Effect of Co-Dopant on the Phase Structure and Photoluminescence Properties of Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$ Phosphors

S.Y. Pung*, C.H. Chang, M.N. Ahmad Fauzi and S.R. Kasim

School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
E-mail: sypung@usm.my

Abstract. The role of co-dopants, i.e. Dy, Ce, Tb or Y in SMS : Eu, RE$^{3+}$ phosphors sintered using solid state reaction method at 1250°C under forming gas was studied. All SMS phosphors exhibited tetragonal Sr$_2$MgSi$_2$O$_7$ as the domain phase and monoclinic SrSiO$_3$ as the minor phase based on XRD analysis. It is noted that only single blue emission (469nm) contributed by Eu$^{2+}$ ions was detected in RTPL measurement regardless types of co-dopants introduced during the sintering process. This result indicates that the co-dopants did not act as luminance centres in the SMS phosphor. The time-decay PL and temperature dependent PL analysis suggest that Ce$^{3+}$ ions acted as sensitizer which improved the luminescence intensity and afterglow property of SMS phosphor. The present of Dy$^{3+}$ ions pro-longed the afterglow property by introducing more traps density in the SMS phosphor structure. The co-doping of Tb or Y into the SMS phosphor generated many non-radiative recombination centres which deteriorated the optical performance of SMS: Eu$^{2+}$, RE$^{3+}$ phosphor.

1. Introduction

Phosphors have been used in architecture, traffic signs, art and graphics, phosphorescent paint, decoration, watch and clock dials, fishing tackles, toys and other goods for daily use [1-3]. Recently, it has been widely applied in phosphor converted white light emitting diodes (white LEDs). The white LEDs have many excellent properties such as long lifetime (> 100,000 hrs), low power consumption and compact size. However, the conventional yellow emitting phosphor based white LEDs have a poor colour rendering index (<65) due to the lacking of red emission. Thus, a new generation of LEDs i.e. near ultraviolet LEDs combined with multiphase phosphor, with a better colour rendering index is developed. The multiphase phosphor consists of blue emission Sr$_2$MgSi$_2$O$_7$(SMS) based phosphor and Eu$^{2+}$-sensitized red-emitting Ca$_3$Mg$_2$(PO$_4$)$_3$ (CMP) phosphor[4-5].

SMS phosphor is an alkaline earth silicate which has attracted attention for the applications in long lasting phosphor too due to its relatively high brightness and chemical stability. Various synthesis methods have been used to prepare this silicate based phosphor material. For examples, sol gel method [6], combustion method [7], and solid state reaction method [8] are the commonly used synthesis techniques for phosphor materials. Nevertheless, these techniques have their own strengths and limitations. The sol gel method requires expensive starting materials and long reaction time whereas the product that synthesized using combustion method has a low brightness and the afterglow lasts shortly. For co-precipitation method, it induces in homogeneity and agglomeration in the powders easily. On the other hand, solid state reaction is the most widely used method even nowadays in the industry due to its simplicity, low cost and easily controlled operation [2, 9].
The blue emission of SMS phosphor could be achieved by doping of Eu$^{2+}$ ions. The Eu$^{2+}$ ion is proposed to substitute into the Sr$^{2+}$ site since it has similar ionic size (1.25 Å) to that of Sr$^{2+}$ ions (1.26 Å) in SMS lattice. The Eu$^{2+}$ ion is unlikely substituted into the Mg$^{2+}$ site (0.72 Å) and Si$^{4+}$ site (0.26 Å) as the ionic radii are small. During the substitution, two Eu$^{3+}$ ions occupy two Sr$^{2+}$ sites and then one Sr$^{2+}$ vacancy is created by charge compensation in vicinity. The Sr$^{2+}$ vacancy acts as electron donor and the two Eu$^{3+}$ ions at the Sr$^{2+}$ sites become acceptors. Thus, two electrons in each vacancy will transfer to two adjacent Eu$^{3+}$ ions and then Eu$^{3+}$ ions are formed [10-11]. The blue emission is produced because of the 5d →4f transition after optical excitation.

As the absorption and emission bands of Eu$^{2+}$ are broad because of the crystal field splitting effect, these ions are well suited for LED characteristics. Nevertheless, the emission peak and its intensity of Eu$^{2+}$ emission can vary as a result of strong dependence on the lattice symmetry, host composition and crystal structure [12-15]. In this work, SMS:Eu$^{2+}$ phosphor co-doped with Dy$^{3+}$, Ce$^{3+}$, Tb$^{3+}$ or Y$^{2+}$ were synthesized by solid state reaction. The SMS:Eu$^{2+}$, Dy$^{3+}$ phosphor was the most studied phosphor [16-17] and thus it was used as control sample. These co-dopants might acts as (i) another luminescent centre, (ii) bridges to transport carriers between trapping and emission centres or (iii) as defect related traps in the host. The influence of co-dopants on their photoluminescence properties, particularly the temperature dependent photoluminescence and time decay photoluminescence were comparatively investigated in detail. The result from these photoluminescent measurements provides a better understanding on the luminescence mechanism and energy transfer in the SMS:Eu$^{2+}$,Re$^{3+}$ phosphor materials.

2. Experimental setup

The SMS: Eu$^{2+}$, RE phosphors were prepared by solid state reaction technique. The precursors were SrCO$_3$, MgO, SiO$_2$, Eu$_2$O$_3$, CeO$_2$, Dy$_2$O$_3$, Y$_2$O$_3$ and Tb$_2$O$_3$ powder. The precursors were weighed according to the given stoichiometric amount (Sr$_{1.96}$MgSi$_2$O$_7$: Eu$_{0.015}$, RE$_{0.005}$) and mixed thoroughly in an agate mortar. A small amount of H$_3$BO$_3$ (10 mol% of silicate) was used as flux. The mixed precursor were sintered at 1250°C for 2 hrs under reductive ambient (95% N$_2$ and 5% % H$_2$). The samples were labelled based on their corresponding co-dopants. For example, SMS co-doped with Ce was labelled as SMSECe.

The X-ray diffraction patterns of SMS phosphors were recorded by Philip model PW 1729 X-Ray powder diffractometer (Cu K$_\alpha$, $\lambda = 0.154$ nm) for structural analysis. The weight percentage of phases present in the as-synthesized samples were estimated based on the area under the diffraction peaks of XRD using XPert Highscore Plus program (version 2.1). The morphology and composition of the SMS phosphors were characterized using Field Emission Scanning Electron Microscopy (FESEM, Zeiss, Supra 35 VP) and Electron Dispersive X-Ray (EDX). The photoluminescence (PL) properties of SMS phosphors were measured by Spectra Fluorolog-3 from Horiba Jobin Yvon using 450 W Xe lamp as the excitation source.

3. Results and discussion

Figure 1(a) gives the XRD patterns of the as-sintered phosphor doped with various types of co-dopants. The results show that the phases present in all the samples are mostly composed of tetragonal Sr$_2$MgSi$_2$O$_7$ and a small amount of monoclinic SrSiO$_3$. Other than these phases, no other phase was observed in any of the samples. It is clearly seen that the positions and intensity of the diffraction peaks for all the samples are almost the same. This implies that the type of co-dopants has no effect on the host structure. The quantitative phase analysis was estimated for all the samples using XPert Highscore Plus program (version 2.1) as shown in Figure 1(b). The weight fraction of Sr$_2$MgSi$_2$O$_7$ phase is slightly different by varying the type of co-dopants. SMSECe exhibits the highest weight fraction of Sr$_2$MgSi$_2$O$_7$ phase (67.1 wt%), followed by SMSED (66.7 wt%), SMSEY (66.4 wt%) and
SMSETb (65.56 wt%). Although the phosphors contained SrSiO\(_3\) phase, it was still named as SMS phosphors throughout the paper for the convenient expression.

The surface morphology of SMS:Eu\(^{2+}\) phosphors co-doped with Ce, Dy, Y and Tb are shown in Figure 2 (a) - (d), respectively. Generally, the morphology of all the samples composed of agglomerated irregular grains. The shape and the size of grains are non-uniform, indicating that the type of co-dopants does not have much influence on the surface morphology and grain shape as well as grain size.

The as-sintered SMS:Eu\(^{2+}\) co-doped with Dy is yellowish in colour. The blue emission was emitted when it was optically excited using UV light (254 nm) for 5 min. Figure 3(a) shows that the emission spectra of all the samples present a single band peaking at 469 nm when excited at 375 nm. The 469 nm broad band corresponds to the \(^{8}\)S\(_{7/2}\) (4f\(^7\)) ground state of Eu\(^{2+}\) ions \([9]\). However, there is no other emission peak observed in the PL result. The emission peaks of Ce\(^{3+}\) (370 nm) \([18]\), Dy\(^{3+}\) (480nm) \([19]\), Tb\(^{3+}\) (542 nm) \([20]\) and Y\(^{3+}\) (601 nm) \([21]\) are absent in the emission spectra. Thus, it indicates that these RE ions did not become the luminescent centres in the SMS host lattice. As no emission in the range of 570 - 750 nm, this suggests that the Eu\(^{3+}\) ions have been reduced completely to Eu\(^{2+}\) ions.

The excitation spectra at the emission wavelength 469 nm are shown in Figure 3(b). The excitation spectrum has a broad band ranges from ultraviolet to visible light and with the main peak at 423 nm. The broad absorption and emission bands of Eu\(^{2+}\) are ascribed to crystal field splitting effect. This phenomenon is suitable for fabrication of white LEDs. In addition, there is no shift of the emission and excitation wavelength in all the samples. This implies that RE co-doping does not cause any significant changes on the emission and excitation spectra.

Time-decay photoluminescence measurement (TDPL) at room temperature was performed to measure the decay of Eu\(^{2+}\) emission at 469 nm upon 375 nm excitation. The time decay of 469 nm of the SMS:Eu\(^{2+}\), Ce\(^{3+}\) phosphor is shown in Figure 4(a). The decay curves can be fitted into a single exponential function as

\[
I(t) = I_o + A \exp \left(-t/t_1\right)
\]

Figure 1. (a) XRD patterns and (b) weight fraction of SMS:Eu\(^{2+}\) phosphor co-doped with Ce, Dy, Y and Tb

Figure 2. Surface morphology of SMS:Eu\(^{2+}\) phosphors sintered at 1250°C co-doped with (a) Ce (b) Dy (c) Y and (d) Tb
where $A_1$ is constant, $I_0$ is the luminescence intensity at time 0, $t$ and $t_1$ are the decay time for the exponential components, respectively. The above fitting is reasonable as only one Sr$^{2+}$ sites is available in the Sr$_2$MgSi$_2$O$_7$ phase [4]. From the fitted function, the measured lifetime of SMS:Eu$^{2+}$, Ce$^{3+}$phosphor is 0.5402 ms. The time decay PL of other SMS:Eu$^{2+}$ phosphors co-doped with Dy, Tb and Y are shown in Figure 4(b). The lifetimes determined from the fittings are 0.44603 ms, 0.31092 ms and 0.26921 ms for SMS:Eu$^{2+}$ phosphors co-doped with Dy, Tb and Y, respectively.

![Figure 3](image1.png)

**Figure 3.** SMS phosphors prepared at different type of co-dopants (a) emission spectra monitored at the excitation wavelength 375 nm and (b) excitation spectra monitored at the emission wavelength 469 nm

![Figure 4](image2.png)

**Figure 4.** Time decay PL of SMS: Eu$^{3+}$ phosphors co-doped with (a) Ce$^{3+}$ and (b) various co-dopants (excitation wavelength 375 nm)

This result is similar with the works of Brito et al. [22] and Guo et al. [23] whereby Ce and Dy co-doping with Eu contribute to a better luminescence property. This could be due to the co-dopant possess energy levels close to that of the intrinsic trap and therefore increasing the trap density. The higher the trap density is, the better the afterglow property of the phosphor. Other co-dopants (i.e Tb and Y) have a lower trap density and therefore contributing to the poor afterglow property. The poor afterglow property (short lifetime) of SMS:Eu$^{2+}$, Y$^{3+}$phosphor could be ascribed to the defect impurities related to Y$^{3+}$ co-dopants that acted as recombination centres rather than traps. It is also suggested that the addition of Tb and Y may destroy some of intrinsic traps in the SMS phosphor. This phenomenon is known as quenching of co-dopants.

Since the afterglow property of SMS phosphor is caused by the thermal detrapping of charge carriers, the intensity of temperature dependent luminescent provides information related to the traps density in the phosphor. Figure 5 (a)-(d) gives the temperature dependent emission spectra of SMS:Eu$^{2+}$ phosphors co-doped with various dopants. It is noted that only one emission peak, i.e 469 nm was observed in all the phosphor samples. Because of the single position of Sr in the SMS host lattice, the 5d states of Eu$^{2+}$ are split into two energy levels, which can be designated by $t_{2g}$ (the lowest) and $e_g$ (the highest). The single blue emission of 469 nm in the phosphors is expected to occur from the lowest $t_{2g}$ level to the 4f$^7$ ground state. It is worth mentioning that the relaxed 5d state of Eu$^{2+}$...
is located 0.29 eV below the bottom of the conduction band, otherwise the luminescence emission would be quenched by rapid auto-ionization process [24].

The variation of the relative emission intensity of these phosphors as a function of temperature is plotted in Figure 5(e). It can be clearly seen that SMSECe phosphor has comparatively good temperature quenching resistance as it is still having 38.8% of normalized emission intensity at 300 K. It is commonly known that the emission band of Ce$^{3+}$ ions normally have two maxima located at the emission wavelength of 420 nm and 450 nm, attributed to the crystal field splitting of the 5d band ($^2F_{5/2}$ and $^2F_{7/2}$ states) and the ground state for the 4f electronic configuration [25]. Since there is no emission peak contributed from Ce$^{3+}$ ions was found in this study, the Ce$^{3+}$ ions were not acted as luminescence centre. Instead, the PL intensity and lifetime of SMS:Eu$^{2+}$ phosphor was enhanced by co-doping with the Ce$^{3+}$ ions as shown in Figure 3(a) and Figure 4(b). Thus, the Ce$^{3+}$ ions was proposed acting as sensitizer. The energy absorbed by the Ce$^{3+}$ ions was transferred to Eu$^{2+}$ ions. This could be verified by the spectral overlap between the PL excitation spectrum of Ce$^{3+}$ and the PL emission of Eu$^{2+}$ in Figure 3(a) and (b). Moreover, the energy transfer rate from Ce$^{3+}$ to Eu$^{2+}$ is generally faster than the emission rate of Ce$^{3+}$ in the dipole-dipole interaction [26], allowing higher emission intensity [Figure 3(a)] and a longer decay lifetime [Figure 4(b)].

In the case of SMS: Eu$^{2+}$ co-doped with Dy, the unique Dy$^{3+}$ emission peak with the wavelength of 486 nm or 577 nm is also not present [27]. Thus, the co-dopant of Dy$^{3+}$ plays a role as electron-trapping centre rather than a luminescent centre in the host crystal lattice [28]. Exposing SMS: Eu$^{2+}$, Dy$^{3+}$ phosphor to ultraviolet light excites Eu$^{2+}$ to a 4f$^{6}$5d state which is located inside the conduction band. A free electron is created by auto-ionization, leaving Eu$^{3+}$ ion behind. The free electron is trapped by Dy$^{3+}$ to form Dy$^{2+}$ (0.66 eV located below the bottom of the conduction band) [24]. The afterglow, i.e. the delay luminescence after excitation, is caused by the thermally activated release of the electron from Dy$^{2+}$ back to the conduction band with subsequent recombination with Eu$^{3+}$ leading to 5d $\rightarrow$ 4f emission at 469 nm. Thus, the persistence time is pro-long. The depth of the trap influences the lifetime of the luminescence of SMS phosphor. In addition to Dy$^{3+}$ ions, other defects such as oxygen vacancies which trap the charge carriers could delay the emission too.

The SMS:Eu$^{2+}$ co-doped with Tb has relatively shorter lifetime, poorer luminescence intensity and thermal quenching resistance in our study. This observation agrees well with the finding of Li et al. that the increase of amount of Tb$^{3+}$ ions reduced the lifetime of Eu$^{2+}$ emission. Under UV irradiation,
electrons were optically excited into the lowest excited state (4f<sup>5d</sup>) of Eu<sup>2+</sup> from the ground state (5d<sup>7S<sub>2</sub></sup>). Some of these excited electrons relaxed back to the ground state, giving the blue emission at 469 nm. The other electrons of Eu<sup>2+</sup> transferred to the excited level (5D<sub>4</sub>) of Tb<sup>3+</sup> ions and could lose its energy as phonon. Therefore, the Tb co-dopants acted as non-radiative recombination centres but not traps/luminescence centres in our work. It is worth mentioning that the weak absorption of Tb<sup>3+</sup> ion at 423 nm due to the 5F<sub>5</sub>→5D<sub>4</sub> transitions and its much narrower FWHM do not favour the co-dopant to act as activator [5]. Lastly, the SMS:Eu<sup>2+</sup>,Y<sup>3+</sup> phosphor has the poorest temperature quenching resistance as it’s relatively emission intensity dropped to 22.6% at 300 K. This is attributed to the effect of Y<sup>3+</sup> ions which acts as the thermal quenching centre and reduces the luminescence.

4. Conclusions

The SMS: Eu<sup>2+</sup>, RE<sup>3+</sup> phosphor were sintered using solid state approach at 1250°C under reducing atmosphere. The effect of co-dopants (RE<sup>3+</sup>), i.e. Ce, Dy, Y and Tb on the luminescence properties of phosphor was studied. Generally, only one blue emission peak centered at 469nm was found regardless the types of co-dopants used in the sintering process. This blue emission was ascribed to the Eu<sup>2+</sup> ion which acts as luminescence centre. The study shows that Ce<sup>2+</sup> ions were the sensitizer in the SMS: Eu<sup>2+</sup>, RE<sup>3+</sup> phosphor by pro-longing the afterglow and by enhancing the luminescence intensity and thermal quenching resistant. The SMS phosphor co-doped with Dy has the comparable emission intensity and long afterglow properties. This is attributed to the Dy ions which introduced more intrinsic traps into the SMS host lattice. The co-doping of Tb or Y was found deteriorated the optical performance of the SMS: Eu<sup>2+</sup>, RE<sup>3+</sup> phosphor with poor emission intensity and short decay lifetime.

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