

Eu³⁺ complex as an Efficient Luminescent Sensitizer for NIR-Emitting Core–Shell Zn_xMg_ySnO₄:Cr³⁺ Persistent Luminescence Materials

Leonardo H. C. Francisco, Renan P. Moreira, Francine F. S. Salvador, Maria C. F. C. Felinto, Veronica C. Teixeira, Oscar M. L. Malta, Lucas C. V. Rodrigues, and Hermi F. Brito*



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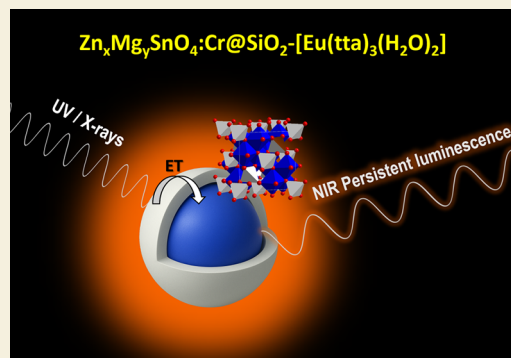
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ABSTRACT: This work presents the development of core–shell Zn_xMg_ySnO₄:Cr³⁺ (40 and 80% Mg) persistent luminescent (PersL) materials prepared by the ceramic method and decorated with the [Eu(tta)₃(H₂O)₂] complex via microwave-assisted silanization, with promising optical properties in the near-infrared (NIR) range. The crystal structure of the prepared materials showed overlapping Mg₂SnO₄ and Zn₂SnO₄ patterns, along with SnO₂, with increasing Mg content. FESEM and TEM microscopy revealed polycrystalline particles with well-defined surfaces and a silica shell in the 5–10 nm range. The optical properties were investigated by UV–vis and synchrotron spectroscopies (VUV, XANES-XEOL, and XRF). The persistent luminescent materials exhibit a noticeable increase in band gap energy with higher Mg content, intense, broadband NIR emission centered at 780 nm from the Cr³⁺ ion in a weak crystal-field environment, as well as longer PersL decay time with a higher Mg/Zn ratio. Core–shell materials decorated with the Eu³⁺-complex indicate energy transfer to the Cr³⁺ ion, resulting in NIR luminescence sensitization by UV and X-ray excitation. Therefore, we demonstrate an effective strategy to sensitize NIR emission by utilizing a highly efficient Eu³⁺ complex in core–shell persistent luminescent materials, which exhibit notable structural and optical properties and hold promise for optical imaging and photonic applications.

KEYWORDS: NIR persistent luminescence, core–shell, europium complex, chromium-doped stannates, luminescent sensitizer



1. INTRODUCTION

Recently, near-infrared (NIR) persistent luminescent materials have been widely investigated due to their expanding range of applications across photonics, optoelectronics, energy conversion and storage, and, notably, biological and biomedical applications. Such materials are promising for theranostics time-gated bioimaging, as persistent luminescent materials offer a significant advantage over luminescent materials that require continuous excitation during signal acquisition, thereby avoiding tissue autofluorescence and improving overall image quality.^{1–12}

Additionally, these luminescent materials may be structurally engineered from a chemical and spectroscopic perspective to yield efficient NIR light emitters in the biological windows, as light absorption and scattering by tissue are significantly reduced compared to other spectral regions in the visible range.^{13–15} Moreover, recent advances in Cherenkov Luminescence Imaging (CLI) further encourage the development of novel NIR persistent luminescent materials to exploit Cherenkov radiation generated by radioisotopes (e.g., ⁶⁸Ga and ¹⁸F), which are frequently used in nuclear medicine for cancer therapy and diagnosis.^{16–18}

Persistent luminescence (PersL) materials continue to emit light for an extended period (from minutes to hours) after the

excitation source (X-ray, UV–vis, electron beam, etc.) has been removed. Therefore, the excitation promotes the trapping of charge carriers (e[−] or h⁺) in defects, which undergo delayed recombination with the luminescent centers via tunneling and/or energy migration via the conduction or valence band, giving rise to PersL.^{19–21}

The NIR-PersL phenomenon has been reported for a series of materials, primarily using Cr³⁺ to achieve efficient light emission for up to several hours. Such materials are commonly based on the spinel ZnGa₂O₄ system, which has been extensively studied by incorporating different cations, such as Mg²⁺ and Al³⁺, to control defect formation and tune light emission from the Cr³⁺ activator by manipulating the crystal-field strength in these compounds.^{22–24}

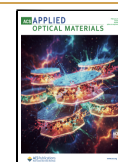
Moreover, recent advances in similar Cr³⁺ mixed-oxide materials have demonstrated promising features for the further development of non-Ga NIR persistent luminescent materials,

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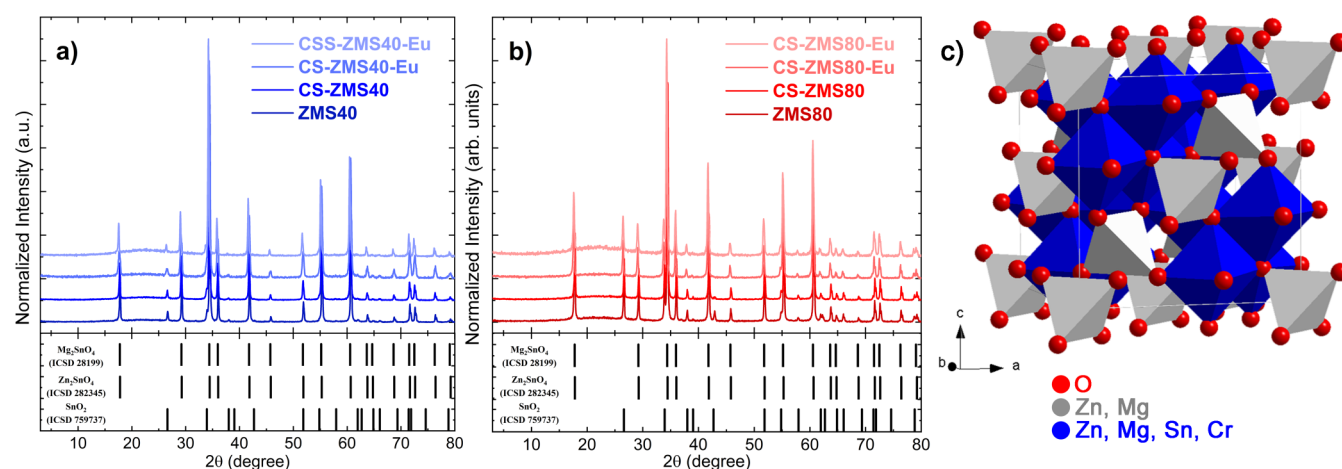


Figure 1. PXRD profiles of the (a) ZMS40 and (b) ZMS80 materials and their core–shell compounds, following the overlapping Zn_2SnO_4 (ICSD 282345) and Mg_2SnO_4 (ICSD 28199) standard patterns, along with SnO_2 (ICSD 759737). (c) Cubic inverse-spinel unit cell of ZMS materials.

exploring different prospects for tuning Cr^{3+} luminescence in more intricate systems, such as inverse-spinel structures, in which the role and rise of equivalent (antisite and exchange) defects are more pronounced compared to the more common nonequivalent (substitutional) defects, which directly affect the PersL properties.^{10,25,26}

Additionally, promising results from ligand-based sensitization of lanthanide-doped nanoparticles suggest different possible mechanisms for luminescence sensitization, including strong absorption and efficient intersystem crossing from $S_1 \rightarrow T_1$ and, subsequently, energy transfer to excited states of Ln^{3+} ions to promote energy migration and increased spectral overlap. This approach can also be extended to lanthanide complexes that serve as sensitizer shells, thereby improving the efficiency of persistent luminescent materials.^{27–29}

Thus, the present work proposes the investigation of structural and spectroscopic properties of mixed-oxide persistent luminescence materials based on cubic inverse-spinel NIR-emitting core–shell $\text{Zn}_x\text{Mg}_y\text{SnO}_4:\text{Cr}^{3+}$ decorated with the $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ hydrate complex, which was successfully prepared by microwave-assisted surface silanization methods. In the proposed system, unlike conventional Ga-based compounds, all cations (Zn^{2+} , Mg^{2+} , and Sn^{4+}) are expected to occupy octahedral sites in the crystal structure, affecting the crystal field around the Cr^{3+} activator as long-range ordering diminishes with increasing Mg/Zn ratio.^{30,31} The high efficiency of the Cr^{3+} luminescence sensitization under excitation at the tta ligand, at the Eu^{3+} ion, and at the Eu L_{III} edge demonstrates europium-to-chromium energy transfer in core–shell persistent luminescent materials.

2. RESULTS AND DISCUSSION

2.1. Crystal Structure

All investigated compounds exhibited diffraction peak profiles (Figure 1a,b) according to the overlapping crystalline phases of inverse-spinel cubic Zn_2SnO_4 and Mg_2SnO_4 (Figure 1c) with the space group $Fd\bar{3}m$ ($Z = 8$) (ICSD standards 282345 and 28199, respectively), alongside tetragonal SnO_2 P42/mmm ($Z = 2$) (ICSD 160667) byproduct formation. Indexed (hkl) for all experimental diffraction data obtained in this work is presented in the Supporting Information (Table S1), as the peak relative intensity ratio to the main (311) reflection of the M_2SnO_4 systems will be discussed next.

The PXRD profiles show the characteristic (311) standard reflection of M_2SnO_4 ($\text{M}: \text{Mg}^{2+}$ or Zn^{2+}) with the highest intensity for all materials (Figure 1). Thus, as (hkl)/(311) ratios were studied to understand crystal growth as Mg concentration increased, the diffraction data present mainly lower values of (hkl)/(311), together with a notable increase in (200)/(311) for the ZMS40 material compared to the ZMS80 material, showing a trend of preferential crystal growth in the $\langle 311 \rangle$ and $\langle 200 \rangle$ directions for ZMS40, in contrast to materials with higher Mg content. Additionally, distinct behavior is noted for SnO_2 indexed diffraction peaks (hkl values indicated by an asterisk), which become more prominent in Mg -rich compounds. Diffraction profiles show that even the usual high-intensity SnO_2 reflection from byproduct formation is very weak for the ZMS40 material, presenting a (100)*/(311) ratio of only 0.05, whereas other SnO_2 -derived reflections are not observed. However, as the Mg content increases, the characteristic SnO_2 pattern becomes visible, as the (100)*/(311) ratio rises to about 0.23 for the ZMS80 material. Several other peaks for SnO_2 are also observed, highlighting the contribution of the $d_{(211)*}$ SnO_2 overlapping with the $d_{(422)}$ of M_2SnO_4 planes and accounting for the increased diffraction intensity compared to ZMS40 in this region.

These structural characteristics are directly correlated to Zn^{2+} substitution by Mg^{2+} ions in the crystal lattice. The incorporation of Mg^{2+} ions into Zn^{2+} sites with no charge compensation is expected due to the same (2+) valence state, and the inverse spinel nature of the prepared materials implies that Mg substitution occurs at both O_h and T_d sites.³⁰ On the other hand, the ionic radius affinity on O_h sites is much higher than for T_d sites for the Zn^{2+} – Mg^{2+} ion pair (O_h : 74 and 72 pm; T_d : 60 and 49 pm for Zn^{2+} and Mg^{2+} , respectively), suggesting preferential substitution in O_h sites. Thus, increasing Mg^{2+} content may result in greater lattice distortions due to its substitution in T_d sites, accounting for the decrease in long-range ordering and potentially inducing the rise of Sn^{4+} vacancies as well as substitution in its O_h sites, given the Sn^{4+} ionic radius in O_h : 69 pm. It is noteworthy that these structural properties can lead to a high defect concentration, thereby improving the persistent luminescence efficiency.

Moreover, charge-compensation defects and further distortions in $\text{Zn}_x\text{Mg}_y\text{SnO}_4:\text{Cr}^{3+}$ materials may also occur due to Cr doping (Cr^{3+} in O_h : 62 pm). Additional defects in the

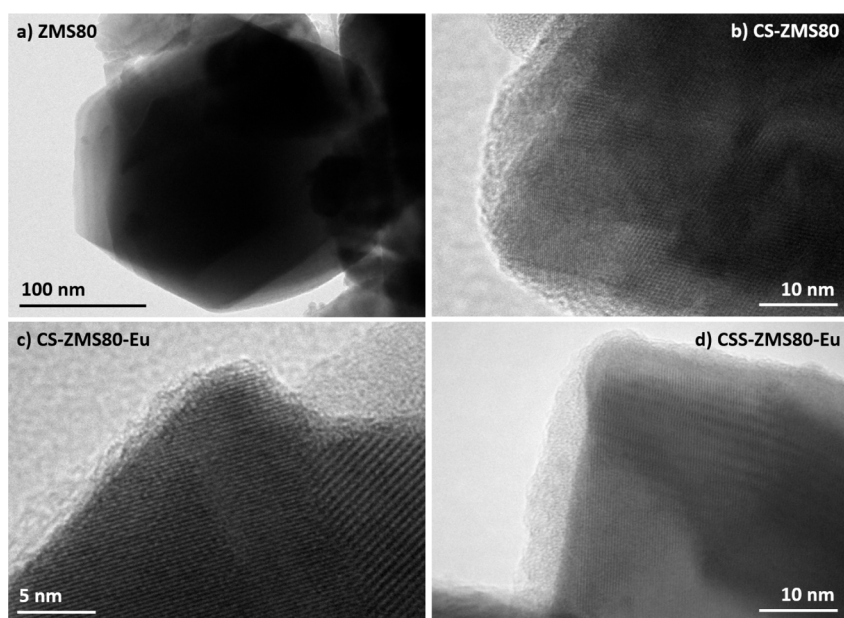


Figure 2. Bright-field TEM images of (a) ZMS80, (b) CS-ZMS80, (c) CS-ZMS80-Eu, and (d) CSS-ZMS80-Eu materials acquired under 200 kV.

crystal structure are due to the intrinsic Zn^{2+} and Mg^{2+} interstitials, together with equivalent octahedral antisite M^{2+} and Sn^{4+} defects (cations that may freely exchange places in the O_h sites), which are likely to play an essential role in the persistent luminescence of the prepared materials.

PXRD data recorded for $\text{Zn}_x\text{Mg}_y\text{SnO}_4:\text{Cr}^{3+}@\text{SiO}_2$ core-shell materials presented no significant alteration compared to their respective “core” precursors, other than the presence of a low-intensity broad band confirming the amorphous polymeric SiO_2 shell. Diffraction peaks from the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex (Figure S1a) were not observed due to the low concentration of the complex in these systems. Furthermore, Rietveld refinement (Figure S2 and Table S2) indicated the relative phase contents of M_2SnO_4 and SnO_2 , confirming that a higher Mg content is associated with higher byproduct formation. Crystallite size (Table S1) distribution was also calculated by the Scherrer method from the experimental diffraction profiles for all indexed reflections, as the full width at half-maximum (FWHM) parameter commonly varies widely with increasing 2θ values. The average crystallite size decreases slightly from 34.4 ± 5.2 nm in ZMS40 to 33.6 ± 3.6 nm in ZMS80, indicating that Mg substitution inhibits crystal growth.

In the FTIR spectra, as the inverse spinel structures have both O_h and T_d sites, it is possible to distinguish the vibrational modes of metal–oxygen bonds in each of these sites (Figure S3). These spectroscopic observations can be rationalized by the different coordination of each site, as in a T_d site with a lower coordination number (CN: 4), each M–O bond has a larger share of the electrostatic character and orbital overlap may be more pronounced compared to that of the O_h sites (CN: 6), hence the different frequency values for each site (of around 575 cm^{-1} and 660 cm^{-1} for the O_h and T_d , respectively) may be attributed to M–O bond stiffness. Lower-frequency modes at around 420 cm^{-1} , assigned to translational and bending modes, are also observed. Additionally, in core-shell materials, while the structural features of the crystal structure are preserved, it is possible to observe vibrational modes of Si–O–Si asymmetric stretching at around 1016 cm^{-1} . However, the vibrational modes that may

arise from the europium complex (Figure S1b) are not easy to distinguish due to the low concentration and overlap of the fingerprint region with the host stretching modes.

2.2. Morphology, Composition, and Size of Core–Shell Materials

The $\text{Zn}_x\text{Mg}_y\text{SnO}_4:\text{Cr}^{3+}$ materials exhibited micrometric-sized particle aggregates observed by FESEM imaging (Figure S4), in which submicron polycrystalline particles presenting well-defined surfaces and grain boundaries, characteristic of highly crystalline materials, are observed. Comparing the ZMS40 and ZMS80 materials, it is possible to directly observe the effect of increasing Mg content, which diminishes crystal growth and yields aggregates of smaller particles. EDS spectra (Figure S5) of ZMS80 and its core-shell compounds were recorded at high voltage to enhance X-ray fluorescence, revealing the chemical composition of the materials, with characteristic X-ray emission peaks from Sn, Mg, Zn, and O dominating the spectra. For core-shell materials, it is also possible to observe a signal of Si from the polymeric surface of the SiO_2 shell. In compounds decorated with the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex, the characteristic F line derived from the $-\text{CF}_3$ (tta) group has been observed.

TEM images (Figure 2) of core-shell materials demonstrated that the surface silanization method used in this work was effective at coating ZMS80 particles with an amorphous silica shell of only a few nanometers (5–10 nm) in thickness. A slight increase in shell thickness is noticed in double-shell compounds compared to single-shell materials, which is expected to increase the distance between the particle surface and the Eu^{3+} -complex embedded in the outer silica shell. Characteristic atomic planes are also visible in the TEM images at higher magnifications, corresponding to the crystalline host lattice. Similarly, the same amorphous silica shell behavior is expected for the ZMS40 materials, based on the other experimental analyses.

2.3. Spectroscopic Properties

The optical properties of the prepared materials were first investigated by Diffuse Reflectance Spectroscopy (DRS)

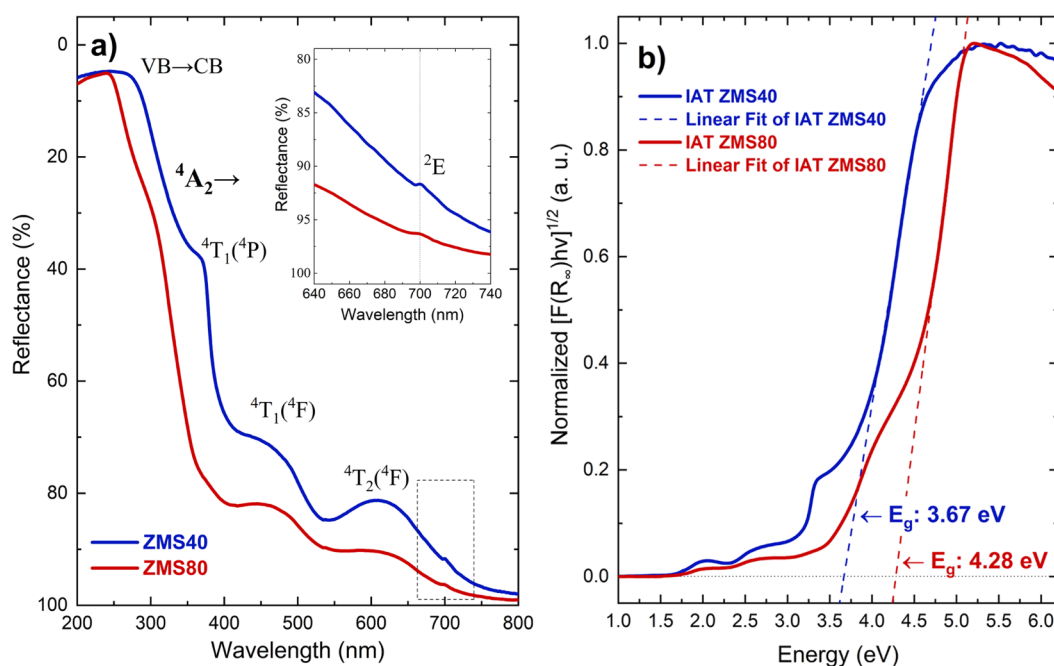


Figure 3. (a) DRS spectra of ZMS40 and ZMS80 materials presenting Cr^{3+} transitions and host matrix absorption. (b) Normalized single-constant Kubelka–Munk fitted profiles of indirect allowed transitions (IAT) from the DRS spectra.

(Figure 3a), which provided information on the positioning of the Cr^{3+} absorption bands: ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{P})$, ${}^4\text{T}_1({}^4\text{F})$, ${}^4\text{T}_2({}^4\text{F})$, and ${}^2\text{E}$ transitions around 350, 450, 610, and 700 nm, respectively. Besides, the host-matrix valence-to-conduction (VB→CB) absorption band is observed at 270 nm. A significant shift in host-matrix absorption is apparent, indicating the band gap energy (E_g) of the $\text{Zn}_2\text{SnO}_4 \rightarrow \text{Mg}_2\text{SnO}_4$ phase transition with increasing Mg concentration from 40 to 80%. To better understand the host matrix absorption energy, E_g values were calculated by the single-constant Kubelka–Munk function (eq 1), considering the experimentally measured reflectance of an infinitely thick (R_∞) specimen.^{32,33}

$$[F(R_\infty)hv]^{1/n} = [(K/S)hv]^{1/n} \quad (1)$$

where K , and S stand for the absorption and scattering parameters, which are represented by $(1 - R_\infty)^2$ and $2R_\infty$, respectively. Additionally, n is the transition constant (assuming values of 1/2 or 2 for direct and indirect allowed transitions, respectively), whereas hv represents the photon energy. Thus, E_g values are given by extrapolating a linear fit of the VB→CB absorption band using the single-constant Kubelka–Munk function versus the photon energy, such that $[F(R_\infty)hv]^{1/n} \rightarrow 0$.

As an indirect band gap is reported for M_2SnO_4 matrices, the calculated E_g values by this method are 3.67 and 4.28 eV for ZMS40 and ZMS80, respectively (Figure 3b). These values corroborate data previously stated in the literature,²⁵ as Zn_2SnO_4 has a lower E_g than the Mg_2SnO_4 host (around 3.7 and 4.6 eV, respectively), as increasing Mg content in ZMS materials accounts for the higher E_g .

Additionally, the DRS spectra of core–shell compounds of ZMS40 and ZMS80 (Figure S6) exhibit similar profiles compared with their core materials, which is expected considering a thin SiO_2 shell. It is also noted that while the DRS spectra of $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ exhibit a broad absorption band in the UV–vis region (Figure S7). However, the

influence of a slight spectral overlap with Cr^{3+} absorption bands is not observed in core–shell compounds as a result of the low Eu-complex concentration.

The luminescent properties of the materials were further investigated by photoluminescence spectroscopy, where it was observed that these materials exhibit the same aforementioned Cr^{3+} absorption bands (characteristic of substitution in a distorted O_h point group) assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{P})$, ${}^4\text{T}_1({}^4\text{F})$, and ${}^4\text{T}_2({}^4\text{F})$ transitions²⁵ in the excitation spectra monitored at 780 nm emission (Figure 4). In fact, the only noticeable change between the spectral profiles of the studied ZMS materials refers to the position and overlap of the host-matrix (VB→CB) absorption and the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{P})$ transition.

As seen in the ZMS40 excitation spectra, the maximum host matrix absorption occurs at around 270 nm, whereas E_g overlaps with the Cr^{3+} absorption band centered at around 330 nm. On the other hand, the ZMS80 material exhibits a higher VB→CB energy, and the host matrix and Cr^{3+} bands have less overlap. In core–shell materials, excitation spectra monitored under Cr^{3+} and Eu^{3+} ions show that while the spectral profiles of Cr^{3+} and host matrix absorption remain the same in functionalized materials, significant interactions with the europium complex embedded into the silica shell seen in the excitation spectra compared to the isolated $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex (Figure S8), when monitoring the characteristic Eu^{3+} emission at 612 nm. This behavior may arise from the interaction of Eu^{3+} ions with Si–OH groups present in the polymeric silica shell, which shift the broad absorption band assigned to the $\text{S}_0 \rightarrow \text{S}_n$ ligand (tta) transition to around 360 nm. The narrow ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transitions of the Eu^{3+} ion are also clearly observed on compounds decorated with the europium complex.

From the Cr^{3+} absorption bands ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{F})$ and ${}^4\text{T}_2({}^4\text{F})$ in the excitation spectra, the crystal field strength was calculated using eqs 2–4.²⁵

$$10\text{Dq} = E(4\text{T}_2) \quad (2)$$

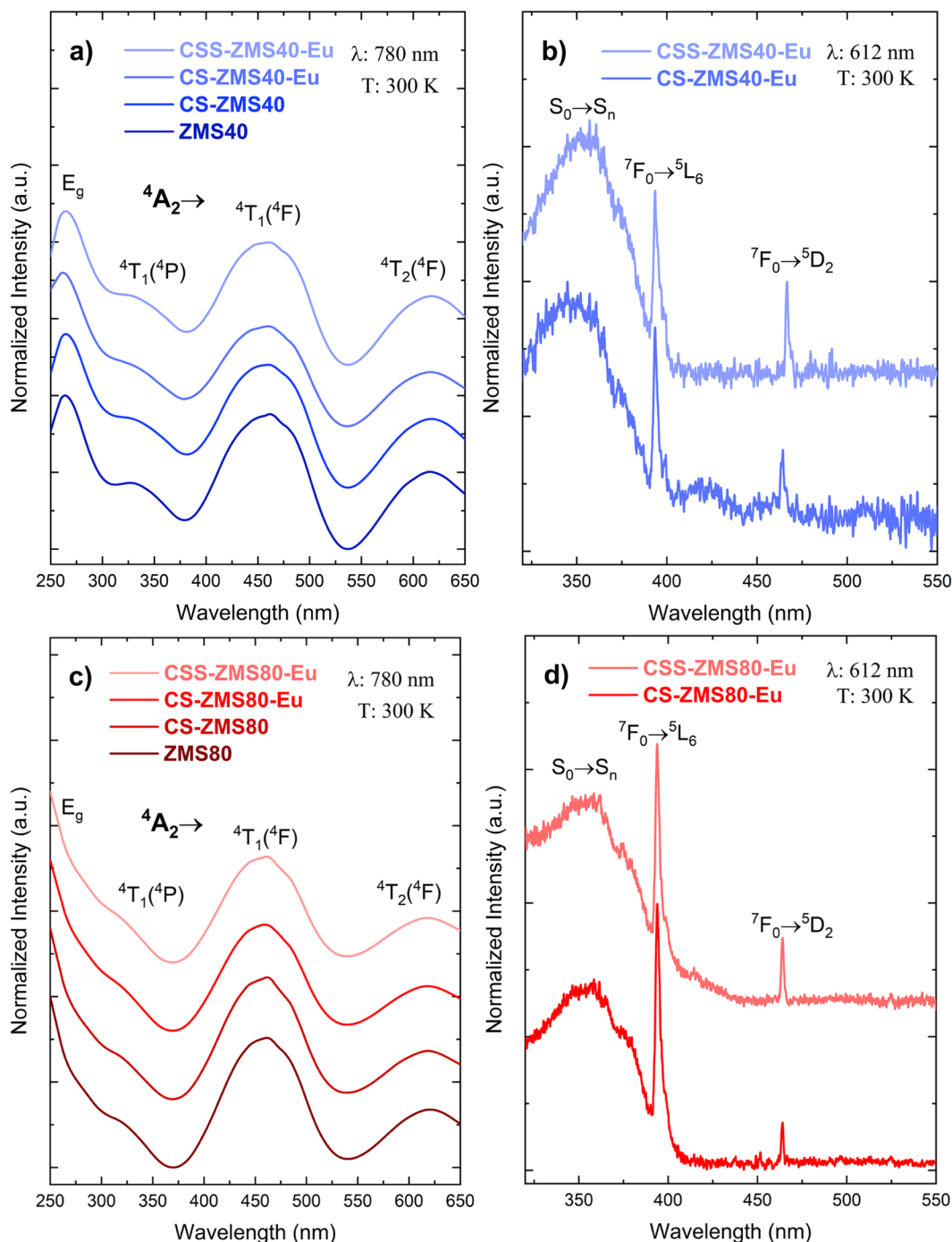


Figure 4. Excitation spectra of a, b) ZMS40, and (c, d) ZMS80 and their core–shell compounds, monitored at 780 nm Cr^{3+} emission and at 612 nm Eu^{3+} emission.

$$x = \frac{E(4T_1) - E(4T_2)}{Dq} \quad (3)$$

$$\frac{Dq}{B} = \frac{15(x - 8)}{x^2 - 10x} \quad (4)$$

In these equations, E denotes the energy related to the maximum of the $\text{Cr}^{3+}4T_1(4F)$ and $4T_2(4F)$ given by the absorption peaks in the excitation spectra. For both ZMS40 and ZMS80 materials, a value of 2.5 Dq/B was obtained, indicating a relatively weak crystal-field environment around the Cr^{3+} ions, as seen in the Tanabe-Sugano diagram for the d^3

configuration (Figure S9). This explains the NIR broadband emission observed in these materials.²⁵ The emission spectra were recorded under different excitation energies corresponding to the observed excitation bands being λ_{exc} : 612, 360, and 394 nm (Figure 5), assigned to the $[\text{Cr}^{3+}] 4A_2 \rightarrow 4T_2(4F)$, $[\text{tTa}] S_0 \rightarrow S_n$, and $[\text{Eu}^{3+}] 7F_0 \rightarrow 5L_6$ transitions, as well as λ_{exc} : 270 and 450 nm (Figure S10), referring to the host E_g and $[\text{Cr}^{3+}] 4A_2 \rightarrow 4T_1(4F)$ transitions, respectively. From these measurements, it is noted that all the studied materials present very similar emission spectral profiles, with a predominant and intense broad NIR emission band (at 780 nm) assigned to the spin-allowed $4T_2(t^2e^1)$ transition of Cr^{3+} ions in a weak crystal-

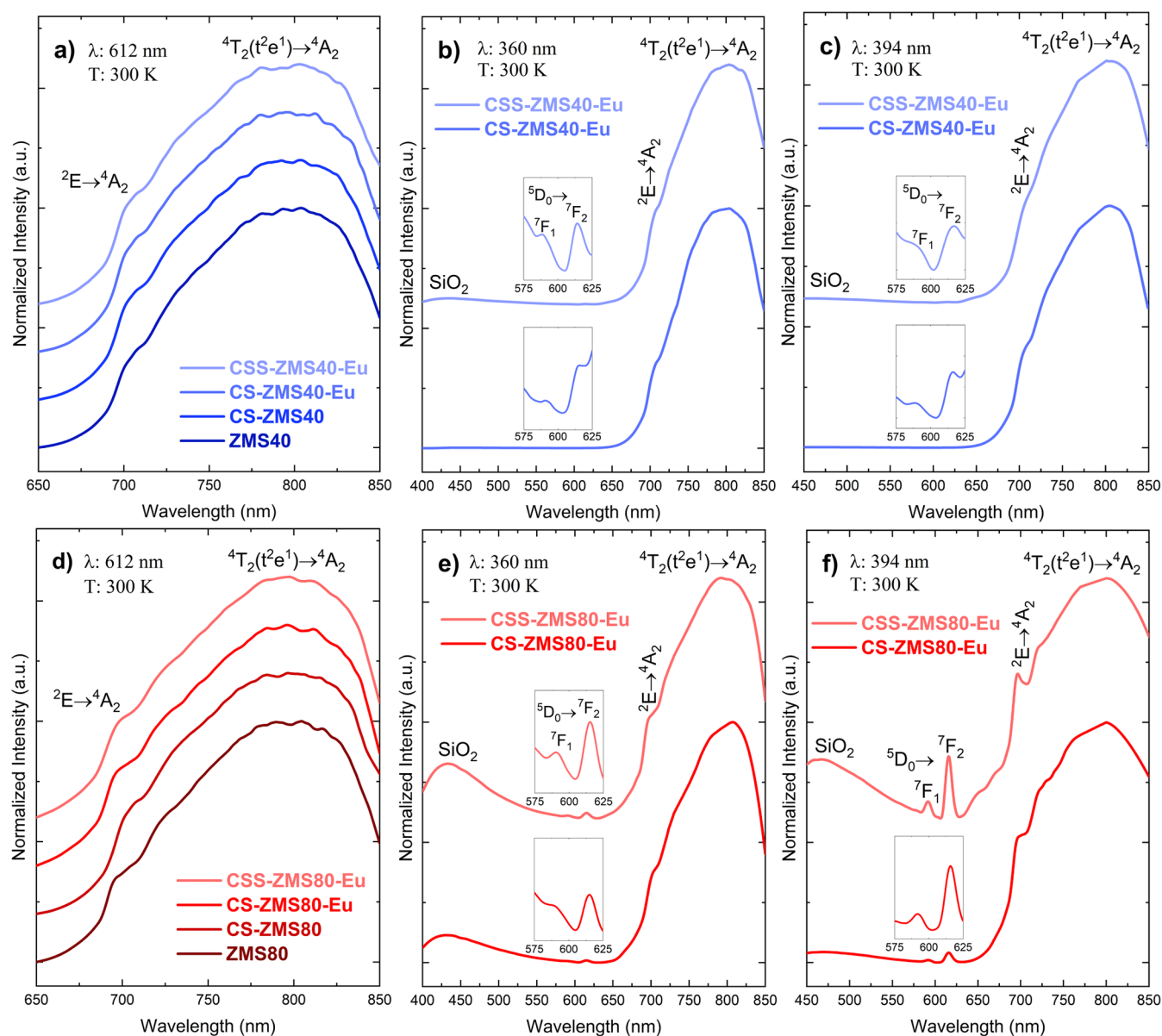


Figure 5. Emission spectra of (a–c) ZMS40, and (d–f) ZMS80 and their core–shell compounds, recorded under 612, 360, and 394 nm corresponding to Cr^{3+} , tta, and Eu^{3+} excitation, respectively.

field environment.^{24–26} In addition, faint narrow vibronic sidebands that usually dominate the emission spectra in Cr^{3+} -doped strong crystal-field hosts were also observed at 700 nm (R_1) and 720 nm (R_2) and assigned to the $^2E \rightarrow ^4A_2$ transition—a consistent optical behavior observed for all compounds.

Interestingly, in the core–shell materials decorated with the Eu^{3+} -complex, NIR Cr^{3+} luminescence remains predominant, suggesting a possible $\text{Eu}^{3+} \rightarrow \text{Cr}^{3+}$ or $T_1 \rightarrow \text{Cr}^{3+}$ energy transfer. While the addition of a SiO_2 single-shell does not significantly change emissions under host matrix excitation, CS-ZMS40-Eu and CS-ZMS80-Eu exhibit intense NIR luminescence even under Eu^{3+} (394 nm) and tta (360 nm) excitation, revealing the ability of the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex to act as a potential sensitizer^{34,35} for NIR luminescence in these materials. On the other hand, the emission profiles observed for double-shell materials decorated with the europium complex show increasing Eu^{3+} emission at

612 nm, arising from the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition, which is characteristic of the europium complex (as seen in Figure S11), alongside significant SiO_2 phosphorescence. The broadening of Eu^{3+} transitions seen in the core–shell materials further suggests interactions of the complex with the polymeric silica network, strongly differing from the emission profile for the isolated $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex (Figure S8). Nevertheless, even under direct excitation of the Eu^{3+} ion, double-shell materials exhibit predominant NIR Cr^{3+} emission, even though it may not be well-sensitized by traditional resonant energy transfer mechanisms due to the increasing distance between the tta ligand and/or Eu^{3+} to Cr^{3+} ion in these compounds.³⁶ (Figure S6) A small contribution of Cr^{3+} absorption may be expected under tta (360 nm) and Eu^{3+} (394 nm) excitation due to a slight spectral overlap with the $^4T_1(^4P)$ and $^4T_1(^4F)$ absorption bands, respectively.

The persistent luminescence decay time of ZMS materials monitored at NIR emission (Figure S12) was recorded for up

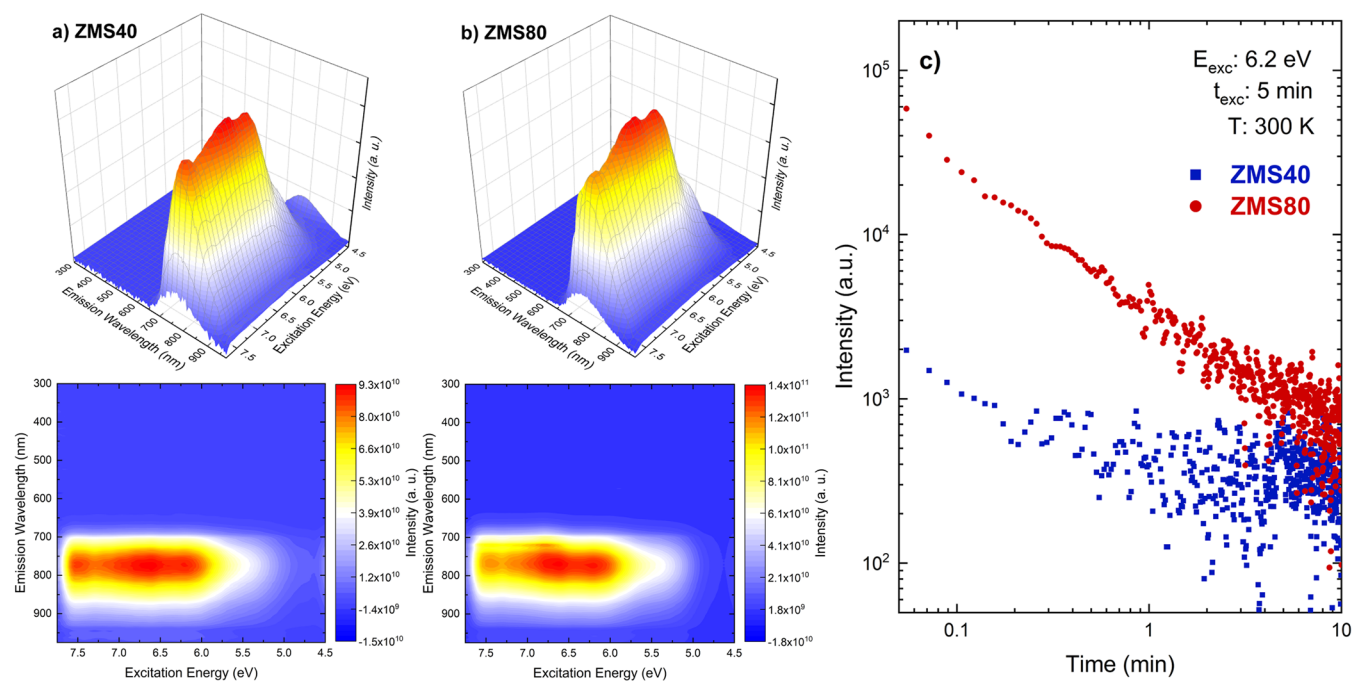


Figure 6. 3D VUV emission spectra of (a) ZMS40 and (b) ZMS80 materials. (c) Persistent luminescence decay time curves of ZMS40 and ZMS80, acquired after excitation above the band gap energy.

to 10 min after UV–vis excitation near the band gap energy, showing that a significant increase in PersL decay time occurs for materials with higher Mg content (80%). This is directly associated with the increasing E_g and trap depth related to the position of the bottom of the conduction band (which will be discussed in the next section), as well as with a higher concentration of crystallographic defects and SnO_2 phase impurities in these materials, as seen in the PXRD data. The PersL decay curves of core–shell materials are similar to those of their “core” counterparts, preserving the optical characteristics of these compounds (Figure S12). It is noteworthy that while Cr^{3+} NIR luminescence may be sensitized by energy transfer via tta ligand and/or Eu^{3+} to Cr^{3+} , direct excitation of the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex does not cause electrons to be photoionized into the CB; however, it can promote OSL through recombination of charge carriers in deeper traps.

3D Vacuum-UV luminescence spectra with excitation above the band gap energy show very similar behavior for ZMS40 (Figure 6a) and ZMS80 (Figure 6b) materials compared to the UV–vis results, as the intense NIR ${}^4\text{T}_2(\text{t}^2\text{e}^1) \rightarrow {}^4\text{A}_2$ spin-allowed Cr^{3+} transition dominates the emission spectra (Figure S13). Also, VUV-UV PersL (Figure 6c) follows the same trend observed under UV–vis excitation when the excitation energy is set above the band gap, corroborating that the photoionization of charge carriers into the conduction band (CB) is essential for achieving PersL in these materials.

Moreover, X-ray spectroscopy experiments were carried out to probe and correlate the local composition with NIR luminescence. For the studied materials, XANES and XEOL spectra reveal that the Cr^{3+} ion is the main radiative recombination optical channel following X-ray excitation. It is noted that the characteristic luminescent behavior of the Cr^{3+} -doped ZMS materials is preserved under both Cr K-edge (Figure S14) and Eu L-edge (Figure S15) excitations of core–shell materials, where maximum absorption was recorded at 5997 and 6984 eV, respectively, yielding the intense NIR

emission centered around 780 nm, which is different from the isolated Eu^{3+} -complex (Figure S16). The XANES spectra of the Eu_2O_3 , Cr_2O_3 , and Cr^0 standards were also obtained for comparison of the edge position energy. Furthermore, by combining the X-ray transmission, XEOL, and XRF mapping data (Figures 7 and S17–S23), it is possible to verify a homogeneous distribution of Cr^{3+} ions in the host lattice and of the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex in core–shell materials. 3D XEOL spectra also show that the NIR emission intensity is directly correlated with the absorption edges seen in the XANES of the Cr K-edge and the Eu L-edge in these materials.

The XANES-XEOL and XRF results (Figures 7 and S17–S23) of ZMS40 and ZMS80 materials and their core–shell systems are in excellent agreement with the data drawn from UV–vis and VUV luminescence spectroscopies (Figures 5 and 6), indicating that the Cr^{3+} ion is the preferred radiative recombination channel in these materials and may be sensitized via photoionization of core electrons of both Cr^{3+} ions doped into the host lattice, as well as by Eu^{3+} ions in the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex.

As previously mentioned, PersL in Cr^{3+} -doped ZMS materials is derived from the trapping of charge carriers in defect states near the bottom of the conduction band (Figure 8). Based on all spectroscopic data, possible energy-transfer mechanisms for the sensitization of NIR luminescence and PersL may be rationalized. It is well established that Cr^{3+} NIR emissions are the predominant pathway for electron–hole pair recombination, regardless of excitation in the host matrix, directly in the Cr^{3+} activator, or by utilizing the europium complex as a luminescence sensitizer as follows:

i) Potential energy transfer in europium complex – ligand strong absorption ($S_0 \rightarrow S_1$), intersystem crossing ($S_1 \rightarrow T_1$), efficient tta ligand-to- Eu^{3+} ion transfer, and subsequently high emission intensity ($4f\text{--}4f \text{ Eu}^{3+}$ ion); (ii) Eu^{3+} complex energy transfer to the Cr^{3+} ion – Eu^{3+} ion can sensitize Cr^{3+} NIR luminescence by distinct mechanisms of quasi-resonant energy

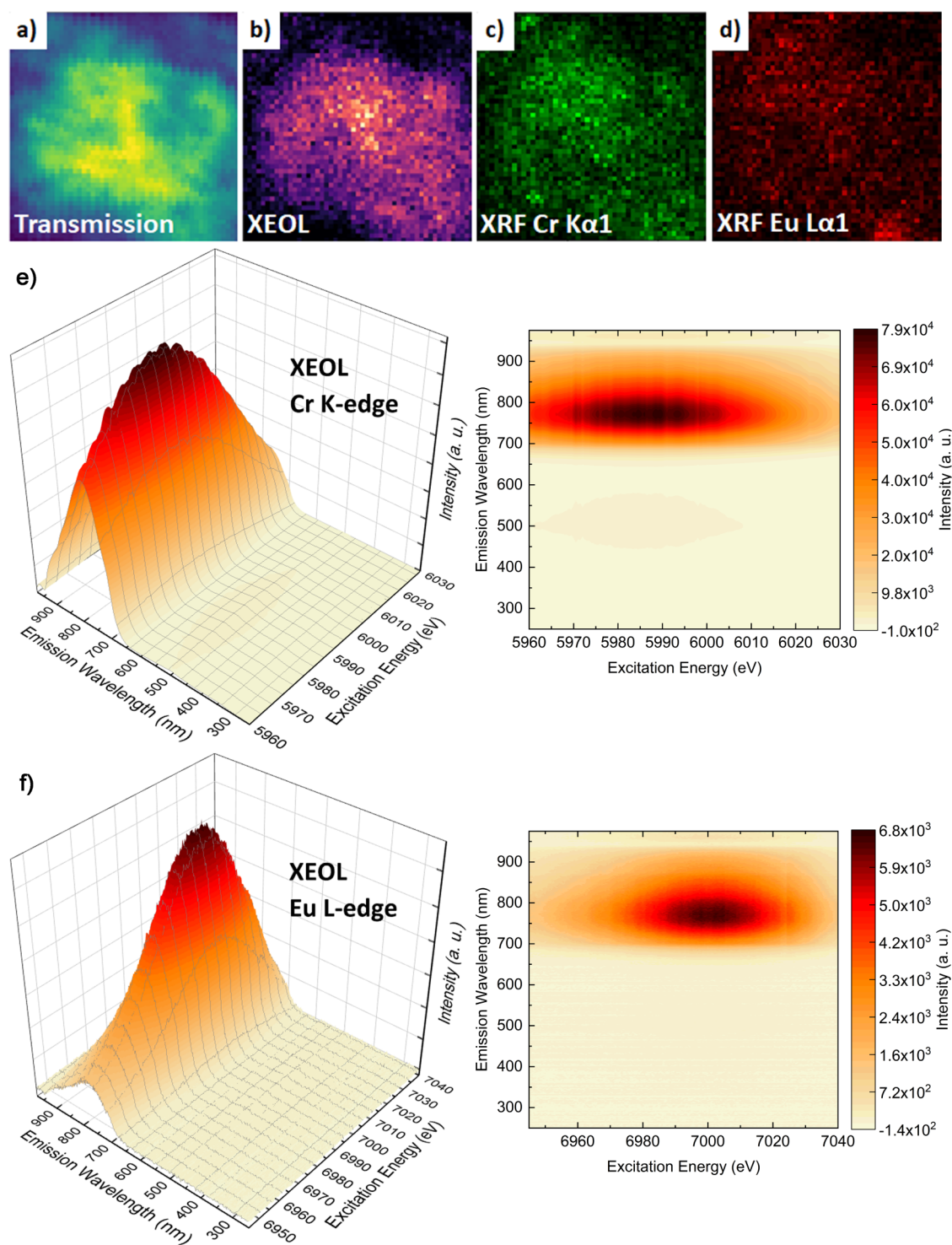


Figure 7. (a) Transmission, (b) XEOL, (c) XRF Cr K α 1, (d) Eu L α 1 distribution maps, (e) 3D XEOL spectra and surface contour under the Cr K-edge, and (f) Eu L-edge excitation of the CS-ZM80-Eu material.

transfer (mainly dependent on the distance of the donor–acceptor pair, less likely to occur in double-shell materials), optically stimulated luminescence (by detrapping electrons in deeper traps), or energy transfer due to spectral overlap of the $\text{Eu}^{3+5}\text{D}_0 \rightarrow {}^7\text{F}_2$ emission and the $\text{Cr}^{3+4}\text{A}_2 \rightarrow {}^4\text{T}_2({}^4\text{F})$ excitation bands. The latter mechanism also results in Eu^{3+} luminescence together with Cr^{3+} NIR luminescence, as best seen in CSS-ZMS80-Eu emission spectra; (iii) UV excitation on the Eu^{3+} ion – direct Eu^{3+} excitation (394 nm) results in similar

behavior of UV excitation on the TTA ligand; however, due to the forbidden nature of $4f-4f$ intraconfigurational transitions, the absorption coefficient of Eu^{3+} is very low. Hence, hence it is an inefficient way to sensitize NIR luminescence, as ligand excitation is preferred; (iv) X-ray excitation on the Eu^{3+} activator – similar to excitation under the Cr K-edge, X-ray excitation on the Eu L $_{III}$ -edge can populate the host-matrix CB by photoionization of core electrons of the Eu^{3+} ion. It is highlighted that, unlike UV–vis emission spectra, no Eu^{3+}

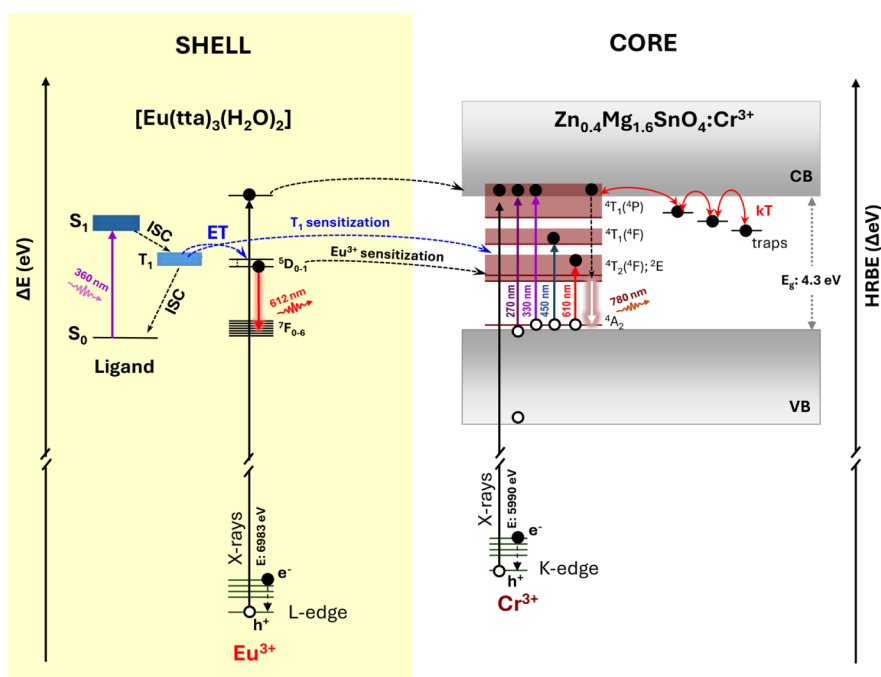


Figure 8. Schematic energy-level diagram for possible optical recombination pathways in Eu^{3+} complex-doped core-shell persistent luminescent materials. In the shell, S_0 and S_1 are the ligand ground and lowest singlet excited states, respectively. T_1 is the lowest triplet ligand level. ISC and ET are intersystem crossing and energy transfer, respectively. Eu^{3+} energy levels and the L edge are also represented. In the core, VB and CB are the host valence and conduction bands, respectively. Cr^{3+} energy levels and K edge are also given. Solid upward arrows represent excitation, while glowing downward arrows represent emission, and dashed downward arrows show nonradiative decay processes. Red curved arrows denote electron trapping and detrapping. Negative (e^-) and positive (h^+) charge carriers are represented by solid black and white circles, respectively. Dashed horizontal arrows show the $\text{tta}/\text{Eu}^{3+}$ sensitization to Cr^{3+} excited states.

emission is observed in the XEOL spectra of the Eu-doped core-shell materials under Eu L_{III} -edge excitation, suggesting that electrons populate the host CB, followed by recombination through the Cr^{3+} optical channel; (v) UV excitation on the Cr^{3+} activator – when the excitation energy is set to the $^4A_2 \rightarrow ^4T_1(^4P)$ transition, persistent luminescence may be achieved depending on the band gap energy. While lower E_g values favor the spectral overlap of this transition with the CB, trap states become shallower, significantly decreasing the PersL decay time. Lower energy transitions of the Cr^{3+} ion have insufficient photon energy to populate the ZMS host matrix CB; (vi) X-ray excitation on the Cr^{3+} activator – excitation under the Cr K-edge can populate the host matrix CB through photoionization, from where electrons may move freely to trap states, resulting in NIR PersL emission; and (vii) Excitation near the band gap – following near- E_g excitation, electrons may move freely through the CB into trap states, yielding the PersL phenomenon.

An energy-level diagram, including the optical recombination pathways in core-shell ZMS materials decorated with the europium complex, is shown in Figure 8.

3. CONCLUSION

NIR persistent luminescent emitting materials $\text{Zn}_x\text{Mg}_y\text{SnO}_4:\text{Cr}^{3+}$ were successfully prepared by a ceramic method. The Mg content was set to 40% and 80% to investigate the role of phase and defect formation in persistent luminescence. Materials with higher Mg concentrations show SnO_2 residue in the PXRD data, owing to the preferential substitution of Mg into Sn octahedral sites. Therefore, Mg substitution above a certain threshold may play a vital role in

breaking long-range ordering and increasing the concentration of localized defects in the inverse-spinel structure of ZMS materials, which improves the persistent luminescence properties. FITR spectroscopy studies also corroborate the PXRD results regarding the phase formation of a highly crystalline inverse-spinel structure. An increase in Mg content in these materials results in a decrease in particle grain size, as demonstrated by FESEM images. After surface silanization of ZMS80 via a microwave-assisted method, TEM images show an amorphous polymeric silica nanoshell with a thickness of 5–10 nm. As expected, the silica shell is found to grow in thickness in “double-shell” materials, owing to the additional surface silanization step in the synthesis procedure. Regarding their optical properties, the characteristic NIR persistent luminescence emission from Cr^{3+} ions doped into the $\text{Zn}_x\text{Mg}_y\text{SnO}_4$ matrix is observed in all the studied materials. Notably, in core-shell ZMS materials decorated with the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex, NIR emission is predominant even on the ligand and/or direct Eu^{3+} ion excitation, which is a potential indicator of the sensitization of Cr^{3+} luminescence by the europium complex. The optical recombination pathways were further investigated with synchrotron-based X-ray absorption techniques, probing both the Cr K-edge and Eu L_{III} -edge, indicating that the spin-allowed $^4T_2(t^2e^1) \rightarrow ^4A_2$ transition of the Cr^{3+} ion is the main radiative recombination pathway. The persistent luminescence decay time increases with Mg content due to a higher band gap energy and additional defect formation, which are expected to increase trap concentration and depth related to the conduction band. In this work, we present an effective approach for assembling NIR-emitting core-shell persistent luminescence materials, in which a Eu^{3+} -based complex may act as a luminescence

sensitizer, providing new insights into the design of hybrid rare-earth-based materials for optical imaging.

4. EXPERIMENTAL SECTION

All reagents used in the synthesis procedures were purchased from Sigma-Aldrich, Synth, and VETEC and used without further purification. The purity of the utilized materials is as follows: zinc oxide (ZnO, 99%), magnesium oxide (MgO, 97.0%), tin oxide (SnO₂, 99%), chromium oxide (Cr₂O₃, 98%), europium oxide (Eu₂O₃, 99.9%), 2-thenoyltrifluoroacetone (tta: C₈H₅F₃O₂S, 99%), 3-amino-propyltrimethoxysilane (APTMS: H₂N(CH₂)₃Si(OCH₃)₃, 97%), hydrochloric acid (HCl aq., 37%), ammonium hydroxide (NH₄OH aq., 30%), and ethanol (C₂H₅OH, 99.5%).

4.1. Synthesis of Zn_xMg_{1-x}SnO₄:Cr Materials

Mixed oxide Zn_xMg_{1-x}SnO₄:Cr 0.5 mol % materials, with 40 and 80% Mg content relative to Zn (ZMS40 and ZMS80, respectively), were prepared by the ceramic solid-state method. Starting from ZnO, MgO, SnO₂, and Cr₂O₃ precursors, the materials were ground together in stoichiometric amounts, followed by powder pressing under 4 t to obtain 8 mm (Ø) pellets that were further sintered in a tubular furnace at 1200 °C for 12 h. The resulting materials were pulverized and maintained under vacuum at room temperature.

4.2. Synthesis of the Eu³⁺(tta) Complex

To prepare the europium complex, a stoichiometric amount of Eu₂O₃ was treated with concentrated HCl to obtain EuCl₃·6H₂O. In a separate vessel, the corresponding stoichiometric amount of the 2-thenoyltrifluoroacetone ligand was dissolved in ethyl alcohol under stirring at 50 °C, and NH₄OH (aq) was added dropwise to the alcohol solution until it reached neutral pH. Afterward, the previously prepared EuCl₃·6H₂O (aq) was added to the alcohol solution, and further NH₄OH (aq) was added to reach a neutral pH. Subsequently, the solution was stirred for 2 h, first yielding a yellowish oil, which was then precipitated. The solid product was washed, filtered, and recrystallized in ethanol, yielding the [Eu(tta)₃(H₂O)₂] complex, which was further dried at 50 °C and kept under a vacuum at room temperature.

4.3. Microwave-Assisted Surface Silanization of Zn_xMg_{1-x}SnO₄:Cr Materials

The surface silanization of Zn_xMg_{1-x}SnO₄:Cr materials was carried out by first suspending the powder in APTMS under stirring at room temperature, where an ethanol solution of 4 mol % [Eu(tta)₃(H₂O)₂] was added dropwise to the suspension. Afterward, APTMS was hydrolyzed (20% v/v H₂O content), and the mixture was then heated in a domestic microwave oven at 1000 W for 1 min to further promote the polycondensation of hydrolyzed APTMS onto the surface of the oxide particles and then transferred to an ultrasonic water bath for 5 min to maintain the solid material in suspension. This process was repeated five times, and afterward, the resulting product was kept at room temperature for 24 h. Subsequently, the samples were dried at 150 °C, then washed with distilled water and ethanol to remove excess APTMS. The solid material was separated by centrifugation to obtain the core-shell Zn_xMg_{1-x}SnO₄:Cr materials decorated with the [Eu(tta)₃(H₂O)₂] complex embedded into a SiO₂ polymeric shell (CS-ZMS40-Eu and CS-ZMS80-Eu). Samples with a silica shell (CS-ZMS40 and CS-ZMS80) were also prepared by skipping the addition of the europium complex, which were utilized as seeds for the synthesis of double-shell materials (CSS-ZMS40-Eu and CSS-ZMS80-Eu), incorporating the [Eu(tta)₃(H₂O)₂] complex on the outer shell with an additional silanization step by using the same procedure.

4.4. Instrumental Analysis

Powder X-ray diffraction (PXRD) analyses were carried out on a Rigaku Miniflex II diffractometer within a 3–80° (2θ) range by K_αCu radiation using a 0.03 degree s⁻¹ step width under 30 kV voltage and 15 mA current. Infrared spectra were acquired on a Bruker ALPHA FT-IR spectrophotometer with a 4 cm⁻¹ point resolution and 64 scans within the 400–4000 cm⁻¹ range. Field Emission Scanning Electron

Microscopy (FESEM) images were acquired with a JEOL JSM-7401F microscope at 5 kV with a working distance (WD) of 8 mm using secondary electron (SE) imaging. TEM images were acquired in a JEOL JEM-2100 electron microscope with a LaB₆ filament at 200 kV. Optical properties were investigated by Diffuse Reflectance Spectroscopy (DRS), recorded on a Shimadzu UV-2600 spectrophotometer using an integrating sphere over the 200–1400 nm spectral range (0.1 nm step width), with BaSO₄ as a standard reference.

Furthermore, luminescence spectroscopy (excitation and emission) measurements were performed on a HORIBA Fluorolog-QM spectrofluorometer with a high-efficiency 75 W xenon lamp as the excitation source, using an axial setup of 22.5° with a blazed holographic grating of 1200 lines/mm, in which excitation and emission spectra were registered by a photomultiplier tube (PMT) with a 0.1 nm s⁻¹ step width. UV-vis PersL decay curves were recorded by a PMT following 5 min of excitation at room temperature, applying a 0.01 s step width. Vacuum-ultraviolet (VUV) spectroscopy experiments were acquired by synchrotron radiation in the Toroidal Grating Monochromator (TGM) beamline at the Brazilian Synchrotron Light Laboratory (LNLS). 3D spectra (excitation energy, emission wavelength, and emission intensity) were measured with a CCD detector (QE 65000, Ocean Optics) over the 300–975 nm range, under 4.5–7.75 eV excitation. In addition, VUV persistence luminescence decay time was recorded by a PMT (R928, Hamamatsu), in which the acquisition of background (dark) spectra was registered for 1 min and was followed by 5 min of excitation at 6.2 eV, where the emission signal was measured for 10 min after terminating excitation. All VUV experiments were performed at room temperature (300 K) and at a pressure below 10⁻⁷ mbar, using a 200-nm-thick quartz slide to avoid second-order harmonics from the beamline optics. In this setup, the acquired signal was collected with an optical fiber (SR UV-vis, 600 μm aperture, Ocean Optics) and further corrected using sodium salicylate (Synth) as a standard reference.

Finally, X-ray Fluorescence (XRF) and X-ray Excited Optical Luminescence (XANES-XEOL) experiments were performed at the Tender-to-Hard X-ray for Submicro Analysis (Taruma)³⁷ station of the Coherent X-ray Nanoprobe Beamline (Carnauba) of Sirius, the Brazilian fourth-generation synchrotron source. In the experimental setup, the powder samples were prepared on carbon tape and aligned with the X-ray beam (beam size: 0.2 × 0.5 μm at 8 keV) using the transmitted X-ray signal. The XRF signal was collected with two Hitachi Vortex ME-4 silicon-drift X-ray fluorescence detectors (SDDs). Simultaneous XANES-XEOL (recorded in fluorescence mode) experiments were performed for Cr K edge and Eu L edge, and the luminescence signal was collected by a XEOL Thorlabs LMM-15X-UVV reflective objective lens, coupled via an optical fiber to an Ocean Insights QE Pro-ABS spectrometer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaoam.5c00612>.

PXRD, FTIR, DRS, Excitation, Emission, and XANES-XEOL spectra of the [Eu(tta)₃(H₂O)₂] complex. Crystallite size, Rietveld refinement, lattice parameters, SEM, DRS, excitation, emission, PersL, VUV-UV, XRF, and XANES-XEOL spectra of ZMS40 and ZMS80 materials and their core-shell compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Hermi F. Brito – Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, São Paulo, São Paulo 05508-900, Brazil; orcid.org/0000-0002-9876-4441; Email: hefbrito@iq.usp.br

Authors

Leonardo H. C. Francisco – Chemistry and Environment Center, Nuclear and Energy Research Institute, National Nuclear Energy Commission, São Paulo, São Paulo 05508-000, Brazil; orcid.org/0000-0002-3929-4478

Renan P. Moreira – Chemistry and Environment Center, Nuclear and Energy Research Institute, National Nuclear Energy Commission, São Paulo, São Paulo 05508-000, Brazil

Francine F. S. Salvador – Chemistry and Environment Center, Nuclear and Energy Research Institute, National Nuclear Energy Commission, São Paulo, São Paulo 05508-000, Brazil

Maria C. F. C. Felinto – Chemistry and Environment Center, Nuclear and Energy Research Institute, National Nuclear Energy Commission, São Paulo, São Paulo 05508-000, Brazil

Veronica C. Teixeira – Brazilian Synchrotron Light Laboratory, Brazilian Center for Research in Energy and Materials, Campinas, São Paulo 13083-100, Brazil; orcid.org/0000-0003-2999-2800

Oscar M. L. Malta – Department of Fundamental Chemistry, Federal University of Pernambuco, Recife, Pernambuco 50740-560, Brazil

Lucas C. V. Rodrigues – Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, São Paulo, São Paulo 05508-900, Brazil; orcid.org/0000-0001-5176-5001

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsaoam.5c00612>

Notes

The authors declare no competing financial interest.

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