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Emission controlled dual emitting Eu-doped CaMgSi₂O₆ nanophosphors



Amol Pawar^a, Abhijit Jadhav^a, Chang Woo Kim^a, Hyun Gil Cha^a,
Umapada Pal^b, Young Soo Kang^{a,*}

^a Department of Chemistry, Sogang University, Seoul 121-742, Republic of Korea

^b Instituto de Física Benemérita, Universidad Autónoma de Puebla, Apodo, Postal J-48, Puebla, Pue 72570, Mexico

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ABSTRACT

Well-dispersed Eu-doped CaMgSi₂O₆ (CMS) nanophosphors of 4–16 nm size range were synthesized by a simple co-precipitation method followed by thermal annealing in controlled ambient. Emission behaviors of the nanophosphors have been studied to optimize and tune their emissions in desired spectral range (red, blue or both). Effects of temperature and calcination atmosphere on the inter-conversion (Eu³⁺ ↔ Eu²⁺) ability of europium ions in CMS matrix have been studied thoroughly. It has been observed that by calcinating the nanophosphors in oxidizing atmosphere like O₂, about 70% of the incorporated europium atoms can be transformed to their trivalent (Eu³⁺) state. On the other hand, calcinating the nanophosphors in reducing atmosphere like H₂+N₂ mixture, about 99% of Eu ions can be transformed to their divalent state (Eu²⁺). It has been demonstrated that by controlling the temperature and ambient of calcination, a dual emitting CMS:Eu nanophosphor could be converted either to blue or red emitting nanophosphor of high emission efficiency. The interchangeable emission characteristic of the size controlled nanophosphor is expected to have immense impact in the fabrication of highly efficient luminescent and display devices.

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1. Introduction

CaMgSi₂O₆ (CMS) pyroxene, known as diopside, has been well studied for different applications such as for the production of high quality glass–ceramics and bioactive materials [1–4]. Recently it has been applied as phosphor material in fluorescent lamps, cathode ray tubes (CRTs), plasma display panels (PDPs) and fabrication of light emitting diodes (LEDs) exploiting its high chemical stability, good thermal stability and relatively high thermal expansion coefficient [5–7]. Introducing suitable impurity, the CMS can be prepared as single emission (e.g. blue emitting CMS:Eu²⁺ or CMS:Eu, Dy/Nd) [8,9], dual emission (blue and red emitting CMS:Eu) [10] or even multi-emission (white emitting CMS:Eu²⁺, Mn²⁺) phosphor [11]. For dual- or multi-emission, the phosphor must contain more than one dopant material or a single dopant at its multiple oxidation states.

Generally, the incorporation of multiple dopants or multi-valent dopant reduces the emission efficiency of CMS due to the large Stokes shift between its emission and absorption bands. Therefore, when it is not absolutely necessary (when both the emissions of the phosphor are not utilized), converting its one

emission to the other, i.e. converting dual emission to single emission would help to increase the quantum efficiency of the phosphor. The divalent Eu²⁺ ions are the well-known blue emitting activators in CMS. On the other hand, trivalent Eu³⁺ ions have been used for inducing red emission in it [12].

Eu²⁺ doping in CMS has been achieved by high temperature thermal treatments in reducing atmosphere such as N₂–H₂ or H₂ [13,14]. On the other hand, an air-annealing process has been utilized to incorporate trivalent europium Eu³⁺ ions in CMS. Due to unsatisfactory charge balance and high thermal energy of formation while calcinating at high temperature, weak oxygen bond of Eu₂O₃ gets to be broken to proportionate one electron to trivalent europium (Eu³⁺), converting a fraction of Eu³⁺ to Eu²⁺ [10]. As the relative intensity of the component emissions depends directly on the fraction of Eu²⁺ and Eu³⁺ ions present in CMS:Eu, it is important to estimate the amounts of incorporated Eu³⁺ and Eu²⁺ ions quantitatively. On the other hand, as the temperature and atmosphere of thermal annealing are the critical parameters which also affect the emission behavior of CMS:Eu, a complete study of the emission behavior dependence on these parameters is essential for its practical applications.

In this paper, we have studied the effects of temperature and annealing atmosphere on the emission behaviors of Eu-doped CMS. Treating the nanophosphors at different temperatures in different atmospheres, the effects of cation vacancy, ionic radius of

* Corresponding author. Tel.: +82 2 705 8882; fax: +82 2 701 0967.

E-mail address: ykang@sogang.ac.kr (Y.S. Kang).

dopant, substitution sites, and charge imbalance in the crystal lattice on the relative emission of their prominent red and blue emissions have been studied. By controlling the temperature and annealing atmosphere, we could control the $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ inter-conversion rate, and hence could control the efficiency of blue to red or vice-versa conversion of the nanophosphors.

2. Experimental section

2.1. Materials

Calcium chloride (CaCl_2 , 95.0%, Junsei Chemicals Co. Ltd.), magnesium chloride (MgCl_2 , extra pure, Junsei Chemicals Co. Ltd.), tetraethylorthosilicate ($(\text{C}_2\text{H}_5\text{O})_4\text{Si}$, TEOS, 98.0%, Samchung Chemicals), europium(III) chloride hexahydrate, ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9% metal basis, Aldrich), ammonium hydroxide (NH_4OH , extra pure, Jin Chemical Pharmaceutical Co. Ltd.), and ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, 94.0%, Samchung Chemicals) were used as received without further purification. Deionized water was used from a Millipore Milli-Q Gradient Water Purification System, installed with a 0.22 μm Millipak membrane filter.

2.2. Synthesis

Eu-doped $\text{CaMgSi}_2\text{O}_6$ nanoparticles were synthesized by a chemical co-precipitation method, modifying the procedure we reported earlier [10]. First a precursor solution was prepared by

dissolving 0.003 mol of CaCl_2 and 0.003 mol of MgCl_2 in 200 mL of DI water. The mixed solution was vigorously stirred for 30 min at room temperature. After that, 0.006 mol of TEOS and 0.0003 mol of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were introduced into the solution and continuously stirred for 2 h. (Practically TEOS is insoluble in water but it slowly decomposes to an adhesive form of silica.) After that, ammonium hydroxide (28–30%) was added drop-wise to the reaction mixture until its pH reached 10. After the addition of ammonia solution, the color of the reaction mixture turned white, indicating the formation of metal hydroxide phase. The white mixture solution was kept at room temperature under magnetic stirring for another 8 h. Finally, the precipitate was separated by centrifuging and washed several times using DI water. The obtained product was dried at 120 $^\circ\text{C}$, and calcined at 1100 $^\circ\text{C}$ for 2 h in air ambient. The resultant phosphor particles were further treated thermally at various temperature range at 600–1000 $^\circ\text{C}$ either in O_2 atmosphere or in $\text{N}_2 + \text{H}_2$ (96:4, v-v) atmosphere for 4 h.

2.3. Characterizations

For structural analysis, powder X-ray diffraction (XRD) patterns of the samples were recorded using the $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) of a Rigaku X-ray diffractometer. A field emission JEOL JEM 2100F transmission electron microscope (TEM) operating at 200 kV was utilized to determine the size and morphology of the nanophosphors. The samples for TEM measurement were prepared by dispersing a small amount of each phosphor sample in ethanol by ultrasonication; spreading a drop of the colloid over

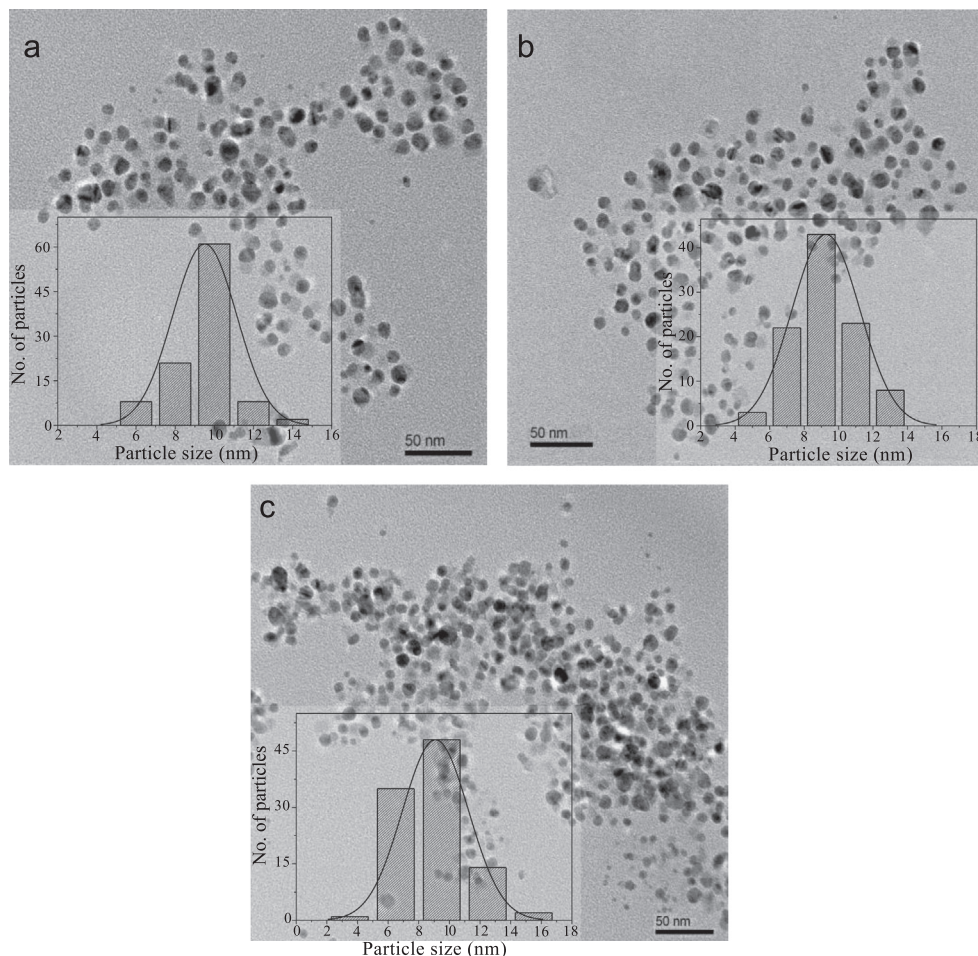


Fig. 1. Typical TEM images of the Eu-doped CMS nanophosphor after calcination: (a) at 1100 $^\circ\text{C}$ in air, (b) re-calcined at 1000 $^\circ\text{C}$ in O_2 , and (c) re-calcined at 1000 $^\circ\text{C}$ in $\text{H}_2 + \text{N}_2$ mixture. Particle size distribution histograms for the samples are presented as insets of the corresponding TEM images.

carbon coated copper grids, and drying under UV lamp. Room temperature photoluminescence (PL) emissions of the powder samples were recorded in a Hitachi F-7000 fluorescence spectrophotometer equipped with ϕ 60 integrating sphere, using the 337 and 395 nm excitations of a Xenon lamp. The excitation wavelengths were selected after careful inspection of the excitation spectra of the samples. Diffuse-reflectance UV–vis spectra of the samples were recorded on a Varian Cary 5000 UV–vis–NIR spectrophotometer equipped with an integrating sphere. Barium sulfate was used as the reference. The diffuse reflectance spectra were treated by the Kubelka–Munk (K–M) formalism. A Thermo VG Scientific (England) Multitab 2000 X-ray photoelectron spectrometer (XPS) was used to estimate the surface elemental composition and chemical state of the elements in the samples. To determine the valence state of the activator Eu in host matrix, X-band electron spin resonance (ESR) spectra of the samples were recorded in a JEOL JEX-FX 200-300 analyzer operating at the microwave frequency of 9.18 GHz, microwave power of 0.99 mW, and modulation field of 100 Hz. The QEs for each sample were measured carefully at least 3 times using a Hamamatsu Absolute PL Quantum Yield Spectrometer equipped with a 150 W Xenon light source, Spectrolon integrated sphere and synthetic quartz as a reference sample.

3. Results and discussion

Typical TEM images of the europium doped CMS samples after calcination at 1100 °C in air and subsequent re-calcination in O₂ or H₂+N₂ (94:6, v-v) atmosphere are presented in Fig. 1. Formation of well dispersed nanoparticles in the 4–16 nm size range with average size of about 9 nm is clear for the air annealed sample (Fig. 1a). As can be observed from Fig. 1b and c, re-calcination of the nanophosphor either in O₂ or in H₂+N₂ ambient does not affect the size or size distribution of the nanoparticles considerably. However, depending on the nature of calcination ambient, the high temperature calcination process induces either reduction or oxidation of the incorporated Eu ions, changing their emission behaviors.

As can be seen from Fig. 2, the air-annealed (at 1100 °C) nanophosphor reveals its dual emission behavior with prominent PL bands in blue (peak at 450 nm) and red (peaks at 590 and 615 nm) spectral regions. However, after re-calcination in O₂ or N₂+H₂ atmosphere, the nanophosphor behaved as single emitting phosphor, revealing only the red emissions (Fig. 3) or blue emission (Fig. 4), respectively.

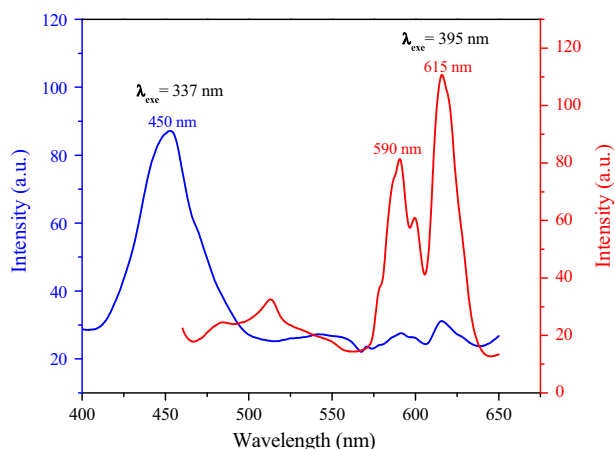


Fig. 2. Emission spectra of the Eu-doped CMS nanophosphor calcinated in air at 1100 °C, under 337 and 395 nm excitations.

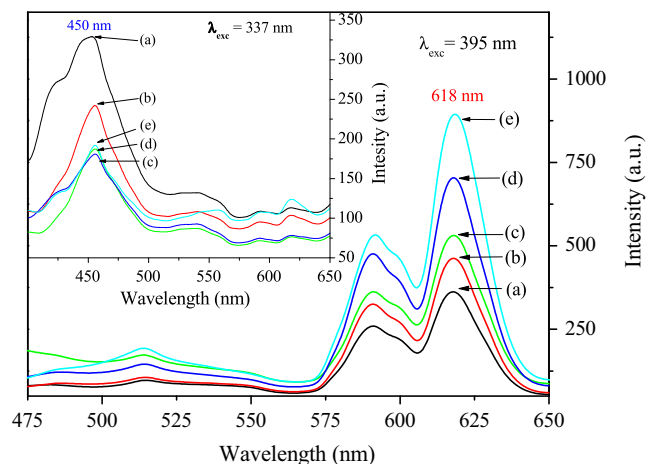


Fig. 3. Emission spectra of the Eu-doped CMS nanophosphor with excitation wavelength 395 nm (inset shows emission spectra with excitation wavelength 337 nm) after re-calcinations at (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C and (e) 1000 °C in O₂ atmosphere.

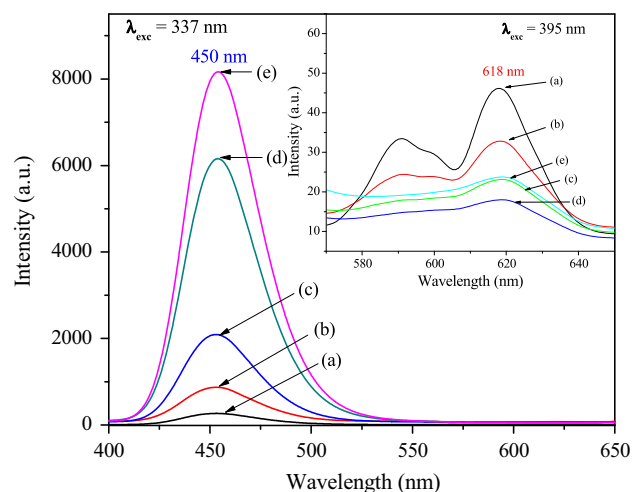


Fig. 4. Emission spectra of the Eu-doped CMS nanophosphor with excitation wavelength 337 nm (and inset shows emission spectra with excitation wavelength 395 nm) after re-calcinations at (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, and (e) 1000 °C in N₂+H₂ (96:4, v-v) atmosphere.

It is well known that Eu³⁺ ions in CMS matrix generate emissions in the red (570–750 nm) spectral region due to their characteristic ⁵D₀–⁷F_J (J=0–4) inter-band transitions. On the other hand, incorporation of Eu²⁺ ions in CMS generates a broad blue emission peak around 450 nm, associated to their characteristic 4f⁶5d → ⁴f₇ inter-band transitions [10]. Due to these distinct characteristics of Eu³⁺ and Eu²⁺ ions, apart from XPS (Figure S1), the oxidation state of Euⁿ⁺ ions in CMS can be monitored easily using spectroscopic techniques such as diffused reflectance spectroscopy (DRS) (Figure S2) and PL spectroscopy. However, incorporating Eu ions fully in trivalent state in CMS is hard to achieve [10].

To study the effect of temperature on the oxidation and reduction ability of europium, the pre-annealed (in air ambient) CMS:Eu nanophosphor was re-calcinated either in O₂ (for red emission) or in N₂+H₂ atmosphere (for blue emission) in between 600 °C and 1000 °C (Figs. 3 and 4). On increasing the temperature of re-calcination in O₂ atmosphere, the intensity of red emission gradually increased at the expense of the blue emission, indicating a gradual transformation of Eu²⁺ ions to Eu³⁺ ions. On the other hand, there are very few conditions reported in the literature suitable for the reduction of trivalent rare-earth ions to divalent

(RE³⁺ to RE²⁺) state in solids [14], basically due to the stringent restrictions like: i) no oxidizing ion should be present in the host crystal, ii) the dopant trivalent RE³⁺ ion must replace the cation of distinct valency in the host lattice, iii) the substituted cations must have similar radii to the dopant ions, and iv) the host lattice must have an appropriate crystal structure [14].

As our synthesized CMS nanocrystals contain Ca²⁺, Mg²⁺ and Si⁴⁺ ions in their lattice sites which are not strong oxidizing agents, condition i) of the above mentioned restrictions is satisfied. Following the condition ii) when Ca²⁺ ions in the CMS lattice sites get replaced by Eu³⁺ ions, to maintain the charge balance, two Eu³⁺ ions are needed to substitute three Ca²⁺ ions. Hence a cation vacancy (V_{Ca}⁰) defect is formed in the lattice. The number of cation vacancies in the lattice depends on available energy, and hence the temperature of thermal treatment or calcination. The relationship between the number of vacancies and temperature can be expressed as [15]

$$N_v = N_0 e^{(-W/kT)} \quad (1)$$

where N_v is the number of vacancy sites, N_0 the total number of atoms in the crystal, W the energy of vacancy formation, k is the Boltzmann constant, and T is the temperature in K. On multiplying the numerator and denominator of the exponent of Eq. (1) by Avogadro's number N , we obtain the relation

$$\frac{N_v}{N_0} = e^{-H_f/RT} \quad (2)$$

where $H_f = WN$ is the activation energy (energy required to form one mole of vacancies), and $R = kN$ is the gas constant (8.31 joules per mole). Considering $H_f = 9.29$ eV/particle [2] for Ca²⁺ self-diffusion in CMS (where Ca²⁺ gets replaced by Eu²⁺/Eu³⁺), the values of N_v/N_0 ratio or the probability of vacancy formation in CMS, which were solely due to thermal treatment (intrinsic defects), was calculated for different temperatures (Table 1). As can be seen, though on increasing the calcination temperature the probability of vacancy formation in CMS increases drastically, the probability of vacancy formation is too low to be considered significantly even for calcination at 1000 °C. Therefore, it is worth to believe that the vacancies in CMS:Eu are formed mainly due to the replacement of Ca²⁺ ions from its crystal lattice by Eu³⁺ ions. In the third column of Table 1, the percent of europium ions in trivalent state (Eu³⁺, the fraction of total europium ions in the host) estimated from the red emission component have been provided. As the incorporation of every two (2) Eu³⁺ ions will create one Ca-vacancy (V_{Ca}⁰), the percent of V_{Ca}⁰ would be half of the percent of incorporated Eu³⁺ ions, provided in the last column of Table 1.

The formation of vacancy at high temperature is the fundamental aspect for any oxide material, which is always limited by the charge balance in the lattice [16]. In fact, the V_{Ca}⁰ values provided in the last column of Table 1 are their maximum possible values in our Eu-doped CMS nanoparticles. Due to the earlier mentioned charge balance limitation, it is impossible to convert all

the europium ions to their trivalent charge state (Eu³⁺) in CMS, i.e. a 100% conversion of Eu²⁺ to Eu³⁺ is impossible. We observed that only about 70% of europium ions can be incorporated in CMS lattice in Eu³⁺ state by producing V_{Ca}⁰ centers.

As the calcination of the Eu-doped CMS nanophosphor in oxidizing environment favors the formation of Eu³⁺ ions, it will enhance the number of cation vacancies in the sample. On the other hand, while annealing in reducing atmosphere, such as in N₂+H₂ ambient, cation vacancies would not be formed due to the charge balance (one Eu²⁺ will replace one Ca²⁺) in the crystal lattice. As can be seen from the XRD spectra presented in Fig. 5, all the samples revealed diffraction peaks related only to the monoclinic CMS phase, with inter-planer spacing closely matching with their standard values (JCPDS #01-070-3482). The nanophosphor re-calcined in H₂+N₂ atmosphere revealed sharper and intense diffraction peaks in comparison to the nanophosphor calcined in air or re-calcined in O₂ atmosphere. Moreover, the weaker and broader diffraction peaks revealed at around $2\theta = 30.30^\circ$ and 30.90° in the former (air-annealed) sample become sharper and well resolved in the latter (re-calcined in H₂+N₂ atmosphere), indicating its lower structural defect content. The fraction of Eu ions incorporated in Eu³⁺ states could be estimated (Table 1 and Figure S1) from the XPS and PL spectra of the CMS:Eu samples calcinated at different temperatures in O₂ ambient. Our PL estimated Eu³⁺ % (Table 1) reveals that even after 4 h of thermal treatment at 1000 °C in O₂ atmosphere, only about 70% of incorporated europium remains in Eu³⁺ state. However, the XPS estimated Eu³⁺ % in the samples are higher (Table 1). The difference between the two sets of Eu³⁺ at% values reduces for

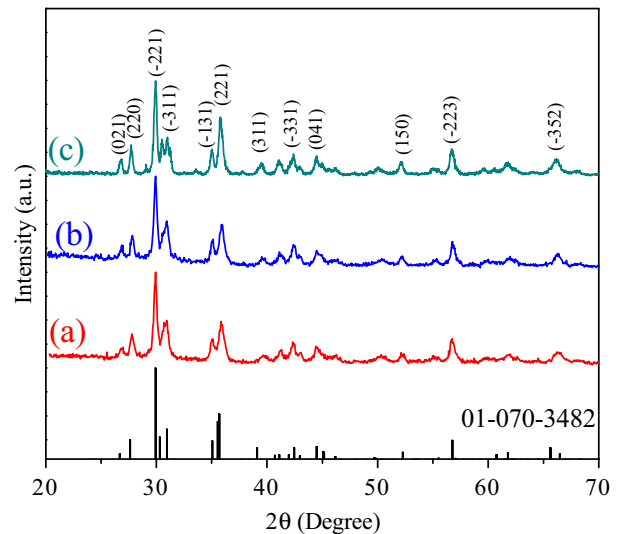


Fig. 5. XRD spectra of the Eu doped CMS nanophosphor: (a) calcinated in air at 1100 °C, (b) re-calcinated at 1000 °C in O₂ atmosphere, and (c) re-calcinated at 1000 °C in N₂+H₂ (96:4, v-v) atmosphere.

Table 1

Estimated vacancy formation probability and Eu³⁺ % in undoped and Eu-doped CMS nanophosphors after calcination in O₂ atmosphere at different temperatures.

| Calcination temperature (K) | Estimated N_v/N_0 in undoped CMS | CMS:Eu re-calcinated in O ₂ ambient | | |
|-----------------------------|------------------------------------|--|----------------------------------|--|
| | | PL estimated Eu ³⁺ % | XPS estimated Eu ³⁺ % | V _{Ca} ⁰ formed due to Eu ³⁺ incorporation (in percent of incorporated Eu ions) (%) |
| 873.15 | 6.16×10^{-39} | 36 | 84.08 | 18 |
| 973.15 | 5.20×10^{-35} | 51 | – | 25.5 |
| 1073.15 | 8.14×10^{-32} | 62 | 87.59 | 31 |
| 1173.15 | 3.64×10^{-29} | 65 | – | 32.5 |
| 1273.15 | 6.23×10^{-27} | 70 | 89.53 | 35 |

the samples calcinated at higher temperatures, though the trend remains as the same. The significant lower Eu^{3+} at% estimated from the red emission band of (PL spectra) the samples calcinated at lower temperatures is due to the presence of Eu ions in both the oxidation states, generating closely spaced energy levels promoting nonradiative recombinations, as has been explained later.

When the CMS:Eu nanophosphor was re-calcinated in N_2+H_2 atmosphere, the neutral V_{Ca}^x vacancies transform to doubly negatively charged V_{Ca}^{2-} vacancies (due to the absence of excess Ca^{2+} ions), behaving as electron donors. At the same time, two Eu^{3+} ions become electron acceptors ($2\text{Eu}_{\text{Ca}}^{\bullet}$). It can be seen that the values of N_v/N_0 , i.e. the fraction of cation vacancy in undoped CMS increases sharply with the increase of annealing temperature. On the other hand, the at% of incorporated europium in Eu^{3+} state in the nanophosphor also increases when annealed in O_2 atmosphere due to $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ transformation. On thermal annealing in N_2+H_2 atmosphere, due to the charge (negative) transfer from the charged vacancy defects to the Eu^{3+} site, the trivalent Eu^{3+} reduces to divalent Eu^{2+} . The whole process can be expressed by Eqs. (3)–(5) [18]. When the trivalent Eu^{3+} ions are doped into CMS, they would replace Ca^{2+} ions with charge imbalance. In order to keep the charge balance, three Ca^{2+} ions get replaced by two Eu^{3+} ions ($2\text{Eu}_{\text{Ca}}^{\bullet}$) creating doubly negatively charged vacancy (V_{Ca}^{2-}). This doubly negatively charged vacancy acts as electron donor, and $2\text{Eu}_{\text{Ca}}^{\bullet}$ acts as electron acceptor. Consequently, on thermal treatment in N_2+H_2 atmosphere, the negatively charged V_{Ca}^{2-} vacancy defect will transfer electron to $2\text{Eu}_{\text{Ca}}^{\bullet}$ and reduce Eu^{3+} to Eu^{2+}



and



By calcinating at 1000 °C in H_2+N_2 atmosphere, about 99% of the incorporated Eu atoms could be transformed to Eu^{2+} state (Table 2).

In the monoclinic crystalline phase of $\text{CaMgSi}_2\text{O}_6$, Ca^{2+} sites have six-fold oxygen coordination. As the radius of Ca^{2+} ion is about 0.100 nm in such coordination [17], they can be replaced by Eu^{3+} (ionic radius=0.0947 nm) or Eu^{2+} (ionic radius=0.117 nm) [18] easily with size-misfits much lower (5.3% and 17%, respectively) than the 30% limit [18]. On the other hand, due to much smaller ionic radius of Mg^{2+} (0.072 nm) and Si^{4+} (0.026 nm) ions in six-fold and four-fold coordination, respectively [19], their size-misfits with the Eu^{3+} or Eu^{2+} ions are much higher (> 30% in both the cases). Therefore, according to the restrictions iii) and iv), substitution of Mg^{2+} or Si^{4+} ions from their lattice sites either by Eu^{3+} or by Eu^{2+} ions is very much unlikely.

Table 2

Quantum efficiency and PL estimated % of $\text{Eu}^{3+}/\text{Eu}^{2+}$ conversion in Eu-doped CMS nanophosphor calcinated at different temperatures. The % conversion of each emission refers to the % of the total Eu ions in the corresponding sample.

| Calcination temperature (°C) | Eu doped CMS re-calcinated in O_2 | | Eu doped CMS re-calcinated in N_2+H_2 | |
|------------------------------|--|------------|---|-------------|
| | % Eu^{3+} conversion | % QE (red) | % Eu^{2+} conversion | % QE (blue) |
| 600 | 36 | 20.4 | 87.26 | 3.4 |
| 700 | 51 | 24.5 | 97.01 | 4.1 |
| 800 | 62 | 28.2 | 98.78 | 5.5 |
| 900 | 65 | 34.3 | 99.63 | 6.8 |
| 1000 | 70 | 39.5 | 99.62 | 9.1 |

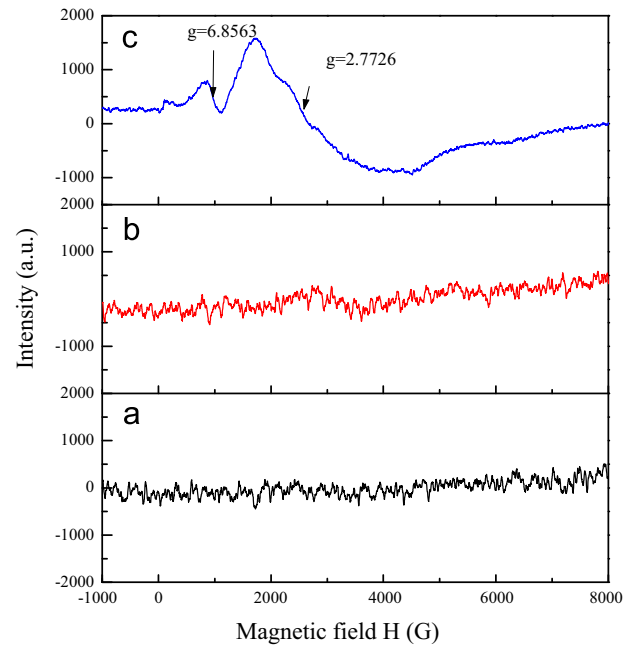


Fig. 6. Room temperature ESR spectra of the Eu-doped CMS nanophosphors: (a) calcinated in air at 1100 °C, (b) re-calcinated at 1000 °C in O_2 , and (c) re-calcinated at 1000 °C in N_2+H_2 (96:4, v-v) atmosphere.

The QEs for each sample were measured carefully at least 3 times using a Hamamatsu Absolute PL Quantum Yield Spectrometer equipped with a 150 W Xenon light source, Spectrolon integrated sphere and synthetic quartz as a reference sample. From Table 2 and Figure S3, it can be seen that the measured QE value increases gradually with an increase in calcination temperature. For lower temperature annealing (calcination) of the nanophosphor, incorporated europium ions exist in both divalent and trivalent states. The mixed oxidation states of Eu ions generate a number of closely spaced energy levels causing the recombination of excited electrons in nonradiative manner, which is the main reason for lower quantum efficiency of the samples calcinated at lower temperatures. In fact, the excitation wavelength, QE of the phosphor, and oxidation state of the dopant are inter-related, and there exists no literature report on the Eu-doped CMS with high QE.

We could monitor the transformation process of Eu^{3+} to Eu^{2+} and vice versa on calcination of the nanophosphor in different atmospheres by electron spin resonance (ESR) spectroscopy (Fig. 6). Electron spin resonance is the process of resonant absorption of microwave radiation by paramagnetic ions or molecules with at least one unpaired electron spin of paramagnetic nuclei species in the presence of a static magnetic field [20]. The relation between magnitude of microwave frequency and crystal field strength is most important for ESR spectrum of Eu^{2+} ion. There are 7 free electrons in the f orbital of Eu^{2+} ion, of which 6 form three electron pairs and one remain unpaired. Due to the presence of this unpaired electron, the X-band ESR spectrum of CMS: Eu^{2+} should reveal a splitted broad signal, characteristic of its hyperfine splitting. On the other hand, as each Eu^{3+} ion has only 6 free electrons in its f orbital, all the electrons remain paired, and hence the CMS: Eu^{3+} sample should not produce any signal in its ESR spectrum. As can be seen from Fig. 6, the ESR pattern of the powder CMS:Eu nanophosphor re-calcinated in N_2+H_2 ambient presents a broad weakly splitted spectrum with g factors 2.7726 and 6.8563 (Fig. 6c). On the other hand, for the CMS:Eu nanophosphors either calcinated in air or in O_2 ambient, the ESR band is almost absent (Fig. 6a and b).

Eu^{2+} ion has ground state term $^8\text{S}_{7/2}$ which means 8-fold degenerate levels for Eu^{2+} as a free ion. When Eu^{2+} ion is

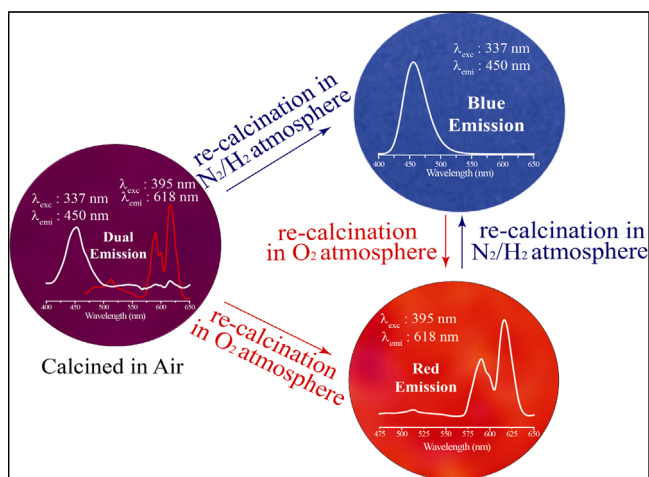


Fig. 7. Schematic presentation of blue and red emissions and the conversion processes for the CMS:Eu nanophosphors. The background color images are the real emission images of corresponding nanophosphors in powder form, digitally photographed under the excitations of 337 and 395 nm of a UV lamp. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

surrounded by strong crystal field, this 8-fold degenerate state will split into four doubly degenerate energy levels and remaining degeneracy will be removed by the Zeeman effect. As a result, the transitions of free electrons would reveal spectral line with $g > 2.0$ and $g < 2.0$. The value of g (less than or higher than 2) depends upon the order of Zeeman microwave frequency and the crystal field strength. If the strengths of both the Zeeman microwave frequency and crystal field are of same order, then we can observe a zero field resonance. Smaller microwave frequency than the crystal field splitting will show ESR signal with g value greater than 2.0 ($g > 2.0$) because of Kramers-conjugate states. The higher microwave frequency than the crystal field splitting would reveal ESR transition with g value close to 2.0 ($g \approx 2.0$) [21]. In this study, resonance signals observed at $g = 2.7726$ and $g = 6.8563$ (Fig. 6c) indicate that there are crystal field splitting higher than the microwave frequency 9.450 MHz. The observed values are quite similar to the reported g values of Eu^{2+} in CMS [22]. While the presence of Eu ions in their divalent state in our sample is clear, the manifestation of two g values can be explained considering two stable isotopes of Eu^{2+} with non-zero nuclear magnetic moments (^{151}Eu and ^{153}Eu with $I = 5/2$). Both the isotopes ^{151}Eu and ^{153}Eu have a similar natural abundance (47.82% and 52.18%, respectively). Caravan et al. have reported that g value of ^{151}Eu is larger by a factor of 2.264 than that of ^{153}Eu [23]. In the case of our Eu doped nanophosphor, as the difference between the two g values is of the same order, we believe the observed ESR peaks with $g = 2.7726$ and $g = 6.8563$ in our sample are related to ^{153}Eu and ^{151}Eu , respectively.

The process of $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ inter-conversion during calcination in different atmospheres, and hence the wavelength inter-change in the emission process of CMS:Eu nanophosphor has been presented schematically in Fig. 7. The pure blue phosphor prepared under calcinations in $\text{N}_2 + \text{H}_2$ atmosphere could be converted to pure red phosphor when it was calcinated again under O_2 atmosphere, and vice versa.

4. Conclusions

In summary, well-dispersed Eu-doped CMS nanophosphor in the 4–16 nm size range could be prepared by chemical co-precipitation

and subsequent high temperature calcination in air. The dual emitting nanophosphor could be transformed to single emitting nanophosphor by re-calcination in suitable oxidizing or reducing atmosphere. While a re-calcination in highly oxidizing atmosphere like O_2 convert it to red emitting phosphor of high QE, a re-calcination in reducing atmosphere (like $\text{H}_2 + \text{N}_2$ mixture) convert it to purely blue emitting. The blue and red emitting nanophosphors are inter-convertible by reversing the atmosphere of their calcination. Higher calcination temperature induces higher conversion efficiencies (dual to red or blue, blue to red, and vice versa) for the nanophosphors. Though the calcination process at temperature as high as 1000°C in O_2 atmosphere cannot transform all the europium atoms to its trivalent state, high temperature calcination in reducing atmosphere can transform almost all the incorporated europium atoms to their divalent state. The method of preparing mono-dispersed CMS:Eu nanophosphors capable of emitting in blue, red or in both the spectral regions with relatively high QE would make them interesting for fabricating efficient display devices.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlumin.2014.08.034>.

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