Tuning the oxidation states of dopants in $\text{Li}_2\text{SrSiO}_4\text{:Eu,Ce}$ and control of the photoemission color

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ABSTRACT: A color-tunable phosphor $\text{Li}_2\text{SrSiO}_4\text{:Eu}^{2+},\text{Eu}^{3+},\text{Ce}^{3+}$ was synthesized by solid state reaction in reducing atmosphere followed by a controlled heating treatment of the compound in air at different temperatures. Due to the different temperatures of oxidation of Eu^{2+} into Eu^{3+} and Ce^{3+} into Ce^{4+} , $\text{Eu}^{2+} / \text{Eu}^{3+} / \text{Ce}^{3+} / \text{Ce}^{4+}$ ions can coexist in the $\text{Li}_2\text{SrSiO}_4$ host and enable a tunable coloration of the “blue-yellow-red” photoemission to obtain white luminescence.

Introduction

White light-emitting diodes (wLEDs) are widely used in solid-state lighting due to their significant advantages, such as long lifetime, and high luminous efficiency.[1–3] Two main strategies are currently used to produce white light: (a) combining a blue InGaN chip with the yellow-emitting YAG:Ce^{3+} phosphor or (b) UV chips exciting three primary phosphors.[4] However, these different methods present various drawbacks. For the first method, the color rendering index (CRI) is low, namely less than 80, due to the lack of a red component. For the second strategy, several parameters have to be controlled such as the reabsorption between different phosphors, the particle size polydispersity and the nonuniformity of luminescence properties, which will directly influence the color and efficiency of wLEDs.[5] Therefore, a single-phase full-color emitting phosphor with high luminous efficiency and excellent CRI is desired for WLEDs.[6]

To obtain a single-phase full-color emitting phosphor, selecting host matrices that exhibit multiple crystallographic sites for the activator is an interesting method. This approach allows the superposition of multiple emission contributions depending on the location of the luminescent center in different environments.[7,8] However, the emission and the occupancy of the dopant in each crystallographic site are difficult to predict/control, making any discovery of a single-phase white phosphor challenging. Another strategy consists in combining in a single host different dopants emitting in different spectral regions[9–11]. However, identifying a single host matrix for multiple dopants remains difficult. An alternative is to tune the oxidation states of the dopants. In previous work, a controlled reduction of dopants enabling to modulate the photoluminescence properties by tuning the ratio of rare-earth elements in different oxidation states has been reported[12,13]. This method was used for $\text{SrAl}_2\text{O}_4\text{:Eu}$, which presents a photoluminescence from green to red

according to the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio.[13] The emission of Eu^{2+} originates from the 4f-5d transitions, and strongly depends on the ions environment (symmetry, covalence, coordination, bond length, and crystal-field strength).[14,15] The emission of Eu^{2+} -doped phosphors commonly occurs in the range of blue to red, such as $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (blue), $\text{M}_2\text{SiO}_4:\text{Eu}^{2+}$ (M = Ba, Ca) (green), $\text{M}_3\text{SiO}_5:\text{Eu}^{2+}$ (M = Sr, Ba) (yellow), or $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M = Sr, Ba) (red).[16–20] On the other hand, the red emission of Eu^{3+} originating from 4f-4f transitions is scarcely influenced by the host matrix. Thus, tuning the ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$ enables to modify the color of photoluminescence. However, designing a white light emission from only Eu^{2+} and Eu^{3+} emissions remains difficult.

In this context, we selected Ce^{3+} ion as an additional activator in a Eu doped phosphor. In this article, the different sensitivity to oxidation of Eu^{2+} and Ce^{3+} ions are explored in order to obtain a significant proportion of Ce^{3+} with a controlled ratio of $\text{Eu}^{2+}/\text{Eu}^{3+}$ ions. As an example, we selected $\text{Li}_2\text{SrSiO}_4$ as host, co-doped with Eu^{2+} , Eu^{3+} and Ce^{3+} ions, leading to yellow, red and blue emissions respectively. Phosphors are firstly synthesized with reduced dopants (Eu^{2+} and Ce^{3+}) in Ar/H_2 atmosphere and then oxidized in air at different temperatures. Finally, the synthesized phosphors doped with Eu^{2+} , Eu^{3+} and Ce^{3+} ions are structurally characterized and the photoluminescence properties are analyzed, showing the possibility of targeting multi emission bands for which the relative intensities can be tuned.

Materials and synthesis

The starting materials were SrCO_3 (analytical reagents, A.R.), BaCO_3 (A.R.), SiO_2 (A.R.), Li_2CO_3 (A.R.), CeO_2 (99.99%) and Eu_2O_3 (99.99%).

$\text{Li}_2\text{SrSiO}_4:\text{Eu}_x\text{Ce}_y$ (with x and y varying from 0.25 to 1.25 mol%) powder samples were prepared via a solid-state reaction process. When not specified, the concentration of the dopants should be considered as 0.5 mol%. SrCO_3 , Li_2CO_3 , SiO_2 , CeO_2 and Eu_2O_3 were weighted based on their stoichiometric ratio, mixed and then transferred to an alumina crucible. The mixture was heated at 550°C with a temperature increase rate of $100^\circ\text{C}/\text{h}$. After 1 h at 550°C , the temperature was increased up to 900°C at the same rate. The samples were kept at this temperature for 6 h and then cooled to room temperature with a rate of $150^\circ\text{C}/\text{h}$. For LSSO doped with Ce^{3+} and/or Eu^{2+} , the mixture should be heated under a reducing atmosphere (95% Ar , 5% H_2) with a flow rate of 30 cc/min, while LSSO doped with Ce^{4+} and/or Eu^{3+} were synthesized in air. In order to synthesize the samples doped with Eu^{2+} , Eu^{3+} and Ce^{3+} ions, the as prepared samples $\text{Li}_2\text{SrSiO}_4:\text{Ce}^{3+},\text{Eu}^{2+}$ were placed into an alumina crucible and heated at $T = 750 \sim 950^\circ\text{C}$ for 2 hours in air.

Phase identification was performed on an X-ray diffractometer (D8 Bruker) with $\text{Cu K}\alpha$ radiation. Diffuse reflection spectra were acquired using a Perkin lambda 1050 equipped with a 150 mm integrating sphere and then using Kubelka-Munk function. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were carried out using a spectrofluorometer Fluorolog-3 from Horiba equipped with a 450 W Xe light source.

Results and discussion

Single doped phosphors $\text{Li}_2\text{SrSiO}_4\text{:Eu}$ and $\text{Li}_2\text{SrSiO}_4\text{:Ce}$ were firstly investigated to determine the temperature ranges in which different oxidation states of the rare earth elements could be stabilized. Concerning $\text{Li}_2\text{SrSiO}_4\text{:Eu}$, X-ray diffraction (XRD) patterns (Figure 1(a)) reveal that the samples synthesized in different atmospheres are pure ($\text{Li}_2\text{SrSiO}_4$, PDF 47-0120). It is interesting to note that the XRD peaks shift to lower angles when samples were synthesized in Ar/H_2 atmosphere vs. air. This observation can be explained by the variation of the Eu oxidation state, since Eu ions substitute Sr^{2+} ions and the ionic radius of Eu^{2+} (1.25 Å) is very similar to Sr^{2+} one (1.26 Å), while the ionic radius of Eu^{3+} (1.07 Å) is smaller. Figure 1(b) shows the diffuse reflection spectra of Eu-doped samples. When LSSO:Eu were synthesized in Ar/H_2 , two absorption bands centered at 320 and 404 nm attributed to the $4f^7 \rightarrow 4f^65d^1$ electronic transitions of the Eu^{2+} ion are observed.[21] For samples synthesized in air, the diffuse reflection spectra is characteristic of the Eu^{3+} ion.[22] Thus, these results suggest that the Eu ions exist almost exclusively in the Eu^{2+} form for samples synthesized in Ar/H_2 , while the emitting ions exist in the Eu^{3+} form for samples synthesized in air. The PLE and PL spectra of LSSO:Eu synthesized under Ar/H_2 atmosphere and under air are shown in Figure 1(c) and 1(d), respectively. A very broad excitation band from 240 nm to 540 nm can be observed for LSSO:Eu prepared under Ar/H_2 due to the $4f^7 \rightarrow 4f^65d^1$ transitions of the Eu^{2+} ion (Figure 1(c)). For an excitation at 310 nm, the emission is centered at 575 nm, corresponding to a yellow emission. The PLE spectrum ($\lambda_{\text{em}}=700$ nm) of LSSO:Eu prepared in air shows a broad band from 240 nm to 300 nm (Figure 1(d)), which originates from the charge-transfer (CT) transitions of O^{2-} to Eu^{3+} , and several sharp peaks from 310 nm to 420 nm, which can be attributed to the $4f-4f$ forbidden transitions of the Eu^{3+} ion.[22,23] Upon excitation at 265 nm, the PL spectrum exhibits a group of emission bands at 578, 593, 616, 651 and 700 nm attributed to $5D_0 \rightarrow 7F_J$ ($J = 0, 1, 2, 3, 4$) transitions, corresponding to a red light emission.[24,25] The evolutions of PL intensity with the Eu^{2+} and Eu^{3+} concentrations (from 0.25 mol% to 1.25 mol%) are shown in Figure S1. The optimal concentration before quenching for Eu^{2+} is 0.5 mol%. For Eu^{3+} , no concentration quenching was observed up to 1.25 mol%. The ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$ can be tuned according to the temperature of oxidation (Figure 1(e)). When the temperature increases, the Eu^{2+} ions are gradually oxidized into Eu^{3+} and the intensity of the Eu^{2+} emission decreases, while the intensity of the Eu^{3+} emission increases. Above 850°C, the emission originating from Eu^{2+} is absent. The chromaticity coordinates ($\lambda_{\text{ex}}=250$ nm) of LSSO:Eu oxidized at different temperatures are represented in Figure S2. The color of emission can be obtained in the “yellow-red” range.

In parallel, single doped LSSO:Ce were synthesized and characterized. XRD patterns of LSSO:Ce synthesized in air and Ar/H_2 atmosphere are shown in Figure 2(a) and confirm the purity of the samples. Compared with undoped samples, the XRD peaks of Ce-doped samples shift to higher angles owing to different ionic radii: Ce^{4+} (0.97 Å) < Ce^{3+} (1.14 Å) < Sr^{2+} (1.26 Å), confirming the Ce doping. The diffuse reflection spectra of the Ce-doped samples are shown in Figure 2(b). LSSO:Ce synthesized in Ar/H_2 presents strong absorption bands at 260 nm and 310 nm, corresponding to the $4f^1 \rightarrow 4f^05d^1$ transition of Ce^{3+} .[26] In the case of

samples synthesized in air, only one absorption band attributed to the $\text{Ce}^{4+}\text{-O}^{2-}$ charge-transfer and located at 350 nm is observed, whereas no specific absorption related to Ce^{3+} can be observed.[27] This result confirms that Ce exists in the oxidized form of Ce^{4+} when synthesized under air. The PL and PLE spectra of LSSO:Ce^{3+} are shown in Figure 2(c). The excitation spectra of LSSO:Ce^{3+} shows three broad bands with maxima at 250 nm, 275 nm and 365 nm. These bands can be attributed to the $4f^1 \rightarrow 4f^0 5d^1$ transitions of Ce^{3+} ions with a crystal-field splitting of the excited $5d$ levels.[26,28–30] Under excitation at 363 nm, an emission centered at 400 nm (blue light) is observed. The evolution of the PL intensity with the Ce^{3+} concentration (from 0.25 mol% to 1.25 mol%) is shown in Figure S3. The optimal concentration for Ce^{3+} was determined to be 0.5 mol%. When LSSO:Ce was synthesized in air, the sample shows no emission because Ce^{4+} is a non-emitting center. Emission spectra of LSSO:Ce^{3+} after treatments at different temperatures in air (Figure 2(d)) suggest the oxidation of Ce^{3+} into Ce^{4+} occurs above 850 °C.

After investigating LSSO:Ce^{3+} (blue emission), LSSO:Eu^{2+} (yellow emission) and LSSO:Eu^{3+} (red emission) phosphors, one can expect that $\text{LSSO:Ce}^{3+}, \text{Eu}^{2+}, \text{Eu}^{3+}$ with the appropriate ratio of dopants could exhibit a white light emission. Interestingly, the investigation on single doped phosphors showed that the oxidations of Ce^{3+} into Ce^{4+} , and Eu^{2+} into Eu^{3+} occur in different temperature ranges (Figure 1(e) and 2(d)), which allows the control of the ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$ without oxidizing Ce^{3+} . To obtain LSSO co-doped with Ce^{3+} , Eu^{2+} , and Eu^{3+} ions, the material was firstly synthesized in reducing atmosphere and treatments under air were performed.

For the synthesis of LSSO:Eu,Ce , the concentration 0.5 mol% was selected for the Eu ions and the Ce ions. The purity of the samples is confirmed by X-ray diffraction (Figure 3(a)). When samples were synthesized under Ar/H_2 atmosphere, the two absorption bands attributed to Eu^{2+} (320 nm, 404 nm) and the absorption bands attributed to Ce^{3+} (260 nm and 355 nm) can be observed, suggesting that the Eu and Ce ions mainly exist in the reduced forms of Eu^{2+} and Ce^{3+} (Figure 3(b)).[26] When samples were synthesized in air, only the absorption bands attributed to Eu^{3+} and Ce^{4+} can be observed, suggesting that the Eu and Ce ions are present in their oxidized form. As expected, the emission bands of Ce^{3+} and Eu^{2+} can be observed in the sample synthesized in Ar/H_2 , while only emission bands associated to Eu^{3+} can be identified for the sample synthesized in air (Figure 3(c)). It is important to note that, for the sample synthesized in Ar/H_2 , the intensity of the PL emission band attributed to Ce^{3+} ions is lower than the intensity of the band attributed to Eu^{2+} ions. Such difference in intensities could be due to an energy transfer from the Ce^{3+} to the Eu^{2+} ions. In addition, low emission bands from Eu^{3+} , which would originate from the metal–metal charge transfer “ $\text{Eu}^{2+} + \text{Ce}^{4+} \leftrightarrow \text{Eu}^{3+} + \text{Ce}^{3+}$ ”, can be observed.[28,31]

To prepare $\text{LSSO:Eu}^{2+}, \text{Eu}^{3+}, \text{Ce}^{3+}$, LSSO:Eu,Ce synthesized in reduced atmosphere was treated in air for 2 hours at different temperatures (Figure 4(a)). The emission bands at 410 nm, 560 nm, and 700 nm were selected to follow the evolution of the emission intensities of the Ce^{3+} , Eu^{2+} and Eu^{3+} ions, respectively (see Figure 4(b)). As the temperature of oxidation increases, the intensity of the Eu^{2+} emission decreases in favor of the Eu^{3+} emission. In parallel, the PL intensity of the emission associated with Ce^{3+} ions increases and then

decreases for temperatures higher than 900°C. This behavior could be explained by the coexistence of two phenomena: (i) an energy transfer (ET) from Ce^{3+} to $\text{Eu}^{2+} / \text{Eu}^{3+}$ (Figure 5(a)) and (ii) the oxidation of Ce^{3+} into Ce^{4+} . From the analysis of the spectral overlaps (Figure 5(c)), one can conclude that the ET from Ce^{3+} to Eu^{2+} is more efficient than the ET from Ce^{3+} to Eu^{3+} . For treatments below 850°C, the oxidation of Eu^{2+} to Eu^{3+} occurs (the ratio $\text{Eu}^{2+} / \text{Eu}^{3+}$ decreases) but Ce^{3+} is not oxidized to Ce^{4+} (Figure 4(b)). The ETs from Ce^{3+} ions to Eu ions (including Eu^{2+} and Eu^{3+}) decrease as the ET of $\text{Ce}^{3+} \rightarrow \text{Eu}^{3+}$ is less efficient than the $\text{Ce}^{3+} \rightarrow \text{Eu}^{2+}$ one. Such decrease of ET leads to an increase of the emission intensity related to Ce^{3+} . For treatments above 900°C, the Eu^{2+} ions are fully oxidized into Eu^{3+} and the decrease of Ce^{3+} PL intensity would be due to the oxidation of Ce^{3+} into Ce^{4+} (Figure 4(b)). The CIE coordinates (0.39, 0.31) have been obtained after a treatment at 800°C under air (Figure 5(b)), which correspond to a warm white light emission. Thus, the control of the oxidation rate of dopant is a simple to implement approach, and allows to quickly and reliably optimize the luminescence properties of LSSO:Eu,Ce phosphor.

Conclusions

LSSO: Ce^{3+} , Eu^{2+} was synthesized under Ar/ H_2 atmosphere and LSSO: Eu^{2+} , Eu^{3+} , Ce^{3+} with a controlled ratio of dopants can be obtained after treatments in air. Owing to the different contributions of each emitting center: Ce^{3+} (blue), Eu^{2+} (yellow) and Eu^{3+} (red), the control of the oxidation states of the Eu and the Ce ions enables to design a white phosphor. Such control was possible owing to different thermal stabilities versus oxidation of the Eu^{2+} and Ce^{3+} species (the oxidation of Eu^{2+} into Eu^{3+} was shown to occur at lower temperatures than the oxidation of Ce^{3+} into Ce^{4+}). The resulting color of photoluminescence for the LSSO:Eu,Ce phosphor can be tuned by varying the temperature of oxidation. We believe such control of the dopants oxidation is a promising method, applicable for most of the phosphors, and could be systematically envisioned for white phosphors synthesis used in wLEDs applications.

Author Contributions

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Figure 1. (a) X-ray diffraction (XRD) patterns and (b) Kubelka-Munk absorption spectra of LSSO:Eu synthesized in air (red) and in Ar/H₂ (blue) ; photoluminescence (PL) and photoluminescence excitation (PLE) spectra of (c) LSSO:Eu²⁺ and (d) LSSO:Eu³⁺. (e) Emission spectra of LSSO:Eu²⁺ after treatment at different temperatures in air. The inset represents the evolution of the emission intensity with the temperature of treatment.

Figure 2. (a) X-ray diffraction (XRD) patterns and (b) Kubelka-Munk absorption spectra of LSSO:Ce synthesized in air (red) and in Ar/H₂ (blue); (c) PL and PLE spectra of LSSO:Ce³⁺. (d) Emission spectra of LSSO:Ce³⁺ after treatments at different temperatures in air. The inset represents the evolution of the emission intensity with the temperature of treatment.

Figure 3. (a) X-ray diffraction (XRD) patterns, (b) Kubelka-Munk absorption and (c) PL and PLE spectra for the LSSO:Eu,Ce samples synthesized in air (red) and in Ar/H₂ (blue).

Figure 4. (a) Emission spectra of LSSO:Eu²⁺,Ce³⁺ after treatments at different temperatures in air, (Ce³⁺: blue arrow at 410 nm, Eu²⁺: yellow arrow at 560 nm, Eu³⁺: red arrow at 700 nm) and (b) evolution of the emission intensities associated with Eu²⁺, Eu³⁺, Ce³⁺ vs. the temperature of oxidation.

Figure 5. (a) Energy level schemes and energy transfers between the Ce^{3+} , Eu^{2+} and Eu^{3+} ions. (b) CIE coordinates of LSSO:Eu²⁺,Ce³⁺ after treatments in air at different temperatures. (c) Spectral overlaps between the Ce^{3+} emission and the Eu^{2+} and Eu^{3+} excitation spectra.