

Synthesis and Luminescence Properties of a Cyan-blue Thiosilicate-based Phosphor $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$

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Abstract

A series of Sr-Si-S compounds was synthesized using an advanced chemical method in which the use of one solution-based process uniformly dispersed the Eu^{2+} activators in the host crystals, to find new compositions that would suit phosphor applications. Particular focus was given to the Si-rich region. This led to the synthesis of a single-phase compound that showed an unknown X-ray diffraction pattern. This compound had a composition close to that of SrSi_2S_5 . When this compound is activated with Eu^{2+} ($\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$), it shows a cyan-blue emission with a main luminescence peak at 495 nm. This emission is excited by wavelengths of 250-440 nm and has a maximum excitation at 350 nm.

Keywords: thiosilicates, new compositions in strontium thiosilicate, cyan phosphor

1. Introduction

In recent years, the development of white LED has had a great impact on phosphor research. White LED is considered a next-generation light source. LEDs have several advantages over conventional incandescent and fluorescent lamps, including low power consumptions, long life, and non-use of toxic mercury. Consequently, white LED is expected to be increasingly used for practical applications. Practical white LEDs currently use a blue or nearly ultraviolet LED to excite a phosphor that emits visible light with the desired wavelengths to generate white light. Therefore, phosphors in white LEDs need to emit visible light at a high efficiency when excited by radiation from a blue or nearly ultraviolet LED. Few phosphors satisfy this requirement, though. Thus, new phosphors are required to increase the efficiency of white LED and to generate different kinds of white light for different applications.

In phosphors with activators, the choice of the activa-

tor and the host crystal greatly affects the fluorescence properties of the phosphor. Divalent europium Eu^{2+} is an activator that luminesces as a result of transitions from the 4f orbital to the outermost 5d orbital. Eu^{2+} is one of the most important activators, since its luminous color ranges from nearly ultraviolet to blue, to red, depending on its host crystal. The excitation energy of Eu^{2+} generally depends on the magnitude of the crystal field and the covalency of the host crystal. For example, many Eu^{2+} -activated oxide phosphors emit blue to purple luminescence when they are excited by high-energy ultraviolet light. In contrast, excitation and emission occur at longer wavelengths for the Eu^{2+} in a sulfide phosphor, which has a higher covalency than that of the corresponding oxide. Many Eu^{2+} -activated sulfide phosphors have green to red emissions when they are excited by nearly ultraviolet to visible light, since the excitation energy of the Eu^{2+} 5d orbital is significantly reduced because sulfur has less electronegativity than oxygen.

Consequently, Eu^{2+} -activated sulfide phosphors are promising phosphors for white LED applications. Alkaline earth metal silicates are considered suitable host crystals for Eu^{2+} -activated phosphors. For example, Sr silicates with many different compositions (e.g., Sr_3SiO_5 , Sr_2SiO_4 , SrSiO_3 and SrSi_2O_5) are known, and they all exhibit different emission characteristics when activated by Eu^{2+} [1-3]. Although diverse fluorescence properties are also expected by varying the composition of Sr thiosilicate systems, only $\text{Sr}_2\text{Si}_4:\text{Eu}^{2+}$ is the commonly known phosphor [4]. There

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has been a report on the photoluminescence of $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$, but there have been no other reports on Sr-Si-S compounds, except for the Sr_2SiS_4 system, even in the ICDD database (PDF-2 Release 2010) [5]. Thus, Sr-Si-S compounds other than Sr_2SiS_4 have been rarely investigated. This is partly due to the greater difficulty in synthesizing multicomponent thiosilicates in their pure forms than their corresponding oxides. $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$ has strong yellow-green luminescence when excited by nearly ultraviolet and visible light.

To facilitate the synthesis of multicomponent thiosilicates, the authors' research group has developed a multiple combination method that is based on inorganic chemistry and that combines a solution method, gas reduction sulfurization, and a solid-state reaction in a vacuum-sealed quartz ampoule [6-8]. This method is meant to be used to discover novel Sr thiosilicates. Accordingly, the three-step multiple combination method was used to synthesize Eu^{2+} -activated Sr thiosilicate phosphors with new compositions that have not yet been studied. This study reports the preparation of an Eu^{2+} -activated Sr thiosilicate with a single phase that has the composition $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$. The structural characteristics and fluorescent properties of the Eu^{2+} -activated Sr thiosilicate are also reported.

2. Experiments

Eu^{2+} -activated Sr thiosilicate phosphors were synthesized using the aforementioned method, which consists of the following three steps (see Fig. 1).

Step 1. A carbonate precursor of $\text{SrCO}_3:\text{Eu}^{3+}$ was synthesized using the polymerizable complex method [9]. Citric acid and propylene glycol were added to an aqueous solution of Sr and Eu nitrates, and this solution was mixed and stirred. The solution was then heated to 353 K to form metal citrate complexes, and was further heated to 393 K to obtain a polyester-resin gel, in which each metal complex is fixed in the polymer in a uniform state. The polyester resin was calcined at 1,073 K to obtain the carbonate precursor of $\text{SrCO}_3:\text{Eu}^{3+}$, in which the Eu ions were uniformly distributed.

Step 2. $\text{SrS}:\text{Eu}^{2+}$ was synthesized by sulfurizing $\text{SrCO}_3:\text{Eu}^{3+}$ using H_2S . The carbonate $\text{SrCO}_3:\text{Eu}^{3+}$ was placed in an alumina boat and heated at 1,223 K for 5 h in a 10% H_2S to 20 ml/min Ar flow in a tube furnace to produce

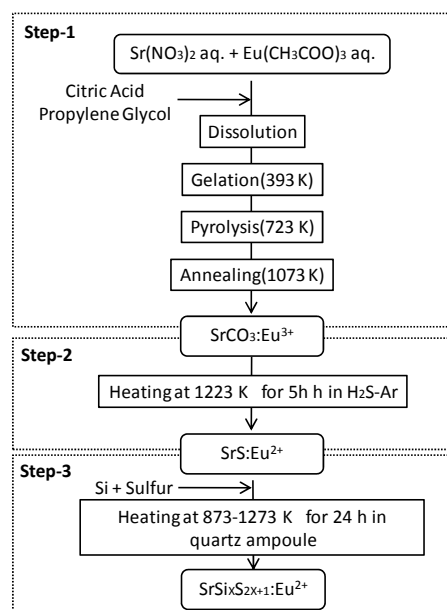


Fig. 1. Flowchart of the $\text{SrSi}_x\text{S}_{2x+1}:\text{Eu}^{2+}$ synthesis.

$\text{SrS}:\text{Eu}^{2+}$, which is a precursor of the synthesis of Sr thiosilicates. During the sulfurization, the Eu^{3+} ions in SrCO_3 were reduced to Eu^{2+} .

Step 3. The Eu^{2+} -activated Sr thiosilicate was synthesized by making the $\text{SrS}:\text{Eu}^{2+}$ interact with Si and sulfur. The $\text{SrS}:\text{Eu}^{2+}$ and the powders of Si and sulfur were mixed to achieve a stoichiometry that corresponded to $(\text{Sr},\text{Eu}):\text{Si}:\text{S} = 1:x:2x$ ($x = 1/3, 1, 2$ and 3). This mixture was pressed into pellets and vacuum-sealed in a quartz ampoule. The samples were heated at 873 to 1,273 K for 24 h to obtain the target materials.

The resulting sample was characterized via X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive X-ray (SEM-EDX) analysis, and fluorescence spectroscopy.

3. Results and Discussion

3.1 Identification of thiosilicate phosphor, $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$

Fig. 2 shows the XRD patterns of the samples with different Sr:Si ratios that were synthesized via calcination at 973 K. The sample with the composition $x = 1/3$, which is Si-deficient relative to Sr_2SiS_4 , was a multiphase that was composed of Sr_2SiS_4 and SrS. Based on this finding, there were no anticipated Sr thiosilicates with Si contents lower

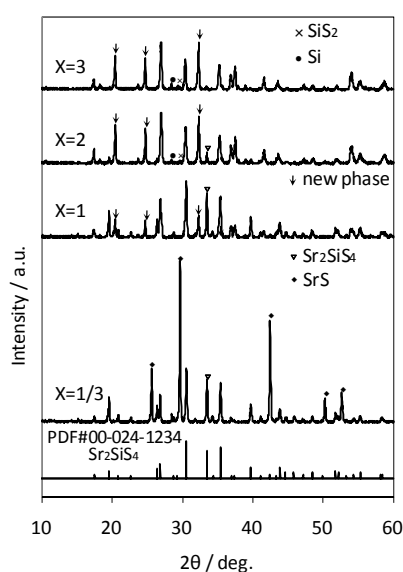


Fig. 2. XRD patterns of the samples with varied compositions of $\text{SrSi}_x\text{Si}_{2x+1}$ that were obtained via annealing at 973 K.

than Sr_2SiS_4 . On the other hand, the samples that were synthesized in the composition range of $x = 1-3$, which contains more Si than Sr_2SiS_4 , had unknown diffraction peaks that were not the characteristic Sr_2SiS_4 peaks at $2\theta = 20.4^\circ$, 24.7° and 32.3° . These observations imply that a novel Sr thiosilicate phase was formed that contains more Si than Sr_2SiS_4 . The intensity of these unknown peaks increased greatly with increasing Si content of $x = 1$ to 2. In contrast, the diffraction peak intensity of the Sr_2SiS_4 phase, which was very noticeable in the XRD pattern for the sample with $x = 1$, was lower in the sample with $x = 2$. Furthermore, while no changes were observed in the diffraction peak intensity of the unknown phase in the sample with $x = 3$ that contained even more Si, some characteristic diffraction peaks of the Sr_2SiS_4 phase (for example, $2\theta = 19.5^\circ$, 33.4° and 39.6°) completely disappeared. Instead, the intensity of the diffractions that originated from the remaining Si and SiS_2 phases increased. Comparison of the XRD patterns of these samples suggested that a novel Sr thiosilicate phase at the Sr-rich end of the Sr-SiS₂ systems had been formed. Its most probable composition is SrSi_2S_5 .

The synthesis conditions were examined for SrSi_2S_5 . Fig. 3 shows the XRD patterns for the samples that were calcined at 873 to 1,223 K. They reveal that Sr_2SiS_4 is present as a major phase, together with Si and SiS_2 , in the sample after heat treatment at 873 K. The Sr_2SiS_4 peak intensity declined remarkably, and the new phase (SrSi_2S_5)

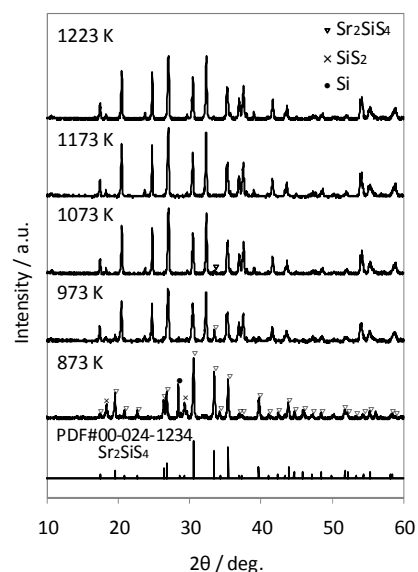


Fig. 3. XRD patterns of the SrSi_2S_5 that was obtained via annealing at various temperatures.

became the main phase as the firing temperature was increased to 973-1,073 K. Furthermore, for the samples that were heat-treated at 1,173 and 1,223 K, the Si, Sr_2SiS_4 , and SiS_2 diffraction peaks disappeared and a diffraction pattern was obtained that did not correspond to that of any known substance. Increasing the temperature to 1,223 K increased the diffraction peak intensity and improved the crystallinity. The sample melted at temperatures greater than 1,273 K. As shown in Fig. 4, the XRD patterns of the new phase were indexed, and the following lattice parameters were obtained: $a = 17.5917 \text{ \AA}$, $b = 10.1647 \text{ \AA}$, $c = 8.8462 \text{ \AA}$, and $\beta = 70.6590^\circ$ in a monoclinic system with the space group C2, which allowed indexing of all the diffraction

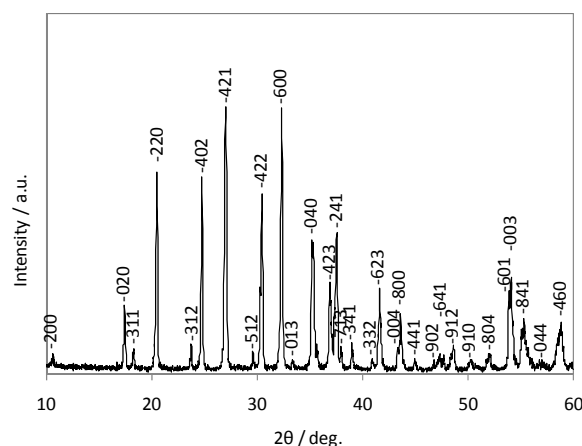


Fig. 4. Full indexing of the XRD patterns of SrSi_2S_5 in a monoclinic system with the space group C2.

peaks. This revealed that the sample that was heat-treated at 1,223 K had a single phase. The analysis of the chemical compositions of the particles of this sample via SEM-EDX revealed that Sr:Si:S is equal to 1:2:5. Therefore, it is concluded that the single-phase Sr thiosilicate SrSi_2S_5 had been synthesized. Detailed XRD analysis using a single crystal is essential for determining the crystal structure of SrSi_2S_5 . Attempts to grow single crystals of SrSi_2S_5 are in progress.

3.2 Luminescence characteristics of the thiosilicate phosphor, $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$

Fig. 5 shows the emission spectra that were obtained when the new Eu^{2+} (1%) -activated samples of $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ ($x = 2$) that had been calcined at 873 to 1,223 K were excited with 350 nm-wavelength light. The samples that were calcined at 1,073 to 1,223 K, in which the SrSi_2S_5 phase was the main phase, had cyan-blue emissions, with a maximum luminescence peak at 495 nm. In contrast, the sample that was calcined at 873 K, in which Sr_2SiS_4 is the main phase, exhibited a yellow-green emission with a maximum luminescence peak at 550 nm, which originated from $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$. The emission intensity at 550 nm that originated from $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$ decreased sharply as the firing temperature increased, and disappeared completely in the samples that were calcined at temperatures above 1,173 K. These observations confirm that $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ formed a new family of Eu^{2+} -activated Sr thiosilicates with luminescence characteristics that differ from those of $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$. The emission property of the present $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ is similar to the previously reported property; i.e., the maximum emission is at 490 nm [5]. The emission intensity of the sample

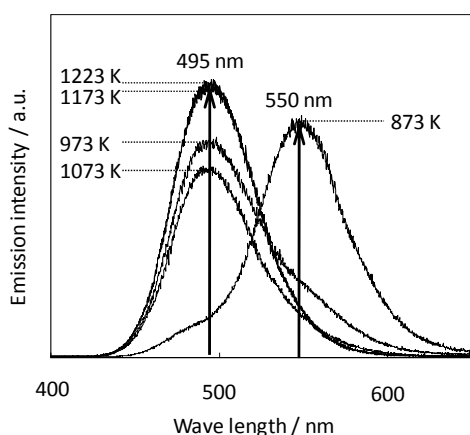


Fig. 5. Emission spectra of the SrSi_2S_5 (1 mol% to Sr) that was obtained via annealing at various temperatures. The samples were excited at 350 nm.

with the highest crystallinity and without detectable impurities after heat treatment at 1,223 K was 24%, higher than that of one of the best commercially available yellow phosphors, $\text{YAG}:\text{Ce}^{3+}$.

The luminescence characteristics of a given Eu^{2+} -activated phosphor generally vary much according to the amount of Eu that is incorporated in the crystal structure. $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ samples with different Eu concentrations were synthesized, and the effect of the Eu concentration on the luminescence characteristics was examined. To obtain the host compound of SrSi_2S_5 with a high crystallinity and with no impurities, $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ (0.5-5%) was synthesized via calcination at 1,223 K. The XRD measurements confirmed that $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ (0.5-5%) was obtained as a single phase, irrespective of the Eu content. Fig. 6 shows the excitation and emission spectra of the prepared $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ (0.5-5%) samples. The sample with an Eu^{2+} concentration of 5% had the highest luminescence intensity of all the samples, at 28% compared with that of the $\text{YAG}:\text{Ce}^{3+}$ phosphor. Although no systematic variation in the luminescence intensity as a function of the Eu concentration was observed, the increase in the Eu concentration tended to significantly enhance the intensity of the excitation spectra of $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ in the region around 400 nm. This was most noticeable in the sample with an Eu^{2+} concentration of 5%. The reason for this remains unclear, but it may be related to an increase in either the crystal field splitting width of the 5d orbital of Eu^{2+} or the probability of energy transfer between Eu^{2+} - Eu^{2+} with the increasing Eu concentration. In the first case, the size of the crystal lattice decreases with the increasing Eu concentration, so the distance between S^{2-} and Eu^{2+} de-

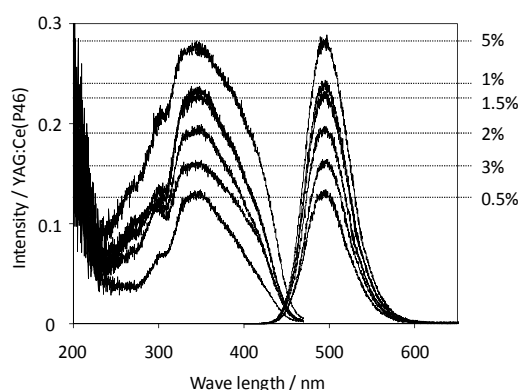


Fig. 6. Excitation and emission spectra of the $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ (0.5-5 mol% to Sr) that was synthesized at 1,223 K. The excitation spectra were monitored for emissions at 495 nm, and the emission spectra were recorded as having been excited at 350 nm.

creases, which increases the crystal field splitting width of the 5d orbital of Eu^{2+} and increases the excitation wavelength range [10]. In the second case, since the distance between Eu^{2+} - Eu^{2+} in the host crystal decreases as the Eu concentration increases, the probability of energy transfer between Eu^{2+} - Eu^{2+} increases, which may increase the energy width of the 5d excitation level of Eu^{2+} .

Fig. 7 shows the variations in the luminescence intensities of $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ and $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$ as a function of the temperature (room temperature to 473 K). $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ exhibits thermal quenching at a lower temperature than $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$. The thermal quenching of an Eu^{2+} -activated phosphor depends on the relationship between the energy difference between the 5d excitation level of Eu^{2+} and the conduction band of the host crystal and on lattice vibrations of the host crystal. Sr^{2+} and Si^{4+} , which are both present in Sr thiosilicate, are considered to possess high lowest-unoccupied molecular orbitals. In addition, the conduction band of the host crystal is thought to have higher energy than the 5d excitation level of Eu^{2+} . Consequently, it is unlikely that the excited electron of Eu^{2+} would be promoted to the conduction band of the host crystal by the excitation heat. Therefore, the difference in the thermal excitation characteristics of $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ and $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$ are assumed to have been due to the different degrees of lattice movement in the two host crystals. To gain a deeper understanding of the thermal quenching characteristics of these

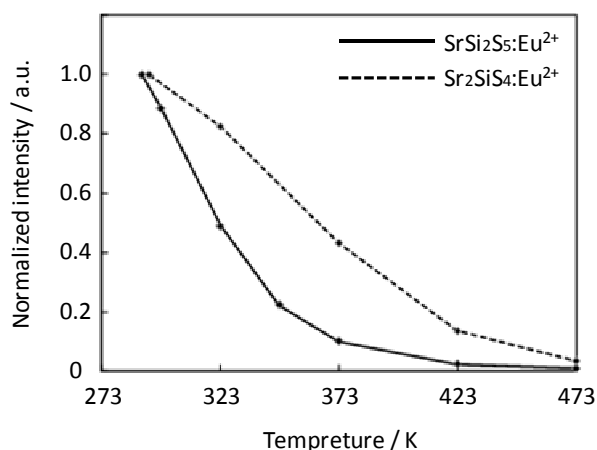


Fig.7. Normalized PL intensity as a function of temperature for $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ and $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$. The samples were excited by each excitation maximum wavelength.

Sr thiosilicate phosphors, it is necessary to have precise knowledge of the band structure of the host crystal, the energy of the 4f-5d level of Eu^{2+} , and the crystallographic arrangement of SiS_4 tetrahedra in the host crystal. These information can be obtained by determining the crystal structures of SrSi_2S_5 as well as Sr_2SiS_4 .

4. Conclusions

A method of synthesizing Sr thiosilicates was developed. The single phase of $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ was synthesized in this study. The luminescence characteristics of the Eu^{2+} -activated phosphor, $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$, were clarified. The phosphor $\text{SrSi}_2\text{S}_5:\text{Eu}^{2+}$ had a cyan-blue emission. Its main luminescence peak at 495 nm was excited by ultraviolet to blue (250-440nm) light. The corresponding maximum excitation was at 350 nm. The results of this study demonstrate that the authors' three-step process, which is based on an advanced chemical method [6-8], can be used to prepare a wide range of complex sulfide-based phosphors. This synthesis technique is considered useful in the search for new sulfide-based phosphors that are suitable for use in white LED and other devices, such as phosphor sensors that can detect temperature changes.

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