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Excitation-Controlled Host–Guest Multicolor Luminescence in Lanthanide-Doped Calcium Zirconate for Information Encryption

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Abstract: Efficient control over lanthanide luminescence by regulating excitations offers a real-time and reversible luminescence-managing strategy, which is of great importance and highly desirable for various applications, including multicolor display and information encryption. Herein, we studied the crystal structure, luminescence properties, and mechanisms of undoped and Tb³⁺/Eu³⁺-doped CaZrO₃ in detail. The intrinsic purple-blue luminescence from host CaZrO₃ and the introduced green/red luminescence from guest dopants Tb³⁺/Eu³⁺ were found to have different excitation mechanisms and, therefore, different excitation wavelength ranges. This enables the regulation of luminescent color through controlling the excitation wavelengths of Tb³⁺/Eu³⁺-doped CaZrO₃. Furthermore, preliminary applications for information encryption with these materials were demonstrated using portable UV lamps of 254 and 302 nm. This study not only promotes the development of multicolor luminescence regulation in fixed-composition materials, but also advances the practical applications of lanthanide luminescent materials in visually readable, high-level anti-counterfeiting and information encryption.

Keywords: luminescence; lanthanide; multicolor emission; luminescence regulation; information encryption

1. Introduction

Luminescent materials that emit various colors of light under different excitation conditions provide a simple and common means of multicolor display, imaging, security, and information encryption [1,2]. Among the various luminescent materials, lanthanide-based materials are one of the most attractive classes for researchers aiming to acquire excitation-dependent luminescence due to their unique and extensive advantages, such as rich and tunable emission bands (covering the near-infrared, visible and ultraviolet regions), narrow excitation and emission bands (for the major 4f–4f transitions), large Stokes or anti-Stokes shift, and high photostability [3,4].

A widely used strategy is integrating downconversion luminescence with upconversion luminescence. For example, NaGdF₄:Yb,Tm@NaYF₄:Tb@EuSe nanocomposites emit blue and purple light under 365 nm UV and 980 nm NIR irradiation, respectively [5]; NaYF₄:Yb/Er@NaTbF₄:Eu microcrystals show green and red light under 980 nm laser and 365 nm UV excitation, respectively [6]. Many similar systems, such as lanthanide-doped NaLuF₄/Y₂O₃ composites [7], NaGdF₄:Yb/Tm@NaGdF₄:Ce/Mn@NaYF₄ nanoparticles [8], CaSc₂O₄:Yb/Tb phosphors [9], and LiYbF₄:Y@LiGdF₄:Yb/Tm@LiYF₄:Eu nanoparticles [10], also generate principally similar upconversion/downconversion emissions by altering excitation wavelengths. Furthermore, designing orthogonal upconversion processes in multilayer nanocrystals [11–14] or nanoclusters [15] can also provide varied colors of luminescence under different excitation wavelengths. For example, NaYF₄:Yb/Tm@NaYF₄@NaYF₄:Er/Ho@NaYF₄ nanocrystals have blue and yellow emissions upon 980 and 1532 nm laser excitation, respectively [16], and LiREF₄-based core/sextuple-shell



Citation: Wang, Y.; Han, Y.; Liu, R.; Duan, C.; Li, H. Excitation-Controlled Host–Guest Multicolor Luminescence in Lanthanide-Doped Calcium Zirconate for Information Encryption. *Molecules* **2023**, *28*, 7623. https://doi.org/10.3390/ molecules28227623

Academic Editors: Claudia Dragonetti and Xingcai Wu

Received: 1 October 2023 Revised: 5 November 2023 Accepted: 13 November 2023 Published: 16 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Yb,Tm/Gd/Yb,Er/Nd/Gd/Er,Tm/Gd nanocrystals emit blue, green, and red light under 980, 800, and 1532 nm excitation, respectively [12]. Although incorporating excitationdependent upconversion has proven to be a robust method, it is obvious that the elaborate construction of a material structure is often necessary in order to prevent cross-relaxationinduced loss of excitation energy, and that excitation lasers of limited wavelengths, such as 808, 980, and 1532 nm, can be selected for upconversion luminescence. In addition, in upconversion-only luminescent systems, modulating the pulse duration or repetition frequency of the excitation laser can tailor the luminescent color efficiently and almost continuously [17,18], but this method undoubtedly relies on a complex excitation light source system.

Another major class of current luminescent materials possessing excitation-dependent luminescence usually incorporates different luminous ions with different excitation wavelengths [19], such as by co-doping Er^{3+} (shows green emission under 360–380 nm excitations) and Eu²⁺ (shows red emission under 250–320 nm excitations) in La₄GeO₈ [20], co-doping Er^{3+} (shows green emission under 362–380 nm excitations) and Pr^{3+} (shows red emission under 200-400 nm excitations) in NaNbO3 and Ca2Nb2O7 [21,22], and co-doping Tb^{3+} and Eu^{3+} for a tunable color from yellow to pink when increasing the excitation wavelength from 254 to 365 nm [23]. This type of luminescence modulation, independent of upconversion, supports a continuous color control when applying a continuous change in excitation wavelengths. Except for the management of luminous ions, the luminescence of host materials may offer new opportunities to achieve excitation-dependent luminescence. However, this has not attracted much attention to date, and there are very few examples: Cs₃TbCl₆ nanocrystals produce blue luminescence of the host under 365 nm excitation, while the green luminescence of Tb³⁺ is produced under 254 nm excitation, enabling colorful luminescence from green to blue under 260–360 nm excitations [24]. KLu_3F_{10} :Tb crystals emit blue light from defects in KLu_3F_{10} under 365 nm excitation and green light from Tb^{3+} under 254 nm excitation, with the luminescence tuning from green to blue under 250–370 nm excitations [25]. Combining the self-trapped exciton luminescence of the matrix and the luminescence of doped lanthanide ions, Cs₂Ag_{0.3}Na_{0.7}InCl₆:Yb³⁺/Eu³⁺/Ho³⁺ microcrystals display yellow, red, and green light under 300, 394, and 980 nm excitations, respectively [26], and a similar phenomenon has been found in $ZrO_2:Gd^{3+}$ nanoparticles [27]. It is obvious that more effort is needed in order to explore host-luminescence-assisted robust luminescence modulation under varied excitation wavelengths.

Previous reports have shown that CaZrO₃, one ABO₃-type perovskite oxide, can emit an intense purple-blue light with a broad emission band ranging from about 350 to 550 nm under excitations of 200–300 nm, where the excitation is derived from the host absorption and the emission derives from the oxygen-defect-related radiative transitions [28,29]. Importantly, the distorted perovskite structure of CaZrO₃ provides two kinds of lattice sites with different symmetries, eight-fold-coordinated Ca²⁺ sites and six-fold-coordinated Zr^{4+} sites to accommodate various trivalent lanthanide ions (Ln³⁺) for multimode and multicolor luminescence [30–35]. Great progress has been made in the research on doping chemistry and luminescence properties in CaZrO₃ in the last decade or so. For example, Kunti et al. investigated the structural and luminescence properties of CaZrO₃:Eu³⁺ phosphors and disclosed the role of oxygen vacancy in the origin of the host CaZrO₃ emissions and the energy transfer mechanism through detailed experimental and theoretical research [36]. Zhang et al. achieved tunable, full-color luminescence by managing the composition and doping concentration in Tb³⁺/Eu³⁺-doped CaZrO₃ phosphors [37]. Very recently, Ueda et al. revealed that doped Eu^{3+} ions occupy not only A sites, but also B sites, in CaZrO₃, and that co-doping ions of different sizes can regulate the site-occupation proportions as well as the site-dependent Eu^{3+} luminescence [38]. However, it is clear that adjusting the dopant concentration [36,39] and introducing ions of different luminous colors, including different Ln^{3+} ions [37,40] and non-rare-earth ions [41,42], are still the principal strategies by which to achieve multicolor luminescence; therefore, multicolor luminescence is still absent in composition-fixed Ln³⁺-doped CaZrO₃. In addition, for

the recently studied Tb^{3+}/Eu^{3+} co-doped colorful phosphors beyond CaZrO₃, such as La₄GeO₈:Tb/Eu [43], K₅Eu(MoO₄)₄:Tb [44], MgF₂:Tb/Eu [45], K₃Lu(PO₄)₂:Tb/Eu [46], Sr₃MgSi₂O₈:Eu/Tb [47], and Gd₂B₂WO₉:Eu/Tb [48], excitation-dependent multicolor luminescence is also very rare.

In this work, we achieved multicolor luminescence in Tb^{3+}/Eu^{3+} -doped CaZrO₃ by managing not only the luminous ions, but also the excitation wavelengths. We introduced green and red luminescence in purple-blue-emitting CaZrO₃ polycrystalline powders by doping Tb^{3+} and Eu^{3+} , respectively. We investigated the doping chemistry of Tb^{3+}/Eu^{3+} in CaZrO₃ and the luminescence properties, as well as the mechanism. The results revealed that the luminescence from the host CaZrO₃ and from guest dopants Tb^{3+} and Eu^{3+} go through completely different energy paths and require excitation light in different wavelength regions. This allows us to control the luminescent color of these materials by succinctly modulating excitation wavelengths. In addition, we demonstrated a group of prototypes to be utilized for anti-counterfeiting and information encryption using undoped and Tb^{3+}/Eu^{3+} -doped CaZrO₃.

2. Results and Discussion

2.1. Structural and Compositional Analysis of Undoped and Tb³⁺/Eu³⁺-Doped CaZrO₃

The CaZrO₃ crystal adopted a distorted perovskite GdFeO₃-type structure (Figure 1a), wherein the array of ZrO₆ octahedra constituted the crystal structure network and Ca²⁺ ions were interspersed among ZrO₆ octahedra [41,49]. The rotation of the ZrO₆ octahedra led to a decrease in the coordination number (CN) of Ca²⁺ from 12 to 8 [39]; thus, the dopants Tb³⁺/Eu³⁺ would theoretically prefer to be located at the asymmetric 8-fold-coordinated Ca²⁺ sites because of a lower degree of mismatch in effective ionic radii (1.18/1.206 Å of Tb³⁺/Eu³⁺ and 1.26 Å of Ca²⁺ when CN = 8) compared with the symmetric 6-fold-coordinated Zr⁴⁺ sites (1.063/1.087 Å of Tb³⁺/Eu³⁺ and 0.86 Å of Zr⁴⁺ when CN = 6) [50].

Powder X-ray diffraction (XRD) patterns of as-synthesized pristine CaZrO₃, CaZrO₃:Tb³⁺, CaZrO₃:Eu³⁺, and CaZrO₃:Tb³⁺/Eu³⁺ powders are shown in Figure 1b and Figure S1a, and all the diffraction peaks of samples with Tb^{3+}/Eu^{3+} concentrations lower than 6% can be well-indexed to the standard diffraction peaks of orthorhombic CaZrO₃ (PDF card No. 35–0645), suggesting the successful integration of Tb^{3+}/Eu^{3+} into the CaZrO₃ matrix. A close observation of the XRD patterns revealed a few negligible impurity peaks at 28.5° – 30.2° when the Tb³⁺/Eu³⁺ concentrations were larger than 6%, which was most likely due to the formation of trace amounts of Tb₂O₃/Eu₂O₃ impurities. The diffraction peak positions of the (202) planes slightly shifted toward the large-angle side after Tb³⁺/Eu³⁺ doping (Figure S1b), implying a shrinking of the crystal lattice owing to the substitution of big Ca²⁺ by small Tb³⁺/Eu³⁺. A reverse shift to the small-angle side was also observed at high Tb^{3+}/Eu^{3+} doping concentrations, which suggests that Tb^{3+}/Eu^{3+} ions occupy not only Ca²⁺ sites, but also Zr⁴⁺ sites. Partial substitution for Zr⁴⁺ sites is reasoned as a selfcompensation for the charge imbalance caused by substituting Ca²⁺ sites, being described as: $Ln_{Ca}^{\bullet} + Ln_{Zr}^{'}$ (Ln = Tb, Eu). This has been definitively verified in recent research [38], and will also be reflected in the latter spectra of CaZrO₃:Eu³⁺.

We conducted Rietveld refinement to evaluate the change in crystal structure induced by Tb³⁺/Eu³⁺ doping. Relevant results for undoped CaZrO₃ and representative CaZrO₃:4%Tb³⁺/0.5%Eu³⁺ are given in Figure 1c,d and Table S2. Based on the reliable refinement and the good agreement between the calculated and measured patterns, both samples possessed pure orthorhombic structures with the *Pnma* space group. It is worth noting that the values of lattice cell parameters, including *a*, *b*, *c*, and *V*, showed only an extremely negligible reduction after Tb³⁺/Eu³⁺ doping. For example, the cell volume *V* shrank very slightly, from 258.39 to 258.08 Å³. This result further confirms the speculation that a fair fraction of Tb³⁺/Eu³⁺ ions substitute smaller Zr⁴⁺ ions to offset the lattice shrinkage caused by substituting bigger Ca²⁺ ions. In the meanwhile, the deviation of lattice cell parameters between doped and undoped samples was less than 1%, implying no second-phase emergence and the successful doping of Tb³⁺/Eu³⁺. The slightly high Rp values for both undoped and Tb³⁺/Eu³⁺-doped samples may have been due to the relatively strong background signal in the XRD patterns, which was likely due to the slightly low crystallinity. However, due to the consistent measurement conditions as well as the refinement results for both the undoped and doped samples, it probably had no effect on the comparison of their crystal structure data.



Figure 1. (a) Crystal structure diagram of CaZrO₃. (b) Powder XRD patterns of representative undoped CaZrO₃, CaZrO₃:4%Tb³⁺, CaZrO₃:4%Eu³⁺, and CaZrO₃:4%Tb³⁺/0.5%Eu³⁺. The bars at the bottom are the reference standard patterns of CaZrO₃ (PDF card No. 35–0645). Rietveld refinement results of (c) undoped CaZrO₃ and (d) CaZrO₃:4%Tb³⁺/0.5%Eu³⁺. (e) SEM image and (f) elemental mapping of CaZrO₃:4%Tb³⁺/0.5%Eu³⁺. (g) EDS spectrum of CaZrO₃:4%Tb³⁺/0.5%Eu³⁺. (h) XPS spectra of CaZrO₃:4%Tb³⁺/0.5%Eu³⁺: the overall spectrum, high resolution spectra of Eu 3d and Tb 3d.

The representative SEM image of CaZrO₃:4%Tb³⁺/0.5%Eu³⁺ shows agglomerates of irregular nanoparticles with sizes about 150–350 nm (Figure 1e), which may indicate slightly low crystallinity of the obtained samples. The two-dimensional elemental mapping results in Figure 1f indicate the existence of Tb and Eu elements in the CaZrO₃ crystals, which was also proven by the clearly identified peaks from Zr, Ca, Tb, and Eu in the EDS spectrum in Figure 1g. This EDS analysis further verified the successful doping of Tb³⁺/Eu³⁺ ions in CaZrO₃. XPS spectra of the representative CaZrO₃:4%Tb³⁺/0.5%Eu³⁺ sample show the peaks of not only the Ca, Zr and O elements from the host, but also Tb and

Eu elements from the dopants (Figure 1h). Two peaks, around 1242.1 and 1277.0 eV, were the typical XPS peaks of Tb³⁺ $3d_{5/2}$ and Tb³⁺ $3d_{3/2}$, and two around 1134.7 and 1164.2 eV were the characteristic peaks of Eu³⁺ $3d_{5/2}$ and Eu³⁺ $3d_{3/2}$ [51], respectively, suggesting the successful introduction of Tb³⁺/Eu³⁺ into CaZrO₃.

2.2. Luminescent Properties and Mechanisms of Undoped CaZrO₃, CaZrO₃:Tb³⁺, and CaZrO₃:Eu³⁺

The undoped CaZrO₃ sample exhibited a broad emission band centered at 392 nm under 312 nm excitation (Figure 2a). A bright purple-blue luminescence is shown in the inset of Figure 2a. When monitoring the 392 nm emission, an excitation spectrum comprising a strong band of around 312 nm, along with a weak band of around 237 nm, was obtained (Figure 2a). The excitation and emission mechanisms of undoped $CaZrO_3$ have been thoroughly explored, both theoretically and experimentally, in previous research. The weak excitation band at 237 nm (5.23 eV) can be attributed to the absorption of CaZrO₃ (that is, the band-gap transition) as a result of $O^{2-} \rightarrow Zr^{4+}$ electron transfer in ZrO₆ octahedra, according to previous reports [28,29]. The similar value of the band gap energy (5.55 eV, 223 nm) obtained from the absorption spectrum of CaZrO₃ verified this definitively (Figure S2). The intense excitation band around 312 nm may have been due to the absorption of oxygen vacancies, which generated defect states in the bandgap of CaZrO₃ [52]. These oxygen vacancies were a singly ionized oxygen vacancy (V_{0}°) and doubly ionized one $(V_0^{\bullet\bullet})$, and occurred in the form of complex $[CaO_7 \cdot V_0^{\bullet}]$, $[CaO_7 \cdot V_0^{\bullet\bullet}]$, $[ZrO_5 \cdot V_0^{\bullet}]$, and $[ZrO_5 \cdot V_0^{\bullet \bullet}]$ clusters generated during the high temperature synthesis processes [29,36]. The emission band stemmed from the radiative transitions of deep oxygen vacancy states.



Figure 2. (a) Excitation and emission spectra of undoped CaZrO₃. (b) Excitation spectra of CaZrO₃:Tb³⁺ (2–8%), obtained by monitoring the emission at 545 nm. (c) Emission spectra of CaZrO₃:Tb³⁺ (0–8%) under 245 nm excitation. (d) Emission spectra of CaZrO₃:Eu³⁺ (0–8%) under 280 nm excitation. The insets in (a,c,d) are photographs of the corresponding samples.

Doping Tb³⁺ or Eu³⁺ ions into CaZrO₃ changed the luminescent properties significantly. The excitation spectra of CaZrO₃:Tb³⁺ (2–8%) monitoring Tb³⁺ emission at 545 nm are presented in Figure 2b. All excitation spectra showed strong and broad excitation bands centered at 245 nm and several weak and narrow excitation peaks in the range of 310–380 nm. These weak and narrow excitation peaks matched a series of Tb^{3+} 4f–4f transitions well. The intense and broad excitation band could be attributed to the characteristic absorption from the 4f–5d transitions of Tb^{3+} [53,54]. The completely different excitation band position around 245 nm compared with the main excitation band around 312 nm of undoped CaZrO₃ could exclude the host's absorption of CaZrO₃. This was further confirmed by the emission spectra under 312 nm excitation (Figure S3a). Obviously, the intense excitation at 312 nm of undoped CaZrO₃ was unable to trigger the luminescence of Tb^{3+} at all. Furthermore, the almost identical excitation band positions at 245 nm for samples with varied Tb³⁺ concentrations also opposed the possible Tb³⁺-doping-induced shift of the host absorption band. Figure 2c compares the emission spectra of $CaZrO_3$:Tb³⁺ (0-8%) under 245 nm excitation, showing that CaZrO₃:Tb³⁺ (2-8%) presented a series of strong and narrow emission peaks originating from the characteristic 4f-4f transitions of Tb^{3+} . The broad emission bands around 392 nm from the host CaZrO₃ still appeared, although the intensity was reduced. This is because the excitation wavelength of 245 nm overlapped with the tail of the excitation band for host emission. The Tb³⁺ luminescence reached the highest intensity in CaZrO₃:4%Tb³⁺, and concentrations greater than 4% led to a decline in intensity due to concentration quenching. Digital photographs display the bright green luminescence of CaZrO₃:Tb³⁺ (2–8%) (the inset in Figures 2c and S3b).

The excitation spectra of CaZrO₃:Eu³⁺ (2–8%) in Figure S4a show a broad band around 280 nm and several narrow peaks. These narrow excitation peaks are all from the 4f-4f transitions of Eu³⁺ as marked. The broad excitation band around 280 nm is ascribed to the charge transfer (CT) transitions from O 2p states to Eu 4f states [38,39,55]. Similarly, the significant difference (about 32 nm) in the excitation band positions between CaZrO₃:Eu³⁺ and undoped CaZrO₃, together with the almost identical excitation band positions at 280 nm for samples with varied Eu³⁺ concentrations, also rule out the possibility of host absorption from CaZrO₃. When excited by 280 nm UV light, CaZrO₃:Eu³⁺ (2–8%) samples showed a series of sharp emissions from Eu^{3+} 4f–4f transitions in the visible region, as well as a weak and wide emission band around 392 nm from the host CaZrO₃ (Figure 2d). The obviously stronger emissions at 593 and 616 nm made the overall luminescence bright red for CaZrO₃:Eu³⁺ (the inset in Figures 2d and S4b). As is known, the local symmetry of Eu³⁺ ions determines the relative intensity between the 616 nm emission from ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ electric dipole transitions and the 593 nm emission from ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole transitions [56]. The emission at 616 nm dominated in the emission spectrum for Eu^{3+} ions in asymmetric lattice sites, while the 593 nm emission was dominant for Eu³⁺ ions in symmetric sites. Herein, the slightly weaker emission intensity at 593 nm compared with 616 nm revealed that a fair amount of Eu^{3+} ions were located at the symmetric centers of the ZrO_6 octahedra. This is consistent with the negligible changes in crystal structure parameters after doping Tb^{3+}/Eu^{3+} . A concentration quenching causing a drop in luminescence intensity was also observed when the Eu^{3+} concentration was greater than 4%. In addition, Eu^{3+} ions could also be efficiently excited by their own 4f-4f transitions, but we did not focus on this in the present research because the sharp excitation peak did not lead to a continuous change in luminescence color when tuning excitation wavelengths.

We explored the mechanism of the concentration-quenching phenomenon in CaZrO₃:Tb³⁺ and CaZrO₃:Eu³⁺. As is well known to us, increasing the doping concentration of activators causes decreased interionic distance and promotes non-radiative energy transfer among activators [57]. We first estimated the critical distance (R_c) among Tb³⁺/Eu³⁺ ions in CaZrO₃ using the Blasse formula [58]:

$$R_c = 2(\frac{3V}{4\pi X_c Z})^{1/3}$$
(1)

where *V* is the unit cell volume (258.3 Å³ for CaZrO₃), *X_c* is the critical doping concentration (0.04 for Tb³⁺/Eu³⁺ herein), and *Z* is the number of lattice sites available for Tb³⁺ or Eu³⁺ occupation per unit cell (*Z* = 4 for CaZrO₃). The calculated *R_c* was about 14.56 Å; thus, the exchange interaction could be excluded from the possible mechanism of concentration quenching because it mainly occurred when *R_c* was less than 5 Å. Therefore, we reasoned that the multipole–multipole interaction was principally responsible for the concentration to be dipole–dipole interaction (find details in the Supporting Information and Figure S5). Therefore, the concentration quenching in CaZrO₃:Tb³⁺ and CaZrO₃:Eu³⁺ can be attributed to electric dipole–dipole interaction.

The mechanisms of luminescence from CaZrO₃, CaZrO₃:Tb³⁺, and CaZrO₃:Eu³⁺ are summarized and depicted in Figure 3. For CaZrO₃, the excitation of electrons from the ground levels to the excited levels of defect states, the subsequent non-radiative transitions to deep defect states, and the following radiative recombinations were the main energy paths, meanwhile weak excitation could also be accessed by the band-gap transitions and the subsequent energy transfer to the defect states (Figure 3a). In CaZrO₃:Tb³⁺, the main mechanism for Tb³⁺ luminescence was the self-excitation of Tb³⁺ through 4f–5d transitions followed by the radiative 4f–4f transitions, accompanied by some non-radiative transitions (Figure 3b). As for CaZrO₃:Eu³⁺, the main luminescent mechanism was the excitation by the O²⁻ \rightarrow Eu³⁺ charge transfer transitions, which led to the described radiative 4f–4f transitions of Eu³⁺ (Figure 3c). It is obvious that the main excitation channels for the luminescence from host CaZrO₃ and dopants Tb³⁺ and Eu³⁺ were completely different, as were the excitation wavelengths.



Figure 3. Schematics of the main luminescence mechanism in (**a**) $CaZrO_3$, (**b**) $CaZrO_3$: Tb^{3+} , and (**c**) $CaZrO_3$: Eu^{3+} . Some of the energy levels of Tb^{3+} and Eu^{3+} are shown and marked. The upward/downward full arrows represent the excitation/emission processes. The curved and straight dash arrows represent the energy transfer and non-radiative transition processes, respectively. CTB: charge transfer band.

2.3. Luminescent Properties and Mechanisms of CaZrO₃:Tb³⁺/Eu³⁺

When co-doping Tb³⁺ and Eu³⁺ ions into CaZrO₃, we obtained the emissions of Tb³⁺ and Eu³⁺ simultaneously in a single material. The excitation spectra of CaZrO₃:4%Tb³⁺/0.5%Eu³⁺ monitoring the 545 nm emission of Tb³⁺ and the 616 nm emission of Eu³⁺ show two broad excitation bands centered at 245 and 273 nm, respectively (Figure 4a). These two bands were almost identical to the excitation bands in Tb³⁺-singly-doped and Eu³⁺-singly-doped CaZrO₃; therefore, it is reasonable to allocate them to the 4f–5d transitions of Tb³⁺ and the O²⁻ \rightarrow Eu³⁺ charge transfer transitions, respectively. The excitation band at 245 nm for Tb³⁺ 545 nm emissions showed no shift in peak position, but only a decrease in intensity when the concentration of Eu³⁺ was increased from 0.5% to 6% (Figure S6a),

because doping Eu^{3+} induces the gradual weakening of Tb^{3+} luminescence. The increase in the excitation band, which was around 273 nm for Eu^{3+} 616 nm emissions, implies an opposite trend regarding Eu^{3+} emission intensity (Figure S6b). To obtain intensitycomparable luminescence from both Tb^{3+} and Eu^{3+} , we selected 255 nm, approximately located at the intersection of the two excitation bands, as the excitation wavelength to obtain the emission spectra.



Figure 4. (a) Excitation and emission spectra of $CaZrO_3:4\%Tb^{3+}/0.5\%Eu^{3+}$. (b) Emission spectra and (c) photographs of $CaZrO_3:4\%Tb^{3+}/xEu^{3+}$ (x = 0–6%) under 255 nm excitation. (d) Schematic of the main luminescence mechanism of $CaZrO_3:4\%Tb^{3+}/xEu^{3+}$. Some energy levels of Tb^{3+} and Eu^{3+} are shown and marked.

As shown in Figure 4b, when increasing the concentration of Eu^{3+} in CaZrO₃:4%Tb³⁺/xEu³⁺ (x = 0-6%), the characteristic emissions of Eu³⁺ became gradually stronger, while the emission intensity of Tb³⁺ showed the opposite trend under the excitation of 255 nm. This fits well with the luminescent color change from green to red (Figure 4c). Additionally, the broad emission band around 392 nm in the host CaZrO₃ maintained a low intensity in all Tb³⁺/Eu³⁺-doubly-doped CaZrO₃ under the excitation of 255 nm. For a Tb³⁺ emission decline by adding Eu³⁺ content, the unchanged content of Tb³⁺ could exclude the possible effect of cross-relaxation (CR) processes (such as familiar CR: ${}^{5}D_{3} + {}^{7}F_{6} \rightarrow {}^{5}D_{4} + {}^{7}F_{0,1}$) between Tb^{3+} ions. Additional Eu^{3+} content could increase the CR processes between Tb^{3+} and Eu³⁺, as in Figure 4d, mainly including CR1: ${}^{5}D_{3}$ (Tb³⁺) + ${}^{7}F_{I}$ (Eu³⁺) $\rightarrow {}^{7}F_{I}$ (Tb³⁺) + ${}^{5}D_{3}$ (Eu³⁺) and CR2: ${}^{5}D_{4}$ (Tb³⁺) + ${}^{7}F_{J}$ (Eu³⁺) $\rightarrow {}^{7}F_{J}$ (Tb³⁺) + ${}^{5}D_{0,1}$ (Eu³⁺). These CR processes would promote the generation of Eu^{3+} -emissive levels of ${}^{5}D_{0}$ and ${}^{5}D_{1}$ while dissipating Tb³⁺-emissive levels of ${}^{5}D_{3}$ and ${}^{5}D_{4}$, leading to the Tb³⁺ \rightarrow Eu³⁺ energy transfer, which is widely considered to be the reason for decreasing Tb³⁺ emissions [59,60]. In addition, the Eu³⁺ emissions of CaZrO₃:4%Tb³⁺/xEu³⁺ samples continue to enhance slightly when the Eu³⁺ concentration is 6%, which exceeds the optimal doping concentration of Eu³⁺ singly-doped samples, which is 4%. This could be attributed to possible compensation by the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer to increased concentration quenching between Eu^{3+}

ions. Therefore, the main luminescent mechanism in CaZrO₃:Tb³⁺/Eu³⁺ can be described as follows (Figure 4d): Being excited by the 4f–5d transitions, Tb³⁺ ions can not only emit light through radiative 4f–4f transitions, but also transfer partial excitation energy to Eu³⁺ through CR1 and CR2 processes. Then, excited Eu³⁺ ions emit light through radiative 4–4f transitions; Eu³⁺ ions can also be excited by $O^{2-} \rightarrow Eu^{3+}$ charge transfer transitions.

The luminescence decay curves monitoring the 545 nm emissions of $CaZrO_3:4\%Tb^{3+}/xEu^{3+}$ (x = 0–6%) under 255 nm excitation are shown in Figure 5a. These decay curves show obvious non-exponential patterns, especially for Tb^{3+}/Eu^{3+} -co-doped samples, so the effective lifetime was adopted and calculated using the following equation:

$$\tau_{\rm eff} = \frac{\int tI(t)dt}{\int I(t)dt}$$
(2)

where I(t) is the luminescence intensity at time t. The calculated values of the effective lifetimes of the Tb³⁺ 545 nm emission decreased from 1.345 to 0.119 ms as the concentration of Eu³⁺ increased from 0 to 6% in CaZrO₃:4%Tb³⁺/xEu³⁺ (Figure 5b). This downward trend in lifetime implies the gradually reduced probability of Tb³⁺ ⁵D₄ \rightarrow ⁷F₅ radiative transitions being due to the energy transfer from Tb³⁺ to Eu³⁺. The efficiency of this energy transfer (η_{ET}) was estimated based on the following equation:

$$\eta_{ET} = (1 - \tau/\tau_0) \times 100\% \tag{3}$$

where τ_0 and τ are the lifetimes of Tb³⁺ 545 nm emissions without and with co-doped Eu³⁺, respectively. The calculated values of η_{ET} were 26.39%, 42.90%, 73.38%, 85.58%, and 91.15% for 0.5%, 1%, 2%, 4%, and 6% Eu³⁺ in CaZrO₃:4%Tb³⁺/xEu³⁺, respectively (Figure 5b).

To determine the energy transfer mechanism, the critical distance between Tb^{3+} and Eu^{3+} was calculated to be 14.00 Å using the Equation (1), indicating that the multipole–multipole interaction dominates the energy transfer processes. The following formula for the relationship between the lifetime and the doping concentration was used to further disclose the mode of multipole–multipole interaction [51]:

$$\frac{1}{2} \propto C^{n/3}$$
 (4)

where *C* is the total concentration of Tb³⁺ and Eu³⁺, and the values of *n* at 6, 8, and 10 correspond to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interaction, respectively. The dependences of τ_0/τ on $C^{n/3}$ were plotted and fitted linearly, as shown in Figure 5c–e. The optimal fitting coefficient R^2 was obtained at n = 6, suggesting that the main energy transfer mechanism was a dipole–dipole interaction.

Luminescence decay analysis according to the Inokuti–Hirayama (I-H) model also revealed the multipole–multipole interaction mechanism between Tb^{3+} and Eu^{3+} [61]. The I-H model described the luminescence decay intensity I(t) at time t using the following equation:

$$I(t) = I_0 \exp\left[-\left(\frac{t}{\tau_0}\right) - Q\left(\frac{t}{\tau_0}\right)^{3/s}\right]$$
(5)

where I_0 is the intensity when t = 0; τ_0 is the intrinsic lifetime of Tb³⁺ without Eu³⁺ (1.345 ms), and Q is the energy transfer parameter, defined as:

$$Q = \frac{4\pi}{3}\Gamma(1 - \frac{3}{s})N_0 R_0^3$$
(6)

where Γ is the Euler function, N_0 is the Eu³⁺ concentration, and R_0 is the critical distance. The values of S at 6, 8, and 10 correspond to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. As shown in Figure 5a, the decay curves of CaZrO₃:4%Tb³⁺/xEu³⁺ (x = 0.5–6%) samples were fitted well by Equation (5) at S = 6. The energy transfer parameter Q, achieved from the fitting process, showed an almost linear dependence on Eu³⁺ concentration (Figure 5b), as reflected by Equation (6). This result further corroborates the notion that the dipole–dipole interaction was mainly responsible for the Tb³⁺ \rightarrow Eu³⁺ energy transfer.



Figure 5. (a) The decay curves monitoring the 545 nm emissions of $CaZrO_3:4\%Tb^{3+}/xEu^{3+}$ (x = 0–6%) under 255 nm excitation. I-H fitting results of the corresponding samples at S = 6 are shown as grey lines. (b) The calculated lifetime values of $Tb^{3+}5D_4 \rightarrow {}^7F_5$ transition, energy transfer parameter Q, and efficiency (η_{ET}) from Tb^{3+} to Eu^{3+} in $CaZrO_3:4\%Tb^{3+}/xEu^{3+}$ (x = 0–6%) as a function of Eu^{3+} concentration. The relationship of τ_0/τ of Tb^{3+} to (c) $C^{6/3}$, (d) $C^{8/3}$ and (e) $C^{10/3}$ in $CaZrO_3:4\%Tb^{3+}/xEu^{3+}$ (x = 0.5–6%).

2.4. Excitation Controlled Multicolor Luminescence

On the basis of the above results, it is clear that the purple-blue luminescence of the host CaZrO₃, the green luminescence of Tb³⁺ and the red luminescence of Eu³⁺ could be achieved under distinctly different excitation wavelengths in Tb³⁺/Eu³⁺-doped CaZrO₃. This allows us to manipulate the luminescence color of these materials by simply controlling the excitation wavelengths, without the need to change the composition of the material. For Tb³⁺-singly-doped, Eu³⁺-singly-doped, and Tb³⁺/Eu³⁺-doubly-doped CaZrO₃, we selected CaZrO₃:8%Tb³⁺, CaZrO₃:6%Eu³⁺, and CaZrO₃:4%Tb³⁺/0.5%Eu³⁺, respectively, for excitation wavelength-dependent luminescence research as the strongest emissions from the host CaZrO₃ at 392 nm in their respective groups (Figure S7). In CaZrO₃:8%Tb³⁺, the optimal excitation wavelengths for 545 nm luminescence of Tb³⁺ and 392 nm luminescence of host CaZrO₃ were 245 and 312 nm, respectively (Figure 6a). Thus, changing the excitation wavelength from 245 to 312 nm led to a gradual decrease in Tb³⁺ luminescence and a gradual increase in CaZrO₃ luminescence (Figure 6b,c). The photographs show a luminescent color evolution from green to purple-blue under excitation at increased wavelengths (Figure 6g). For CaZrO₃:6%Eu³⁺, we tuned the luminescent color from red to wine red by gradually increasing the excitation wavelength from 280 to 312 nm (Figure S8). Purple-blue emissions

were not obtained due to the relatively large degree of overlap between the two excitation bands for the 616 and 392 nm emissions (Figure S8a). In CaZrO₃:4%Tb³⁺/0.5%Eu³⁺, richer emission color variations were achieved. As shown in Figure 6d, the most effective excitation wavelengths for green emission at 545 nm, red emission at 616 nm, and purple-blue emission at 392 nm were 245, 273, and 312 nm, respectively. Therefore, when the excitation wavelengths were set to vary from 245 to 312 nm, the emissions of Tb³⁺ were gradually reduced. The emissions of host CaZrO₃ were first slightly reduced, then significantly enhanced, while the emissions of Eu³⁺ experienced a significant rise and then a significant decline (Figure 6e,f). For the overall luminescence, the color varied from white to red, and to purple in the end (Figure 6h). A white, instead of green, luminescence was obtained under the 245 nm excitation, as it was a mixture of several intensity-comparable emissions in the range of 400–550 nm from both the CaZrO₃ and Tb³⁺ hosts.



Figure 6. (a) Excitation spectra of CaZrO₃:8%Tb³⁺, obtained by monitoring emissions at 545 and 392 nm. (b) Emission spectra and (c) intensity variation of CaZrO₃:8%Tb³⁺ under 245–312 nm excitations. (d) Excitation spectra of CaZrO₃:4%Tb³⁺/0.5%Eu³⁺, obtained by monitoring emissions at 545, 616 and 392 nm. (e) Emission spectra and (f) intensity variation of CaZrO₃:4%Tb³⁺/0.5%Eu³⁺ under 245–312 nm excitations. Digital photographs show the color evolution of (g) CaZrO₃:8%Tb³⁺ and (h) CaZrO₃:4%Tb³⁺/0.5%Eu³⁺ under different excitation wavelengths.

2.5. Cases of Information Encryption

The excitation-dependent multicolor luminescence of Tb^{3+}/Eu^{3+} -doped CaZrO₃ suggests possible applications in the fields of optical anti-counterfeiting and information encryption. We established a series of luminescent patterns by selectively coating slurries of luminescent samples on PMMA plates engraved with designed patterns. As shown in Figure 7a, the "LCU" patterns, composed of CaZrO₃:8%Tb³⁺, CaZrO₃:6%Eu³⁺,

and CaZrO₃:4%Tb³⁺/0.5%Eu³⁺, were green, red, and light-red under 254 nm UV light, and blue, wine-red, and purple-blue under 302 nm UV light, respectively. This demonstrates the potential application of these materials in high-level anti-counterfeiting. In Figure 7b, it is shown that all signal points in a 3×8 dot matrix composed of both CaZrO₃ and CaZrO₃:8%Tb³⁺ emitted blue light under 302 nm UV light; however, the points of CaZrO₃:8%Tb³⁺ turned to green, while the points of CaZrO₃ remained blue under 254 nm UV light. This reveals latent optical information and can be decoded as a binary code using "1" and "0"; furthermore, the obtained 8-bit ASCII codes from the three rows of light signal can be read out as "LCU". This preliminary experiment may provide great opportunities for optical information encryption and storage.



Figure 7. (a) Photographs of "LCU" patterns composed of $CaZrO_3:8\%Tb^{3+}$, $CaZrO_3:6\%Eu^{3+}$, and $CaZrO_3:4\%Tb^{3+}/0.5\%Eu^{3+}$ under 254 and 302 nm UV light. (b) Photographs of array patterns composed of $CaZrO_3$ and $CaZrO_3:8\%Tb^{3+}$ under 302 and 254 nm UV light; ASCII codes revealed by the luminescent color, and cryptographic information of "LCU".

3. Materials and Methods

3.1. Materials and Synthesis

The reagents used in the synthesis of undoped CaZrO₃, CaZrO₃:Tb³⁺, CaZrO₃:Eu³⁺, and CaZrO₃:Tb³⁺/Eu³⁺ phosphors include CaCO₃ (99.99%, Aladdin), ZrO₂ (99.99%, Aladdin), Tb₂O₃ (99.99%, Aladdin), and Eu₂O₃ (99.99%, Aladdin). All reagents were used without further purification. The high temperature, solid-state reaction method was used for sample synthesis. The stoichiometric contents of CaCO₃, ZrO₂, Tb₂O₃, and Eu₂O₃ were weighed and ground completely for 30 min with an agate mortar (details of each doped sample can be found in Table S1 of the Supporting Information). Note that all of the doping percentages of lanthanide ions are atomic percentages in this work, and lanthanide ions were supposed to replace calcium ions. The mixture was transferred into an aluminum oxide crucible and sintered at 600 °C for 5 h. Then, the cooled mixture was ground again for 20 min using an agate mortar and heated to 1200 °C for 6 h. After cooling down to room temperature, the product was ground for another 10 min and collected for further use. All the sintering processes occurred under atmospheric conditions, and all heating and cooling rates were set to 5 °C/min.

3.2. Characterization

Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer with Cu K α radiation as the incident beam. Scanning electron microscopy (SEM) measurements and the energy-dispersive X-ray spectroscopy (EDS) elemental analysis were conducted using a field emission scanning electron microscope (Thermo Fisher Scientific (Waltham, MA, USA) FIB-SEM GX4). X-ray photoelectron spectroscopy (XPS) analysis was carried out using an XPS Microprobe (Thermo SCIENTIFIC ESCALAB Xi+). The absorption spectra were collected with a UV-3600 UV-VIS-NIR spectrophotometer from Shimadzu (Kyoto, Japan). The excitation and emission spectra were measured by means of a Hitachi (Chiyoda City, Japan) F-7000 fluorescence spectrophotometer. The decay curves were obtained using an Edinburgh Instruments (Livingston, UK) FLS920 fluorescent spectrometer with a μ s flash lamp as the excitation source.

3.3. Methods to Establish the Luminescent Patterns for Anti-Counterfeiting and Optical Information Encryption

Firstly, 2 g of as-prepared undoped CaZrO₃, CaZrO₃:8%Tb³⁺, CaZrO₃:6%Eu³⁺, or CaZrO₃:4%Tb³⁺/0.5%Eu³⁺ was mixed with 5 g of PVA aqueous solution, then underwent ultrasonic treatment to form a slurry. Then, the slurry was selectively coated on the patterned PMMA plate by dripping before being dried at 70 °C for 1 h. Photographs of the luminescent patterns were taken with a smartphone under 254 or 302 nm UV light in a dark box.

4. Conclusions

In summary, we synthesized undoped CaZrO₃ with purple-blue luminescence and introduced green and red luminescence by doping lanthanide ions Tb^{3+} and Eu^{3+} , respectively. In-depth research revealed the distinctly different excitation energy paths for luminescence from host CaZrO₃ and dopants Tb^{3+} and Eu^{3+} . This allowed the optimal excitation wavelengths to move away from each other to achieve luminescence in host CaZrO₃ and dopants Tb^{3+} and Eu^{3+} , which allowed us elaborative control of the luminescent color by modulating excitation wavelengths only in composition-fixed CaZrO₃: Tb^{3+} , CaZrO₃: Eu^{3+} and CaZrO₃: Tb^{3+} . Thereafter, we demonstrated preliminary cases of applications for optical anti-counterfeiting and information encryption using this group of materials and common UV lamps. This study not only offers a generally applicable design strategy for multicolor luminescent regulation without the need to change the composition of the material, but will also help to develop advanced luminescent multi-functional rare-earth materials.

Supplementary Materials: The following supporting information can be downloaded at https:// www.mdpi.com/article/10.3390/molecules28227623/s1: Figure S1: Powder XRD patterns; Figure S2: Absorption spectrum and plot of $(\alpha hv)^2$ versus photo energy of CaZrO₃; Figure S3: Emission spectra of CaZrO₃:Tb³⁺ under 312 nm excitation, photographs of CaZrO₃:Tb³⁺ under 245 nm excitation; Figure S4: Excitation spectra of CaZrO₃:Eu³⁺ (2–8%), photographs of CaZrO₃:Eu³⁺ (0–8%) under 280 nm excitation; Figure S5: Dependences of Log (*I*/*x*) against Log (*x*) for CaZrO₃:Tb³⁺ (2–8%) and CaZrO₃:Eu³⁺ (2–8%); Figure S6: Excitation spectra of CaZrO₃:4%Tb³⁺/xEu³⁺ (x = 0.5–6%); Figure S7: Emission spectra of CaZrO₃:Eu³⁺ and CaZrO₃:4%Tb³⁺/xEu³⁺ under 312 nm excitation; Figure S8: Excitation spectra, emission spectra, emission intensity variation, and luminescent photographs of CaZrO₃:6%Eu³⁺; Table S1: Products and the detailed dosages of precursors for their synthesis; Table S2: Rietveld refinement results.

Author Contributions: Conceptualization, Y.W.; methodology, Y.W., Y.H., R.L. and C.D.; validation, Y.W.; formal analysis, Y.H.; investigation, R.L. and C.D.; resources, Y.W.; data curation, Y.W., R.L. and C.D.; writing—original draft preparation, Y.W.; writing—review and editing, Y.W., Y.H. and H.L.; supervision, Y.W.; project administration, Y.W. and H.L.; funding acquisition, Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Shandong Province (grant number ZR2021QA057) and the Research Fund for the Doctoral Program of Liaocheng University (grant number 318051832).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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