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Full-Color Mesophase Silicate Thin Film Phosphors Incorporated with Rare Earth Ions and Photosensitizers**

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Many studies have been performed recently in an attempt to produce full-color phosphors,^[1–3] especially those with white color emissions,^[4] due to their important role in the field of display systems and lighting technologies. Various colors can be achieved by adjusting the relative red, green and blue luminescent components. Thus, full-color phosphors could be obtained by controlling the relative amounts of these components to achieve multicolored photoluminescence. The sharp and intense line-emissions of rare earth (RE) complexes have been of great interest in the luminescence material science field.^[1,5] In the RE complex, an organic ligand is employed as an energy absorption antenna to photosensitize the RE ion in the center of the complex. The trivalent RE ion absorbing the energy can exhibit a highly efficient and narrow emission via an effective intermolecular energy transfer from the ligand to the luminescent center.^[6] In addition, some ligands like salicylic acid show strong blue emission under UV excitation. This suggests that some organic ligands can serve as blue components in addition to being photosensitizers. Among RE complexes, trivalent europium (Eu) and terbium (Tb) ions exhibit bright red and green emissions when they are linked to a suitable ligand. Therefore, Eu and Tb complexes accompanied by excess blue light emitting ligands can be co-doped and served as red, green, blue luminescent components for multicolored photoluminescence. The color can be controlled by changing the composition of the RE ions and the photosensitizers which affect the energy transfer to the various components resulting in a full-color phosphor. Recently, Wada et al. reported the multicolored photoluminescence of zeolite powders incorporated with Tb³⁺ and Eu³⁺ ions and photosensitizers exhibiting red-green-blue (RGB) photoluminescence.^[1] The color was finely tuned by changing the composition of the RE ions and the photosensitizers, the temperature, and the excitation wavelength. However, a white color was only observed at a temperature of 77 K. In this pa-

per, we present mesophase silicate thin films incorporated with RE ions and organic ligands that successfully exhibit multicolored photoluminescence including white at room temperature.

The use of ordered mesophase silicate thin film as a matrix material in which to incorporate photoactive molecules is attracting increasing interest.^[7–9] In the present study, RE complexes are incorporated into films of this type. The luminescent dopants can easily be incorporated into nano-sized mesopores to obtain homogeneous thin films. The rigid inorganic framework, which can protect the dopants in the silicate mesophase matrix, can improve the stability of the RE complexes. Also, the advantages of using the silicate mesophase matrix to incorporate the complexes include the local separation of organic/inorganic regions, the prevention of dopant aggregation, the chemical inertness and the controllable porosity of the silicate framework.^[9] Furthermore, the hydrophobic core of the surfactant micelle increases the solubility of the RE complexes during the synthesis of the mesophase thin film. In addition, the mesophase silicate thin film is optically transparent in the visible region making full-color photoluminescence possible. It should be noted that in the multicolored photoluminescence system, the energy transfer is very sensitive to the chemical environment due to the existence of multiple components. The control of energy transfer to the multiple components for multicolored luminescence is also difficult.^[1,10] However, mesophase thin films incorporated with Eu³⁺, Tb³⁺ and organic ligands can present various colors of photoluminescence. Under UV excitation, the mesophase thin films show bright distinguishable colors which cover the whole visible range including green, cyan, yellow, orange, red, pink to purple, as well as white at room temperature. The color can be finely tuned by varying the relative concentrations of the RE trivalent ions and photosensitizers, as well as by changing the excitation wavelength. Thus, the ordered mesophase silicate thin film appears to be an ideal matrix as it provides a suitable luminescence environment for multiple luminescence dopants and for controlling the energy transfer processes. The use of these full-color mesophase thin film phosphors in multicolor displays is promising.

The mesophase thin films incorporated with RE ions and photosensitizers were synthesized by an in-situ synthesis method. In our experiments, surfactant Pluronic P123 triblock copolymer (P123) was employed as a template and spin-coating was used to produce homogeneous mesophase thin film on a silicon substrate. The schematic diagram of experiment process is shown in Figure 1. The silicate precursor was hydro-

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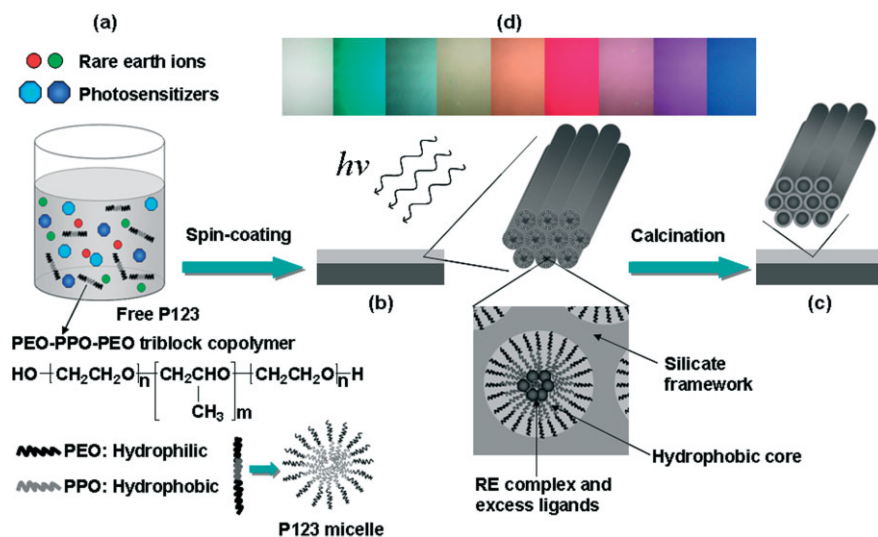


Figure 1. Schematic diagram of the experiment process. a) Original homogeneous solution of soluble silicates, surfactant P123, rare earth ions and photosensitizers. b) As-deposited mesophase thin film. Right top: magnified picture of the 2-d hexagonal mesophase structure. Right bottom: enlarged view of the cross section of the mesophase thin film incorporated with RE ions and photosensitizers. c) Calcined mesopore thin film. Top: magnified picture of the 2-d hexagonal mesopore structure, after the as-deposited mesophase thin film calcined at 550 °C in air. d) Photoluminescence from the as-deposited thin films under the UV excitation, with colors varying from white to blue depending on the ratios of incorporated RE ions and photosensitizers.

lyzed in distilled water containing hydrochloric acid. Then P123 methanol solution and luminescence dopants, i.e., $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, 1,10-phenanthroline (phen), and salicylic acid (SA) methanol solution were added to form homogeneous transparent sol (Fig. 1a). The P123 template is composed of a hydrophobic central part (PPO) and hydrophilic end (PEO). In the fabrication of the mesophase thin films, it acts as the structure-directing agent for the mesophase structure. The original concentration of P123 (c_0) was lower than the critical micelle concentration (cmc). In the evaporation-induced self-assembly (EISA) process for the synthesis of silica thin film, the PEO moieties of the P123 are associated with hydronium ions under acid condition and the cationic silica species are combined with these charge-associated PEO units through noncovalent interactions (electrostatic, hydrogen bonding, van der Waals forces, etc.).^[11a,12] During coating, as the methanol preferentially evaporated, the concentration of the P123 began to exceed the cmc, the micelles formed, concurrently partitioned the luminescence dopants into micellar interiors by hydrophobicity and the inorganic silica species surrounding the micellar exteriors. With the evaporation continued these micellar species were co-assembled into 2-d hexagonal mesophases. After spin coating, the luminescence dopants were combined at the nanoscopic level and incorporated into the hydrophobic core of the

template and a continuous homogenous 2-d hexagonal mesophase thin films was formed (Fig. 1b).

For tuning the color, the ratios of the luminescent components were varied and marked as sample A to I as listed in Table 1. Under the UV excitation, the mesophase thin films display various colors depending on the different ratios of incorporated RE ions and photosensitizers (Fig. 1d). All the as-deposited thin films incorporated with various ratios of luminescent dopants show similar X-ray diffraction patterns (XRD), which suggests that they have similar mesophase structures. In this paper, we choose sample A as a typical thin film whose reactant composition containing all the luminescent components including Eu^{3+} , Tb^{3+} , phen and SA.

The typical as-deposited thin film is dense, continuous, and homogeneous on silicon wafer, which can be verified by the scanning electron microscopy (SEM) image of a cross-section of as-deposited sample A shown in Figure 2a. The thickness of sample A is about

439 nm and the thickness of all as-deposited thin films is similar because all the as-deposited samples were prepared under the same spin-coating conditions. The 2-d hexagonal mesophase structure of the thin films shown in Figure 1b can be confirmed by both XRD and transmission electron microscopy (TEM). To study the mesophase structure, we calcined the as-deposited thin films at 550 °C in air and also synthesized the as-deposited undoped mesophase thin film as references. The XRD curves in Figure 2b were obtained from the as-deposited undoped thin film (curve I), the as-deposited thin film of sample A (curve II) and the calcined thin film of sample A

Table 1. Composition of mesophase thin films from A to I incorporated with different mole ratios of multiple luminescence dopants and corresponding XRD data for the as-deposited samples.

Thin Film	Mole ratio of multiple luminescent dopants				XRD data (100)		
	Eu	Tb	phen	SA	d-spacing [nm]	2θ [degree]	a_0 [a] [nm]
A	0.5	1.5	4.5	7.5	9.59	0.92	11.1
B	0	2	0	6	9.81	0.90	11.3
C	0.75	1.25	2.25	3.75	9.11	0.97	10.5
D	1	1	3	3	8.83	1.00	10.2
E	1	0.5	3	1.5	9.01	0.98	10.4
F	2	0	6	0	9.59	0.92	11.1
G	2	0.5	6	1.5	10.1	0.87	11.6
H	1	0	2.25	3.75	9.69	0.91	11.2
I	0	0	0	7.5	9.19	0.96	10.6

[a] The unit cell parameter (a_0) is calculated using $a_0 = 2d(100)/3^{1/2}$.

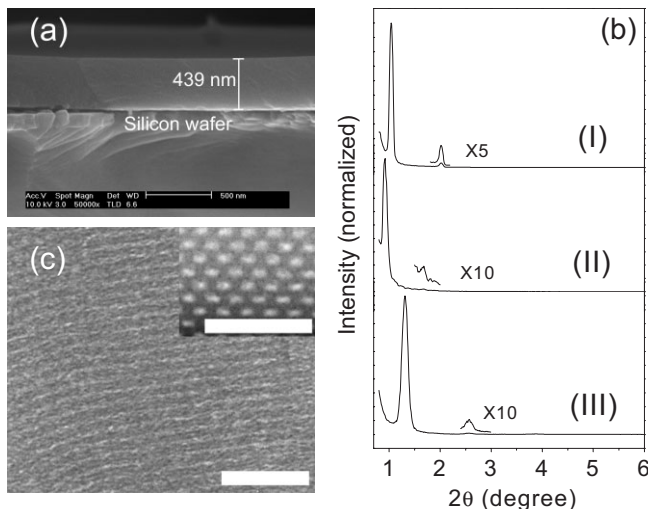


Figure 2. a) Cross-section SEM image of a typical as-deposited mesophase thin film. b) XRD patterns of (I) the as-deposited undoped mesophase thin film, (II) the as-deposited mesophase thin film of sample A, (III) the calcined mesopore thin film of sample A. c) Planar-section and cross-section (inset) TEM images of sample A after calcination at 550 °C. Both scale bars are 50 nm.

(curve III). The XRD curve II shows a very intense (100) peak at $2\theta = 0.920^\circ$ and a weak (200) peak at $2\theta = 1.660^\circ$ (shown enlarged). If the two peaks still remain in the calcined thin film, it suggests the formation of oriented hexagonal meso-structured silica in the as-deposited thin film,^[11b] because the surfactants and organic dopants were decomposed and only silica framework left after calcinations at 550 °C in air. In the XRD pattern of the calcined thin film for sample A (curve III), the (100) and (200) reflections still remained. These results confirm the formation of 2-d hexagonal mesophase structure in the original as-deposited thin film. TEM images are other evidences for the 2-d hexagonal mesophase structure. Figure 2c shows the typical planar-section and cross-section (inset) TEM images of the calcined thin film of sample A with a pore size about 7 nm. The images corroborate the suggested $p6mm$ symmetry of the mesoporous thin film.^[8] The XRD patterns and TEM images prove that the as-deposited mesophase thin films having a 2-d hexagonal structured silicate framework were formed by using the P123 block copolymer template even when multiple components of RE ions and organic ligands were incorporated. The incorporation of RE complexes did not disrupt the structure.

From XRD patterns, d spacing is obtained from the 2θ value of (100) peak using $d(100) = \lambda/2 \sin\theta$. For 2-d hexagonal structure, the unit cell parameter (a_0) including the internal pore diameter and silica wall thickness can be calculated using $a_0 = 2d(100)/3^{1/2}$. The d value and the calculated a_0 of the as-deposited mesophase sample A to I are listed in Table 1. For the as-deposited undoped mesophase thin film that acts as the reference, the d spacing $d(100) = 8.49$ nm and $a_0 = 9.74$ nm. Both the d spacing value and the pore size of each as-deposited mesophase sample incorporated with luminescence dop-

ants are bigger than those of the as-deposited undoped mesophase thin film. These facts are consistent with what the references reported.^[9] Such increases may originate from the incorporation of the hydrophobic luminescence components within the P123 micelles when they are formed at the early stage of the film coating process. It indicates that the in-situ synthesized RE complexes and photosensitizers ultimately occupy the interior organic region of surfactant micelles and reside inside the pores of the silica framework (as shown in Fig. 1b). In addition, in the similar one step, one pot EISA process, it has been demonstrated that if the 2-d hexagonal structure of the as-deposited thin film is retained, all RE complex or organic molecules should reside within the surfactant micelles.^[9] Otherwise, the 2-d hexagonal structure of the as-deposited mesophase thin film will be disrupted if the loading of metal complexes or organic molecules in films exceeds the limit incorporation by hydrophobicity alone, because an excess of such hydrophobic molecules will prevent the formation of micelles and their organization into hexagonal arrays.^[9]

Figure 3 shows the photoluminescence spectra and the colors obtained from the as-deposited mesophase thin films at room temperature. All the photoluminescence spectra in Figure 3a were performed with a 290 nm UV excitation and normalized to their respective maximum intensities. They present different emission peak ratios creating different colors depending on the composition of the luminescent components. The as-deposited mesophase thin film doped with a single kind of RE ion exhibits the characteristic sharp emission peaks. For sample B, which contains only Tb^{3+} ion complexed with SA, characteristic sharp emission peaks at 488, 544, 584, and 622 nm are attributed to the f-f transitions of the Tb^{3+} ion ($^5D_4 \rightarrow ^7F_J (J=3-6)$).^[13] Also, in the spectra of sample F and H which contain only Eu^{3+} ions complexed with phen, the characteristic emission peaks at 579, 590, 618, 655 and 701 nm are attributed to transitions of Eu^{3+} ion ($^5D_0 \rightarrow ^7F_J (J=0-4)$).^[14] In addition, SA causes a strong blue photoluminescence with UV excitation. Thus, sample I, which includes only SA ligand without doping of any RE ions, gives a broad blue emission band centered around 430 nm. However, for the samples accommodating all the multiple luminescent dopants such as samples A, C, D, E, and G, the emission spectra involve all the emission peaks of the Tb^{3+} , Eu^{3+} ions and ligands to provide mixed peak contributions. All the peaks have similar emission wavelengths but various relative intensities depend on the different concentrations of the luminescent dopants responsible for their respective colors. The organic photosensitizers incorporated with RE ions into the mesopores also give rise to blue emissions in addition to acting as energy absorption antenna for the red and green emissions of the RE ions. The relatively broad emission band in the range 400 to 470 nm in all the spectra is attributed to the luminescence of excess photosensitizers.

According to energy transfer mechanism in the RE complex system, to achieve efficient luminescence from RE ions, the lowest triplet energy level state of the ligand should be nearly equal to or lie above the resonance energy level of the

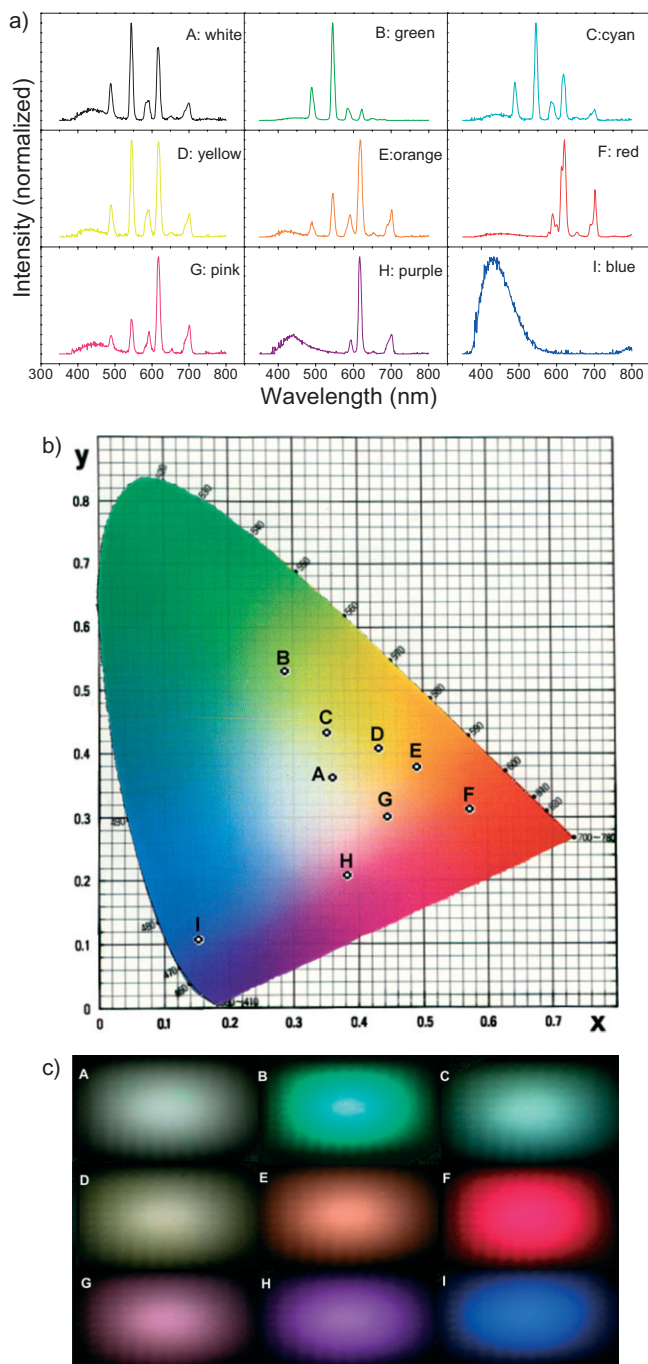


Figure 3. a) Photoluminescence spectra of the mesophase thin films incorporated with various ratios of luminescent dopants at room temperature with UV excitation at 290 nm. b) CIE x-y chromaticity diagram showing the location of the multicolored photoluminescence from the mesophase thin films. c) Photographs of the photoluminescence colors from the mesophase thin films with the UV excitation using a Hg/Xe lamp as the excitation source. All labels A to I corresponding to the samples listed in Table 1.

RE ions.^[6] In the present study, SA was selected as a photosensitizer for the Tb³⁺ ion. The energy transfer from SA to the Tb³⁺ ion is quite efficient and results in the emission of a

strong green color when excited by UV light. Simultaneously, the excess SA has a strong blue luminescence under UV excitation. However, SA is not suitable for the Eu³⁺ ion because the distance between the lowest triplet energy level state of SA (23 300 cm⁻¹) and the resonance energy levels of the Eu³⁺ ion (19 100 cm⁻¹ for ⁵D₁, 17 400 cm⁻¹ for ⁵D₀) is too far to transfer energy efficiently. Thus, phen which also emits low blue light was also added to form a complex with the Eu³⁺ ion in order to emit a red color under UV excitation. As a result, green and red emissions were obtained from Tb³⁺ and Eu³⁺ ions complexed with photosensitizers, respectively, accompanied by a blue emission from the excess organic ligands. This led to simultaneous RGB photoluminescence in the as-deposited mesophase thin films.

Various colors could be obtained by adjusting the RGB luminescent components and thus varying the intensity ratio of RGB emissions. Multiple colors from white (A), green (B), cyan (C), yellow (D), orange (E), red (F), pink (G) to purple (H) and blue (I) in different as-deposited mesophase thin films were achieved by incorporating different ratios of the luminescence dopants. All the colors are illustrated in the Commission Internationale de L'Eclairage (CIE) x-y chromaticity diagram shown in Figure 3b. The CIE color coordinates of each sample are listed in Table 2. It can be seen that the color of the as-deposited mesophase thin films cover the whole visible range. For direct evidence of the full-color photolumines-

Table 2. Luminescence properties of the as-deposited thin films incorporated with luminescence dopants.

Thin film	CIE [a] (x, y)	Colors under UV excitation	Quantum yield [b] η_{PL} [%]
A	(0.3648, 0.3799)	white	9.0
B	(0.2870, 0.5296)	green	35.2
C	(0.3599, 0.4373)	cyan	8.6
D	(0.4224, 0.4126)	yellow	12.8
E	(0.4929, 0.3742)	orange	15.0
F	(0.5765, 0.3127)	red	28.8
G	(0.4258, 0.3124)	pink	13.3
H	(0.3846, 0.2049)	purple	4.3
I	(0.1534, 0.1002)	blue	19.4

[a] CIE (x, y) color coordinate is obtained from the spectrometer under the 290 nm excitation. [b] Quantum yield is measured using integrating sphere and 325 nm HeCd laser as excitation source.

cence in the as-deposited mesophase thin films, photographs of the samples are presented in Figure 3c where a Hg/Xe lamp (confined spectral range of 220–260 nm) was used as an excitation source. It is clearly observed by the naked eyes that the as-deposited mesophase thin films exhibit distinct bright colors. In particular, the as-deposited mesophase thin film sample A exhibits a white color at room temperature.

The photoluminescence quantum yield (η_{PL}) that is a principal characteristic of luminescent materials can quantify the efficiency of the energy transfer. The absolute quantum yield is defined as the number of photons emitted in photolumines-

cence per absorbed photon. In our experiments, the absolute quantum yield of the as-deposited mesophase thin film was measured using an integrating-sphere technique similar to that described elsewhere.^[15] The excitation source is a 325 nm cw HeCd laser. The obtained quantum yields of all samples A to I are listed in Table 2. The quantum yields of these as-deposited thin films which emit multicolored luminescence are between 4.3 % to 35.2 %. In particular, the quantum yield of white luminescence thin films is 9.0 %. It is worth mentioning that under the UV excitation, the sample B emits green luminescence and the absolute quantum yield reaches 35.2 %. The quantum yield of this as-deposited mesophase thin film is higher compared with the traditional green material used in light emitting diodes (LEDs), the tris (8-hydroxyquinoline) aluminum complex (Alq3) with a photoluminescence quantum yield of 8 % in the solid state according to Tang^[16] and of 20 % in thin film according to the more recent work of Kawamura.^[15c] And the quantum yield of sample B is also higher than that of the similar thin film doped with Tb complex reported in the reference^[8] (the quantum yields for the thin films doped with terbium-phen complex are between 17 and 25 % according to the Tb complex concentrations ranging from 2 to 6 wt %). For the sample F which emits red luminescence, the quantum yield is 28.8 %. It is similar with the quantum yield of the same material reported in the above reference^[8] (the quantum yields are between 22 and 24 % in the case of their europium-phen doped thin films). The absolute luminescence quantum yield informs the photophysical characteristics of the luminescence materials. These results indicate that the full-color mesophase silica thin film phosphors incorporated with RE ions and photosensitizers have promising applications in display field.

The intensity ratio of the red, green and blue emissions in an as-deposited mesophase thin film depends not only on the composition of luminescence dopants but also on the UV excitation wavelength. Figure 4a shows the change in the photoluminescence spectra of sample A obtained at room temperature with a UV excitation wavelength varied between 240 and 330 nm. The emission intensities of the green and red components increase with increasing excitation wavelength up to 300 nm, after which they begin to decrease as shown in Figure 4b. Conversely, the blue component reaches a maximum at an excitation wavelength of 310 nm. Thus, the color of the sample A varies with the changed relative intensities of the RGB emissions by varying the UV excitation wavelength. Figure 4c illustrates the corresponding CIE x-y chromaticity diagram and shows the color of the sample as a function of the UV excitation wavelength. The color moves from white to yellow, then returns to light blue as the excitation wavelength increases from 240 nm to 330 nm. Taking into account the difference in the lowest triplet energy level state between the two organic ligands, the absorbed energy from the excitation transferred to the Eu^{3+} and Tb^{3+} ions may be through different routes, according to the energy transfer mechanism of the RE complex system. The absorption efficiencies of the phen and the SA are various under a certain UV excitation wave-

length due to their different absorption peak wavelengths around 270 nm and 310 nm, respectively. As a result, the energies which transfer to the two RE ions are different, which cause the variation of the intensity ratios of the RGB luminescent components depending on the UV excitation. In addition, the mesophase silicate thin films which incorporate the luminescence dopants inside the mesopores provide an ideal environment to control the energy transfer processes that occur between the multiple luminescent components as a function of the UV excitation wavelength. Also, many possible energy transfer mechanisms may take place, not only between organic ligands and RE ions, but also between RE ions, the so-called “cofluorescence effect”. This is because all the luminescence dopants are incorporated in the same nano-sized mesopores and the distance between RE ions is short enough to promote an intermolecular energy transfer in the solid state.^[17] Thus, the complex energy transfer mechanisms between the various luminescent components in the mesophase thin films may allow color tuning by changing the UV excitation wavelength.

In summary, we have demonstrated a novel approach to the synthesis of full-color phosphor thin films by using Eu^{3+} , Tb^{3+} and two organic ligands incorporated into the as-deposited mesophase silica thin films. The in-situ synthesized RE complexes serve as green and red luminescence components, respectively, and the organic ligands give rise to blue emissions in addition to acting as luminescence photosensitizers. Various colors covering the whole visible range can be finely tuned by changing the ratios of RE ions and organic ligands as well as by changing the UV excitation wavelength. In particular, we observed white photoluminescence in the as-deposited mesophase thin film at room temperature. The synthesis of the novel photoluminescent mesophase thin films incorporated with RE ions and photosensitizers, and the fine control of the emission color provides a promising strategy in the development of RGB-photoluminescent materials for use in full-color displays, indicators and backlights.

Experimental

Instrumentation: The film-thickness measurement was carried out using a Philips XL 30 scanning electron microscope (SEM). The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-RC diffractometer (40 kV, 80 mA) with CuK radiation ($\lambda = 0.15417$ nm) with a 0.01° step width and 1 s step time. Transmission electron microscope (TEM) images of the calcined films were obtained by a JEOL JEM-2000EX electron microscope operating at 200 kV. The photographs of the photoluminescence from the mesophase thin films were taken by a standard camera using a Hg/Xe lamp (Oriel 82511, with a power density of 70 mW cm^{-2} with a spectral range of around 220–260 nm) as the excitation source at room temperature. Room-temperature photoluminescence spectra were examined under continuous (500 W) Xe lamp excitation with a DARS PRO 5100 PL System (Professional Scientific Instrument Co, Korea). The absolute quantum yield of the as-deposited thin films was measured using a 6-inch integrating sphere with a HeCd laser as an excitation source.

Material Synthesis: The mesophase silicate thin films incorporated with RE ions and organic ligands were prepared using a one-step syn-

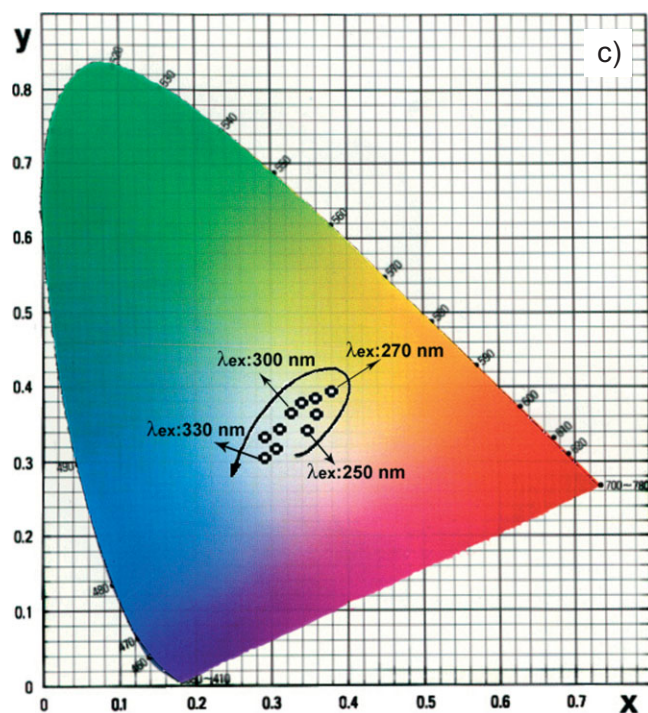
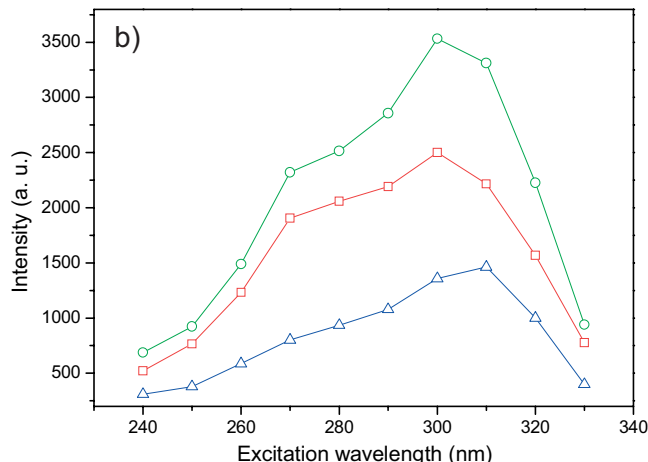
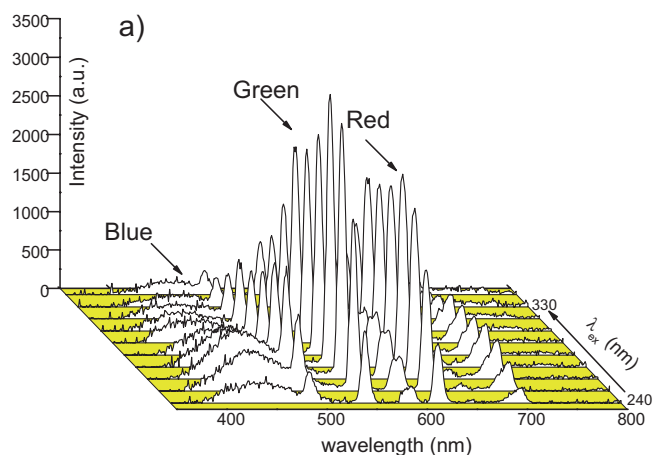


Figure 4. a) Photoluminescence spectra of sample A at room temperature with UV excitation wavelength changing from 240 nm to 330 nm. b) Changes in the emission intensity of the RGB components ($\lambda_m = 544$ nm for Tb^{3+} (green), $\lambda_m = 617$ nm for Eu^{3+} (red), and $\lambda_m = 435$ nm for organic ligands (blue)) at various excitation wavelengths (λ_{ex}) over the range 240–330 nm. c) CIE x-y chromaticity diagram showing the changes in the photoluminescence color from sample A at different UV excitation wavelengths from 240 to 330 nm at room temperature.

thesis method at room temperature. For the synthesis procedure, tetramethylorthosilicate (TMOS, Aldrich, 98 %) was hydrolyzed in distilled water containing hydrochloric acid (HCl, Aldrich, 37 %) at room temperature. Pluronic P123 (BASF, $M_{AW} = 5750$) was dissolved in methanol (CH_3OH , Merck, 99.8 %) to form a template solution. Europium(III) chloride hexahydrate ($EuCl_3 \cdot 6H_2O$, Aldrich, 99.9 %), terbium(III) chloride hexahydrate ($TbCl_3 \cdot 6H_2O$, Aldrich, 99.9 %), 1,10-phenanthroline (phen, Aldrich, 99+ %) and Salicylic acid (SA, Aldrich, 99+ %) were dissolved in methanol (MeOH) to form the complex solution. After the hydrolyzation of TMOS, the template solution was added while stirring the solution. The complex solution was then added into the mixture. For sample A, the final reactant mole ratios of the various components in solution before spin-coating were $0.5EuCl_3 \cdot 6H_2O : 1.5TbCl_3 \cdot 6H_2O : 4.5phen : 7.5SA : 100TMOS : 833H_2O : 0.9HCl : 1.05P123 : 2469 MeOH$. The mole ratios of these components for other samples are listed in Table 1. The transparent solutions were stirred for 15 minutes and filtered through a $0.22 \mu m$ -sized Teflon filter to remove impurities and gas bubbles. These solutions were then deposited onto p-type Si(100) wafers by spin coating at 4000 rpm for 40 s to form the mesophase thin films. To measure the

absolute quantum yield of samples, the as-deposited thin films were also spin-coated on transparent quartz substrates. The as-deposited thin films were heated at $550^\circ C$ in air to obtain the calcined samples. The as-deposited mesophase thin film without any luminescence dopants was synthesized as the same process. The final reactant mole ratios of all the components in solution before spin-coating for the as-deposited undoped thin film were $100TMOS : 833H_2O : 0.9HCl : 1.05P123 : 2469 MeOH$.

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