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Broad luminescence of \( \text{Ce}^{3+} \) in multiple sites in \((\text{La},\text{Ce},\text{Y})_6\text{Si}_4\text{S}_{17}\)

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Abstract. We have developed novel broad luminescent phosphors \((\text{La},\text{Ce},\text{Y})_6\text{Si}_4\text{S}_{17}\) including multiple substituted sites of \(\text{Ce}^{3+}\). They have been formed a triclinic structure (\(P-1\)) with three kinds of coordination structures around \(\text{Ce}^{3+}\) ions. The broad photoluminescence (PL) spectra at the range from 430 nm to 700 nm were observed, and they can be respectively decomposed into three PL bands. Moreover, the correlation between the three PL bands and the three substitution sites for \(\text{Ce}^{3+}\) were confirmed through the PL spectra at 78 K and a Van Uitert’s universal equation.
1. Introduction

Along with the development of GaN-based light-emitting diodes (LED) [1, 2], white LEDs have attracted much interest as energy-saving, reliable and environmentally friendly light sources. Commercial white LED consists of a blue-LED and one or more phosphor materials, and is usually called phosphor converted LED (pc-LED). The phosphor materials partially convert the blue-LED emission. Ce$^{3+}$, Eu$^{2+}$ and Mn$^{2+}$ ions are well used as the activator for such broad luminescent phosphors. Because the emission band width can be expanded to some extent through the applied crystal field in hosts. The typical phosphor is a YAG:Ce$^{3+}$-based yellow phosphor [3, 4, 5]. However, this phosphor has less red fluorescence. So it exhibits low color rendering index and high correlated color temperature. To improve the color characteristics for better lighting systems, the phosphors having wide emission bandwidth are required. Recently, oxide, sulfide, nitride and oxy-nitride phosphors have been reported as candidates for such the phosphors. They are classified into the following two types.

The first group of phosphor contains multiple activator ions in a host [6, 7, 8, 9]. They have several luminescence peaks originating from 4f-5d transition (Ce$^{3+}$ or Eu$^{2+}$) or 3d-3d transition (Mn$^{2+}$). For example, $Y_{10}(Si_8O_{22}N_2)O_2$:Ce$^{3+}$,Mn$^{2+}$ shows wide luminescence ranging from 350 nm to 700 nm, originating from $5d^1 \rightarrow 4f^1$ transition of Ce$^{3+}$ and $4T_1(4G) \rightarrow 6A_1(6S)$ transition of Mn$^{2+}$ [6].

The second group phosphor contains a single activator ion in the host having multiple substitution sites [10, 11, 12, 13, 14]. $Y_3Si_8N_9O$:Ce$^{3+}$ phosphor, a representative example, has two different substituted sites of Ce$^{3+}$ [13]. This shows a broad luminescent band covering from blue to deep red light (450-850 nm) with the internal quantum efficiency (17.2%). A disappointing feature of this phosphor is that it requires high temperatures and reducing atmosphere to produce. On the other hand, thiosilicate phosphors also have multiple substitution sites and can be fabricated at relatively low temperature [15, 16, 17, 18, 19, 20, 21]. Especially, we have confirmed that the monoclinic (Gd,Ce)$_4$(SiS)$_3$ and (Y,Ce)$_4$(SiS)$_3$ show broad luminescence originated from Ce$^{3+}$ ions replaced with the multiple Y or Gd sites in $Y_4(SiS)_3$ and $Gd_4(SiS)_3$ [20]. They have high internal quantum efficiency (62%) and host excitation efficiency, and also high water-resistance. The superior luminescence properties and the water-resistance depend on the host materials. However, there is no report other efficient phosphors using rare-earth thiosilicate hosts.

There are many rare-earth thiosilicate crystals. The fabrication processes have been reported for monoclinic Ln$_4$(SiS)$_3$ (Ln = Gd, Tb or Dy) [22, 23, 24], Ln$_9$Si$_5$ (Ln = La, Ce) [25, 26], Eu$_2$Si$_4$ [27], Eu$_4$Si$_5$ [18], hexagonal Ln$_6$Si$_{2.5}$S$_{14}$ (Ln = Y, Gd, Tb or Dy) [28], trigonal Ln$_4$Si$_3$S$_{12}$ (Ln = Ce, Pr, Nd, Sm or Gd) [26, 29] and triclinic Ln$_6$Si$_4$S$_{17}$ (Ln = Ce, Pr, Nd or Sm) [26, 30].

The triclinic thiosilicate crystals have distinct six rare-earth sites, categorized into three kinds of coordination structures around rare-earth ions. A triclinic phosphor Ce$_6$Si$_4$S$_{17}$ (space group P-1) exhibits much broad luminescence at the range from 443 nm
Broad luminescence of Ce$^{3+}$ in multiple sites in (La,Ce,Y)$_6$Si$_4$S$_{17}$ to 668 nm. In addition, it has been confirmed from differential thermal analysis and thermogravimetry analysis that this has a good thermal stability up to 500°C [26]. However, the internal quantum efficiency is quite low (10%) due to concentration quenching of Ce$^{3+}$. If the quenching can be eliminated, Ce$^{3+}$-doped triclinic rare-earth thiosilicates will be promising broad luminescent and high efficiency phosphors. A possible solution is to replace most of the six sites with different ions.

In this paper, we report novel broad luminescent phosphors (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ (0 ≤ x ≤ 0.2). These were prepared by replacing the most sites of Ce with La or Y in Ce$_6$Si$_4$S$_{17}$ and maintaining a triclinic structure (P-1). The photoluminescence (PL) spectra were observed from blue to red region, originating from the electron transition from 5d$^1$ excited state to 4f$^1$ ($^2F_J, J = 5/2, 7/2$) ground state in Ce$^{3+}$ ions. The photoluminescence excitation (PLE) spectra were broadened with increase of Ce concentration. It was found from the PL measurements at low temperature that three different PL and PLE bands are included in the spectra. Here, we discuss the correlation between the PL bands and the substitution sites of Ce$^{3+}$ in La$_6$Si$_4$S$_{17}$.

2. Experimental Procedure

For the fabrication of polycrystalline (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ powders, we used the solid state reaction technique in vacuum-sealed silica-glass ampoule. A mixture of La$_2$S$_3$, Ce$_2$S$_3$, Y$_2$S$_3$, Si and S powders in the molar ratio of La$_2$S$_3$ : Ce$_2$S$_3$ : Y$_2$S$_3$ : Si : S = 3(0.9 − x) : 3x : 0.3 : 4.4 : 8.8 was prepared. The total weight of the powder was ∼300 mg. The value x refers to Ce concentration in the range of 0-0.2. To obtain the single phase triclinic (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ phosphors, additional Y$_2$S$_3$ was needed. When the phosphors were fabricated without the addition, monoclinic La$_2$Si$_5$ phase was appeared in them (experimental data are not shown here). To avoid a residual of rare-earth sulfide after thermal heating, a 10% molar excess of Si and S were added in the starting mixture. The mixture was sealed in a silica-glass ampoule in a vacuum of 10$^{-2}$ Pa. For the first annealing, the ampoule was heated for 24 h at 1050°C. Since a trace of other phase still existed in the powders after the annealing, the powders and additional sulfur (20 mg) were milled and heated again for 24 h at 1050°C after sealing in a vacuum silica tube.

X-ray diffraction (XRD) patterns were recorded using a Rigaku Rint2000 diffractometer in standard θ-2θ geometry using Cu K$_\alpha$ radiation. Structural information such as lattice constants was obtained through the Rietveld method. The atomic positions and thermal expansion factors were not refined, because they require higher quality XRD patterns.

The third harmonic of a pulsed Nd:YAG laser (355 nm, 10 kHz) and monochromatic output from a xenon arc lamp were used as the excitation source for PL measurements. The latter was also used for PLE measurements. A charge-coupled device camera and a photomultiplier were used for photo-detection in the PL and PLE measurements. The second harmonic of a pulsed Ti:sapphire laser (400~440 nm, 82 MHz, pulse duration <
130 fs) and a spectrometer with a streak camera (Hamamatsu-Photonics C5680) were used for time-resolved PL measurements. An excitation pulse was picked up by using a Pockels cell. The system time resolution was 0.8 ns. These measurements were carried out with a cryostat in a temperature range of 78-300 K. Internal quantum efficiency was measured using a spectrophotometer (Hamamatsu C11347-01) having an integrating sphere. Sample powder (~20 mg) was put on a quartz Petri dish which was placed within the integrating sphere. Monochromatic output from 300 nm to 500 nm of a xenon arc lamp was used for the excitation. Details of the measurement can be found in [18].

3. Results and discussion

3.1. XRD results

Figure 1 shows XRD patterns of (La_{0.9-x}Ce_xY_{0.1})_6Si_4S_{17} (x = 0-0.2). In the top of this figure, a simulated XRD pattern for Ce_6Si_4S_{17} is placed. The simulation was conducted using the crystallographic data of Ce_6Si_4S_{17} [26] and the RIETAN-FP program [31]. Line shapes were models by pseudo-Voigt profile functions. For the all of samples, the XRD pattern are well understood only shifts from that of Ce_6Si_4S_{17}, and no peak for starting materials and no unidentified peak were confirmed. This indicates that single phase triclinic (La_{0.89-x}Ce_xY_{0.1})_6Si_4S_{17} powders were obtained in this work. Ce^{3+} and Y^{3+} ions would be substituted for La sites in La_6Si_4S_{17} hosts. At present, the triclinic-type lanthanum thiosilicate has not been reported. From the diffraction peak positions of the XRD pattern for (La_{0.9}Y_{0.1})_6Si_4S_{17}, the lattice constants were estimated at a = 8.99 Å, b = 10.02 Å, c = 14.28 Å, α = 82.21°, β = 86.96°, γ = 89.47°, respectively. With the increase in x, the lattice constants a, b and c are decreased. For example, the lattice constants of (La_{0.7}Ce_{0.2}Y_{0.1})_6Si_4S_{17} were estimated at a = 8.98 Å, b = 10.01 Å, c = 14.27 Å, α = 82.22°, β = 86.96°, γ = 89.45°, respectively. This can be understood as arising from the substitution of La^{3+} by Ce^{3+}, since the ionic radius of Ce^{3+} is 2% smaller than that of La^{3+} [32]. It can be also understood that the lattice constants a, b and c of (La_{0.9}Y_{0.1})_6Si_4S_{17} are 0.3%, 0.2% and 0.1% larger than that of Ce_6Si_4S_{17}, respectively, considering their ionic radii.

3.2. Photoluminescence at room temperature

Figure 2 shows PL spectra and PLE spectra of (La_{0.9-x}Ce_xY_{0.1})_6Si_4S_{17}. This broad PL band from 420 nm to 720 nm originates from 5d\rightarrow 4f^1 (2F, J = 5/2, 7/2) transition of Ce^{3+} replaced with La sites in the hosts. With the increase in x, the PL peak slightly shifts from 532 nm to 536 nm, while the full width at half maximum (FWHM) of the PL band decreases from 107 nm to 97 nm. The maximum internal quantum efficiency was found to be 59\% for x = 0.07, and kept after immersion in distilled-water for a day at room temperature (details on the measurement can be found in [20]). It could be confirmed that the phosphors also have high water resistance, same as (Gd,Ce)_{4}(SiS)_{3}
Broad luminescence of Ce$^{3+}$ in multiple sites in (La,Ce,Y)$_6$Si$_4$S$_{17}$ and (Y,Ce)$_4$Si$_3$S$_{17}$ [20]. For the PLE band, the FWHM significantly increases from 70 nm to 129 nm with the increase in $x$. The complicated dependence of PL and PLE spectra on Ce concentration can be explained by the multiple substitution sites of Ce$^{3+}$ in (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$. The atomic positions of La$_6$Si$_4$S$_{17}$ have not yet been refined by the XRD patterns. Thus, we discuss the S$^{2-}$ coordination structures around rare-earth ions in La$_6$Si$_4$S$_{17}$ with reference to those of Ce$_6$Si$_4$S$_{17}$ having similar triclinic structure.

The Ce-S coordination structures around each Ce sites in Ce$_6$Si$_4$S$_{17}$ are summarized in table 1. The volume ($V_c$) of the Ce-S coordination structure and the average distance ($R_a$) between Ce and S were estimated by VESTA [33]. Ce$_6$Si$_4$S$_{17}$ has distinct six Ce sites, and they are mainly classified into three types according to their coordination structure and number. The schematic of the three coordination structures, mono-capped trigonal prism (1ctp), bi-capped trigonal prism (2ctp) and tri-capped trigonal prism (3ctp), are shown in figure 3. There are one 1ctp, three 2ctp and two 3ctp in Ce$_6$Si$_4$S$_{17}$. The Ce sites belonging to the same prism group have almost the same $V_c$ and $R_a$. La$_6$Si$_4$S$_{17}$ has also six distinct La sites similar to Ce$_6$Si$_4$S$_{17}$. The 4f-5d transitions in Ce$^{3+}$ related to the PL and PLE bands depend on the coordination environment around the ion, which causes the 5d level splitting through crystal field. Therefore, it can be assumed that the PL and PLE spectra of (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ contain three types of PL and PLE bands, which are related to the three prism structures. In the next subsection, we will discuss the validity of this assumption through fine analysis of the spectra measured at 78 K.

3.3. Photoluminescence at low temperature (at 78 K)

Figure 4 shows excitation wavelength ($\lambda_{ex}$) dependence of PL spectra for (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ ($x = 0.01$ (a) and 0.2 (b)) at 78 K. They have a few peaks commonly and their spectral shapes were changed dramatically as the excitation wavelength was shifted from 410 nm to 480 nm. These indicate that the PL spectrum includes several intrinsic PL bands. The PL spectrum from Ce$^{3+}$ in a La site consists two bands, corresponding to the transitions from 5d$^1$ to $^2F_{7/2}$ and $^2F_{5/2}$ levels in the 4f$^1$ configuration, respectively. The energy level of $^2F_{7/2}$ is higher than that of $^2F_{5/2}$, so the PL band for the former is placed at longer wavelength side. From now on, we will treat the two PL bands originating from Ce$^{3+}$ in a La site as one unit. At first, we discuss the PL spectra shown in figure 4 (a). The spectrum for 480 nm excitation clearly shows simple double peaks, so this can be ascribed to Ce$^{3+}$ ions in a La site. We termed the PL unit "X1" band. As for the excitation at 440 nm, the PL spectrum shifts to lower wavelength and has a tail on the long wavelength side. From now on, we will discuss the PL spectra shown in figure 4 (a). The spectrum for 480 nm excitation clearly shows simple double peaks, so this can be ascribed to Ce$^{3+}$ ions in a La site. We termed the PL unit "X1" band. As for the excitation at 440 nm, the PL spectrum shifts to lower wavelength and has a tail on the long wavelength side. From now on, we will discuss the PL spectra shown in figure 4 (a). The spectrum for 480 nm excitation clearly shows simple double peaks, so this can be ascribed to Ce$^{3+}$ ions in a La site. We termed the PL unit "X1" band. As for the excitation at 440 nm, the PL spectrum shifts to lower wavelength and has a tail on the long wavelength side. From now on, we will discuss the PL spectra shown in figure 4 (a). The spectrum for 480 nm excitation clearly shows simple double peaks, so this can be ascribed to Ce$^{3+}$ ions in a La site. We termed the PL unit "X1" band. As for the excitation at 440 nm, the PL spectrum shifts to lower wavelength and has a tail on the long wavelength side. From now on, we will discuss the PL spectra shown in figure 4 (a). The spectrum for 480 nm excitation clearly shows simple double peaks, so this can be ascribed to Ce$^{3+}$ ions in a La site. We termed the PL unit "X1" band. As for the excitation at 440 nm, the PL spectrum shifts to lower wavelength and has a tail on the long wavelength side. From now on, we will discuss the PL spectra shown in figure 4 (a). The spectrum for 480 nm excitation clearly shows simple double peaks, so this can be ascribed to Ce$^{3+}$ ions in a La site. We termed the PL unit "X1" band. As for the excitation at 440 nm, the PL spectrum shifts to lower wavelength and has a tail on the long wavelength side. From now on, we will discuss the PL spectra shown in figure 4 (a). The spectrum for 480 nm excitation clearly shows simple double peaks, so this can be ascribed to Ce$^{3+}$ ions in a La site. We termed the PL unit "X1" band. As for the excitation at 440 nm, the PL spectrum shifts to lower wavelength and has a tail on the long wavelength side.
Broad luminescence of Ce\textsuperscript{3+} in multiple sites in (La, Ce, Y)\textsubscript{6}Si\textsubscript{4}S\textsubscript{17} to Ce\textsuperscript{3+} in a third kind of La site. In figure 4(b) for \(x = 0.2\), the PL peak located at 460 nm was not observed even when excited at 410 nm. This might be due to the concentration quenching of Ce\textsuperscript{3+} related to X3 band, and will be discussed in the next measurement of PL decay curves. The spectra for 440 and 480 nm excitation had no change from those of \(x = 0.01\). The result indicates that X1 and X2 bands would not shift with increasing Ce concentration. Thus, it is considered that the spectral change, varying with the excitation wavelength as shown in figure 2 and figure 4, is due to the intensity ratio of the X1, X2 and X3 bands.

Detection wavelength dependence of PLE spectra for (La\textsubscript{0.89}Ce\textsubscript{0.01}Y\textsubscript{0.1})\textsubscript{6}Si\textsubscript{4}S\textsubscript{17} at 78 K is shown in figure 5. The PLE peaks in the long wavelength region are located at 410, 440 and 475 nm for the PL detection at 460, 500 and 620 nm, respectively. They would originate from the 4f\textsuperscript{1}(\textsuperscript{2}F\textsubscript{5/2}) \(\rightarrow\) 5d\textsuperscript{1} transition for Ce\textsuperscript{3+} in three different La sites. The excitation wavelengths used for the PL measurement in figure 4 were located near these peaks. Thus, it can be assumed that the discussion about PL spectra in figure 4 is plausible. That is, the observed PLE peaks at 475, 440 and 410 nm are the origins of the X1, X2 and X3 PL bands, respectively.

To assign the X1, X2 and X3 bands, we demonstrated fitting the PL spectra shown in figure 4(a) using Gaussian curves. Figure 6(a), (b) and (c) show the fitting result for the PL spectrum, shown in figure 4(a), excited at 480, 440 and 410 nm, respectively. Here, the PL spectra are represented by open circles and the fitting results are shown by solid lines. The bottom axis was changed to the photon energy for the fitting. Firstly, it is found that the PL spectrum in figure 6(a), having narrow two peaks, could be fitted by just two Gaussian curves, as represented by a dashed-dotted line. This indicates that the PL spectrum induces from the X1 band, belonging to the lowest energy site. Secondly, the PL spectrum in figure 6(b), showing blue shift and broadening of the spectral shape, could be clearly represented by the two curves and additional two Gaussians. In this fitting, we fixed the peak widths, positions and intensity ratios between these two peak intensities of the former, corresponding to the X1 band. The additional two curves, as represented by a dashed line, would be assigned to the X2 band. Finally, the PL spectrum in figure 6(c) could be also reproduced by the same manner. Before the fitting, we fixed the peak widths, positions and intensity ratios between these two peak intensities for the X1 and X2 bands. Then the spectrum was well fitted with additional two Gaussians. The additional two, as represented by a dotted line, could be assigned to the X3 band. The obtained parameters, peak positions and their energy differences, are summarized in table 2. As mentioned before, the lower side peak in the curve pairs corresponds to the transition from 5d\textsuperscript{1} to 4f\textsuperscript{1}(\textsuperscript{2}F\textsubscript{7/2}), while the higher comes from 5d\textsuperscript{1} to 4f\textsuperscript{1}(\textsuperscript{2}F\textsubscript{5/2}) transition. The energy differences, corresponding to the spin-orbit splitting of the 4f\textsuperscript{1} level in Ce\textsuperscript{3+} ion, are similar with that for (Gd, Ce)\textsubscript{4}(SiS\textsubscript{4})\textsubscript{3} (0.24 eV) and (Y, Ce)\textsubscript{4}(SiS\textsubscript{4})\textsubscript{3} (0.24 eV) [20]. This indicates that our deconvolution process is adequate for the analysis of the emission bands in (La\textsubscript{0.89}Ce\textsubscript{0.01}Y\textsubscript{0.1})\textsubscript{6}Si\textsubscript{4}S\textsubscript{17}.

In the previous paragraph, the PL spectrum of (La\textsubscript{0.89}Ce\textsubscript{0.01}Y\textsubscript{0.1})\textsubscript{6}Si\textsubscript{4}S\textsubscript{17} could be divided into three PL bands. However, the PL bands have not yet been associated with
the each specific La sites. To clarify the correspondence between the three PL bands and the three kinds of Ce ions substituted for La sites in La₆Si₄S₁₇, we discussed with the following empirical equation [34].

\[ E/Q = \left[1 - \left(\frac{V}{4}\right)^{1/V}10^{-10(nrA/20)}\right], \tag{1} \]

where \(E\) is the lowest emission or excitation energy of a Lanthanide ion taken in a host crystal, and \(Q\) is the d-band energy when the ion is in free space. \(V\) is the valence of the ion. \(A\) is the electron affinity of a ligand anion. \(n\) is the coordination number around the ion. \(r\) is the ionic radius of a host cation substituted by the ion. This formula gives the correspondence between the emission energy and the anion coordination around the host cation in the first approximation. What matters in this correspondence is not details of the coordination structure but the type and number of anions and the ionic radius of host cations. Van Uitert have succeeded in explaining the emission peak and/or excitation edge energies for Eu²⁺ or Ce³⁺ systematically by using this equation in many hosts such as sulfide, oxide, halide and alumina [34]. In this report, we attempt to relate the three PL bands to the three coordination structures, based on the equation. Here, the peak energies of 5d¹ → 4f¹ (2F₅/₂) transition in table 2 were substituted in \(E\). The units of the peak energies were changed to wavenumber. The \(Q\) value is 50,000 cm⁻¹ and \(V = 3\) for Ce³⁺. According to Van Uitert, the \(A\) value is uniformly constant in the same host materials. Thus, it is assumed that \(A\) of S²⁻ anions in La₆Si₄S₁₇ is also constant. However, it is difficult to estimate \(A\) for sulfur in (La₀.₉₋₋₋₂Ce₀.₂Y₀.₁)₀Si₄S₁₇ from other experiments. The ionic radius \(r\) of the La ion increases with increasing \(n\) [32]. Hence, the value of \(E/Q\) for the PL band in (La₀.₈₉Ce₀.₀₁Y₀.₀₁)₀Si₄S₁₇ increase with the coordination number of the La site. According to table 1 and 2, X₁, X₂ and X₃ bands should correspond to 1ctp, 2ctp and 3ctp structures of the La sites, respectively.

Figure 7 depicts \(E/Q\) versus \((nrA)/80\) for (La₀.₈₉Ce₀.₀₁Y₀.₀₁)₀Si₄S₁₇ and other rare-earth thiosilicate phosphors. The data and references for them are summarized in table 3. The solid curve represents equation (1) for Ce³⁺ (\(V = 3\)). The \(A\) value was estimated as 1.56 eV by least squares fitting for the data of (La₀.₈₉Ce₀.₀₁Y₀.₀₁)₀Si₄S₁₇. To check the validity of this estimation, the corresponding data for (Gd₀.₉₉Ce₀.₀₁)₄(Si₄S₄)₃ and (Y₀.₉₉Ce₀.₀₁)₄(Si₄S₄)₃ with the same \(A\) value were plotted in this figure. All the points line up on the solid curve with good accuracy. Van Uitert described that the \(A\) values for oxy-anion complexes involving the highly charged central cations, such as SiO₄³⁻, PO₄³⁻ and WO₄³⁻, were generally greater than those of CaO, Y₃Al₅O₁₂ and Gd₃Al₅O₁₂ without such cations [34]. Thus, it is assumed that sulfide hosts have also the same tendency. Because the \(A\) value for binary sulfide hosts, such as CaS, ZnS and La₂S₃, is 1.0 [34], the thiosilicates with SiS₄⁻ anion, which is also highly charged complex, should have larger \(A\) value. This indicates that the estimated value of 1.56 is reasonable as the effective electron affinity of such the thiosilicate hosts. Thus, we conclude that the X₁, X₂ and X₃ bands originate from the Ce³⁺ ions in 1ctp, 2ctp and 3ctp structures of the La sites, respectively.

To discuss the concentration quenching of the phosphor, we measured the PL decay
profiles of the X1, X2 and X3 bands. As shown in figure 6, the PL spectrum contains the
three emission bands. When the phosphor is excited at 410 nm, the PL spectral part
below 2.00 eV (620 nm) and above 2.69 eV (460 nm) consist only of X1 and X3 band,
respectively. Then, the X2 band emission can be observed by monitoring the PL region
above 2.48 eV (500 nm) with excitation at 2.81 eV (440 nm). Figure 8 shows the PL decay
profiles of (a) X1, (b) X2 and (c) X3 bands in (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ for $x = 0.01$, 0.03,
0.07 and 0.20, which were obtained at 78 K based on the method described above. In
figure 8 (a), the excitation pulse shape is also appended. The excitation pulse is followed
by a tiny pulse appeared at 10 ns. The second pulse is the residual left after the Pockels
cell operation and does not affect the PL decay profiles. The PL data were calculated
through integration of the spectral region above 620 nm (a), below 500 nm (b) and below
460 nm (c) at each delay time. These measurement conditions are summarized in table 4.

Their decay times were obtained through curve fitting with the following single or
double exponential function.

$$I(t) = \sum_{i=1}^{N} I_i e^{t/\tau_i} + b \quad (N = 1 \text{ or } 2, \tau_1 < \tau_2). \quad (2)$$

The decay profiles of X1 and X2 band could be fitted by a single exponential regardless
of the Ce concentration. The decay profile of X3 band for $x = 0.01$ sample could be also
fitted by this way. However, the X3 profiles for $x = 0.03$ and 0.07 samples had to be
fitted by double exponential. The X3 band was not observed for the $x = 0.20$ sample
because of the concentration quenching of Ce$^{3+}$. The fast components ($\tau_1$) of the decay
times are summarized in figure 9. The decay time of X3 band decreased from 20.5 ns
to 4.8 ns with the increase of Ce concentration, while those of X1 and X2 band did not
change for any concentration samples as 33.9 ns for the X1 band and 28.5 ns for the X2
band.

To understand these results, we discuss the energy transfer among Ce$^{3+}$ ions in
La$_6$Si$_4$S$_{17}$ based on Dexter’s theory [35]. The deconvolution analysis for the X1, X2 and
X3 bands in figure 6 indicates that the peaks at the right end of the PLE spectrum
in figure 5, 475 nm, 440 nm and 410 nm, correspond to the Ce$^{3+}$ ions substituted for
1ctp, 2ctp and 3ctp, respectively. According to Dexter’s theory, the energy transfer
to neighboring ions can occur when the luminescence band of donor ion overlap the
excitation band of acceptor ion [35]. As shown in figure 5 and 6, there is no spectral
overlap between PL and PLE spectra originating from the Ce$^{3+}$ in the same coordination
structure. Thus, the energy transfer between Ce$^{3+}$ ions in the same coordination
structure does not occur. On the other hand, the X3 PL band has overlaps with the
excitation bands for X1 and X2 band. Therefore, the energy transfer from Ce$^{3+}$ in 3ctp
sites to Ce$^{3+}$ in 2ctp or 1ctp sites is possible. The energy transfer from Ce$^{3+}$ in 2ctp
sites to Ce$^{3+}$ in 1ctp sites can also occur because the X2 PL band overlaps a little with
the excitation band for the X1 band, while the energy transfer from Ce$^{3+}$ in 1ctp to
others are impossible.
The Dexter’s theory also indicates that the probability of the energy transfer increases in proportion to $R^{-6}$ (electric dipole-dipole interaction), where $R$ is the distance between donor ion and acceptor ion [35]. This leads to the prospect that the energy transfer from 2ctp or 3ctp sites to 1ctp sites hardly occur even when the Ce$^{3+}$ ions are highly doped in the host, since the number of 1ctp site is smaller than that of 2ctp or 3ctp site, as shown in table 1. On the other hand, the energy transfer from 3ctp sites to 2ctp sites increases with increase of Ce concentration because the number of those sites is comparable. That is, the energy transfer from 3ctp sites to 2ctp sites is selectively promoted when Ce$^{3+}$ ions are highly doped in the host. This leads to the experimental results that only the decay time of the X3 band become faster when the Ce concentration is increased.

4. Conclusions

In conclusion, we introduced novel broad luminescent phosphors $(La_{0.9-x}Ce_xY_{0.1})_6Si_4S_{17}$ ($x = 0-0.2$). The observed broad PL spectra at the range from 430 nm to 700 nm were originated from $5d^1 \rightarrow 4f^1$ transition in Ce$^{3+}$. They could be excited by near-UV, violet and blue LEDs and have maximum internal quantum efficiency of 59% for $x = 0.07$. We clarified the presence of three PL bands, each consisting of two peaks, through the PL spectra at 78 K. The correlation between the PL bands and the Ce substitution sites in the matrix could be well explained with a universal formula. The three PL bands directly correspond to the three kinds of Ce$^{3+}$ ions replaced at the characteristic La sites in $La_6Si_4S_{17}$, whose coordination number is 7, 8 or 9. These indicate that $(La_{0.9-x}Ce_xY_{0.1})_6Si_4S_{17}$ are promising broad luminescent, efficient and stable phosphors for white LED with high color rendering.

Acknowledgments

XRD patterns and PL efficiency were measured at the Center for Instrumental Analysis in the University of Electro-Communications.
References

[31] Izumi F and Momma K 2007 Solid State Phenom. 130 15
[34] Van Uittert L G 1984 J. Lumin. 28 1
### Table 1.

Ce-S coordination structures in Ce₆Si₄S₁₇ [26]. The volume ($V_c$) and the average distance ($R_a$) between Ce and S of Ce-S coordination structures were estimated by VESTA [33].

<table>
<thead>
<tr>
<th>Sites</th>
<th>Coordination structure and (number)</th>
<th>$V_c$ / Å³</th>
<th>$R_a$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce4</td>
<td>1ctp (7)</td>
<td>36.8</td>
<td>2.94</td>
</tr>
<tr>
<td>Ce3</td>
<td>2ctp (8)</td>
<td>46.6</td>
<td>3.00</td>
</tr>
<tr>
<td>Ce5</td>
<td>2ctp (8)</td>
<td>46.5</td>
<td>3.00</td>
</tr>
<tr>
<td>Cr6</td>
<td>2ctp (8)</td>
<td>47.8</td>
<td>3.00</td>
</tr>
<tr>
<td>Ce1</td>
<td>3ctp (9)</td>
<td>55.5</td>
<td>3.05</td>
</tr>
<tr>
<td>Ce2</td>
<td>3ctp (9)</td>
<td>57.1</td>
<td>3.07</td>
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</table>
**Table 2.** The peak positions of the PL bands and the separation between $^4F_{5/2}$ levels and $^4F_{7/2}$ levels ($\Delta E$).

<table>
<thead>
<tr>
<th>PL band</th>
<th>$5d^1 \rightarrow 4f^1(^2F_{5/2})$ / eV</th>
<th>$5d^1 \rightarrow 4f^1(^2F_{7/2})$ / eV</th>
<th>$\Delta E$ / eV</th>
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</thead>
<tbody>
<tr>
<td>X1</td>
<td>2.30</td>
<td>2.04</td>
<td>0.26</td>
</tr>
<tr>
<td>X2</td>
<td>2.47</td>
<td>2.23</td>
<td>0.24</td>
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<tr>
<td>X3</td>
<td>2.69</td>
<td>2.42</td>
<td>0.27</td>
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Table 3. Data for Figure 8. Host cation radii $r$ are given from [32].

<table>
<thead>
<tr>
<th>Host materials</th>
<th>$n$</th>
<th>$r$ / Å</th>
<th>$A$ / eV</th>
<th>$E$ ($\times 10^4$) / cm$^{-1}$</th>
<th>$nrA/80$</th>
<th>$E/Q$</th>
<th>Ref. of $E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_6$Si$<em>4$S$</em>{17}$</td>
<td>9</td>
<td>1.216</td>
<td>1.56</td>
<td>2.17</td>
<td>0.213</td>
<td>0.434</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.16</td>
<td>1.56</td>
<td>1.99</td>
<td>0.181</td>
<td>0.399</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1.10</td>
<td>1.56</td>
<td>1.86</td>
<td>0.150</td>
<td>0.371</td>
<td>This work</td>
</tr>
<tr>
<td>Ga$_4$(SiS$_4$)$_3$</td>
<td>8</td>
<td>1.053</td>
<td>1.56</td>
<td>1.78</td>
<td>0.164</td>
<td>0.357</td>
<td>[20]</td>
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<tr>
<td></td>
<td>7</td>
<td>1.00</td>
<td>1.56</td>
<td>1.59</td>
<td>0.137</td>
<td>0.318</td>
<td>[20]</td>
</tr>
<tr>
<td>Y$_4$(SiS$_4$)$_3$</td>
<td>8</td>
<td>1.019</td>
<td>1.56</td>
<td>1.83</td>
<td>0.159</td>
<td>0.366</td>
<td>[20]</td>
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<tr>
<td></td>
<td>7</td>
<td>0.96</td>
<td>1.56</td>
<td>1.64</td>
<td>0.131</td>
<td>0.328</td>
<td>[20]</td>
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Table 4. Measurement conditions for the PL decay of X1, X2 and X3 band at 78 K.

<table>
<thead>
<tr>
<th>PL band</th>
<th>Coordination structure</th>
<th>Excitation wavelength / nm</th>
<th>Integral region of PL spectrum at each time point</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1</td>
<td>1ctp</td>
<td>410</td>
<td>&gt; 620 nm</td>
</tr>
<tr>
<td>X2</td>
<td>2ctp</td>
<td>440</td>
<td>&lt; 500 nm</td>
</tr>
<tr>
<td>X3</td>
<td>3ctp</td>
<td>410</td>
<td>&lt; 460 nm</td>
</tr>
</tbody>
</table>
Figure captions

**Figure 1.** XRD patterns of (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ ($x = 0$ to 0.2). In the top panel, the simulated pattern of Ce$_6$Si$_4$S$_{17}$ and the indices of the diffraction peaks are shown.

**Figure 2.** Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ ($x = 0.01$ to 0.2). The value of $x$ is shown in the figure. Excitation wavelength for the PL spectra is 355 nm. Detection wavelength for PLE spectra is 535 nm.

**Figure 3.** Schematic of S$^{2-}$ coordination structures around Ce$^{3+}$ ions in Ce$_6$Si$_4$S$_{17}$ [26]. (a) mono-capped trigonal prism (1ctp). (b) bi-capped trigonal prism (2ctp) (c) tri-capped trigonal prism (3ctp).

**Figure 4.** Excitation wavelength dependence of PL spectra for (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ ($x = 0.01$ (a), 0.2 (b)) at 78 K. The excitation wavelengths were 410 nm (dotted lines), 440 nm (dashed lines) and 480 nm (dashed-dotted lines).

**Figure 5.** Detection wavelength dependence of PLE spectra for (La$_{0.89}$Ce$_{0.01}$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ at 78 K. Detection wavelengths were 460 nm (dotted lines), 500 nm (dashed lines) and 620 nm (dashed-dotted lines). Up arrows represent the PLE peaks in the long wavelength region located at 410, 440 and 475 nm.

**Figure 6.** Deconvolution results of PL spectra (circles) for (La$_{0.89}$Ce$_{0.01}$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ at 78 K. The excitation wavelengths ($\lambda_{exc}$) are shown in the figure. X1 (dashed-dotted line), X2 (dashed line) and X3 (dotted line) are PL bands originated from 5d$^1 \rightarrow$ 4f$^1$ ($^2$F$_J$, $J = 7/2, 5/2$) transition of Ce$^{3+}$ ions replacing different La sites in La$_6$Si$_4$S$_{17}$. (a) X1, (b) X1 and X2 or (c) X1, X2 and X3 bands are included in each PL spectra. Solid lines represent sum of the PL bands.

**Figure 7.** $E/Q$ versus $nrA/80$ for (La$_{0.89}$Ce$_{0.01}$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ (circles), (Gd$_{0.99}$Ce$_{0.01}$)$_4$(SiS$_4$)$_3$ (squares) and (Y$_{0.99}$Ce$_{0.01}$)$_4$(SiS$_4$)$_3$ (triangles). The solid curve is calculated from equation (1) with $V = 3$. Coordination numbers $n$ of La, Gd and Y sites are denoted near the corresponding marks.
Figure 8. PL decay curves of (a) X1, (b) X2 and (c) X3 bands in (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ for $x = 0.01$ (circles), 0.03 (squares), 0.07 (triangles) and 0.20 (rhombuses) at 78 K. Solid lines are fitted curves by single exponential functions (equation (2), $n = 1$). Dotted lines are the fitted curves by double exponential functions (equation (2), $n = 2$). The X3 band decay for $x = 0.20$ is not observed because of quenching.

Figure 9. Changes in the decay times of X1, X2 and X3 bands for (La$_{0.9-x}$Ce$_x$Y$_{0.1}$)$_6$Si$_4$S$_{17}$ with Ce concentration $x$ at 78 K. For $x = 0.20$, that of X3 band couldn’t be plotted because it was quenched.
Broad luminescence of Ce$^{3+}$ in multiple sites in (La, Ce, Y)$_6$Si$_4$S$_{17}$
Broad luminescence of Ce$^{3+}$ in multiple sites in $(La,Ce,Y)_6Si_4S_{17}$
Broad luminescence of $\text{Ce}^{3+}$ in multiple sites in $(\text{La}, \text{Ce}, \text{Y})_6\text{Si}_4\text{S}_{17}$

Figure 3.
Broad luminescence of $\text{Ce}^{3+}$ in multiple sites in $(\text{La}, \text{Ce}, \text{Y})_6\text{Si}_4\text{S}_{17}$

Figure 4.
Figure 5.
Broad luminescence of Ce³⁺ in multiple sites in (La, Ce, Y)₆Si₄S₁₇

Figure 6.
Broad luminescence of $\text{Ce}^{3+}$ in multiple sites in $(\text{La, Ce, Y})_6\text{Si}_4\text{S}_{17}$

Figure 7.
Figure 8.
Broad luminescence of Ce$^{3+}$ in multiple sites in (La,Ce,Y)$_{6}$Si$_{4}$S$_{17}$

Figure 9.