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## Eu and Dy co-activated $\text{SrB}_2\text{Si}_2\text{O}_8$ Blue Emitting Phosphor: Synthesis and Luminescence Characteristics

(Fosfor  $\text{SrB}_2\text{Si}_2\text{O}_8$  didopkan dengan Eu dan Dy yang Memancarkan Cahaya Biru: Sintesis dan Ciri-ciri Luminesen)

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### ABSTRACT

The main focus in this research was to understand the influence of  $\text{Dy}^{3+}$  and  $\text{Eu}^{3+}$  doping/co-doping and sintering atmosphere on the luminescence properties of  $\text{SrB}_2\text{Si}_2\text{O}_8$ . Single phase Eu and Dy doped/co-doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  ceramics were synthesized in different atmosphere through solid state reaction technique. An inexpensive method was occupied to provide reducing sintering atmosphere. Europium doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  exhibit unusual reduction from trivalent to a divalent oxidation state even in an oxidizing atmosphere. We also discovered co-doping with  $\text{Dy}^{3+}$  ions produced further europium reduction in this phosphor. By manipulating the sintering condition and co-doping, a reddish-purple to blue tune-able phosphor under 390 nm excitations were produced and their Commission International del'Eclairage (CIE) color coordination were calculated and plotted in a CIE 1931 diagram. Photoluminescence spectra of the  $\text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  co-doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  phosphor showed energy transfer from  $\text{Dy}^{3+}$  to  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  which was observable in  $\text{Dy}^{3+}$  f-f excitation transitions and the Dy-O charge transfer bands. A weak 777 nm emission from  $3p^5P$  to  $3s^5S^0$  transition of  $\text{O}^{2-}$  ions were observed in all the samples. The excitation and emission peaks of f-f transition from  $\text{Dy}^{3+}$  and  $\text{Eu}^{3+}$  as well as 4f - 5d transition of  $\text{Eu}^{2+}$  were also discussed. The long excitation band in ultraviolet (UV) region from these doped/co-doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  ceramics produced phosphors with efficient UV excitation for solid state lighting.

**Keywords:** Co-doping; energy transfer;  $\text{Eu}^{3+}$  reduction in air; photoluminescence;  $\text{SrB}_2\text{Si}_2\text{O}_8$

### ABSTRAK

Fokus utama dalam kajian ini adalah untuk memahami pengaruh pengedopan  $\text{Dy}^{3+}$  dan  $\text{Eu}^{3+}$  dan juga atmosfera pensinteran pada ciri-ciri luminesen  $\text{SrB}_2\text{Si}_2\text{O}_8$ . Fasa tunggal seramik  $\text{SrB}_2\text{Si}_2\text{O}_8$  yang didopkan dengan Eu dan Dy telah disintesis dalam suasana yang berbeza melalui teknik tindak balas keadaan pepejal. Kaedah yang berkos rendah telah digunakan untuk menyediakan suasana pensinteran menurun.  $\text{SrB}_2\text{Si}_2\text{O}_8$  yang didopkan dengan europium menunjukkan penurunan yang luar biasa daripada keadaan pengoksidaan trivalen kepada dwivalens walaupun dalam suasana pengoksidaan. Kami juga mendapati pengedopan bersama dengan ion  $\text{Dy}^{3+}$  menghasilkan lebih penurunan europium dalam fosfor ini. Dengan memanipulasikan atmosfera pensinteran dan pengedopan, sinaran merah-ungu ke biru diperolehi apabila fosfor dipancarkan dengan ujaan sinaran 390 nm. Koordinasi warna Jawatan kuasa Antarabangsa del'Eclairage (CIE) fosfor tersebut telah diambil dan diplotkan dalam gambar rajah CIE 1931. Spektra fotoluminesen fosfor  $\text{SrB}_2\text{Si}_2\text{O}_8$  yang didopkan bersama dengan  $\text{Eu}^{2+}/\text{Eu}^{3+}$  dan  $\text{Dy}^{3+}$  menunjukkan pemindahan tenaga daripada  $\text{Dy}^{3+}$  ke  $\text{Eu}^{3+}$  dan  $\text{Eu}^{2+}$  yang boleh diperhatikan dalam transisi pengujaan f-f dari  $\text{Dy}^{3+}$  dan Dy-O band pemindahan caj. Sinaran 777 nm yang lemah daripada transisi ion  $\text{O}^{2-}$   $3p^5P$  ke  $3s^5S^0$  juga diperhatikan dalam semua sampel. Puncak pengujaan dan pemancaran transisi f-f dari  $\text{Dy}^{3+}$  dan  $\text{Eu}^{3+}$  disertakan dengan transisi 4f - 5d dari ion  $\text{Eu}^{2+}$  juga dibincangkan. Jalur pengujaan yang panjang dalam rantau ultraungu (UV) daripada seramik  $\text{SrB}_2\text{Si}_2\text{O}_8$  didopkan dengan logam nadir bumi menghasilkan fosfor yang boleh diuja dalam UV dengan berkesan demi kegunaan dalam pencahayaan keadaan pepejal.

**Kata kunci:**  $\text{Eu}^{3+}$  pengurangan udara; fotoluminesen; pemindahan tenaga; pengedopan;  $\text{SrB}_2\text{Si}_2\text{O}_8$

### INTRODUCTION

Borosilicate glass or ceramic system has been the center of interest in many applications including laboratory glassware and optical glass, mainly due to its chemical durability and abundance of  $\text{SiO}_2$  while attaining a low temperature synthesis due to borate as modifier (Sembiring 2011; Zawrah & Hamzawy 2002). Moreover, further investigation into alkaline earth borosilicate system had been a field of interest for its potential in application

such as low cost optical connectors, optical amplifiers and phosphor materials (Jean & Chang 1999; Rao et al. 2014). Also, the applications of low-temperature co-fired ceramics (LTCC) of alkaline earth borosilicate in wireless communication and microwave products has recently immersed (Chen et al. 2013; Krzhizhanovskaya et al. 2010). One of the naturally occurring alkaline earth borosilicate minerals were the danburites ( $\text{CaB}_2\text{Si}_2\text{O}_8$ ). Maleevite ( $\text{BaB}_2\text{Si}_2\text{O}_8$ ) and pekovite ( $\text{SrB}_2\text{Si}_2\text{O}_8$ ) were

analogous species to danburite where the  $\text{Ca}^{2+}$  cations are replaced by  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , respectively. Syntheses of pekovite were firstly performed by Verstegen et al. (1972). However, structural and luminescence investigations on  $\text{SrB}_2\text{Si}_2\text{O}_8$  crystals were very limited. Several researchers has reported on  $\text{Sr}_3\text{B}_2\text{SiO}_8$ ,  $\text{SrB}_2\text{Si}_2\text{O}_8$ , and  $\text{BaB}_2\text{Si}_2\text{O}_8$  crystals for its potential in phosphor applications and showed promising result (Sabikoglu 2013; Saradhi et al. 2010; Wang & Wang 2011; Wang et al. 2009). Additionally, few researchers demonstrated that rare earth doped alkaline earth borosilicate possess good luminescence properties, namely by  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Dy}^{3+}$  ions. Rare earth doped phosphor has always been of significant interest for its long wavelength excitation in UV. This feature is important for application in fluorescent lighting, plasma display phosphor, LED and bills marking. However, to the best of our knowledge, co-doping of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  in a single  $\text{SrB}_2\text{Si}_2\text{O}_8$  host crystal had never been reported before. Also, the search for new and more efficient phosphor material is ongoing.

This current work investigated the luminescence properties of rare earth doped ( $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$ )  $\text{SrB}_2\text{Si}_2\text{O}_8$  for phosphor applications.  $\text{SrB}_2\text{Si}_2\text{O}_8$ :  $\text{Dy}^{3+}$ ,  $\text{SrB}_2\text{Si}_2\text{O}_8$ :  $\text{Eu}^{2+}/\text{Eu}^{3+}$ , and  $\text{SrB}_2\text{Si}_2\text{O}_8$ :  $\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  polycrystalline samples were synthesized under oxidizing atmosphere of air and reducing atmosphere of carbon monoxide (CO). In this study, instead of using sophisticated  $\text{N}_2$  or Ar gas flow system, we provided reducing atmosphere into the sintering vicinity through an inexpensive technique using carbon powder. Luminescence properties were described in terms of possible excitation and emission transitions of the doped/co-doped rare earth ions in  $\text{SrB}_2\text{Si}_2\text{O}_8$  system. Moreover, the influence of CO in sintering atmosphere and  $\text{Dy}^{3+}$  co-doping on the unusual  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  reduction that were reported earlier were also discussed (Saradhi et al. 2010; Verstegen et al. 1972; Wang et al. 2009). By manipulating the sintering atmosphere and  $\text{Dy}^{3+}$  co-doping, a reddish-purple to blue emissions from  $\text{Eu}^{2+}/\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  co-doped phosphor were achieved. As such, these phosphors show potential for use in white light generation.

## EXPERIMENTAL DETAILS

$\text{SrB}_2\text{Si}_2\text{O}_8$  phosphor samples of 1 mol%  $\text{Eu}^{2+}/\text{Eu}^{3+}$  and 1 mol%  $\text{Dy}^{3+}$  doped/co-doped were prepared via solid state reaction method. Strontium carbonate ( $\text{SrCO}_3$ , 98%), boric acid ( $\text{H}_3\text{BO}_3$ , 99.8%), silicon dioxide ( $\text{SiO}_2$ , 99%), europium oxide ( $\text{Eu}_2\text{O}_3$ , 99.9%), dysprosium oxide ( $\text{Dy}_2\text{O}_3$ , 99.9%) and activated charcoal powder were employed as the precursor material. The precursor materials were weighted and ball milled to assure homogeneous mixture, which was then subjected to calcination to remove moisture. Calcined cakes were grounded in mortar and pelletized to promote intimate contact before sintering at  $1000^\circ\text{C}$  for 5 h in porcelain crucibles. Two series consisting of three samples each were synthesized in air and in carbon monoxide (CO). To create CO reducing atmosphere, smaller crucibles containing phosphor samples were inserted into a larger crucible containing activated charcoal powder and lid-closed. Sintered samples were cooled to room temperature and grounded in mortar for characterizations.



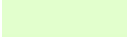



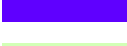


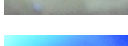


Powder X-ray diffraction data (XRD) were collected by a Siemens Diffractometer D5000 with Cu  $K\alpha$  source ( $\lambda = 1.5406\text{\AA}$ ) at 40 kV tube voltage and 30 mA tube current to verify the phase as well as to study the structure of the samples. Photoluminescence spectra were obtained by a JASCO FP-8500 Series fluorescence spectrometer occupying a 150W xenon arc lamp source. All measurements were carried out at room temperature.

## RESULTS AND DISCUSSION

Table 1 summarized the doping/co-doping material of the  $\text{SrB}_2\text{Si}_2\text{O}_8$  (SBS) phosphor.  $\text{Eu}^{2+}/\text{Eu}^{3+}$  doped SBS were denoted as SBSE, while  $\text{Dy}^{3+}$  singly doped represented by SBSD and lastly  $\text{Eu}^{3+}/\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$  co-doped were SBSED. Small letter 'a' or 'c' denotes the sintering atmosphere for air and CO, respectively.

All the sintered samples were white in colour regardless of doping and sintering condition. Figure 1 showed the X-ray powder diffraction data of the collected samples and PDF card no. 25-1288. The results showed

TABLE 1. Summary of the doping/co-doping material of the  $\text{SrB}_2\text{Si}_2\text{O}_8$  (SBS) phosphor

Sample	$\text{Eu}_2\text{O}_3$ (mol%)	$\text{Dy}_2\text{O}_3$ (mol%)	Sintering atmosphere	Chromaticity coordinate		Calculated Color	Actual color under 390 nm irradiation
				x	y		
SBSE-a	1		Air	0.2398	0.0832		
SBSD-a		1	Air	0.3426	0.3892		
SBSED-a	1	1	Air	0.1645	0.0349		
SBSE-c	1		CO	0.1604	0.0348		
SBSD-c		1	CO	0.3463	0.4208		
SBSED-c	1	1	CO	0.1554	0.0322		

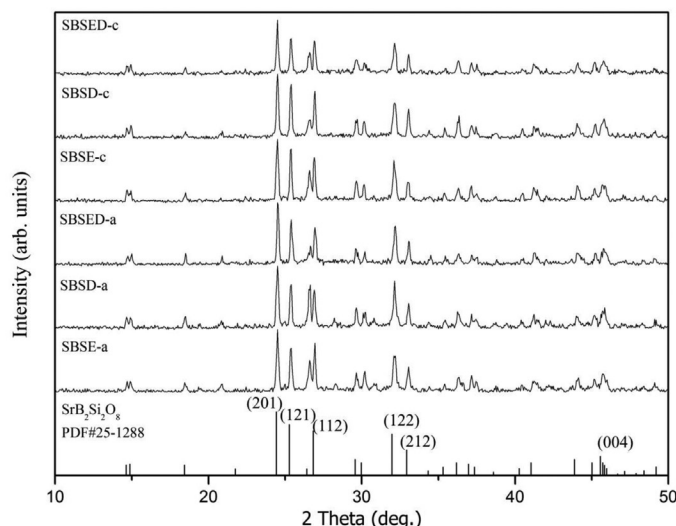


FIGURE 1. XRD patterns of  $\text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  doped/co-doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  compared with PDF#25-1288

that most of the peaks matched with  $\text{SrB}_2\text{Si}_2\text{O}_8$  phase, PDF card no. 25-1288. Moreover, no impurity phase or  $\text{Eu}_2\text{O}_3$  or  $\text{Dy}_2\text{O}_3$  phases were detected up to 1 mol% Eu ions and Dy ions doping or co-doping. Both the air sintered and carbon monoxide sintered sample showed no obvious change in XRD pattern. However, the europium ions doping changed in oxidation state which was displayed by photoluminescence spectra discussed later in this section. The  $\text{SrB}_2\text{Si}_2\text{O}_8$  is a member of Pnma (62) space group, with unit cell dimension of 8.187 Å (a) x 8.948 Å (b) x 7.957 Å (c) and cell volume 582.9 Å<sup>3</sup>.

Figure 2 shows the excitation and emission PL spectra of 1 mol%  $\text{Dy}^{3+}$  doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  phosphor sample. Four emission narrow band from trivalent dysprosium were observed in the PL emission at ~482, 575, 661 and 754 nm which corresponded to  $^4\text{F}_{9/2}$  to  $^6\text{H}_j$  transitions where  $j = 15/2, 13/2, 11/2$  and  $9/2$ . Two most prominent emission

were the renowned blue (482 nm) and yellow (575 nm) emissions of  $\text{Dy}^{3+}$ , intensity of these two emission was utilized to determine the local host site surrounding the rare earth ions. Blue emissions from  $^4\text{F}_{9/2}$  to  $^6\text{H}_{15/2}$  were magnetic dipole transition that was independent of crystal environment. Conversely, the  $^4\text{F}_{9/2}$  to  $^6\text{H}_{13/2}$  yellow emission were electric dipole transition that were only allowed when  $\text{Dy}^{3+}$  ions resides in low site symmetry surrounding (Hussin et al. 2010). Since 575 nm emissions were stronger than 482 nm emissions, we can conclude that the  $\text{Dy}^{3+}$  resided at low symmetry site that lacked inversion center. The fact that  $\text{Dy}^{3+}$  doped phosphor emits blue and yellow light suggests  $\text{SrB}_2\text{Si}_2\text{O}_8:\text{Dy}^{3+}$  to be a potential candidate for use in white LED.

On top of that, a weak emission narrow band centered at 777 nm appeared in the NIR region. Closer inspection of the spectra led us to discover that the 777 nm emission

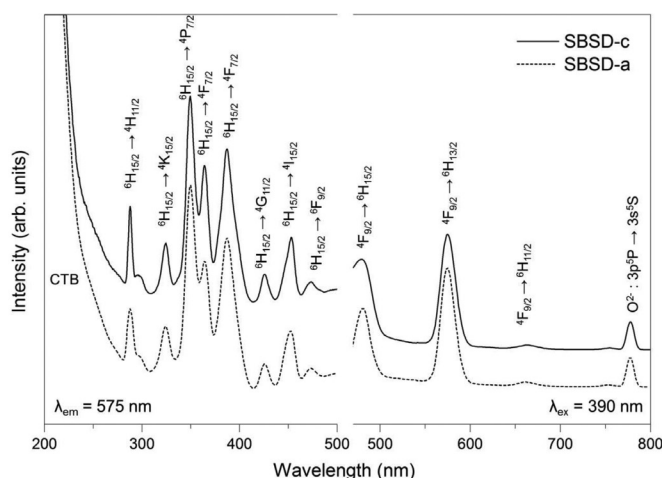


FIGURE 2. Excitation spectra observing 575 nm (left) and emission spectra under 390 nm excitation (right) of 1 mol%  $\text{Dy}^{3+}$  doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  synthesized under air and carbon monoxide atmosphere

appeared in all samples regardless of doping composition. Literature reviews showed that the 777 nm emissions was a result of  $3p^5P$  to  $3s^5S^0$  transition from  $O^{2-}$  ions that was reported before in thin film systems (Iwata et al. 2000; Li et al. 2013; Zhang et al. 2007). This phenomenon may have been overlooked by other researchers as the emission from  $O^{2-}$  ions were very weak compared to the rare earth ions emissions. Dominance of rare earth ions emissions forces charge transfer from  $O^{2-}$  ions to rare earth ions, therefore only weak 777 nm emissions were observed.

The excitation spectra were obtained by observing the most prominent emission at 575 nm peak, which featured multiple narrow bands ranging around 288 to 473 nm and a strong broad absorption band around 250 nm. Three strongest excitation were detected around 350, 364 and 387 nm which corresponded to the transition from  $^6H_{15/2}$  ground state to  $^6P_{7/2}$ ,  $^4I_{11/2}$  and  $^4F_{7/2}$  excited state, respectively. In addition to that, weaker excitation narrow bands detected around 288, 324, 426, 452 and 473 nm were assigned to the  $^6H_{15/2} \rightarrow ^4H_{11/2}$ ,  $^4K_{15/2}$ ,  $^4G_{11/2}$ ,  $^4I_{15/2}$  and  $^6F_{9/2}$ , respectively. Subsequently, the broad band excitation from 200 to 250 nm range was induced by host charge transfer. Energy was being absorbed by the host and transferred to  $Dy^{3+}$  for radiative emission, this observation suggest that interaction between  $Dy^{3+}$  and host lattice was strong. The broad band excitations at short wavelength range were ascribed to the  $Dy^{3+} - O^{2-}$  charge transfer. Weak narrow emission band around 777 nm were the result of residue from  $O^{2-}$  charges that failed to transfer to  $Dy^{3+}$ , this further asserts the  $Dy^{3+} - O^{2-}$  charge transfer occurrence.

Furthermore, no noticeable difference was found between  $SrB_2Si_2O_8:Dy^{3+}$  sintered in oxidizing and reducing atmosphere. The CIE coordination coordinates were calculated and tabulated in Table 1. The coordinates were plotted in 1931 CIE color space in Figure 7.

Figure 3 showed four emission spectrum comprising of  $SrB_2Si_2O_8:Eu^{2+}/Eu^{3+}$  and  $SrB_2Si_2O_8:Eu^{2+}/Eu^{3+}, Dy^{3+}$  that

were synthesized under oxidizing atmosphere of air and reducing atmosphere of carbon monoxide. All the samples exhibited blue emission broad band centred around 435 nm and red emissions from 590 to 700 nm that decreased in intensity in relative to blue emission traversing from SBSE-a to SBSED-c. The blue emission was identified to be presence of  $Eu^{2+}$  while red emission was due to  $Eu^{3+}$ . The presence of  $Eu^{2+}$  showed that  $Eu^{3+}$  was reduced to  $Eu^{2+}$  in the  $SrB_2Si_2O_8$  host even in oxidizing atmosphere. Unusual reduction of  $Eu^{3+}$  to  $Eu^{2+}$  with high temperature sintering in air had been reported by other researcher on similar crystal (Saradhi et al. 2010; Wang et al. 2009). Whilst other host such as  $Sr_2B_5O_9$  (Pei et al. 1999),  $Sr_4A_{11}4O_{25}$  (Peng et al. 2003) and  $SrB_4O_7$  (Liang et al. 2002) were reported to exhibit such behaviour. According to Pei et al. (1999) there are four conditions needed for this to occur. Firstly, doped rare earth ions must replace cations with lower valencies such as alkaline earth ions. Secondly, no other reducible ions are present in the vicinity. Thirdly, ionic radius of cation ( $Sr^{2+}$ , 0.120 nm) replaced by  $Eu^{2+}$  (0.121 nm) (Shannon 1976) should be close and lastly, host crystal structure should stabilize the  $Eu^{2+}$  ions with three dimensional network of  $MO_4$  tetrahedral ( $M = B, Si, Al, P, S$ ). Similar work by Saradhi et al. (2010) and the present work satisfied all of the above requirements.  $Eu^{3+}$  emissions were seen to decrease further in samples synthesized under carbon monoxide atmosphere. This showed that more  $Eu^{3+}$  ions were reduced to a divalent oxidation state by the reducing atmosphere of carbon monoxide to the point that in SBSED-c, almost negligible amount of  $Eu^{3+}$  existed and pure blue emission were observed. However, it is worth mentioning that incorporation of  $Dy^{3+}$  ions further reduced the  $Eu^{3+}$  ions in both samples sintered in air and carbon monoxide.  $Eu^{3+}$  reduction effect by co-doping was firstly reported by Pei et al. (1999) and Peng et al. (2003). They proposed a model in which the more electrons on negative defect were created; more  $Eu^{3+}$  ions were reduced. They

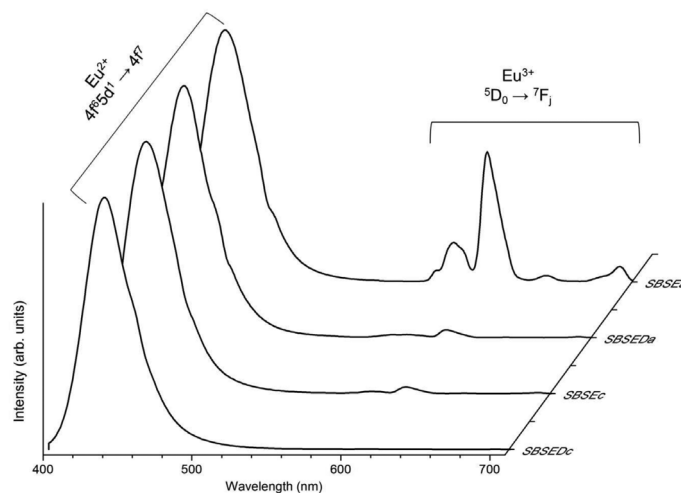


FIGURE 3. PL emission spectra under 390 nm excitation of  $SrB_2Si_2O_8:1 \text{ mol\% } Eu^{2+}/Eu^{3+}$  and  $SrB_2Si_2O_8:1 \text{ mol\% } Eu^{2+}/Eu^{3+}, 1 \text{ mol\% } Dy^{3+}$  synthesized under air and carbon monoxide atmosphere



demonstrated the effect by co-doping with  $\text{La}^{3+}$  ions. However such phenomena originating from  $\text{Dy}^{3+}$  ions were first ever reported.

The broad band blue emission that peaked at 435 nm was assigned to the  $4f_65d_1$  to  $4f_7$  allowed transition of  $\text{Eu}^{2+}$  ions. Divalent europium were widely known for its  $4f \leftrightarrow 5d$  transition, its ability to emit light in different wavelength responding to different crystal field strength had allowed researchers to tune its emission centre using different host material. Inner  $4f$  electrons from  $4f_65d_1$  were shielded from the  $5d$  orbital and were therefore immune to the host crystal environment. However, the  $5d$  electrons were not shielded and therefore were sensitive to influence from crystal lattice environment (Nazarov et al. 2013). Due to this, energy level splitting of  $5d$  orbital occurred and gave rise to a broad band emission centred at 435 nm (Huang et al. 2011). The peak position of the  $\text{Eu}^{2+}$  emission was determined by the crystal environment surrounding the rare earth ions. In the present case,  $\text{Sr}^{2+}$  and its short ionic radius was believed to be the main contributor to crystal field splitting of  $5d$  orbital, hence resulted in 435 nm emission centre. It is mentioned in many research that  $\text{Eu}^{2+}$  occupies the  $\text{Sr}^{2+}$  vacancy in the host lattice due to their similarity in ionic radius between  $\text{Eu}^{2+}$  and  $\text{Sr}^{2+}$  (Hölsä et al. 2009; Lin et al. 2001), the present case was believed to be the same.

Figure 4 showed the emission spectra of  $\text{Eu}^{2+}/\text{Eu}^{3+}$  doped and  $\text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  co-doped  $\text{SrB}_2\text{Si}_2\text{O}_8$  normalized at 613 nm intensity to show the emissions of  $\text{Eu}^{3+}$ . Actual intensities were shown in Figure 3. All samples exhibited typical  $\text{Eu}^{3+}$   $4f-4f$  emission narrow band from 578 – 702 nm range, with exceptions of SBSED-c only showing emissions after 613 nm as the  $\text{Eu}^{3+}$  emissions were relatively lower to  $\text{Eu}^{2+}$  (shown in Figure 3) and being overlapped by  $\text{Eu}^{2+}$   $4f$  to  $5d$  emission. The sharp peaks observed at 578, 590, 613, 653 and 702 nm

were ascribed to the energy transitions between the first excited state to the  ${}^5\text{D}_0$  to  ${}^4\text{F}_j$  multiplet ground states of  $\text{Eu}^{3+}$  ions, where  $j = 0, 1, 2, 3, 4$ . Emission bands that come into interest were the highest emission intensity at 613 nm, followed by 590 and 560 nm bands. Emission band around 560 nm was assigned to the  ${}^5\text{D}_0$  to  ${}^4\text{F}_0$  transition; this transition was usually forbidden in the presence of centre of symmetry. The narrow band around 613 nm corresponds to  ${}^5\text{D}_0$  to  ${}^4\text{F}_2$  electric dipole transition;  ${}^5\text{D}_0$  to  ${}^4\text{F}_2$  transition with  $\Delta J = 2$  was profound to be hypersensitive to site symmetry, its intensity increases along with low site symmetry surrounding  $\text{Eu}^{3+}$ . On the other hand, orange emission around 590 nm was ascribed to  ${}^5\text{D}_0$  to  ${}^4\text{F}_1$  magnetic dipole transition. Due to parity-allowed in the selection rule, the intensity was irrelevant to host crystal environment. As the 613 nm emissions were stronger than 590 nm emission, this proved that  $\text{Eu}^{3+}$  in  $\text{SrB}_2\text{Si}_2\text{O}_8$  occupied a low site symmetry, the existence of 560 nm emissions (forbidden transition) strongly supports this finding. This finding was in agreement with PL spectra from  $\text{Dy}^{3+}$  doped samples. Aside from that, weak emission bands were observed around 653 nm and 702 nm which were assigned to  ${}^5\text{D}_0$  to  ${}^4\text{F}_3$  and  ${}^5\text{D}_0$  to  ${}^4\text{F}_4$  transition, respectively.

Figure 5 presented the excitation spectra of SBSE and SBSED samples sintered in air and carbon monoxide atmosphere, left figure showed  $\lambda_{\text{em}} = 435$  nm and right figure showed  $\lambda_{\text{em}} = 613$  nm. The broad excitation bands with acromion located around 296, 341, 359 and 370 nm from  $\lambda_{\text{em}} = 435$  nm figure corresponded to the  $4f^7 \rightarrow 4f^65d^1$  excitation of  $\text{Eu}^{2+}$ . The influence of crystal field splitting was responsible for the broad excitation bands, which was similarly responsible for the broad emission bands of  $\text{Eu}^{2+}$  as well. No charge transfer bands were involved in  $\text{Eu}^{2+}$  excitation. Excitation spectra from  $\lambda_{\text{em}} = 613$  nm in singly doped SBS phosphor observed typical excitation

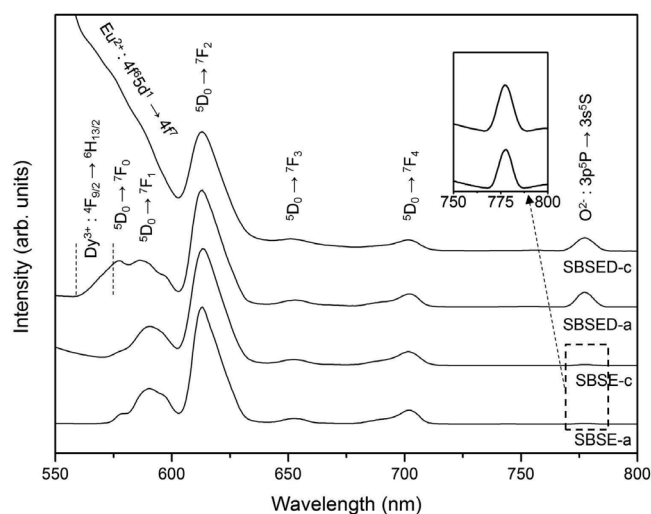


FIGURE 4. 613 nm normalized emission spectra of  $\text{SrB}_2\text{Si}_2\text{O}_8:1 \text{ mol}\% \text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{SrB}_2\text{Si}_2\text{O}_8:1 \text{ mol}\% \text{Eu}^{2+}/\text{Eu}^{3+}, 1 \text{ mol}\% \text{Dy}^{3+}$  synthesized under air and carbon monoxide atmosphere,  $\lambda_{\text{ex}} = 390$  nm

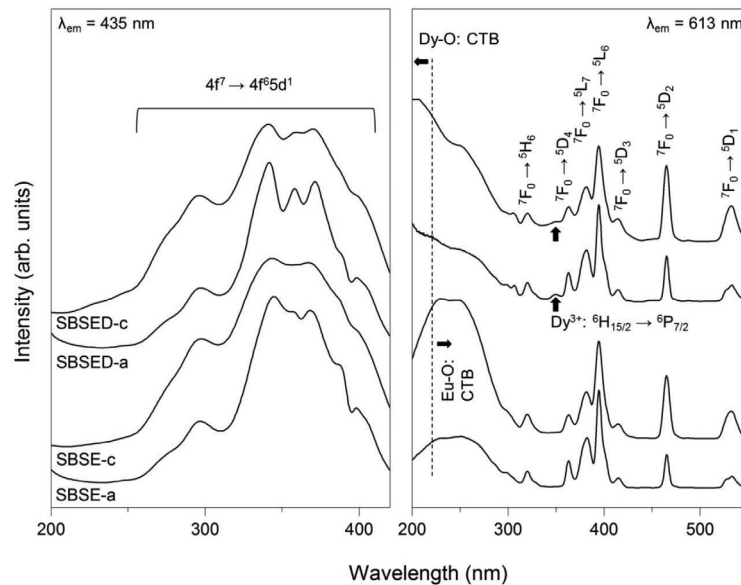


FIGURE 5. Excitation spectrum of  $\text{SrB}_2\text{Si}_2\text{O}_8:1 \text{ mol\% Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{SrB}_2\text{Si}_2\text{O}_8:1 \text{ mol\% Eu}^{2+}/\text{Eu}^{3+}, 1 \text{ mol\% Dy}^{3+}$  synthesized under air and carbon monoxide atmosphere.  $\lambda_{\text{em}} = 435 \text{ nm}$  (left),  $\lambda_{\text{em}} = 613 \text{ nm}$  (right)

narrow bands from f - f transitions of  $\text{Eu}^{3+}$ . Narrow bands arising from around 320, 363, 382, 394, 414, 465 and 532 nm were assigned to the transition from the ground state  $7F_0$  to  $5H_6$ ,  $5D_4$ ,  $5L_7$ ,  $5L_6$ ,  $5D_3$ ,  $5D_2$  and  $5D_1$  excited states of  $\text{Eu}^{3+}$ , respectively. Broad band excitations arising from 300 to 200 nm region were caused by Eu-O charge transfer band. Besides that,  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  co-doped SBS phosphor showed excitation from  $\text{Dy}^{3+}$  transitions, the charge transfer bands were extended into VUV region in  $\text{Dy}^{3+}$  co-doped samples, corresponding to the Dy - O charge transfer band. Such charge transfer bands were also observed in  $\text{Dy}^{3+}$  singly doped excitation spectrum as shown in Figure 2. Additionally,  $\text{Dy}^{3+}$  co-doped samples also showed excitation around 350 nm which corresponded to the  $6H_{15/2}$  to  $6P_{7/2}$  transition. Observing the overlapped  $\text{Eu}^{3+}$  excitations by  $\text{Dy}^{3+}$  excitations indicated the energy transfer from  $\text{Dy}^{3+}$  to  $\text{Eu}^{3+}$  in co-doped samples. Occurrence of  $\text{Dy}^{3+}$  energy transfer to  $\text{Eu}^{3+}$  had been reported by Cai et al. (2012) in alumino borate glass. However neither the  $6H_{15/2}$  to  $6P_{7/2}$  transition nor the CTB of  $\text{Dy}^{3+}$  ions were reportedly involved in energy transfer process. The extended excitation towards the VUV region will provide a more efficient excitation for  $\text{Eu}^{3+}$  based phosphors. CIE color coordinate of these samples were calculated and plotted as in Figure 7 and Table 1.

Figure 6 showed the excitation spectra of  $\text{SrB}_2\text{Si}_2\text{O}_8: \text{Eu}^{2+}/\text{Eu}^{3+}, \text{Dy}^{3+}$  samples sintered under air and carbon monoxide atmosphere where  $\lambda_{\text{em}} = 575 \text{ nm}$ . Excitation narrow bands of  $\text{Dy}^{3+}$  were observed from air sintered SBSED similar to the  $\text{Dy}^{3+}$  singly doped SBS phosphor. This showed that emission at 575 nm were due to  $\text{Dy}^{3+}$  ions. However, carbon monoxide sintered SBSED phosphor showed  $\text{Eu}^{2+}$  broad excitation bands combined with  $\text{Dy}^{3+}$

narrow excitation bands, which can be observed from the shoulders along the broad band around 289, 351, 365, 387, 452 and 473 nm. The corresponding transitions were discussed earlier in this section. Dy - O charge transfer bands around 200 - 250 nm were also detected. These results indicated that emission around 575 nm was a combined emission from both  $\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$ . It was thought that the 575 nm emissions from  $\text{Eu}^{2+}$  ions as a result of  $\text{Dy}^{3+}$  energy transfer may be possible, further experimental evidence is needed.

Table 1 tabulated the CIE color coordinate and its simulated color, as well as the actual color under 390 nm illuminations. The color coordinate of  $\text{Dy}^{3+}$  singly doped SBS phosphor were (0.3426, 0.3892) for air sintered and (0.3463, 0.4208) for CO sintered, both phosphor emitted yellowish-white color under 390 irradiation. On the other hand, SBS phosphor doped with  $\text{Eu}^{2+}/\text{Eu}^{3+}$  emit reddish-purple to blue color under irradiation of 390 nm UV light, the color was dependent on the sintering condition and  $\text{Dy}^{3+}$  co-doping. Samples doped with  $\text{Eu}^{3+}/\text{Eu}^{2+}$  under air synthesis emits reddish-purple for its high  $\text{Eu}^{3+}$  content. While CO synthesized  $\text{Eu}^{3+}/\text{Eu}^{2+}$  and  $\text{Eu}^{3+}/\text{Eu}^{2+}, \text{Dy}^{3+}$  co-doped ceramics showed bluish-purple emission. Lastly,  $\text{Eu}^{3+}/\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$  co-doped ceramics under CO synthesized emitted pure blue emission due to its high  $\text{Eu}^{2+}$  content. Therefore this study presented a possible reddish-purple to blue tunable phosphor by manipulating CO sintering atmosphere and  $\text{Dy}^{3+}$  co-doping. White phosphor were usually produced by RGB (red green blue) method (Liang et al. 2009). The presence of blue ( $\text{Eu}^{2+}$ ) and red ( $\text{Eu}^{3+}$ ) emission in the same host crystal offered itself as a promising candidate for white phosphor application.

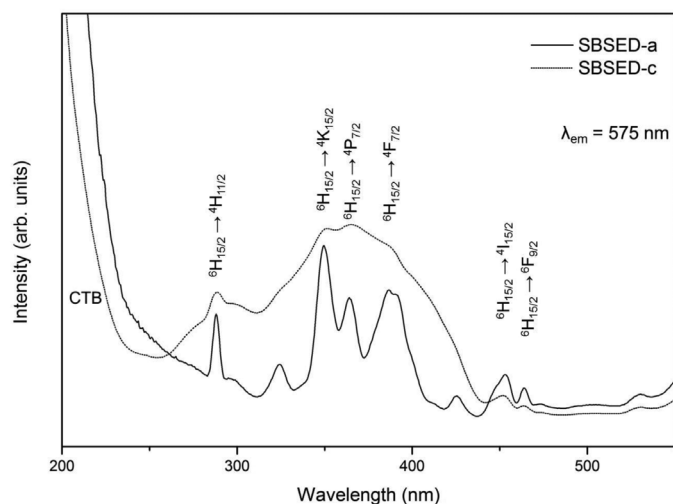


FIGURE 6. Excitation spectra of  $\text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  co-doped SBS samples synthesized under air and carbon monoxide atmosphere,  $\lambda_{\text{em}} = 575$  nm

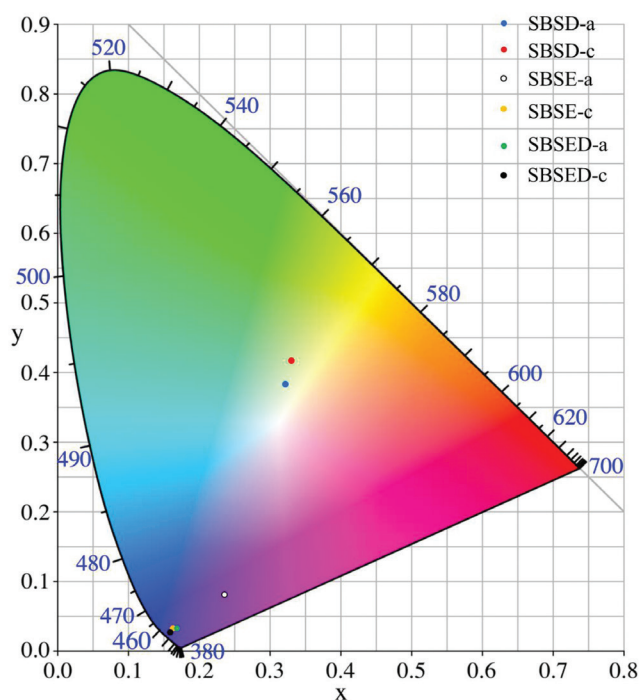


FIGURE 7. Color coordinates of  $\text{SrB}_2\text{Si}_2\text{O}_8: \text{Dy}^{3+}$ ,  $\text{SrB}_2\text{Si}_2\text{O}_8: \text{Eu}^{2+}/\text{Eu}^{3+}$ , and  $\text{SrB}_2\text{Si}_2\text{O}_8: \text{Eu}^{2+}/\text{Eu}^{3+}, \text{Dy}^{3+}$  phosphor synthesized in air and CO atmosphere plotted in CIE 1931 chromaticity diagram

## CONCLUSION

In this report,  $\text{SrB}_2\text{Si}_2\text{O}_8: \text{Dy}^{3+}$ ,  $\text{SrB}_2\text{Si}_2\text{O}_8: \text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{SrB}_2\text{Si}_2\text{O}_8: \text{Eu}^{2+}/\text{Eu}^{3+}, \text{Dy}^{3+}$  phosphor were synthesized by solid state reaction in air and CO atmosphere. The  $\text{Dy}^{3+}$  singly doped phosphor gave rise to yellowish white emission. We showed that co-doping of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  in  $\text{SrB}_2\text{Si}_2\text{O}_8$  system is possible and they exhibited reddish-purple to blue emissions. They also showed energy transfer from  $\text{Dy}^{3+}$  to  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ . Unusual  $\text{Eu}^{3+}$

to  $\text{Eu}^{2+}$  reduction was also displayed in these samples, and that its reduction was affected by co-doping of  $\text{Dy}^{3+}$ . To the best of our knowledge, this phenomenon was first ever reported and is worthwhile for further in-depth research to study its mechanism. Future research on  $\text{Eu}^{2+}/\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  co-doped in other host lattice is also recommended to confirm the occurrence of energy transfer as well as the  $\text{Eu}^{3+}$  reduction in air.

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