

Photoluminescent properties of $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+},\text{Eu}^{3+}$ phosphor

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Abstract. Terbium (Tb^{3+}) and europium (Eu^{3+}) co-doped strontium silicate ($\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+},\text{Eu}^{3+}$) phosphor was prepared via solid state reaction and its structure, particle morphology and photoluminescent properties were investigated. The X-ray diffraction patterns show phases associated with monoclinic ($\beta\text{-Sr}_2\text{SiO}_4$) and orthorhombic ($\alpha'\text{-Sr}_2\text{SiO}_4$) structures of strontium silicate. Scanning electron microscopy images showed agglomerated particles with irregular shapes, encrusted with nanorods. The Tb^{3+} single doped Sr_2SiO_4 gave predominantly green emission at 546 nm ascribed to the $^5\text{D}_4 - ^7\text{F}_5$ transition of Tb^{3+} while the Eu^{3+} single doped Sr_2SiO_4 gave a predominantly red emission at 616 nm ascribed to the $^5\text{D}_0 - ^7\text{F}_2$ transition of Eu^{3+} . The $\text{Tb}^{3+}\text{-Eu}^{3+}$ co-doped system gave simultaneous emission of blue, green and red with the green emission dominating the blue and the red. We speculate that the blue, green and red emissions can be balanced to get white emission by using a single excitation wavelength where the excitation spectra of these emissions overlap provided the right concentration ratio of $\text{Tb}^{3+}:\text{Eu}^{3+}$ is used.

1. Introduction

Solid state host materials have attracted extensive attention because of their diverse applications in lighting. Strontium silicate (Sr_2SiO_4) is one of the examples of the solid state materials used as a host for rare-earth ions to prepare light emitting materials or phosphors. It has stable crystal structure, good mechanical strength and high thermal stability provided by the tetrahedral silicate (SiO_4^{2-}) group [1]. Currently, rare earths orthosilicate based phosphors are being developed and investigated for application in white LEDs (Light emitting diodes) due to their high durability against high power, high temperature, and the packaging resins. The luminescent properties of many silicate phosphors such as $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ ($\lambda_{\text{em}} = 490\text{-}580$ nm), $\text{Mg}_2\text{SiO}_4:\text{Mn}^{2+}$ ($\lambda_{\text{em}} = 680$ nm), $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ ($\lambda_{\text{em}} = 500\text{nm}$), $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ ($\lambda_{\text{em}} = 490$ nm), $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ ($\lambda_{\text{em}} = 524$ nm), and $\text{Zn}_2\text{SiO}_4:\text{Tb}^{3+}$ ($\lambda_{\text{em}} = 545$ nm) have been studied because of their ability to be efficiently excited by blue and ultraviolet (UV) lights [2-7]. Kim et. al investigated the white LEDs where a blue LED was combined with a yellow YAG:Ce phosphor which can be applied as a color-tunable phosphor for green or greenish white light emitting diode based on ultraviolet chip/phosphor technology [8]. Although YAG exhibits high luminescence efficiency and chemical stability, the combination of blue chip and YAG showed a lower color rendering index due to the lack of red color contribution [9, 10]. To get an excellent color index it is necessary to develop a single host phosphor that can absorb in the UV region and emit blue, green and red light simultaneously whose combination gives white light. The primary objective of this study was to develop such phosphor for LEDs by co-doping a single host (Sr_2SiO_4) with Tb^{3+} and Eu^{3+} .

When two kinds of rare-earths are co-doped into a single host material one of them sometimes acts as a sensitizer and the other acts as an activator for excitation energy transfer after photoexcitation. Examples such as $\text{LaPO}_4\text{:Tb}$, Ce phosphors where Ce^{3+} ions are efficient sensitizers to Tb^{3+} emission has been reported [11]. In this paper, we studied the structural and photoluminescent properties of $\text{Sr}_2\text{SiO}_4\text{:Tb}^{3+}\text{:Eu}^{3+}$ phosphor and we observed simultaneous emission of blue and green from Tb^{3+} , and red from Eu^{3+} when the phosphor was excited at different wavelengths using a monochromatized xenon lamp.

Preparation and Characterization Techniques

$\text{Sr}_2\text{SiO}_4\text{:Eu}^{3+}$, Tb^{3+} phosphors were prepared at a temperature of 1000 °C using solid state reaction process. The starting materials used in the preparation process were SrCO_3 , SiO_2 and Eu_2O_3 and Tb_4O_7 which were weighed stoichiometrically and mixed thoroughly using a mortar and pestle. The concentrations of Eu^{3+} and Tb^{3+} were 0.5 mol% of Sr^{2+} ions in the Sr_2SiO_4 lattice. The mixture was sintered at 1000 °C for 3 hrs in air. The crystal structure and particle morphology were analyzed by an Advanced D8 Bruker powder X-ray diffractometer (XRD) and a Shimadzu Superscan ZU SSX-550 scanning electron microscope (SEM). The room temperature photoluminescence (PL) excitation spectra and PL emission were recorded from the Cary Eclipse fluorescence spectrophotometer using a monochromatized xenon lamp as the excitation source.

2. Results and discussion

2.1. Structure and morphology

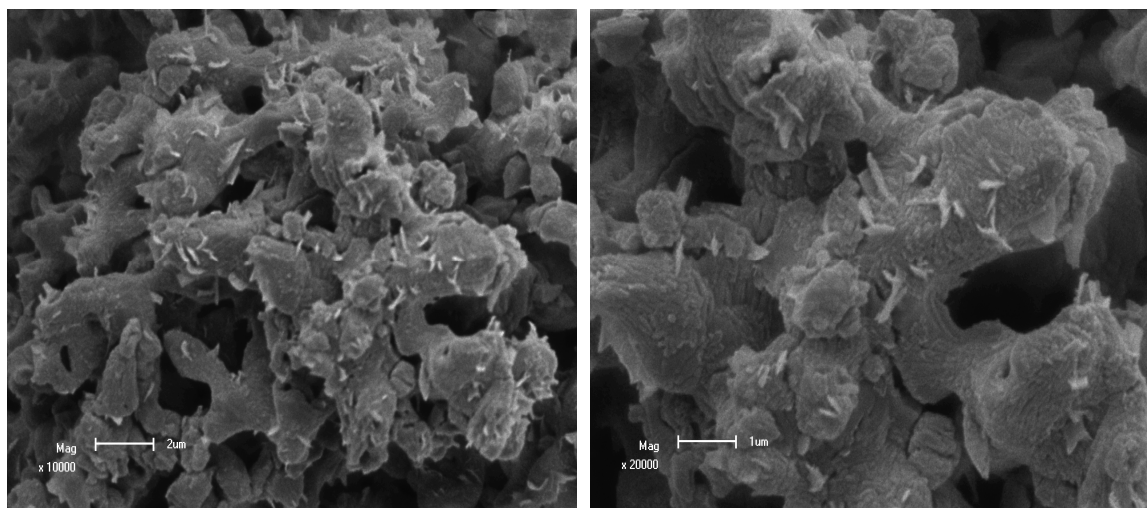


Figure 1. SEM micrographs of $\text{Sr}_2\text{SiO}_4\text{:Tb}^{3+}\text{:Eu}^{3+}$ at different magnifications.

It is known that the luminescence characteristics of phosphor particles depend on the morphology of the particles such as size, shape size distribution and defects. Figure 1 shows the SEM images of $\text{Sr}_2\text{SiO}_4\text{:Tb}^{3+}\text{:Eu}^{3+}$ with different magnification. The images show an agglomeration of irregular particles, which are encrusted with nanorods. The agglomeration of these particles is a result of overlapping of small particles.

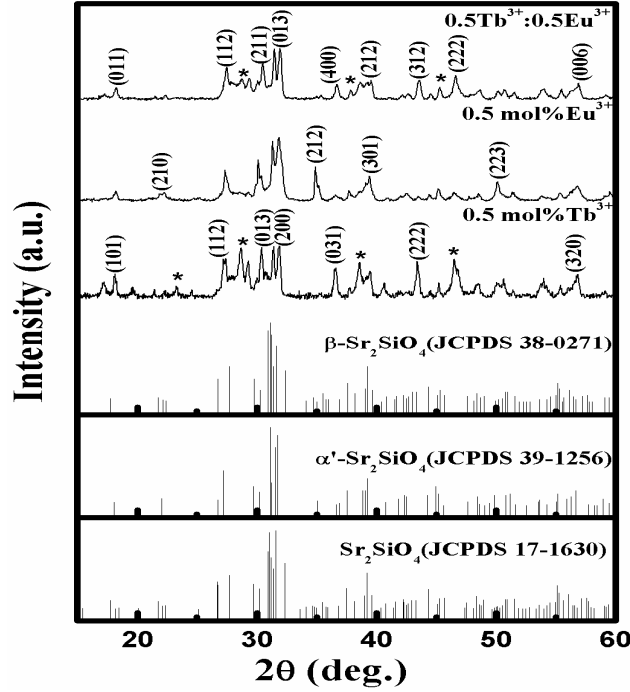


Figure 2. XRD spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$, $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}, \text{Tb}^{3+}$ phosphors.

Figure 2 shows the XRD patterns of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$, $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$ (Eu^{3+} and Tb^{3+} were 0.5mol %) phosphors. It has previously been reported that the crystal structures of α' - Sr_2SiO_4 and β - Sr_2SiO_4 are very similar, and the XRD peaks are therefore also similar in the JCPDS cards of both phases, and both structures can co-exist [12]. The α' and β phases are the two modifications of Sr_2SiO_4 , and the phase transition between low temperature β phase and high temperature α' phase, whereas α' phase can also be stabilized at room temperature by substituting more Eu ($0.1 \geq$) or small amounts of Sr^{2+} [13]. As seen from Figure 2, $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}$ is consistent with the standard JCPDS card no. 76-1630, while the $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$ agrees with the pure phase of α' - Sr_2SiO_4 (JCPDS card no. 39-1256). On the other hand, $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$ agrees with the standard diffraction data of both α' - Sr_2SiO_4 (JCPDS card no. 39-1256) and β - Sr_2SiO_4 (JCPDS card no. 38-0271), so it can be concluded that the co-doped phosphor sample is a mixture of orthorhombic α' - $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$ and monoclinic β - $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$. There were secondary phases marked with asterisks (*), which may be due to the un-reacted SrCO_3 (JCPDS card no. 05-0418) and SiO_2 (JCPDS card no. 85-0462). These extra peaks indicate that the reaction of raw materials was not complete.

2.2. Photoluminescence analysis

Figure 3 illustrates the photoluminescent excitation (PLE) and (PL) emission spectra of $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}$. The excitation spectrum was recorded when monitoring the green emission at 546 nm and the excitation peak at 227 nm is assigned to the f-f transitions of Tb^{3+} . The PL spectrum consists of one major emission peak at 546 nm which is assigned to the $^5\text{D}_4 - ^7\text{F}_5$ transition of Tb^{3+} , the second major

emission at 382 (violet) and minor emissions at 415 nm (blue) and 435 nm (bluish-green) are due to $^5D_3 - ^7F_J$ ($J = 6, 5, 4$) transitions of Tb^{3+} . Additional minor emissions at 490, 585 and 621 nm are due

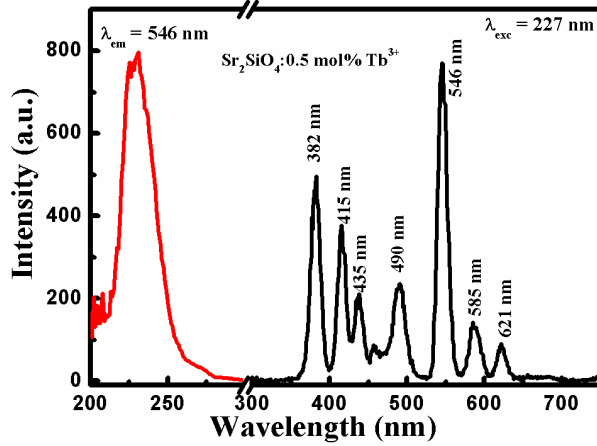


Figure 3. PLE and PL emission spectra of $Sr_2SiO_4:Tb^{3+}$ excited at 227 nm.

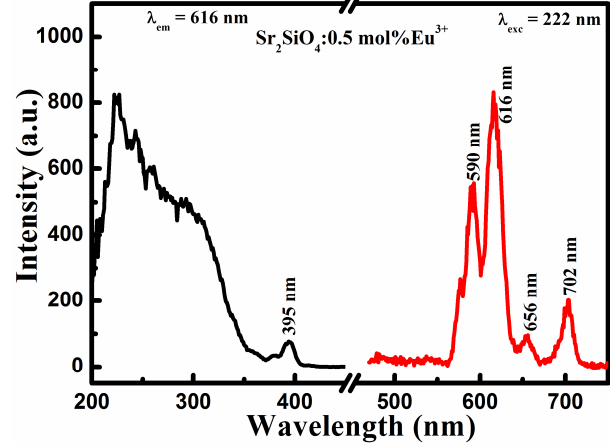


Figure 4. PLE and PL emission spectra of $Sr_2SiO_4:Eu^{3+}$ excited at 222 nm.

to $^5D_4 - ^7F_J$ ($J = 6, 4, 3$) transitions of Tb^{3+} . Figure 4 shows the PLE and PL emission spectra of the $Sr_2SiO_4:Eu^{3+}$ phosphor. The excitation spectrum is asymmetrical with sharp peaks protruding from the broad excitation band extending from 200 – 400 nm [14]. The broad spectrum is due to $Eu^{3+} \rightarrow O^{2-}$ charge transfer states while the protruding sharp peaks are due to $f \rightarrow f$ transitions of Eu^{3+} . The PL spectra shows major red emission at 616 nm corresponding to $^5D_0 - ^7F_2$ transition of Eu^{3+} , and a few minor peaks at 590, 656, and 702 nm assigned to the $^5D_0 - ^7F_J$ ($J = 1, 3, 4$) transitions of Eu^{3+} .

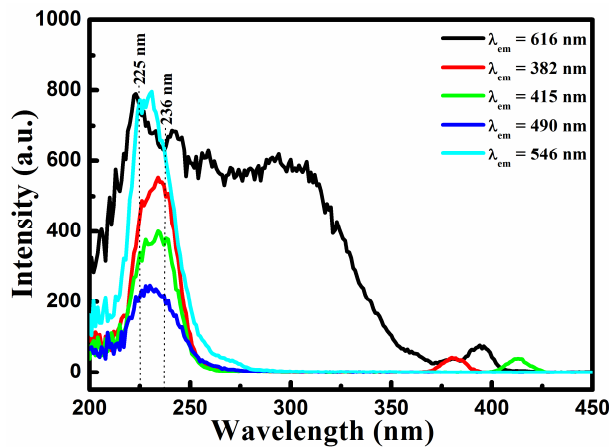


Figure 5. PLE spectra of $Sr_2SiO_4:Tb^{3+}:Eu^{3+}$ phosphor.

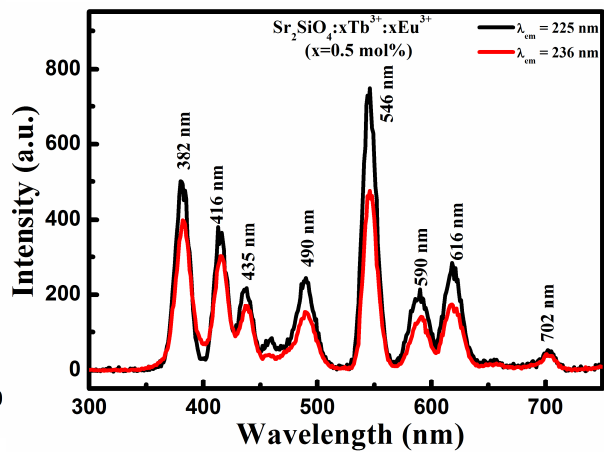


Figure 6. PL emission spectra of $Sr_2SiO_4:Tb^{3+}:Eu^{3+}$ phosphor.

Figure 5 and 6 shows respectively the PLE and PL spectra of $Sr_2SiO_4:Tb^{3+}, Eu^{3+}$ (Eu^{3+} and Tb^{3+} were 0.5 mol %) phosphor. The PLE spectra were recorded when monitoring emission peaks at 382, 415, 546 coming from Tb^{3+} and 616 nm coming from Eu^{3+} . There were other weak excitation peaks located at 380, 394 and 413 nm when monitoring the peaks at 382, 616 and 415 nm which are related to the

intra-4f transitions of Eu^{3+} ions in the host lattice, which can be assigned to ${}^7\text{F}_0\text{-}{}^5\text{G}_2$, ${}^7\text{F}_0\text{-}{}^5\text{L}_6$ and ${}^7\text{F}_0\text{-}{}^5\text{D}_2$ transitions. The PL spectra were recorded when exciting the phosphor at 225 and 236 nm, which are the wavelengths where the Tb^{3+} and Eu^{3+} excitations are overlapping as shown in the figure. The reason for choosing these wavelengths was to find common wavelengths that can lead to simultaneous emission of blue and green emission from Tb^{3+} and red emission from Eu^{3+} as previously observed by Shaat et al [15]. For both excitations, the blue, green and red emissions from Tb^{3+} and Eu^{3+} were observed. However, the spectrum is dominated successively by the green and violet-blue emissions from Tb^{3+} when exciting at 225 nm and when exciting at 236 nm, the green emission is reduced considerably but the red emission from Eu^{3+} is still less intense than the green and violet-blue emissions from Tb^{3+} . The reason why Tb^{3+} emission are more intense especially when exciting at 225 nm is because of the fact that this excitation is in the same location as the $f \rightarrow f$ transitions of Tb^{3+} at 227 nm as observed in figure 3, and therefore it makes sense to have the green emission dominating other emissions. Although we could not get a balance of blue, green and red emission to get white light, these preliminary data serve as a good platform to help us get white emission in our future experiments. We believe that by getting a good balance of the concentration of Tb^{3+} and Eu^{3+} will improve the blue emission from Tb^{3+} and the red emission from Eu^{3+} . This study is in progress and we are optimistic about producing a single host phosphor that can be excited in the UV region and give white emission that can be used in LEDs.

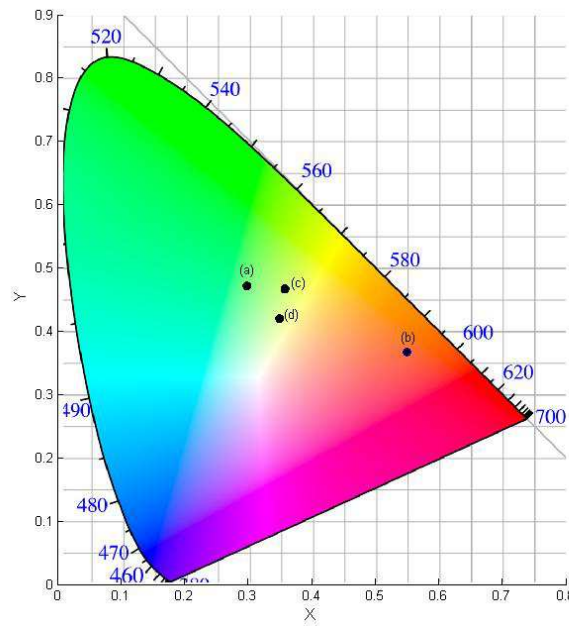


Figure 7. The CIE diagram showing coordinates of (a) $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}$, (b) $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$ and (c) $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$ ($\lambda_{\text{exc}} = 225$ nm) and (d) $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$ ($\lambda_{\text{exc}} = 236$ nm) phosphors.

To evaluate the material performance on color luminescent emission, Commission International de l'Eclairage France (CIE) x-y color coordinates diagram was used. Figure 7 showed the CIE coordinates of the $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+},\text{Eu}^{3+}$ phosphor at different excitation wavelengths 225 and 236 nm which was found to be (c) $x = 0.375$, $y = 0.446$ and (d) $x = 0.369$, $y = 0.424$. The Figure also shows the chromaticity coordinates of (a) green $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}$ and (b) red $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$.

3. Conclusion

The phosphors $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$, $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$ were successfully synthesized by solid-state reaction technique. The particles were agglomerated and have irregular shapes. The structures of the materials showed phases associated with monoclinic ($\beta\text{-Sr}_2\text{SiO}_4$) and orthorhombic ($\alpha'\text{-Sr}_2\text{SiO}_4$) structures of Sr_2SiO_4 with secondary peaks suggesting that some of the precursors did not react completely. Although the presently studied $\text{Sr}_2\text{SiO}_4:\text{Tb}^{3+}:\text{Eu}^{3+}$ did not give white emission that can be used in white LED, the study serves as a good platform to developing such phosphor in our future experiments.

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