Synthesis and photoluminescence study of CE^{3+} doped strontium silicate as blue light emitting phosphor under ultraviolet excitation

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Abstract:

Using the conventional solid state reaction approach, a series of Ce^{3+} doped $Sr_{(2-x)}SiO_4$ phosphors (x=Ce=0.02, 0.03, 0.04, 0.05, and 0.06 mole) were created. Through X-ray diffraction (XRD) investigation, the crystalline phase of the Sr_2SiO_4 host was confirmed. Additionally, the morphology and composition of the produced sample were examined using scanning electron microscopy (SEM) and EDAX. The average particle size on the SEM measurement was between one and three micrometers. We examined the excitation (em = 472 nm) and emission (ex = 310 nm) of $Sr_{(2-x)}SiO_4:xCe^{3+}$ in photoluminescence (PL). At an emission wavelength of 472 nm, the broad excitation spectra of $Sr_2SiO_4:Ce^{3+}$ phosphors are seen, cantered at 304 nm. The phosphor emission spectrum is an isolated broad emission band with a peak at 472 nm, which was studied at 304nm excitation.

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Keywords: $Sr_2SiO_4:Ce^{3+}$; solid state reaction; XRD; SEM; EDAX; n-UV LEDs

Introduction:

Strontium orthosilicate (Sr_2SiO_4) has garnered interest due to its unique structural characteristics and exceptional chemical and physical stability [1–6]. According to He and Song [7], Sr_2SiO_4 absorbs ultraviolet (UV) light and emits blue visible light when triggered by Eu^{2+} ions. Yang and Liu [8] claim that Sr_2SiO_4 exhibits significant red emission when activated by Eu^{3+} ions. Numerous studies have examined the luminescent characteristics of $Sr_2SiO_4:Eu^{3+}$, a red-emitting phosphor for white LEDs [9–11]. A near ultraviolet chip utilizing a green-yellow emitting β- $Sr_2SiO_4:Eu^{2+}$ phosphor S. Xiaoyuan et al. reported a white-light-emitting diode [12]. In 2014, M. Pardha Sarthi et al. reported enhanced luminosity of $Sr_2SiO_4:Dy^{3+}$ through sensitization (Ce^{3+}/Eu^{2+}) and the creation of white light-emitting diodes [13].

For various plant growths, Ce^{3+}-doped orthosilicate solid solution phosphors have been created with fine controlled blue emission and its mechanism [13]. The structural and spectral characteristics of Ce^{3+} in strontium silicate phosphors were effectively investigated in an ab-initio investigation [14]. The synthesis of Ce^{3+} doped Sr_2SiO_4 using a traditional solid state reaction approach is the main topic of this paper. The phase, morphology, EDAX, and photoluminescence properties of the blue-emitting Sr_2SiO_4: Ce^{3+} phosphor are also studied. CIE color coordinates confirm the phosphor's blue emission.

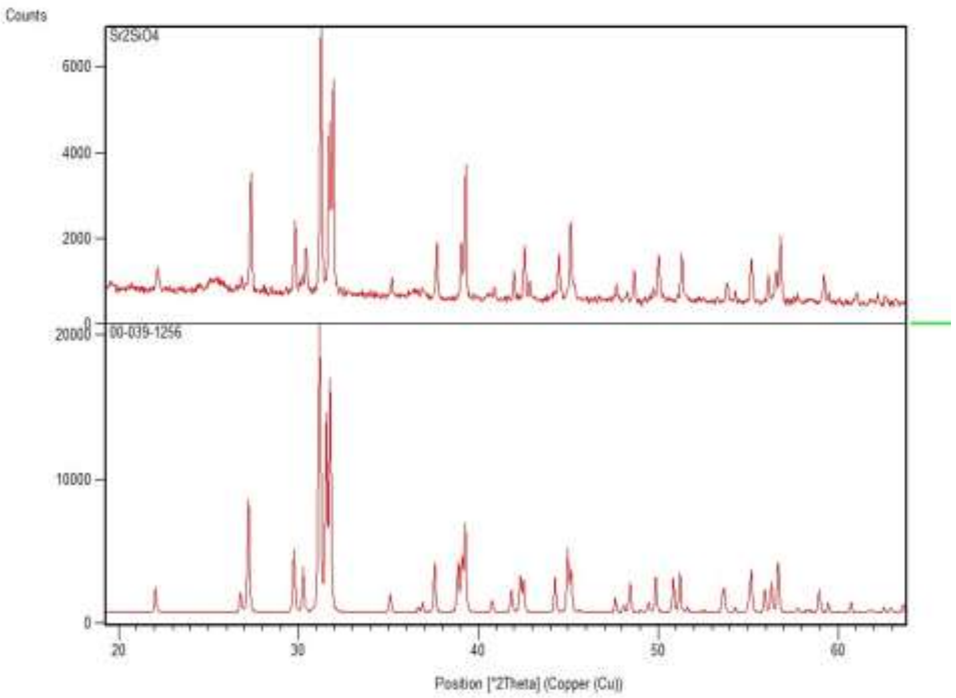
Materials and Methods:

Phosphors of $Sr_{(2-x)}SiO_4$:xCe^{3+} (x=0.02,0.03,0.04,0.05,0.06) were synthesized using the conventional solid state reaction method. As starting materials, high purity $SrCO_3$ (99.9%), SiO_2 (99.9%), and CeO_2 (99.9%) were utilized. Eight milliliters of H_3BO_3 were used as a flux. Ball milling was used to completely mix a small amount of ethanol with stoichiometric amounts of starting ingredients for two hours. After two hours of calcination at 1000 ^{o}C, the mixture was sintered for four hours in air at 1250 ^{o}C. Natural cooling was used to gradually bring the phosphor down to room temperature.

The traditional x-ray diffraction method was used to determine the final product's crystal structure. (Cu Kα, 40kV, XRD, XPERT PRO). High-resolution XRD patterns were gathered between 10 and 85 degrees in the 2θ range. EDAX, or energy dispersive x-ray analysis, was used to examine the phosphor's chemical constituents. Scanning electron microscopy, Quanta 200 with EDS (SEM), was used to examine the size and shape of the obtained sample. A Hitachi F-7000 fluorescence spectrofluorometer fitted with a 150W Xe lamp was used to measure the excitation and emission spectra. Every experiment was carried out at room temperature.

Results and Discussion :

a) X-RAY DIFFRACTION



(XRD)

Fig.1 XRD pattern of $Sr_{1.98}SiO_4$:0.02Ce^{3+}

The XRD pattern of Sr_2SiO_4:0.2mole% Ce^{3+} phosphor is shown in Fig. 1. The phosphor is in good accord with the JCPDS card number 00-039-1256 and has the orthorhombic structure α-Sr_2SiO_4. In strontium silicate, there are two kinds of strontium sites, one is a more symmetric 10 coordinated site [Sr(1)] and the other is a less symmetric 9 coordinated site [Sr(2)]. While the nine coordinated Sr(2) sites form zigzag chains of (Sr(1)–O–Sr(2)–O–Sr(1)) along the b-axis, the ten coordinated Sr(1) sites form linear three-membered rows of (Si–O–Sr(1)–O–Sr(2)) [15].

The 9 and 10 coordinated Sr^{2+} have ionic radii of 131 and 136 pm, respectively. The Sr(2) polyhedron is significantly less symmetrical and shares neither edges nor faces with any SiO_4 tetrahedra, according to a thorough structural analysis of α- Sr_2SiO_4 [16]. Ce^{3+} has an average ionic radius of roughly 103 pm, which is close to 9-coordinated Sr^{2+} (131 pm), unfavourable geometry in 10-coordinated Sr^{2+} (136 pm), and Si^{4+} (26 pm). As a result, the majority of Ce^{3+} in strontium silicate occupies 9-coordinated Sr^{2+}. The local field is uneven because the Ce^{3+} and Sr2+ sites have different ionic sizes and charges. However, 0.2 moles of Ce are insufficient to change the structure of Sr_2SiO_4.

b) SCANNING ELECTRON MICROSCOPY (SEM)

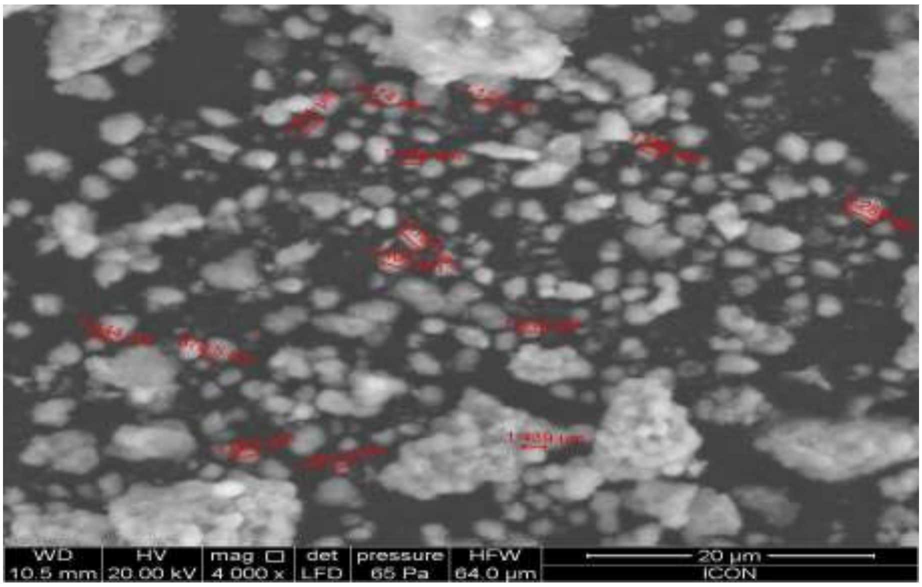


Fig.2. SEM images of Sr_2SiO_4:2%Ce^{3+} phosphor.

Fig. 2 displays the shape of $Sr_2SiO_4:Ce^{3+}$ phosphor made using a solid-state reaction technique. The SEM examination is performed on the sample exactly as it was received, without any modifications. The phosphor's shape can be inferred from the SEM image. The phosphor exhibits some form of aggregation. Although the particles' sizes and shapes vary, they are generally spherical and range in size from 1 to 3 µm on average.

c) ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

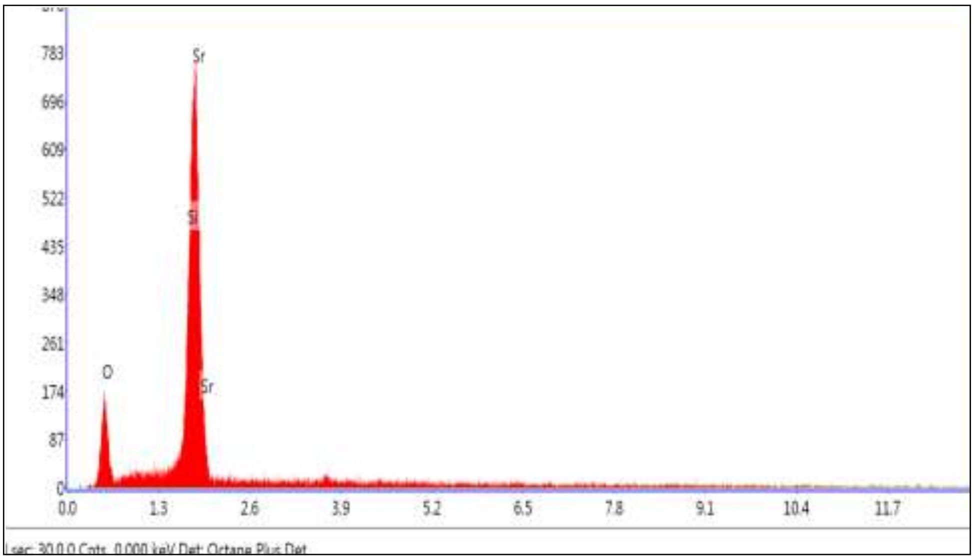


Fig.3. EDAX images of Sr_2SiO_4:2%Ce^{3+} phosphor.

The prepared EDAX of the sample is displayed in Fig. 3. The observation is conducted for 30 seconds at a magnification of 4000. The energy lines Lα (1.806 eV) for strontium, Kα (0.523 eV) for oxygen, and Kα (1.740 eV) for silicon atoms are represented by the graph's peaks. This indicates that Sr_2SiO_4 is the sample's chemical makeup.

d) PHOTOLUMINESCENCE: EXCITATION AND EMISSION SPECTRA

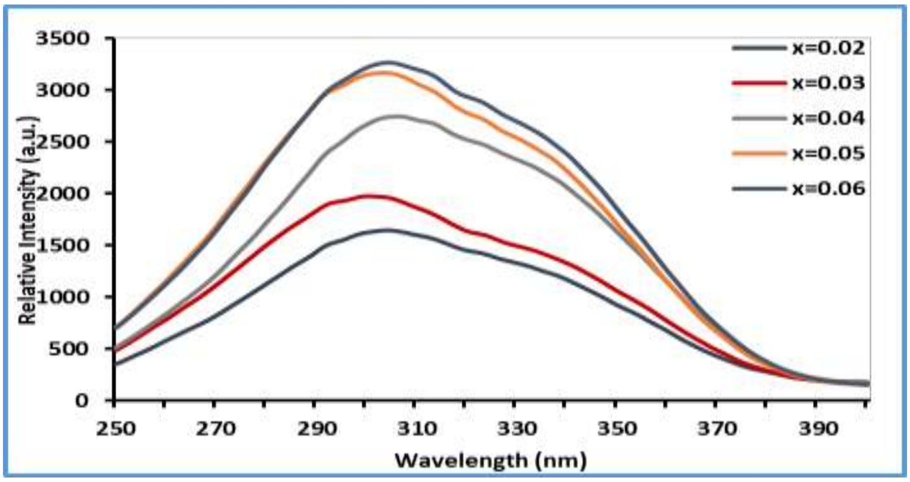


Fig.4. Photoluminescence Excitation spectra observed at 472nm emission wavelength

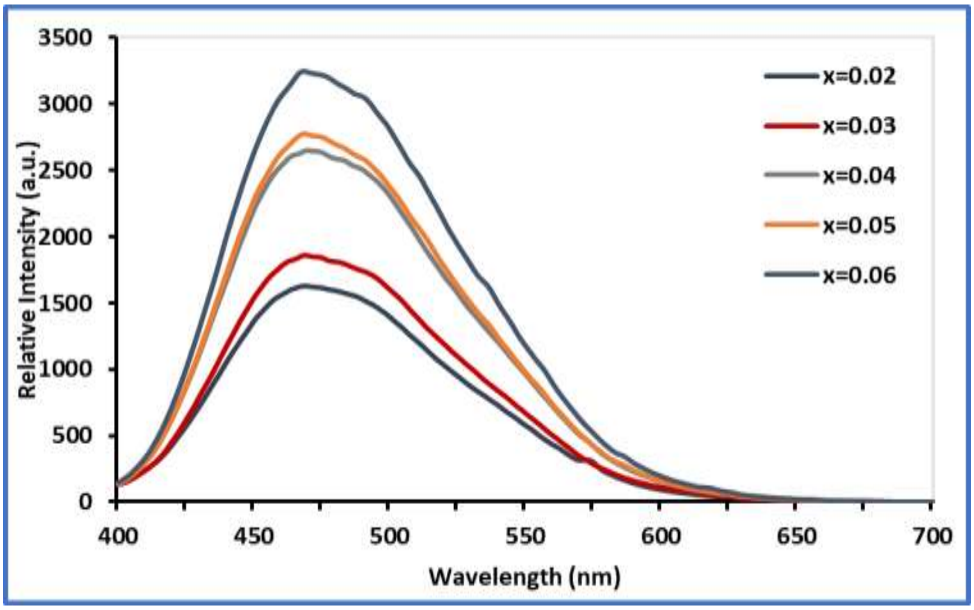


Fig.5. Photoluminescence Emission observed at 310nm excitation wavelength

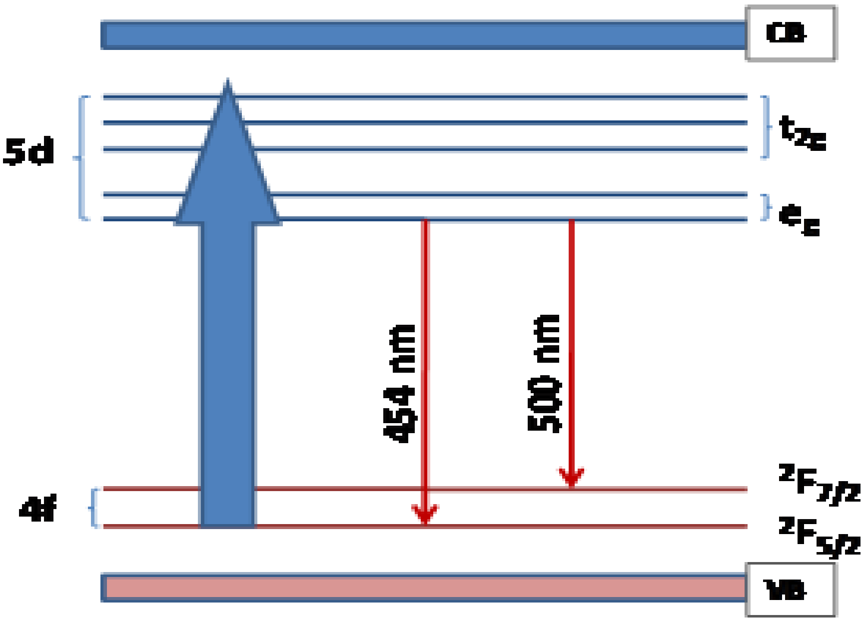


Fig.6. Energy level diagram of Ce^{3+} ion

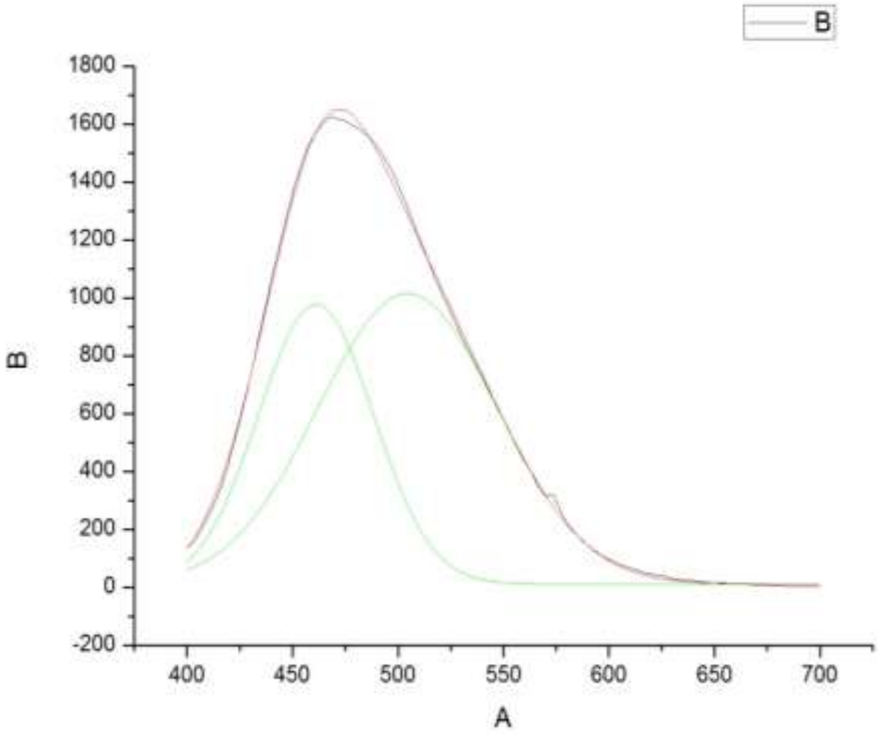


Fig.7. Gaussiun fitting of emission spectra(A- Wavelength and B- relative intensity)

The broad excitation spectra of $Sr_2SiO_4:Ce^{3+}$ phosphors with a center at 310 nm and a fixed emission wavelength of 472 nm are shown in Fig. 4. The 5d-4f transition of Ce^{3+} ions is represented by a single broad emission band at 472 nm in phosphor emission spectra. Depending on the host lattice, Ce^{3+} emission is primarily seen in the ultraviolet to visible portion of the spectrum, according to a review of the literature on numerous Ce^{3+} doped inorganic host lattices. The lowest 4f level is the ground state, which separates into two components, $^2F_{7/2}$ and $^2F_{5/2}$, because of spin-orbit coupling (2000cm–1). The 5d state is the excited state with crystal field splitting, which splits the levels into two to five components (18000 cm–1).

Because of these ground state splitting levels, Ce^{3+} typically produces doublet bands. This is depicted in Figure 5. Therefore, the emission of Ce^{3+} ions toward these terminating ground state levels originates from the lowest crystal field components of the 5d state. Since the distinctive doublet bands of Ce^{3+} are absent from the $Sr_2SiO_4{:}Ce^{3+}$ phosphors that we generated, an isolated broad band can be seen because of the spectral overlap of two ending levels. However, it can be fixed by fitting Gaussian curves, as Fig. 7 illustrates.

Therefore, we separate the emission bands into two bands at 454 nm (22026 cm^{-1}) and 500 nm (20000 cm^{-1}) using Gaussian curve fitting. Therefore, 2026 cm^{-1} is the measurement of the spin orbit splitting difference in these two 4f levels. Ce^{3+} ions may choose to occupy the smaller site of Sr^{2+} in the host lattice and create the emission centers because their ionic radii are much closer than those of Si^{4+}. These emission bands are nearly reliant on the splitting difference of the crystal fields; if it is considerable, the effect of Ce^{3+} in the host lattice causes emission to shift towards longer wavelengths.

As a result, the Ce^{3+} emission band is highly dependent on its immediate surroundings. It is discovered that the emission intensity increases up to 6% as the doping concentration rises. Up to 6 moles of Ce, concentration quenching is not seen in this scenario.

e) COLOR COORDINATES

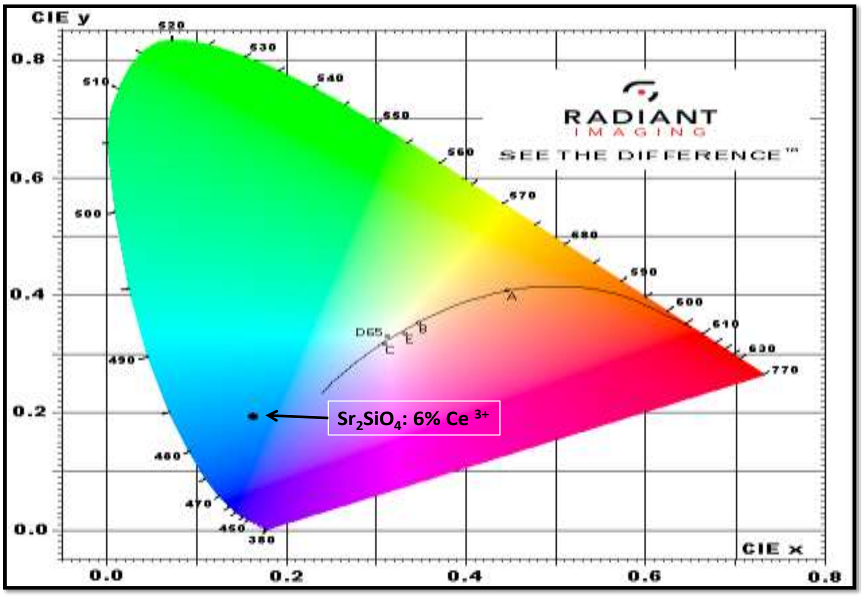


Fig.8. CIE coordinates of the $Sr_{1.94}SiO_4$:$0.06Ce^{3+}$

Fig. 8 displays the chromaticity coordination of the $Sr_{1.94}SiO_4$:0.06 Ce^{3+} phosphor according to the Commission International de'Eclairage (CIE). The chromaticity coordinates of the blue-emitting $Sr_{1.94}SiO_4$:0.06 Ce^{3+} phosphor are x=0.162 and y=0.194.

Conclusion :

$Sr_{(2-x)}SiO_4$:Ce^{3+} phosphors with particle sizes between 1-3 µm were successfully created using the solid-state reaction technique. The chemical composition of Sr_2SiO_4 was determined using EDAX analysis. XRD investigation confirmed the precise phase formation of Sr_2SiO_4. According to a photoluminescence investigation, when excited by n-UV light (310 nm), the phosphor showed blue color emission at 472 nm. n-UV, which closely matches the wavelength of the n-UV chip, could efficiently stimulate the $Sr_{(2-x)}SiO_4$:Ce^{3+} phosphors. $Sr_{1.94}SiO_4$:0.06 Ce^{3+} phosphor's CIE color chromaticity coordinates are x=0.162 and y=0.194, which indicate blue emission. Ce^{3+}-doped Sr_2SiO_4 is a viable option for a phosphor that emits blue light.

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