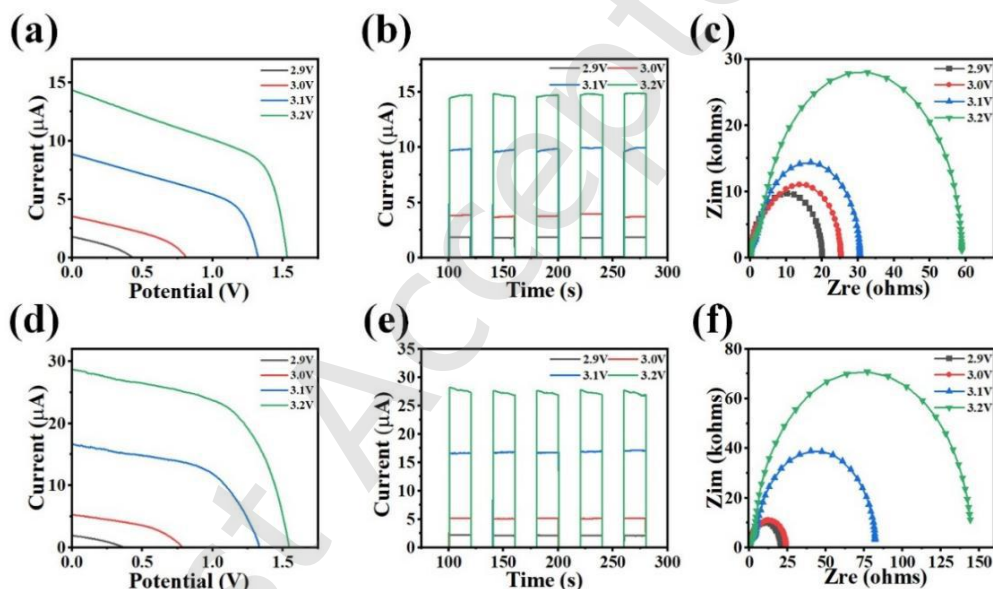


Figure S24. The photocurrent-voltage (I-V) curves, transient photocurrent curves, and Nyquist diagrams of silicon solar cells under illumination from LEDs composed of (a-c) uncompensated and (d-f) charge-compensated Eu³⁺ doped phosphors.

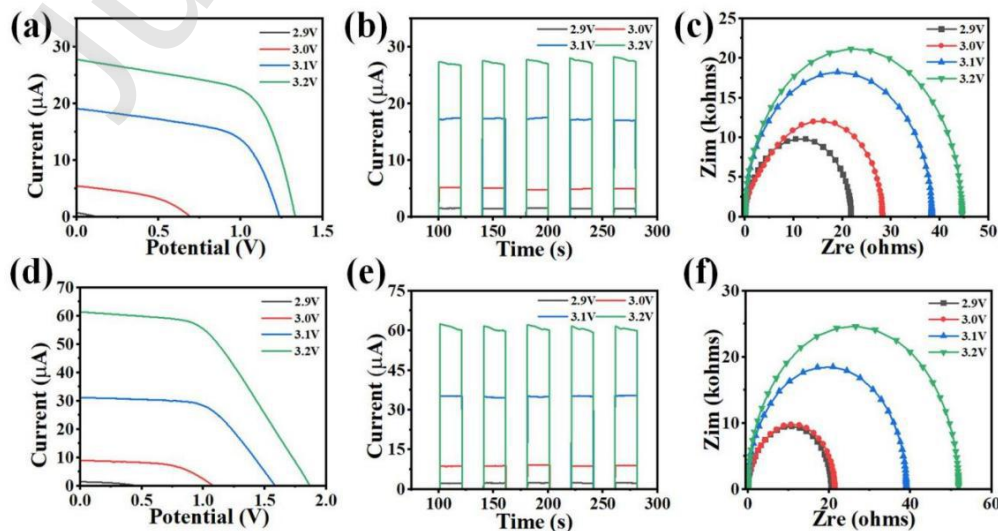


Figure S25. The photocurrent-voltage (I-V) curves, transient photocurrent curves, and Nyquist diagrams of silicon solar cells under illumination from (a-c) LED-4 in Figure 7a and (d-f) LED-E in Figure 7b.