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Red-Emitting Coatings for Multifunctional UV/Red Emitting LEDs Applied in Plant Circadian Rhythm Control

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Multifunctional light-emitting diodes (LEDs) formed by coating deep-UV-emitting (<300 nm) LED chips with downshifting phosphors are of great interest for applications in indoor farms as both antibacterial (UV radiation) and photosynthetic agent (red light). Challenges include the fabrication of high-brightness downshifting converter films with controlled thickness excited in the deep-UV spectral region. We address it by optimizing the amount of Ba₂SiO₄:Eu(III) red-emitting phosphor dispersed in poly(methyl) methacrylate (PMMA), yielding luminescent films with tunable thickness. Taking advantage of the intra-4f⁶ transitions, the Eu(III) luminescence is used as local probe, pointing out the presence of 8 non-equivalent local sites for the lanthanides. PMMA enables the processing of flexible films and simultaneously acts as a selective filter to deep-UV radiation, controlling the amount of UV radiation for indoor farm applications. Moreover, after the dispersion in PMMA, the Eu(III)-based luminescence remains analogous to that of the isolated phosphor with an absolute emission quantum yield of 0.11 ± 0.01, confirming that Ba₂SiO₄:Eu(III)/PMMA films display desirable features to be used as coatings of deep-UV emitting LEDs toward multifunctional devices for indoor farm application.

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After just over two decades since the first commercialization,¹ white light-emitting diodes (WLEDs) became the main white-light source for electronic devices (backlighting for displays, digital cameras, security equipment, mobile phone, etc.) and lighting, namely indoor (offices, homes, shops) and outdoor (streets, traffic signals) applications,^{2,3} being estimated to achieve nearly 60% of penetration in the lighting market in 2020.^{4,5} Nonetheless, their commercial use is not limited to lighting since the current concern on improving life quality is catalyzing the solid-state lighting technology to come up with multifunctional light-emitting diodes (LEDs) that regulate human and plant circadian rhythm, as highlighted in Table I.⁶⁻¹³

In what concerns plant growth, the regulation of the circadian rhythm by light exposition from LEDs appears as an option to enhance the biomass production rate, especially in indoor farms, as an attractive alternative to supply the food world demand.¹⁴ In this case, the quality of the produced biomass depends on the light source characteristics, such as wavelength and intensity.¹⁵ Taking into account the impact of the emission wavelength on the plant circadian rhythm, red light is the most suitable one to regulate the photoreceptor phytochrome, that, in its turn, is directly correlated with photosynthesis, germination, flowering, as well as aerial architectural development.¹⁶ Extra UV radiation (~250 nm) would also make a worthwhile contribution to food production since low doses of deep-UV radiation (40 mJ.cm⁻²)¹⁷ are helpful to disinfection, water treatment, and purification by inactivating bacteria, spores, and viruses.¹⁷⁻¹⁹ It is worth pointing out it is essential to dose the amount of UV radiation, avoiding disturbs in the natural plant growth.²⁰

Currently, deep-UV radiation is not applied in indoor farms due to the low external quantum efficiency (EQE) of deep-UV emitting LEDs, making its use quite expensive. The disinfection process in indoor farms is made chemically (ethanol, bleach, quaternary ammonium chloride salt, hydrogen peroxide) or physically (soil solarization and steam sterilization) prior the cultivation and then, the sanitizing control is done only by keeping the environment clean, to which may lead to contaminations.²¹ In this regard, we note that if the indoor farm is exposed to controlled doses of deep-UV radiation, its environment could be free of microorganisms over the time of use. There-

fore, the combination of a deep-UV emitting LED (250 nm) and a deep-UV-to-red downshifting converter phosphor allows fabricating a multifunctional prototype with controlled UV radiation emission and simultaneous red light suitable for indoor farming, Figure 1.

To accomplish the multifunctional device fabrication, two main challenges need to be addressed: i) fabrication of compact and higher output power deep-UV LEDs and (ii) choice of efficient monochromatic downshifting phosphors easily processed as coatings with adjustable thickness. Regarding issue (i), some progress has been achieved in the last 10 years,²² despite low energy conversion efficiency (1%),²³ so that, this is still a challenge. In this study, we propose to address challenge (ii), in particular, by the utilization of the Ba₂SiO₄:Eu(III) phosphor, whose Ba₂SiO₄ matrix is well-known for LED application.^{24,25} The rationales behind its selection lie on the low phonon frequency of the matrix (~900 cm⁻¹), and high thermal stability (up to 1 000°C, with no changes in the structure or decom-

Figure 1. Scheme of the UV and red-emitting multifunctional LED architecture for a potential application in indoor farming.

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Table I. LED emission features for human and plant circadian rhythm control.

LED maximum emission wavelength	Human circadian rhythm control	Application for human healthy	Plant circadian rhythm control	Application for plant and food technology
Red (630 nm)	It induces melatonin production, human circadian system photopigment, important at bedtime ⁷	Rhinitis treatment, wound healing and anti-inflammatory ¹¹	It efficiently drives photosynthesis and photomorphogenesis ¹²	Algae growth, microalgae cultivation, plant tissue culture ¹¹
Green (550 nm)	It is the second most effective in suppressing melatonin, helpful to reset body clock ⁸	Correct hyperpigmentation, eliminate skin spots ⁸	Photosynthesis (less than blue and red colors) ¹²	Algae growth, bacteria and microalgae cultivation ¹¹
Blue (480 nm)	The most effective in suppressing melatonin. It activates melanopsin, responsible for alertness, attention, and emotional processes. Desirable during the day but not at night ⁹	Seasonal Affective Disorder (SAD), non-seasonal depression and bipolar disorder therapies ⁹	It improves growth (dry mass gain) and minimize excessively elongated stems ¹²	Algae growth, astaxanthin production ¹¹
UV (250 nm)	It is not well-understood, since just 2% of UV radiation survives after filtration through the eye lens ¹⁰	Disinfection, water treatment ¹¹	Carotenoids and polyamines induction, damage to photosynthetic apparatus ¹³	Disinfection, water treatment and purification ¹¹

position processes)^{26–29} when compared to Mn(IV)-doped fluorides or Eu(II)-doped matrixes, due to the larger melting point of Ba₂SiO₄. Moreover, the Ba₂SiO₄:Eu(III) phosphor displays higher efficiency under excitation at 250 nm, and the emission deviates to the visible, in particular, the radiative emission occurs at higher energies in the red spectral region (~610 nm) compared with that of the Mn(IV)-based systems, whose emission peaks ~700 nm, and partially lies within the NIR spectral region.^{30–32}

In order to dose the UV radiation, the phosphor was dispersed in poly(methyl methacrylate) (PMMA) since it absorbs deep-UV radiation (Figure S1), acting as photo-selective coating to UV radiation through film thickness control. Moreover, PMMA is environmentally friendly, lightweight, low-cost and has high mechanical and optical resistance to UV radiation exposure.³³ Therefore, inspired in the possibility of fabricating photo-selective films to be applied as coatings of multifunctional red-emitting LEDs, the Ba₂SiO₄:Eu(III) phosphor was prepared by sol-gel at distinct calcination times (2 h and 10 h) and dispersed in PMMA films with tunable thickness. Taking advantage of the Eu(III) photoluminescence properties, the intra-4f⁶ transitions were also used as a local probe to further investigate the role of Eu(III) doping on the optical features as function of the calcination time interval.

Experimental

Synthesis and processing.—The Eu(III) (4%)-doped silicate phosphors were synthesized from an adapted sol-gel route by using C₈H₂₀O₄Si₂ (TEOS, Fluka, 99.9%), CH₃COOH (Acetic acid, VETEC, 97%), Eu₂O₃ (Europium oxide, Aldrich, 99.99%), Gd₂O₃ (Gadolinium oxide, Aldrich, 99.99%), and Ba(CH₃COO)₂ (Barium acetate, VETEC, 99.9%) as starting reactants.³⁴ The synthesis was designed in order to keep the overall charge. Since Ba(II) and Eu(III) have distinct charges, the following equation was considered: $2n_{Ba} + 3n_{Eu} = 4$, where n_{Ba} and n_{Eu} are the mol number of Ba(II) and Eu(III), respectively, yielding Ba_{1.88}Eu_{0.08}SiO_{4.00}.

First, stoichiometric amounts of Ba(CH₃COO)₂ (2.6494 g) and Eu₂O₃ (0.0777 g) were dissolved in 10 mL of acetic acid at 70°C to obtain 2.0000 g of the final product. Then TEOS in isopropyl alcohol solution (8.83 mL, 0.55 mol/L) was added. The solution was kept under stirring for 4 h at 70°C until the gel formation. The gel was dried at 100°C for 2 h, yielding the xerogel precursor. Finally, the

xerogel was calcined in two different ways: (1) 450°C for 2 h with a heating ramp of 10°C/min and 1 100°C for 2 h with a heating ramp of 10°C/min and (2) 450°C for 2 h with a heating ramp of 10°C/min, 1 000°C for 2 h with a heating ramp of 10°C/min and 1 100°C for 10 h with a heating ramp of 10°C/min. After each annealing step, samples were brought back to room temperature, without reground.

To support the assignments of the luminescent features, Ba_{1.88}Gd_{0.08}SiO_{4.00} sample was synthesized in the same way of Ba_{1.88}Eu_{0.08}SiO_{4.00}, replacing Eu₂O₃ by Gd₂O₃. The samples will be hereafter designated as Ln-X, where Ln = Eu or Gd and X = 2 h and 10 h indicates the thermal treatment time at 1100°C.

PMMA-based film.—The PMMA matrix was produced mixing methyl methacrylate (10 g) with benzoyl peroxide (0.6 g) in a glass vial. The mixture was heated at 80–90°C for 30 min and then, placed in an oven at 40°C until the complete polymerization. The films containing the Ba_{1.88}Eu_{0.08}SiO_{4.00} phosphor were deposited by drop-casting. First, PMMA (0.6069 g) was dissolved in dichloromethane (10 mL), and 1.7 mL of this solution was deposited in a 2.2 × 2.2 cm² glass substrate (thickness of 0.1 cm) forming the undoped PMMA film (0.1042 g). This PMMA weight was considered as the reference of 100 wt%. Then, stoichiometric amounts of Eu-2h and PMMA/dichloromethane solution were mixed to produce films with tunable PMMA:Eu2h weight proportions, namely 1:M, where M = 0.25, 1.00, 2.00, 3.00 and 4.00 (20, 50, 66, 75 and 80 wt%, respectively). These suspensions were deposited in a 2.2 × 2.2 cm² glass substrate (thickness of 0.1 cm) and dried at 300 K for 24 h. Finally, the optimized deposition condition (1:2) was used to fabricate the film using the Eu-10h phosphor. The films will be hereafter designated as PMMA:MEu-X, where M = 0.25, 1, 2, 3 and 4 and X = 2 h or 10 h.

Structural and optical characterizations.—**X-ray diffraction (XRD).**—The diffractograms were acquired in a PANalytical Empyrean diffractometer at 300 K, from 9.0000° to 99.9000°, step size of 0.0260°, scan step time of 67.0650 s using CuK_α radiation (1.54060 Å). Crystalline structure and phase composition of Eu-2h and Eu-10h were refined according to the Rietveld method (Table S1, Supporting Information).

Optical microscopy.—The thickness of the films was measured through optical microscopy using an Olympus BX51 bright field mi-

Figure 2. (a) Powder XRD of the Eu(III)-based phosphors calcined for 2 h and 10 h compared to the JCPDS-26-1403 Ba_2SiO_4 pattern (the asterisks represent the peaks assigned to the BaSiO_3 spurious phase). (b) Ba_2SiO_4 unit cell representation based on the CIF file available on Inorganic Crystal Structure Database (ICSD); Ba1 and Ba2 are the notation for sites with CN 9 and 10, respectively.

croscope (10 × objective), in the reflection mode, equipped with a hyperspectral imaging system (CytoViva Inc., Auburn, AL). The system integrates an optical imaging CCD camera (QImaging Retiga 4000R), a visible/near-infrared hyperspectral camera (CytoViva), a motorized stage and a halogen light source (Fiber-lite, DC-950).

Absorption spectroscopy.—UV/visible absorption spectra were recorded using a Lambda 950 dual-beam spectrometer (Perkin-Elmer) from 200 nm to 800 nm, step size of 1 nm.

Photoluminescence spectroscopy.—The spectra were recorded at 14 and 300 K with a modular double-grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 Hamamatsu photomultiplier. The reciprocal Linear Dispersion of the diffraction gratings is $2.66 \text{ nm} \cdot \text{mm}^{-1}$, and for the high-resolution emission spectra (14 K), the excitation and emission slits were placed at 2×10^6 and $3 \times 10^4 \text{ nm}$, respectively, which results in a spectral resolution of 0.079 nm. Lifetime measurements for the Eu(III)-doped samples were carried out at 14 K by using a pulsed Xe arc lamp (6 mJ/pulse) coupled to a Kratos GM-252 monochromator and a Spex 1934 C phosphorimeter. The widths of the slits of the excitation and emission monochromator were placed at 2×10^6 and $1 \times 10^5 \text{ nm}$, respectively, resulting in a spectral resolution of 0.27 nm. The emission color coordinates (x,y) were calculated accordingly to the 1931 Commission Internationale de l'Éclairage (CIE) chromaticity standards defined for the 2° observer.³⁵

Luminous flux.—The luminous flux was measured using an integrating sphere ISP 150L-131 from Instrument Systems with internal diameter of 150 mm (BaSO_4 coating) and coupled to an array spectrometer MAS 40 from Instrument Systems. A lamp emitting at 254 nm and optical power of $3.2 \pm 0.1 \times 10^{-3} \text{ W}$ was used as excitation source. The accuracy is 5%, accordingly to the manufacturer.

Absolute emission quantum yield.—The absolute emission quantum yields were measured at 300 K using a system (Quantaaurus-QY Plus C13534, Hamamatsu) with a 150 W xenon lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as the sample chamber, and a multichannel analyzer for signal detection. The accuracy is 10%, accordingly to the manufacturer.

Results and Discussion

Eu(III)-doped Ba_2SiO_4 phosphor.—The local structure was characterized by powder XRD measurements, Figure 2. For the samples calcined during 2 h (Eu-2h), the diffraction pattern is indexed to the or-

thorhombic Ba_2SiO_4 phase (JCPDS 26–1403, number 62, P_{nma} space group) as the major phase (82.9 wt%) and two other secondary ones identified as $\beta\text{-BaSiO}_3$ (JCPDS 26–1402, number 19, $P2_12_12_1$ space group) (16.8 wt%) and SiO_2 (quartz, JCPDS 46–1045, number 152, $P3_121$ space group) (0.3 wt%). No diffraction peaks indexed to the Eu_2O_3 phase were observed. At longer calcination time, the diffractogram of Eu-10h only reveals the orthorhombic Ba_2SiO_4 phase (JCPDS 26–1403), pointing out that the increase of the calcination time is crucial to decrease the quantity of spurious phases.

According to the phase diagram of the BaO-SiO_2 binary mixture,³⁶ the suitable molar proportion of Si in relation to Ba to form Ba_2SiO_4 without spurious phases is 33.3 %, under heating of 1 100°C. However, due to the doping with the activator ion, to compensate the charge difference between Eu(III) and Ba(II), the Si molar proportion is 35 %, enabling the formation of low amounts of BaSiO_3 . Because of this non-stoichiometry, it will be always possible to find BaSiO_3 in the phosphor composition regardless of the calcination condition.

The structural parameters (Table S1) are in accordance with those previously found in the literature for Ba_2SiO_4 ³⁷ and BaSiO_3 ³⁸ matrices. The Si(IV) ions are in tetrahedral coordination sites with oxygen ions in the tetrahedra vertices and ionic radius of 40 pm. The Ba(II) occupies two crystallographic positions with analogous occurrence in the Ba_2SiO_4 structure, Figure 2b. One position with coordination number CN = 10 and ionic radius of 166 pm forms a chain along the c-axis and other structurally distorted with CN = 9 and ionic radius of 161 pm establishes chains along the b-axis.

In turn, in the BaSiO_3 lattice, the Ba(II) occupies a single site with CN = 8 and ionic radius of 142 pm. Eu(III) has ionic radius of 131 pm (CN = 10), 126 pm (CN = 9), and 107 pm (CN = 8) and even that the rare-earth ionic radius is smaller than that of Ba(II), the substitution is favored since the ionic radii difference between both is lower than 30 %.³⁹ Due to the large difference between the ionic radii of Eu(III) and Si(IV), the replacement of Si(IV) by Eu(III) is unlikely to take place.

Due to the charge compensation mechanism considered in the Eu(III)-based phosphor synthesis, structural defects arise in the lattice since two Eu(II) replace three Ba(II), as previously noticed.²⁶ As consequence, a doubled negative Ba-related vacancy (V_{Ba}'') defect and two positive defects arising from Eu(III) occupying Ba(II) sites ($\text{Eu}_{\text{Ba}}^\bullet$) are generated, as represented in Eq. 1.

The V_{Ba}'' leads to a local expansion in its environment due to the oxygen negative charge repulsion, and in the $\text{Eu}_{\text{Ba}}^\bullet$ sites, there is a local compression due to the positive charge increase. This compression is also favored because Eu(III) ionic radius is smaller than that of Ba(II). Furthermore, due to the non-stoichiometry of the synthesis, distorted Eu(III) or Ba(II) sites (local sites named as $\text{Eu}_{\text{D1-D3}}$) are formed, leading to the appearance of Eu(III) sites different from that typically expected by the replacement of Ba(II) in the Ba_2SiO_4 and BaSiO_3 structures (local sites named as Eu_{1-3}).⁴⁰ In this context, considering the XRD data, we expect that Eu(III) occupies six non-equivalent sites (Eu_{1-3} and $\text{Eu}_{\text{D1-D3}}$) in Eu-2h and four non-equivalent sites (Eu_{1-2} and $\text{Eu}_{\text{D1-D2}}$) in Eu-10h.

Under UV irradiation, all the samples display an intense red emission color, as illustrated in Figure 3a. To infer the preferential excitation optical paths, excitation spectra were monitored at 610.4 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition), Figure 3b, exhibiting a broad excitation band in the deep-UV region assigned to the $\text{Eu}^{3+} \rightarrow \text{O}^{2-}$ charge transfer band (CTB)⁴¹ and narrow lines attributed to the Laporte's forbidden Eu(III) f - f transitions. The main excitation path at $\sim 250 \text{ nm}$ is fundamental to use these materials as coatings of deep-UV emitting LEDs. We notice that Mn(IV) or Eu(II)-based red-emitting phosphors typically feature weak absorption in this spectral region.³⁰⁻³²

The phosphor emission spectra under deep-UV excitation reveal a series of Eu(III) transitions from the $^5\text{D}_0$ excited level to the $^7\text{F}_j$ ($j = 0-4$) levels, Figure 3c. The high number of components for each transition, in particular, the presence of more than one com-

Figure 3. (a) Photo of the Eu-10 h sample under UV radiation (255 nm). (b) Absolute emission quantum yield (q) of the Eu(III)-based phosphors compared to the excitation spectra. (c) Emission spectra (300 K) excited at 255 nm of the Eu(III)-based phosphors. (d) CIE chromaticity diagram of Eu-2h and Eu-10h.

ponent for the non-degenerated $^5D_0 \rightarrow ^7F_0$ transition, readily indicates that Eu(III) is inserted in more than one non-equivalent local coordination site, as detailed below. The red emission was quantified by the calculation of CIE color coordinates, Figure 3d. For Eu-2h/Eu-10h, the (x,y) color coordinates are within the red spectral region, (0.659;0.324)/(0.686;0.315) and (0.569;0.316)/(0.622;0.310) under excitation at 255 nm and 393 nm, respectively.

To further discuss the Eu(III)-local environments as function of the heat-treatment, low-temperature high-resolution emission spectra under 255 nm and 393 nm excitation were collected in the $^5D_0 \rightarrow ^7F_0$ transition range, Figure 4a. The $^5D_0 \rightarrow ^7F_0$ transition exhibits at least five and eight components under excitation at 255 and 393 nm respectively, suggesting that Eu(III) is, at least, inserted in 8 non-equivalent

local sites without inversion center. In accordance, we note that the $^5D_0 \rightarrow ^7F_1$ transition, that occurs by a magnetic dipole mechanism and exhibits up to three components per each Eu(III) non-equivalent site, shows at least eight and eleven well-defined components at 255 and 393 nm excitation, respectively, Figure 4b. Likewise, the $^5D_0 \rightarrow ^7F_2$ transition has a maximum of five components per each Eu(III) non-equivalent site. In both Eu-2h and Eu-10h, at least ten components are noticed in the emission spectra, Figure 4c, under both 255 and 393 nm excitation.

Focusing our attention into the eight components found for the $^5D_0 \rightarrow ^7F_0$ transition, the components at 580.1 nm and 508.6 nm are tentatively assigned to the Eu₁ and Eu₂ local sites, respectively, Table II and Figure 4d, based on the changes in their intensities with

Table II. Energy (cm^{-1}) of the components for the $^5D_0 \rightarrow ^7F_0$ transitions and 5D_0 lifetime (τ) values of each component excited at 393 nm (14 K) for Eu-2h, Eu-10h and PMMA:Eu-10h.

Notation for Eu ions	Wavelength/ ± 0.08 nm	Energy/ ± 3 cm^{-1}	τ/ms		
			Eu-2h	Eu-10h	PMMA:Eu-10h
Eu ₁	578.22	17 295	1.60 ± 0.03	1.73 ± 0.03	0.903 ± 0.015
Eu ₂	579.56	17 256	1.19 ± 0.04	1.50 ± 0.02	0.846 ± 0.014
Eu ₃	580.12	17 238	1.36 ± 0.03	0.79 ± 0.02	0.495 ± 0.032
Eu _{D1}	580.62	17 223	1.22 ± 0.03	1.13 ± 0.01	-
Eu _{D2}	581.54	17 196	0.60 ± 0.02	0.66 ± 0.03	-
Eu _{D3}	582.35	17 173	0.28 ± 0.02	0.11 ± 0.02	0.016 ± 0.001
Eu _{A1}	572.64	17 464	0.77 ± 0.02	0.68 ± 0.01	0.628 ± 0.009
Eu _{A2}	573.13	17 448	0.69 ± 0.01	-	-

Figure 4. High-resolution emission spectra (14 K) excited at different excitation wavelength for Eu(III)-based phosphors and the PMMA:2Eu-10h film in the (a) $^5D_0 \rightarrow ^7F_0$, (b) $^5D_0 \rightarrow ^7F_1$, and (c) $^5D_0 \rightarrow ^7F_2$ transition region. (d) Representation of Eu(III) local sites (Eu₁₋₃, Eu_{D1-3} and Eu_{A1,2}) in the Eu(III)-doped phosphors.

the increase of the calcination time. The XRD data establishes six and four non-equivalent $^5D_0 \rightarrow ^7F_0$ components for Eu-2h and Eu-10h, respectively. However, both samples show the same number of $^5D_0 \rightarrow ^7F_0$ transitions with the same energy, whose relative intensity variation indicates that there are some BaSiO₃ traces in the sample composition, even for Eu-10h, evidencing the greater sensitivity limit of the spectroscopic technique in detriment of XRD. When the calcination time increases from 2 h to 10 h, the $^5D_0 \rightarrow ^7F_0$ components at 580.1 nm (Eu₃), 580.6 nm (Eu_{D1}), 581.5 nm (Eu_{D2}) and 582.3 nm (Eu_{D3}) have their relative intensity decreased compared to the other components, Figure 4a. Besides that, the relative intensity of the components at 578.2 nm (Eu₁) and 579.5 nm (Eu₂) increases. These observations suggest that the components at 580.1 nm (Eu₃), 580.6 nm (Eu_{D1}), 581.5 nm (Eu_{D2}) and 582.3 nm (Eu_{D3}) correspond to the BaSiO₃ spurious phase or defect sites, and for the other 2 components, they arise from the Ba₂SiO₄ phase since the fraction of the BaSiO₃ phase decreases as the calcination time increases, according to the XRD data.

In order to further assign the remaining $^5D_0 \rightarrow ^7F_0$ transition components, site-selective excitation spectra were monitored around each $^5D_0 \rightarrow ^7F_0$ transition, around 578.2 nm (Eu₁), 579.6 nm (Eu₂), 580.1 nm (Eu₃), 580.6 nm (Eu_{D1}), 581.5 nm (Eu_{D2}), and 582.3 nm (Eu_{D3}), Figure 5. The excitation spectra are similar, indicating analogous 5D_0 population paths being tentatively ascribed to Eu(III) located within the Ba₂SiO₄ or BaSiO₃ matrices. For these components, it is also possible to distinguish two different bands in the excitation spectra at 255 nm and 275 nm assigned to the CTB arising from Eu replacing Ba sites in the Ba₂SiO₄ or BaSiO₃ matrices (CTB1).

It is feasible to assign the CTB1 band (~275 nm) to the Eu_{D1-3} sites since the CN of these sites is lower than the Eu₁₋₃ ones⁴² and it is well-known that a decrease in CN leads to a decrease of the CTB energy.⁴³ This premise confirms that the sites at 578.2 nm (Eu₁), 579.5 nm (Eu₂) and 580.1 nm (Eu₃) come from the Ba₂SiO₄ or BaSiO₃ structures since we cannot notice them in the emission spectra under 255 nm excitation

for Eu-2h, Figure 4a. However, they are noticed for Eu-10h, where the concentration of Eu₁₋₃ local sites is larger than that in Eu-2h.

The excitation spectra monitored around 572.6 nm (Eu_{A1}) and 573.1 nm (Eu_{A2}), Figure 5, reveals an additional broadband peaking at ~330 nm (hereafter designated as CTB2), similar to that found in the excitation spectra of Eu³⁺-O²⁻ associates,⁴⁴ suggesting that in the Eu_{A1} and Eu_{A2} sites, Eu(III) is bonded to oxygen ions that do not belong to the silicate network. The formation of the Eu³⁺-O²⁻ associates is usually related to a charge compensation mechanism, but they may also be formed when the matrix is rather loosely packed or contain chains formed by M-O polyhedral with unfilled spaces that may locate oxygen ions in their interstices.⁴⁵ In the present case, whereas the Ba₂SiO₄ and BaSiO₃ matrices contain Ba-O polyhedral chains with unfilled spaces, it is feasible to assume the presence of Eu³⁺-O²⁻ associates (Eu_{A1} and Eu_{A2}). Under excitation at 330 nm (CTB2), the $^5D_0 \rightarrow ^7F_0$ transition at 572.6 nm (Eu_{A1}) dominates the emission profile, characteristic of the Eu³⁺-O²⁻ associate emission, Figure 6. Moreover, two $^5D_0 \rightarrow ^7F_2$ components (621.8 nm and 623.9 nm) are only noticed under CTB2 excitation.

To further discuss the nature of the bands at 255 nm, 275 nm and 330 nm in the excitation spectra (Figure 5), the diffuse reflectance spectra of the isostructural Gd-2h sample were measured. The energy of the Gd(III) excited levels is much higher than the typical energy of defects-related bands, inhibiting any energy transfer process, and therefore the spectrum of Gd-2h is free from any CTB contribution.⁴⁶

Like the excitation spectra in Figure 5, the diffuse reflectance spectrum of Eu-2h, Figure 7a, shows three broad bands and a series of low-intensity lines assigned to the Eu(III) *f-f* transitions. The high energy band (~217 nm) is attributed to transitions from the valence band to the conduction band of the matrix.²⁶ Regarding the two bands at ~250 nm and ~320 nm, the spectrum of the Eu-2h was compared with that of the analogous Gd-2h. Interestingly, the arithmetical difference between them, Figure 7b, reveals two bands at ~250 nm (CTB1) and ~320 nm (CTB2) confirming that they arise from CTB processes between the matrix and Eu(III), supporting the assignments in the excitation spectra, Figure 5. The band at 250 nm (CTB1) displays a component at 275 nm, also discerned in the excitation spectra, Figure 5.

To further examine the Eu(III) local sites, selective emission decay curves (Figures S2 and S3) were monitored around each of the eight $^5D_0 \rightarrow ^7F_0$ components at 14 K since, at 300 K, it is not possible to distinguish all the eight $^5D_0 \rightarrow ^7F_0$ components. All the decay curves reveal a single exponential behavior in good agreement with experimental site-selective conditions. From the data best fit, the 5D_0 lifetime (τ) values were calculated for each Eu(III) local environment, Table II. The 5D_0 lifetime values for Eu₁₋₃ local sites are similar to those found in other silicate-based matrices,^{47,48} and for the Eu_{A1} and Eu_{A2}, they are faster, in accordance with the Eu³⁺-O²⁻ associate assignment.⁴⁴

The distinct values found for the 5D_0 lifetime at 14 K (Eu-2h) compared to those ones at 300 K give further evidence for the proposed assignment of the eight Eu(III) local sites. However, it was only possible to estimate the 5D_0 lifetime value (300 K) for the component at 578.2 nm (Eu₁) through a biexponential fit, Figure S4, due to the superposition of the Eu₁ and Eu₂ components at 300 K; therefore, the values obtained through the biexponential fit may be associated to the Eu₁ and Eu₂ local sites. The 5D_0 lifetime values at 300 K of the Eu₁ and Eu₂ local sites are to be found as 1.55 ± 0.04 ms and 0.0568 ± 0.005 ms and they are shorter than the values found at 14 K, Table II. The Eu₂ local site displays shorter 5D_0 lifetime than Eu₁, indicating that the Eu₂ site is more influenced by thermally activated non-radiative pathways. Attending to the fact that the experimental transition probability may be expressed as $\tau^{-1} = \tau_{nr}^{-1} + \tau_r^{-1}$, where τ_{nr} and τ_r represent the non-radiative and radiative lifetimes, respectively, and that at 14 K $\tau^{-1} \sim \tau_r^{-1}$, the increase in τ as the temperature decreases suggests the presence of competing thermally activated non-radiative mechanisms.

Eu(III) at defect-related local sites are characterized by larger τ_{nr} due to semi-filled coordination sphere.⁴⁹⁻⁵¹ Thus, a decrease in the lifetime value is expected. In this way, among the series of 5D_0 lifetimes measured for the Eu(III) local sites, we can correlate the shortest

Figure 5. Excitation spectra (14 K) of the (a) Eu-2h and (b) Eu-10h samples monitored at distinct wavelengths around the $^5D_0 \rightarrow ^7F_0$ transitions. CTB1 arises from Eu in Ba sites, CTB2 comes from $\text{Eu}^{3+}\text{-O}^{2-}$ associates and the black arrows represent the two components of the CTB1.

5D_0 lifetimes monitored around the components at 580.6 nm (Eu_{D1}), 581.5 nm (Eu_{D2}) and 582.3 nm (Eu_{D3}) to Eu(III) sites associated to the structural defects. Previously, we concluded that the components at 578.2 nm (Eu_1) and 579.5 nm (Eu_2) come from Eu(III) in the usual sites of the Ba_2SiO_4 network and the lifetime values are in accordance with this assignment. In addition, by increasing the calcination time to 10 h, the lifetime of the $^5D_0 \rightarrow ^7F_0$ components at 578.2 nm (Eu_1) and 579.5 nm (Eu_2) increases.

As temperature is a crucial parameter in what concerns the balance between radiative and non-radiative transition probabilities, high-resolution emission spectra were measured by changing the temperature from 14 K up to 300 K, Figure 8. The $^5D_0 \rightarrow ^7F_0$ lines at 580.6 nm (Eu_{D1}), 581.5 nm (Eu_{D2}) and 582.3 nm (Eu_{D3}) are favored only at low temperatures, Figure 8a, when the non-radiative losses are minimized.

Figure 6. High-resolution emission spectra (14 K) of the Eu(III)-based phosphors monitoring different excitation wavelengths. The * represents the $^5D_0 \rightarrow ^7F_2$ transition components that come from the Eu_{A1} and Eu_{A2} Eu(III) local sites.

This observation is in accordance with our previous assignment for the nature of the $^5D_0 \rightarrow ^7F_0$ transition components. The components at 590.4 nm ($^5D_0 \rightarrow ^7F_1$ transition), 593.3 nm ($^5D_0 \rightarrow ^7F_1$ transition), 595.8 nm ($^5D_0 \rightarrow ^7F_1$ transition), 610.4 nm ($^5D_0 \rightarrow ^7F_2$ transition) and 623.9 nm ($^5D_0 \rightarrow ^7F_2$ transition) reveal analogous thermal dependence, Figures 8b and 8c, thus, being related to the Eu_{D1-3} local sites.

Focusing our attention to the potential use of those materials as coatings of deep-UV emitting LEDs, the quantification of the emission is fundamental. The absolute emission quantum yield (q) was measured as a function of the excitation wavelength, namely around 250 nm (CTB) and within the f - f levels (5L_6) at 393 nm and (5D_2) at 464 nm, Figure 3b. The maximum q values are found at deep-UV excitation (CTB) and increase from 0.058 ± 0.006 to 0.11 ± 0.01 as the calcination time increases from 2 h to 10 h, respectively, in good agreement with the above suggestion that the spurious phase contributes to a decrease of the non-radiative decay probability. The achieved q values resemble those of other silicate-based Eu(III)-phosphors,⁵² but they are lower than those found for classic Eu(III)-based phosphors, such as $\text{Y}_2\text{O}_3\text{:Eu(III)}$ and YOF:Eu(III) , Table S2.⁵³

Figure 7. (a) Diffuse reflectance spectra of Gd-2h and Eu-2h. (b) Arithmetic difference between Gd-2h and Eu-2h-related reflectance spectra in the range of 200–360 nm. CTB 1 comes from Eu inserted in Ba sites and CTB 2 arises from $\text{Eu}^{3+}\text{-O}^{2-}$ associates.

Figure 8. Temperature-dependent emission spectra monitored at 393 nm of the Eu-2h phosphor in the (a) $^5D_0 \rightarrow ^7F_0$, (b) $^5D_0 \rightarrow ^7F_1$ and (c) $^5D_0 \rightarrow ^7F_2$ transitions region. The black arrows represent the transition components that disappear as the temperature increases.

Ba₂SiO₄:Eu(III)/PMMA film characterization.—Featuring the fabrication of the multifunctional UV and red-emitting LED, red-emitting films were fabricated with controlled thickness. To optimize the deposition conditions, the Eu-2h was selected as the red-emitting phosphor since it is easier to process due to its lower calcination time (lower energetic outlay than that of Eu-10h). Then, the best condition (1PMMA:2Eu-2h) was applied to fabricate the PMMA:2Eu-10h film. To optimize the UV absorption, the PMMA:Eu-2h film growth was monitored by UV/visible absorption spectroscopy, Figure S5. The intense band in the deep-UV region at ~ 225 nm, Figure S5 (a) is attributed to the PMMA absorption⁵⁴ whereas the band ~ 265 nm is related to the above mentioned CTB1, confirming that the phosphor particles are incorporated in the membrane.

The UV absorption spectra were also used to evaluate the optical features as the composite films grow, by monitoring the film absorption in a region (600 nm) that neither the phosphor nor the polymer absorb, Figure S5 (b). In this case, the absorption increase is mainly ascribed to light scattering by the phosphor particles.^{55,56} The absorbance of the films at 600 nm reveals a linear increase up to the PMMA:2Eu-2h film, and then tends to a saturation regime at larger phosphor content, suggesting that the phosphor dispersion is homogeneous until the PMMA:2Eu-2h. As the phosphor particles are micro-sized (diameter of 1 μm),²⁶ it is expected that the precursor suspension becomes unstable as the phosphor amount increases, leading to a non-homogeneous deposition of the particles. Also, considering that the phosphor particle surface is non-ionic, weak interactions like Van der Waals forces are the main driving forces that maintain the suspension stable, being strongly influenced by the particle concentration, and leading to particle coagulation at high concentration.^{55,57}

The film thickness decreases as the phosphor amount increases from the proportion of 1 PMMA:1 Eu-2h, Table III. This tendency is correlated with the decrease of the PMMA content in the film composition.²⁸

Under UV exposition (255 nm), the PMMA:2Eu-10h exhibits bright red luminescence at naked eyes, Figure 9a, confirming the successful incorporation of the Eu-10h phosphor in the polymeric matrix. The excitation spectrum, Figure 9b, of PMMA:2Eu-10h, is dominated by the $\text{Eu}^{3+} \rightarrow \text{O}^{2-}$ CTB1 and $f-f$ Eu(III) transition in accordance with the previously reported Eu-10h excitation spectra, Figure 3b.

All films emit red light upon 255 nm radiation exposition, Figure 9c, but there is a deviation of the overall emission color from the red toward the blue spectral region as the phosphor particle concentration decreases in the PMMA matrix, as represented in CIE chromatic-

ity diagram, Figure 9d. This deviation is associated with the intrinsic PMMA emission (Figure S6) in the blue spectral region that has high contribution in the emission pattern as the phosphor content decreases.

The luminous flux of the films enhances as the phosphor amount increases up to the proportion of PMMA:2Eu-2h, Table III. This tendency is directly correlated with the above-mentioned film coagulation as the phosphor amount increases. The PMMA:2Eu-10h film showed the best luminous flux, confirming that this is the ideal condition. Furthermore, the luminous flux values of PMMA:2Eu-2h and PMMA:2Eu-10h are higher than the values found for the powder phosphors, Table III, suggesting that the phosphor dispersion in PMMA affects the Ba₂SiO₄ surface since as the particles are micro-sized, it is expected that PMMA does not penetrate inside the particles.

To understand the changes in the Ba₂SiO₄ structure after the phosphor dispersion in PMMA, the PMMA:2Eu-10h film was chosen as a representative sample since it showed the highest luminous flux. The excitation and emission spectra of the PMMA:2Eu-10h film, Figure S7, are similar to those ones related to the Eu-10h sample, except in the relative intensity of some $^5D_0 \rightarrow ^7F_0$ transitions, Figure 4a. For the PMMA:2Eu-10h film, only five components for the $^5D_0 \rightarrow ^7F_0$ transition at 572.6 nm (Eu_{A1}), 578.2 nm (Eu₁), 579.6 nm (Eu₂), 580.1 nm (Eu₃), and 582.3 nm (Eu_{D3}) are noticed, Figure 4a.

The excitation spectra monitored around each $^5D_0 \rightarrow ^7F_0$ components (Figure S7) are quite similar to those ones acquired for Eu-10h (Figure 5), confirming the preservation of the Eu(III) local environ-

Table III. Film thickness and luminous flux compared to the powder phosphors.

Sample	Thickness/ μm	Luminous flux/ $\times 10^{-4}$ lm
PMMA:0.25Eu-2h	26 ± 2	0
PMMA:1Eu-2h	88 ± 4	3.8 ± 0.1
PMMA:2Eu-2h	72 ± 3	5.9 ± 0.2
PMMA:3Eu-2h	55 ± 6	4.3 ± 0.2
PMMA:4Eu-2h	17 ± 2	2.5 ± 0.1
PMMA:2Eu-10h	68 ± 2	7.9 ± 0.3
Eu-2h	*	4.5 ± 0.2
Eu-10h	*	5.4 ± 0.2

*Samples as powders.

Figure 9. Photo of the PMMA:2Eu-10h film under UV radiation (255 nm) exposition. (b) Absolute emission quantum yield (q) for the PMMA:2Eu-10h film compared to its excitation spectrum. (c) Emission spectra (300 K) monitored at 255 nm of the films. (d) CIE chromaticity diagram of the films monitored at 255 nm.

ment after the dispersion in PMMA. Yet, the $^5D_0 \rightarrow ^7F_0$ transitions at 580.2 nm (Eu_{D1}), 581.6 nm (Eu_{D2}), and 582.3 nm (Eu_{D3}) reveal a decrease in their relative intensity after the dispersion in PMMA, when compared to the component at 578.2 nm (Eu_1), Figure 4a, suggesting that the phosphor dispersion fills the lacking oxy ion positions, suppressing defects, probably located on the surface of $Ba_2SiO_4 \cdot Eu(III)$ particles. Thus, the $Ba_2SiO_4 \cdot Eu(III)$ dispersion in PMMA confirms that the Eu_{D1-3} defects are located mostly on the particle surface.

Selective emission decay curves (Figures S8) for the PMMA:2Eu-10h sample were monitored around each one of the five $^5D_0 \rightarrow ^7F_0$ components at 14 K and the calculated 5D_0 lifetime values are also included in Table II. The 5D_0 lifetime values of the components at 580.2 nm (Eu_{D1}) and 582.3 nm (Eu_{D3}) decrease after the Eu-10h dispersion in PMMA, Table II, confirming that the concentration of these defects decreases, in accordance with the above-cited structural changes. Finally, the emission quantum yield of the PMMA:2Eu-10h film is statistically the same compared to the Eu-10h phosphor, Figure 9b, confirming that the dispersion of the phosphor does not quench the Eu(III) emission.

Therefore, the finds reported here confirm that by dispersing $Ba_2SiO_4 \cdot Eu(III)$ red-emitting phosphors in PMMA, high-brightness deep-UV-to-red downshifting converter films were fabricated, with potential to be applied in the future as coatings of multifunctional UV/red-emitting LEDs for indoor farming, being that PMMA decreases the concentration of defect-related Eu(III) local sites without any quenching of the Eu(III) emission, that is a remarkable ad-

vantage taking into consideration the balance between non-radiative and radiative decay probabilities from the Eu(III) 5D_0 emitting state.

Conclusions

Herein, $Ba_2SiO_4 \cdot Eu(III)$ deep-UV-to-red downshifting converter phosphor was synthesized by the sol-gel route and its incorporation in the PMMA polymer was introduced, producing films with tunable red-emission intensity and thickness. The phosphor, in both powder or film forms, emits in the red spectral region characteristic of Eu(III) into the Ba_2SiO_4 network. The sol-gel synthesis was carried out at 100°C and the increase of the annealing time from 2 h to 10 h decreases the amount of $BaSiO_3$ spurious phase and enhances the absolute quantum yield from 0.058 ± 0.006 to 0.110 ± 0.010 . Eu(III) is inserted in 8 non-equivalent local sites, 2 coming from $Eu^{3+} \cdot O^{2-}$ associates, 2 arising from the Ba site replacement in the Ba_2SiO_4 matrix, 1 from the Ba site replacement in the $BaSiO_3$ network and 3 defect-related sites. The phosphor dispersion in PMMA does not quench the Eu(III) emission and also undoes the Eu defect sites. Therefore, the $Ba_2SiO_4 \cdot Eu(III)$ /PMMA films show potential to be used as coatings of deep-UV-emitting LEDs (250 nm), making a device that combines both UV and red-emission, important to disinfection and plant circadian rhythm control applications in indoor farms.

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