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Salt-assisted combustion synthesis of Ca- α -SiAlON:Eu²⁺ phosphors

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Abstract

In this study, Ca- α -SiAlON:Eu²⁺ yellow phosphors for white light-emitting diodes (LEDs) were synthesized via a facile combustion synthesis method by using CaO, Eu₂O₃, Si, and Al as raw materials, while NaCl and Si₃N₄ were utilized as diluents to contain the combustion temperature. The concentration of Eu was varied, and the resulting changes in phase purity, photoluminescence properties, and thermal quenching were investigated. We observed that the increase in lattice constant depended on the amount of Al, while the Ca sites were partially substituted by Eu ions. The synthesized Ca- α -SiAlON:Eu²⁺ powders exhibited emission wavelength at 556–560 nm and high thermal stability, revealing high potential for application in white LEDs.

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1. Introduction

White light-emitting diodes (LEDs) are considered the next-generation solid-state lighting sources, and are widely used owing to their high light efficiency, low energy consumption, and long service lifetime. To adjust the complex LED white color light, various materials such as rare earth hosts, ceramics, and quantum dots have been used [1-3]. Generally, LEDs use rare earth (RE) doped oxynitride phosphors, which exhibit high photoluminescence (PL) intensity and outstanding thermal and chemical stabilities due to the stiff framework consisting of Si–N, or Al–N, bonding in the crystal structure of the host lattice. Among these oxynitride phosphors, Eu-doped phosphors show a strong absorption in the ultraviolet (UV) to visible spectral region and exhibit broad emission bands from blue to red. Recently, Ca- α -SiAlON:Eu²⁺, which exhibits yellow emission, has attracted considerable attention for application in white LEDs [4-7].

Usually, a solid-state reaction [8-12], gas pressure sintering [13, 14], or gas-reduction nitrogen [15-17] method is used to synthesize Ca- α -SiAlON:Eu²⁺. However, these methods involve the use of high-purity expensive α -Si₃N₄ and AlN as starting materials, and require prolonged high-temperature (1900–2000 °C) sintering under nitrogen pressure, which is an energy- and time-consuming process. Combustion synthesis, or self-propagation high-temperature synthesis (SHS), established by Merzhanov et al. [18, 19], exploits a self-sustaining regime that utilizes the heat generated during a strongly exothermic reaction. This method is a proven effective energy- and time-saving process for producing various industrial materials, owing to advantages such as high-purity products, low energy investment, and short processing time. Therefore, the SHS process has been applied to the powder production of various kinds of materials including metallic alloys [20, 21], and ceramics [22, 23], etc.

In our previous work, we successfully prepared Eu-doped β -SiAlON green phosphors using inexpensive Si, Al, and SiO₂ as raw materials along with a small amount of NaCl as diluent at relatively low nitrogen pressure [24]. Among the various techniques available today for the synthesis of Ca- α -SiAlON:Eu²⁺ [13, 16, 25], the combustion synthesis method has not been thoroughly investigated, despite offering advantages such as: 1) self-sustaining and self-propagating reaction with no external heating; 2) low energy investment; 3) short processing time. Owing to the high combustion temperature reached during the combustion synthesis process, the β -SiAlON phase tends to be stabler than the α -SiAlON phase. Therefore, to contain the combustion temperature, NaCl and Si₃N₄ were added to the raw materials as diluents. In this study, we prepared Ca- α -SiAlON:Eu²⁺ phosphors via a new synthesis route and investigated the properties of the obtained materials. To optimize the composition, we varied the Eu concentration from 0.00 to 0.15, based on previous works.

2. Material and methods

In this work, Ca_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}:Eu_y (x = 0.625, y = 0.00, 0.05, 0.075, 0.1, and 0.15; m = 2x + 3y, m = 2n) was prepared. The raw materials included Si (>99.9% purity, 5 μ m), Al (99.9% purity, 3 μ m), CaO (99.9% purity), Eu₂O₃ (99.9% purity), and α -Si₃N₄ (99.9% purity, 0.5 μ m) powders, as well as NaCl (99.9% purity); α -Si₃N₄ and NaCl were used as diluents. When designing the compositions, Eu³⁺ was assumed to be the Eu ion, as Eu₂O₃ was the starting material [26]. The starting materials were mixed and mechanically activated via planetary ball milling (Gokin Planetaring Inc., Japan) at a ball-to-sample mass ratio of 10:1 for 15 min. The activated mixture was loaded into a cylindrical carbon crucible with vents through which nitrogen gas was introduced. The combustion reaction was conducted at a nitrogen (purity: 99.999%)

pressure of 1 MPa by passing current through a carbon foil. The details of the planetary milling and equipment for the combustion synthesis are described elsewhere [27]. After the reaction, the products were washed with distilled water to remove the NaCl residues, and then dried at 110 °C.

The product phases were analyzed by using X-ray diffraction (XRD, Miniflex, Rigaku) with Cu K α radiation ($\lambda = 1.54056$ nm) and a sampling step of 0.02°. Structural refinements were performed by applying the Rietveld method to powder XRD patterns by means of the PDXL program (Rigaku) [28, 29]; the crystal structure of Ca_{0.67}Si₁₀Al₂N_{15.7}O_{0.7} (ICDD 01-084-0785) with space group P31c (No.159) was used as the starting structure model. The phase purity of the product was analyzed by using X-ray fluorescence spectroscopy (XRF, ZSX Mini II, Rigaku). Field emission scanning electron microscopy (FE-SEM, JSM-7001FA, JEOL) and transmission electron microscopy (TEM, JEM-2010F, JEOL) were used to characterize the microscopic morphology. High-resolution scanning TEM (STEM) images were acquired using a C_s-corrected STEM system (FEI Titan Cubed G2 60-300 300 kV). To distinguish the atoms, high-angle annular dark-field (HAADF) technique was used, in which the image contrast is roughly proportional to the square of the atomic number Z [30]. For STEM observation, the obtained particle was mixed with fine copper powder, and then hot pressed for 1 h at 800 °C to form a bulk sample, which was thinned via cutting, grinding, and ion milling by using a Gatan precision ion polishing system. The PL properties were measured using a fluorescence spectrometer (FP-6400, JASCO) at room temperature with an excitation wavelength of 380 nm. The obtained chromaticity values were plotted on a color diagram by using the ColorAC software. Temperature-dependent PL was measured using a multichannel spectrometer (USB 2000+, Ocean Optics) in the temperature range of 25–260 °C, with a LED as the excitation source.

3. Results and Discussion

In our previous work on the combustion synthesis of Ca- or Y-doped α -SiAlON [31], single-phase α -SiAlON could not be easily obtained when NaCl was added by itself to the starting materials, as α -SiAlON precipitated from the liquid M–Si–Al–O–N mixture. When a large amount of NaCl was added to the raw materials, the reaction heat released from the nitridation of Al could be reduced through the NaCl (solid) $\rightarrow$ NaCl (liquid) reaction ($\Delta H = 82.1$ kJ); however, owing to the increased amount of liquid NaCl, the infiltration of N_2 for the nitridation of Si was inhibited. Therefore, in this study, to achieve a complete nitridation of Si, the content of NaCl was fixed at 10 mass%; meanwhile, different amounts of α -Si₃N₄ as diluent were added to the raw materials. NaCl not only acts as a diluent to decrease the combustion temperature, but also as a shell to prevent self-sintering of the products, facilitating post-synthesis treatments such as milling. The intensity of the Si peak in XRD decreased as the amount of α -Si₃N₄ increased, and disappeared at 40 mass%.

Fig. 1 shows the XRD patterns of the $Ca_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}:Eu_y$ ($x = 0.625$, $y = 0.00$ – 0.15) powders synthesized with the addition of NaCl and Si₃N₄. The as-prepared powders consisted of a single α -SiAlON crystalline phase at all Eu concentrations, and there was no detectable β -SiAlON phase. In the case of $y = 0$, the small amount of AlN was due to the igniter near the carbon foil. Fig. 2a shows the enlarged XRD pattern of α -SiAlON (222), in which the diffraction peaks of α -SiAlON gradually shifted to lower diffraction angles with the increase of the Eu content, indicating an expansion of the crystal lattice. When the Eu content rose, m in $Ca_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}:Eu_y$ increased, and thus the molar ratio of Al in the material

became accordingly larger. As the bonding distances of Al–O (1.75 Å) and Al–N (1.87 Å) are larger than that of Si–N (1.74 Å) [14], the crystal lattice expanded. From the Rietveld analysis shown in Fig. 2b and Table 1, the lattice constant c of the samples linearly increased with the increase of y . This tendency agreed with previously reported data [32]. In addition, after analyzing the phase purity by XRF, impurity phases (e.g., iron) were not detected. The quantitative analysis of the Eu concentration was performed by adopting the calibration curve method shown in Fig. 3, in which a calibration curve was prepared by using standard samples with different Eu concentrations. The Eu concentration almost matched that of the raw materials and had a ~15% margin of error. These results indicated that Ca- α -SiAlON:Eu²⁺ phosphors can be successfully prepared by using the combustion synthesis method with the addition of NaCl at low nitrogen pressure (1 MPa).

The SEM images showed similar morphologies for Ca- α -SiAlON:Eu²⁺ samples synthesized with different amounts of Eu. Fig. 4a shows a SEM image of Ca- α -SiAlON:Eu_{0.075} powders synthesized upon addition of NaCl under 1 MPa of nitrogen; mainly equiaxed particles, along with a few rod-like particles, can be observed. A TEM image of a Ca- α -SiAlON:Eu_{0.075} particle is shown in Fig. 4b; the inset shows the selected area electron diffraction pattern of the same particle along with a high-resolution TEM image. These results revealed that α -SiAlON single crystals grew along the [001] direction. Generally, trigonal α -SiAlON tends to grow along the [001] direction. Notably, understanding the atomic sites for dopant ions in a host crystal is critical. In the case of β -SiAlON, the Eu dopant is located in a continuous atomic channel in the β -Si₃N₄ structure [33]. In contrast to β -SiAlON, which has a hexagonal structure [24], α -SiAlON has a trigonal P31/c crystal structure and contains two large interstices in a (Si,Al)₁₂(N,O)₁₆ unit cell; the centers of the interstitial holes are located at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4) [34]. Metallic ions

such as Li, Mg, Ca, and Y, or RE metals such as Ce and Eu, can be accommodated into these holes [34, 35]. The HAADF-STEM image shown in Fig. 5a, projected along the [001] direction, revealed that the Eu atoms substituted the Ca sites without segregation. The bright dots marked with solid circles correspond to the Eu-substituted Ca columns, as the atomic number of Eu (63) is significantly larger than that of Ca (20). This image is in good agreement with the structure model shown in Fig. 5b.

The excitation and emission spectra of the prepared Ca- α -SiAlON:Eu²⁺ phosphors with different Eu concentrations are shown in Fig. 6. The samples exhibited a wide excitation band ranging from the UV to the blue region, with two peaks at 280 and 380 nm. These two excitation bands correspond to the 4f⁷ $\rightarrow$ 4f⁶5d transition absorption of Eu²⁺ [26, 36, 37]. In this case, the Eu²⁺ 5d orbitals may split into t₂ and e orbitals. According to the local structure of the Eu ion with cubic symmetry, the t₂ orbit has a lower energy level, as shown in the schematic diagram of Fig. 7. The emission spectra show a single broad peak in the range of 400–700 nm, which corresponds to the allowed 4f⁶5d $\rightarrow$ 4f⁷ transition of Eu²⁺. When Eu³⁺ is present, a sharp peak between 560 and 630 nm is observed [36]. This result suggests that Eu doped the α -SiAlON host as Eu²⁺ ion. By increasing the Eu concentration, the emission intensity of the phosphors decreased, owing to concentration quenching [32, 38]. When the concentration of Eu²⁺ increases, the distance between Eu²⁺ ions is reduced, and thus the probability of nonradiative energy transfer between neighboring doped ions increases. The maximum emission peak wavelength ranged from 556 nm (Eu = 0.05) to 560 nm (Eu = 0.15). This red shift might be caused by the following reasons: 1) change in the crystal field strength surrounding Eu ions; 2) difference in the Stokes shift; 3) increase in reabsorption with the increase in Eu concentration [14,

25, 26, 37, 39]. However, further studies are required to clarify the origin of the red shift at high doping concentrations.

Fig. 8 shows the Commission Internationale de l'Eclairage (CIE) 1931 chromaticity diagram, in which the black squares indicate the chromaticity points of the obtained Ca- α -SiAlON:Eu²⁺ phosphors. The black solid line shows the blackbody locus curve. The intersection of the dashed line—which connects blue LED ($\lambda_{\text{ex}} = 450$ nm) and Ca- α -SiAlON:Eu²⁺ phosphor chromaticity points—with the blackbody locus curve indicates the corresponding color temperature. Notably, the phosphor investigated here could not provide warm white light when combined with a 450 nm blue LED, owing to emission wavelengths shorter than those of other Ca- α -SiAlON:Eu²⁺ phosphors reported elsewhere[13, 25]. In the combustion synthesis process, the reaction time is relatively short, which might induce defect formation, inhomogeneous distribution of Eu dopant and low crystallinity. To improve the performance of phosphors produced by combustion synthesis, further improvement, including thermal insulation, is thus necessary.

For practical white or high-power LED applications, the phosphors must sustain emission efficiency at temperatures of ~ 200 °C over a long period. Fig. 9 displays the gradual decrease of the normalized PL emission intensity of as-prepared Ca_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}:Eu_y ($x = 0.625$, $y = 0.075$) and silicate phosphors as the temperature increases. At 200 °C, the PL emission intensity of the as-prepared Ca- α -SiAlON:Eu²⁺ phosphor was 88% of that measured at room temperature, which is $\sim 30\%$ higher than that of the silicate green phosphors (Sr₂SiO₄:Eu²⁺). When the temperature increased to 260 °C, the remaining PL emission intensity of the silicate green phosphors was only $\sim 10\%$ of the original value, which is far less than the 73% observed for the as-prepared Ca- α -SiAlON:Eu²⁺ phosphor. The activation energy of the thermal quenching was determined by the Arrhenius equation, as shown in Fig. 7b.

Theoretically, the relationship between temperature and intensity can be described by the following equation (1) [40, 41]:

$$I(T) = \frac{I_0}{1 + A \exp\left(\frac{-\Delta E}{k_B T}\right)} \quad (1)$$

where I_0 is the initial intensity, $I(T)$ is the intensity at each temperature, A is a constant, ΔE is the activation energy of thermal quenching, and k_B is the Boltzmann constant. The plot of $\ln[(I_0/I) - 1]$ against $1/(k_B T)$ shows a straight line (Fig. 9b). The obtained apparent activation energy was 0.17 eV for as-synthesized Ca- α -SiAlON ($x = 0.625$, $y = 0.075$), which is close to the reported values of 0.189 eV (Ca- α -SiAlON:Eu, $x = 1.25$) [32] and 0.202 eV (Sr- α -SiAlON:Eu, $x = 0.725$) [36]. The activation energy of the thermal quenching is related to the interaction between electrons and phonons. At high temperature, the nonradiative transition is enhanced, owing to the higher density of the phonons. The small activation energy suggests a weak electron-phonon interaction in α -SiAlON. This minimal thermal quenching of the PL emission efficiency is attributed to the rigid crystal structure of the host lattice, which comprises a network of linked (Si, Al)(O, N)₄.

4. Conclusions

In this study, Ca_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}:Eu_y ($x = 0.625$, $y = 0.00, 0.05, 0.075, 0.1$, and 0.15) was successfully prepared by using the salt-assisted combustion synthesis method. The lattice constant increased, owing to the increases of the Al–O and Al–N bonding distances. STEM-HAADF observations clearly revealed that the Eu ions substituted the Ca sites. The as-synthesized phosphor exhibited a single emission peak at 556–560 nm under 380 nm excitation. Compared with the silicate (Sr₂SiO₄:Eu²⁺) phosphor, the as-synthesized Ca- α -SiAlON:Eu²⁺ showed a superior thermal stability.

According to these results, the new combustion synthesis method using low-cost raw materials, and NaCl and Si₃N₄ as diluents, can find application in the production of α -SiAlON phosphors.

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Figure captions

Fig. 1. X-ray diffraction patterns of combustion synthesized Ca- α -SiAlON:Eu_y powders with y values of 0, 0.05, 0.075, 0.10, and 0.15, obtained under 1 MPa of nitrogen.

Fig. 2. (a) Enlarged X-ray diffraction pattern of Ca- α -SiAlON (222); (b) lattice constant c of samples with different compositions evaluated from Rietveld analysis.

Fig. 3. Quantitative analysis of Eu concentration evaluated by X-ray fluorescence spectroscopy. The inset table shows the analytical results for the Eu concentration.

Fig. 4. (a) Scanning electron microscopy image of combustion synthesized Ca- α -SiAlON:Eu_{0.075} powders obtained under 1 MPa of nitrogen; (b) transmission electron microscopy image of a Ca- α -SiAlON:Eu particles along with the corresponding selected area electron diffraction pattern and high-resolution image.

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Fig. 5. (a) High-angle annular dark-field scanning transmission electron microscopy image of synthesized Ca- α -SiAlON:Eu_{0.075} projected along the [001] direction; the doped Eu ions marked with solid circles have brighter contrast due to the difference in

atomic number between Ca (20) and Eu (63). (b) Structural model of [001] projected Ca- α -SiAlON:Eu.

Fig. 6. Room temperature excitation and emission spectra of as-prepared Ca- α -SiAlON:Eu_y powders with y = 0.05, 0.075, 0.10, and 0.15, obtained at nitrogen pressure of 1 MPa. The emission spectrum was measured by using 380 nm excitation wavelength (λ_{exc}), while the excitation spectrum was monitored at 580 nm (λ_{emi}).

Fig. 7. (a) Local structure of Ca or Eu site in the α -SiAlON structure. The oxygen can substitute the nitrogen site. (b) Configuration coordinate model for absorption and emission.

Fig. 8. Calculated Commission Internationale de l'Eclairage coordinate diagram of Ca- α -SiAlON:Eu²⁺ and YAG:Ce³⁺ phosphors.

Fig. 9. (a) Temperature dependences of the relative photoluminescence (PL) peak intensities of the as-prepared Ca- α -SiAlON:Eu phosphor and a commercial silicate green phosphor (Sr₂SiO₄:Eu²⁺), measured at temperatures in the range of 25–260 °C. (b) Arrhenius fitting of the PL peak intensity in the measured temperature range. Activation energies for thermal quenching (ΔE) are shown.

Table captions

Table 1. Lattice constants of samples with different Eu contents.

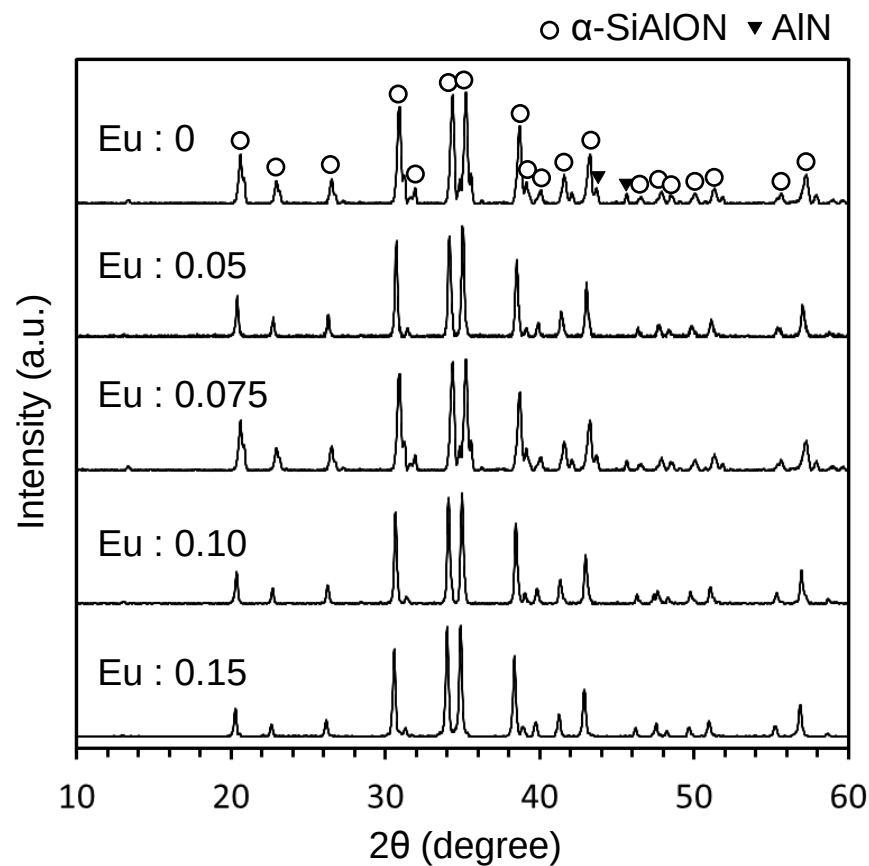


Fig. 1. X-ray diffraction patterns of combustion synthesized $\text{Ca-}\alpha\text{-SiAlON:Eu}_y$ powders with y values of 0, 0.05, 0.075, 0.10, and 0.15, obtained under 1 MPa of nitrogen.

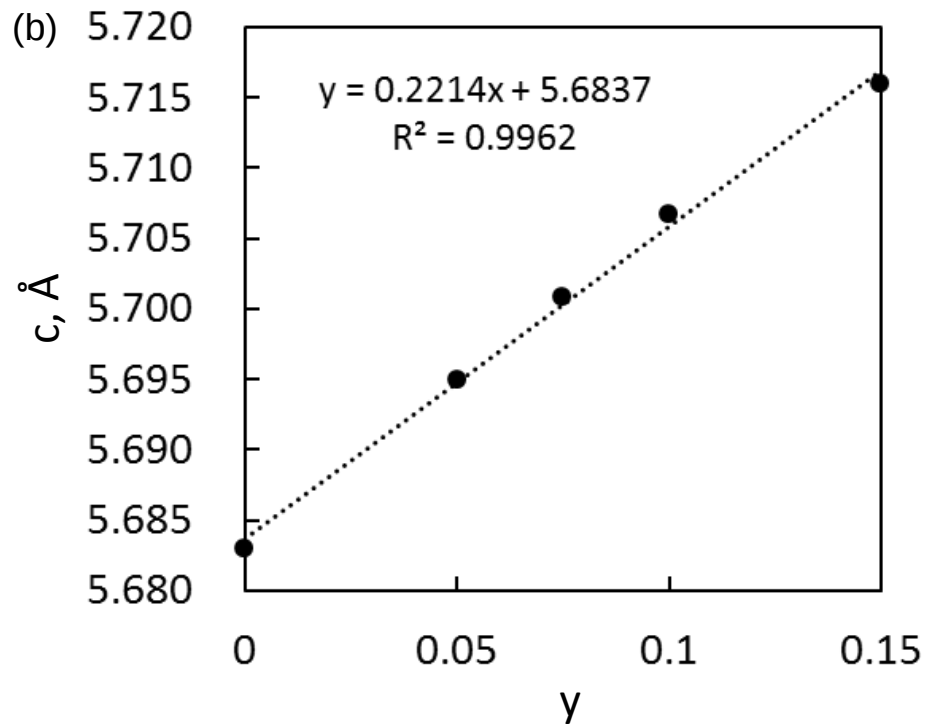
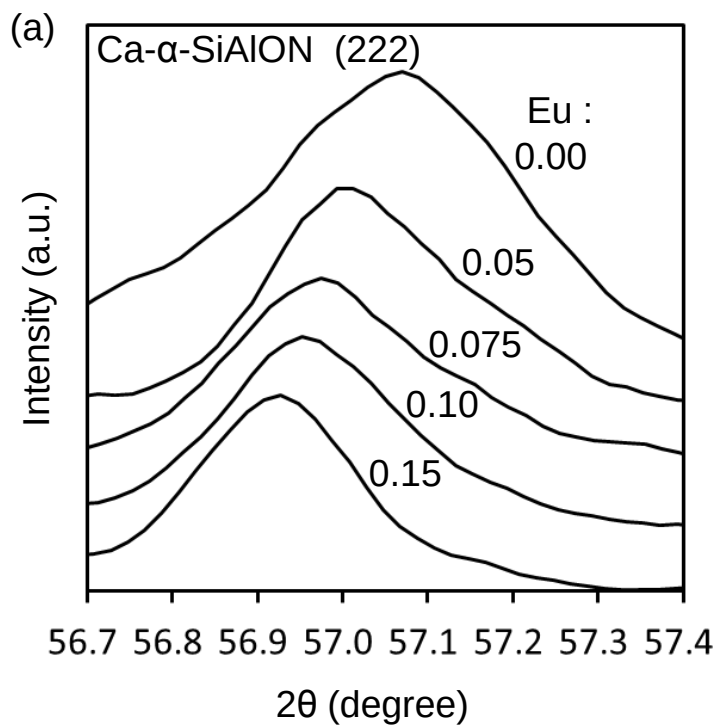


Fig. 2. (a) Enlarged X-ray diffraction pattern of Ca- α -SiAlON (222); (b) lattice constant c of samples with different compositions evaluated from Rietveld analysis.

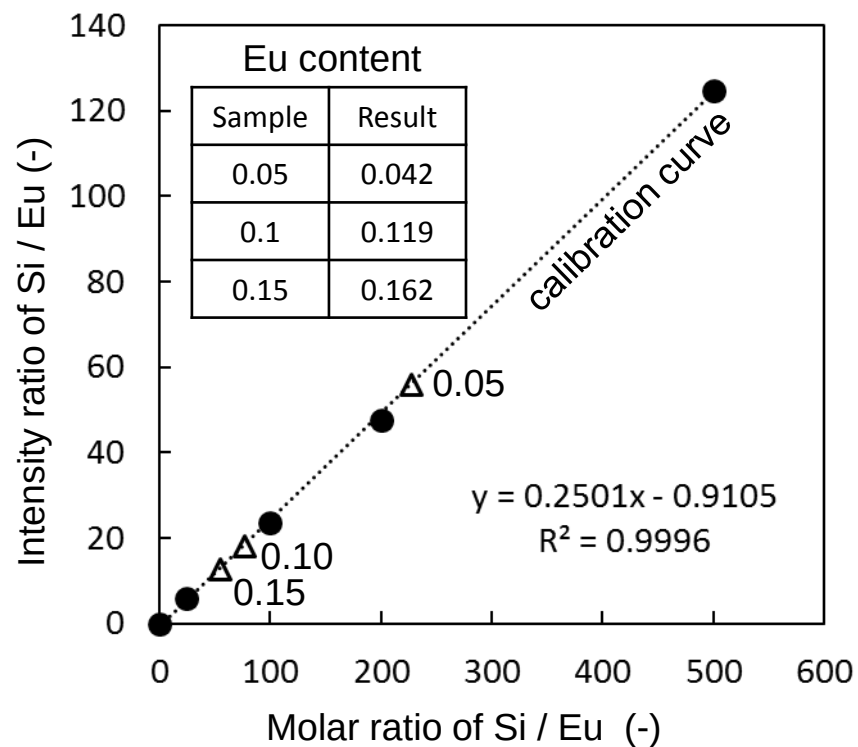


Fig. 3. Quantitative analysis of Eu concentration evaluated by X-ray fluorescence spectroscopy. The inset table shows the analytical results for the Eu concentration.

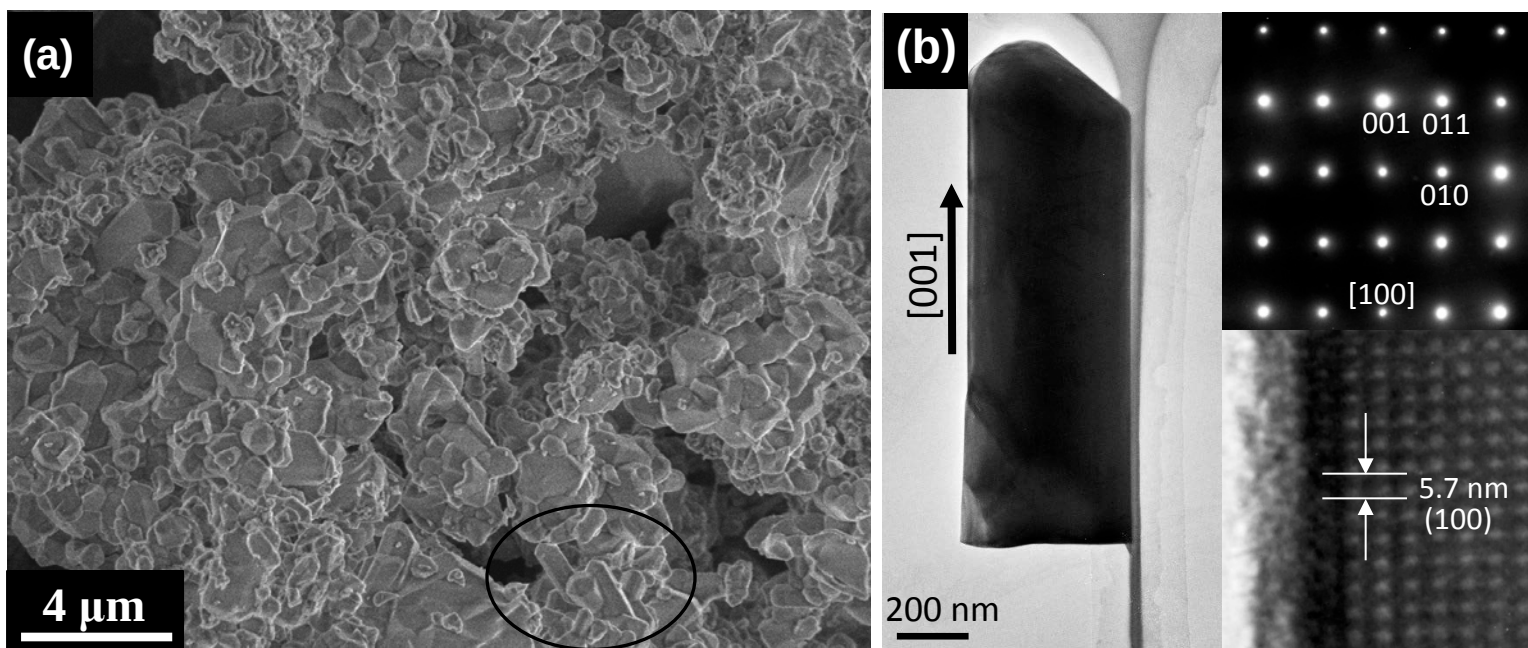


Fig. 4. (a) Scanning electron microscopy image of combustion synthesized Ca- α -SiAlON:Eu_{0.075} powders obtained under 1 MPa of nitrogen; (b) transmission electron microscopy image of a Ca- α -SiAlON:Eu particles along with the corresponding selected area electron diffraction pattern and high-resolution image.

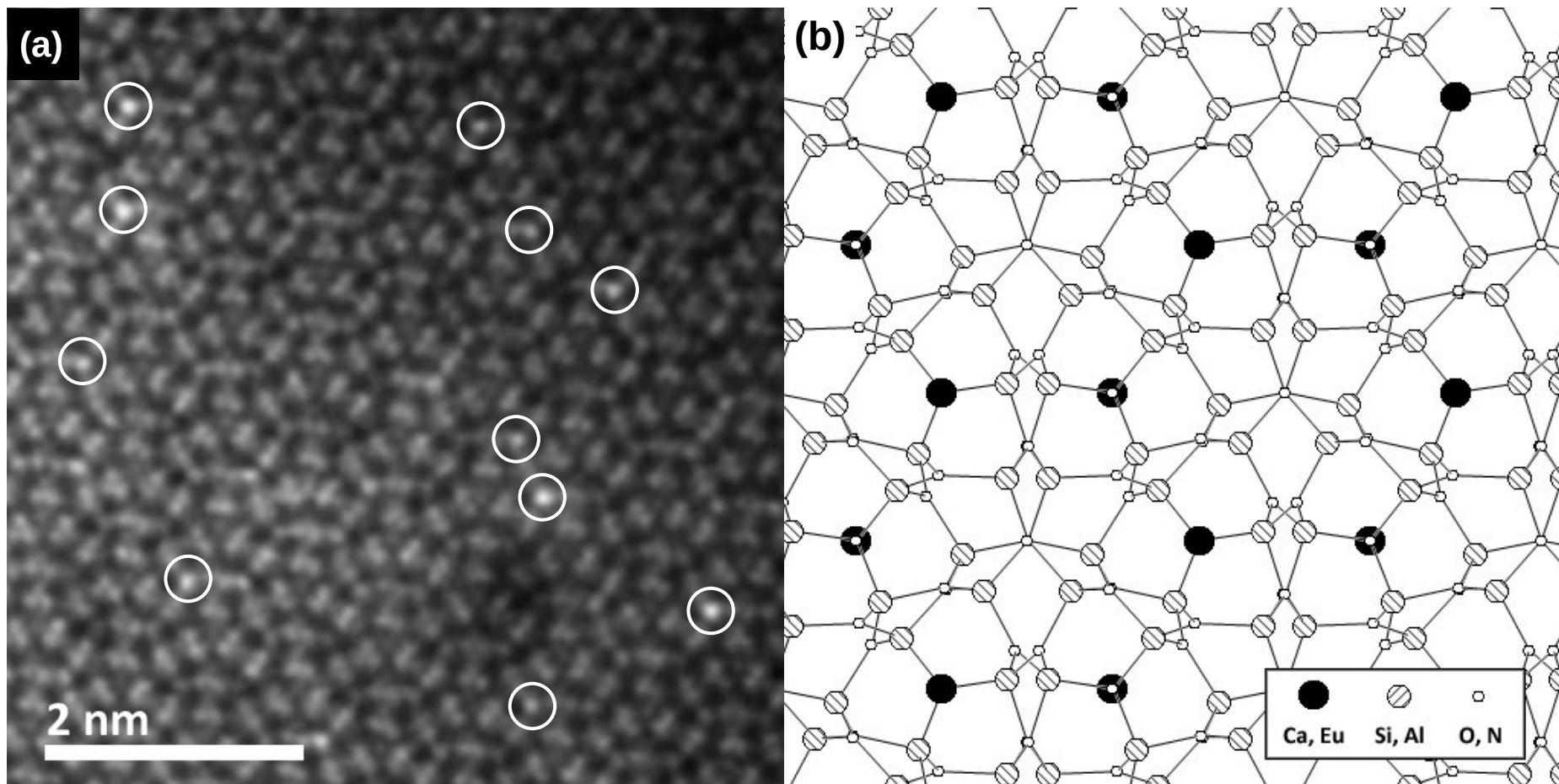


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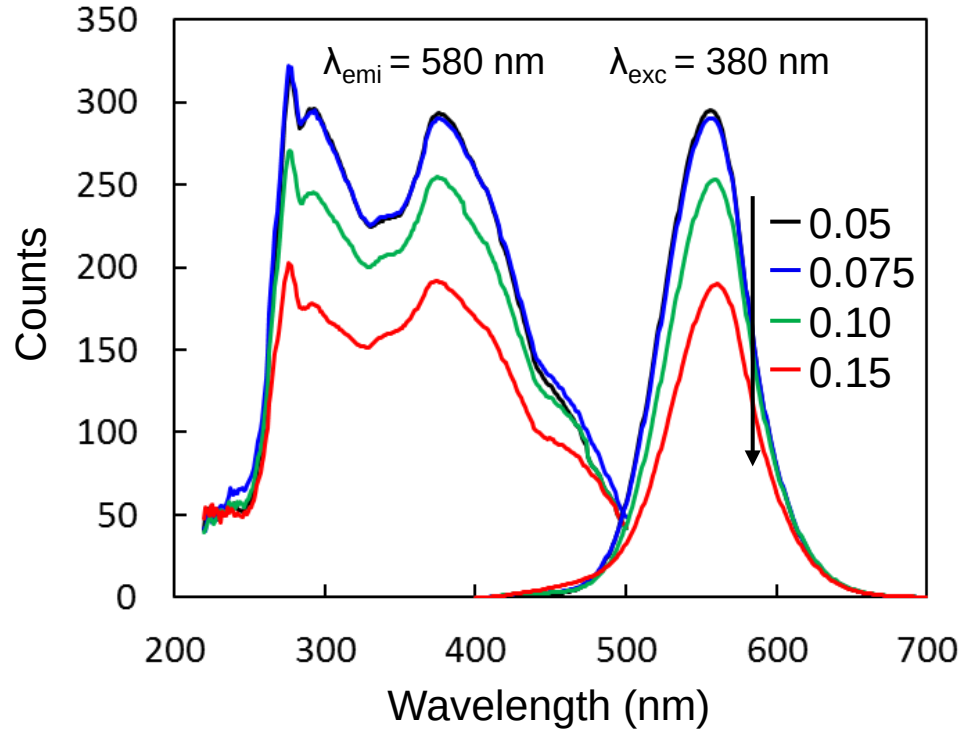


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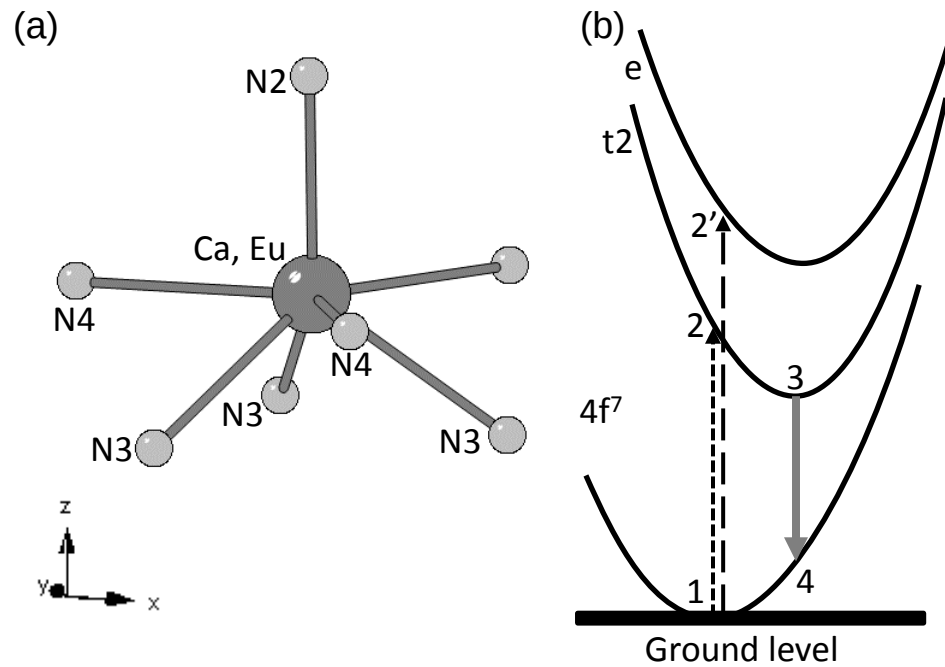


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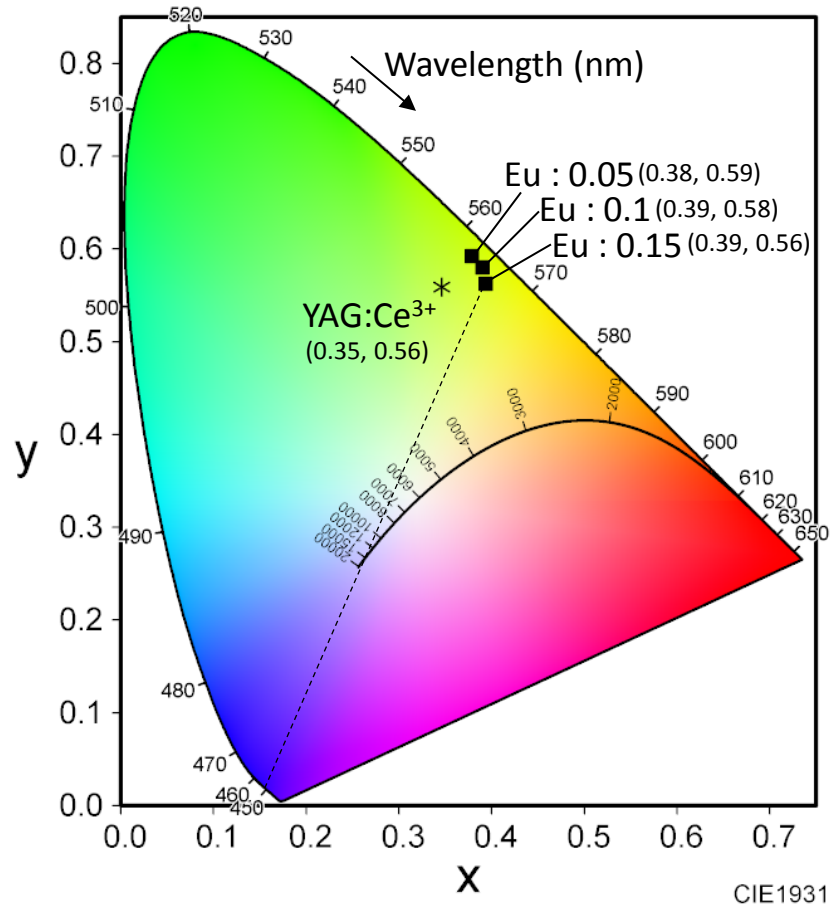


Fig. 8. Calculated Commission Internationale de l'Eclairage coordinate diagram of Ca- α -SiAlON:Eu²⁺ and YAG:Ce³⁺ phosphors.

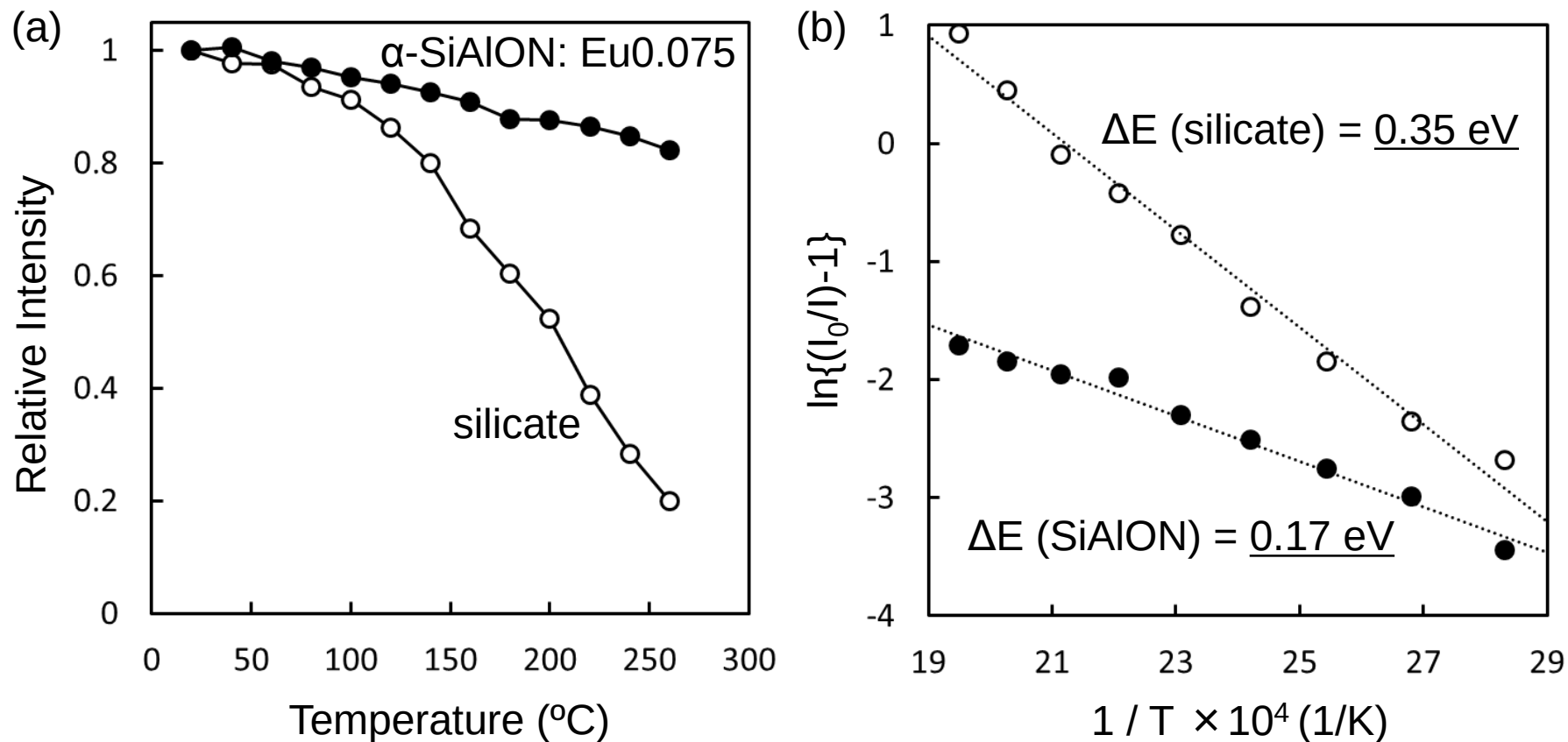


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