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Preparation of Eu-doped β- and 15R-SiAlONs by Ammonia Nitridation of the Precursor obtained using Aluminum Glycine Gel

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Abstract

Synthesis of Eu-doped β- and 15R-SiAlONs was studied by the ammonia nitridation of precursors derived from an α-Si_3N_4 fine powder dispersed in aluminum glycine gel with various Si/Al ratio and post-annealing in a nitrogen pressure furnace. The largest amount of β-SiAlON was observed in the product at 1750 °C for Si/Al = 1/1 with small amounts of both α- and 15R-SiAlON impurities. The product showed two emissions at around 420 nm and 560 nm. The emission intensities decreased with increasing amount of β-SiAlON. The former and latter emissions were assigned to Eu^{2+} in the 15R- and α-SiAlONs impurities. A mixture of Eu-doped 15R-SiAlON with α-Al_2O_3 impurity was obtained for Si/Al = 1/6, using AlN together with $Al(NO_3)_3$•$9H_2O$ in a 2/1 atomic ratio as the aluminum source. It showed a bluish-white emission at 450 nm under 254 nm radiation.

Keywords:

nitride materials, chemical synthesis, luminescence, X-ray diffraction

1. Introduction

Silicon aluminum oxynitrides (SiAlONs) have been used for structural engineering applications, because of their excellent mechanical and thermal stability over periods of several decades. Recently, rare-earth doped nitride or oxynitride compounds have been reported as promising host materials for phosphor applied in white light emitting diodes (LEDs) [1,2]. In white LED applications, blue LED light is combined with yellow light emitted from the phosphor to generate white light [3]. Divalent Eu-doped α-SiAlONs have been reported to show strong yellow light emission under UV and blue light radiation [4,5]. To improve the color rendering properties of LEDs, appropriate amounts of phosphors emitting green and red lights have been used with yellow light phosphor. These phosphors have been developed among the SiAlON-related compounds to further improve the color rendering in white LEDs. The kinds of their variants are limited [6-8].

Hirosaki et al. reported that Eu^{2+} doped β-SiAlON emitted green light under either UV or blue light radiation [9]. β-SiAlON is isostructural with β-Si_3N_4 and has the chemical composition $Si_{6-z}Al_zO_zN_{8-z}$ with $0 < z \leq 4.2$ [10,11]. The hexagonal β-SiAlON lattice is in either space group $P6_3$ or $P6_3/m$. There are no apparent available sites to accommodate rare-earth ions in the structure. The situation is different from α-SiAlON, which has large sites to incorporate rare-earth ions. β-SiAlON has been obtained in high purity only at

compositional range with low z values ($z \leq 1.0$), and exhibited a strong emission with a Eu^{2+} concentration of <0.3 at% [12,13]. At high z composition, the product was contaminated with SiAlON polytypoids [12,14]. Most recently, K. Kimoto et al. proposed that Eu^{2+} ions were located in the channel parallel to c-axis of the β-SiAlON crystal structure using scanning transmission electron microscopy [15].

Several kinds of SiAlON compounds have been reported in addition to the β-phase in the quaternary phase diagram of SiO_2-Si_3N_4-AlN-Al_2O_3 [10]. There are compounds named as SiAlON polytypoids, such as 8H, 15R, 12H, and so on, at the AlN-rich corner in the phase diagram. The 15R-SiAlON polytypoid neighboring β-SiAlON can be formulated as $Si_{6-y}Al_{4+y}O_yN_{12-y}$ with y = 3 to 4.9. These polytypoids have a layered structure closely related to wurtzite-type AlN. As an example, the 15R-SiAlON has a large rhombohedral unit cell (a= 0.301 nm, c= 4.181 nm). Every 15 layers of $(Si,Al)(O,N)_4$ tetrahedra similar to AlN structure interleaves an AlO_6 octahedral layer in the unit cell along its c-axis [16]. A polytypoid containing a small amount of Sr^{2+} has also been reported [17]. The Sr cations were assumed to be located at cubo-octahedral sites formed in stacking faults of the $(Si,Al)(O,N)_4$ tetrahedral layers [18]. Similar polytypoids with rare-earth ions have been very preliminary reported as impurities in α-SiAlON ceramics [19]. The Eu^{2+} doped AlN emitted strong blue light in electron beam of 5 kV and 400 pA [20], and blue-green emission at 495 nm under

290 nm excitation [21]. These investigations suggested that the Eu ions were incorporated in the layered structure of AlN, although their accurate sites were not clarified. There has been no report on Eu^{2+} doped 15R-SiAlON phosphor.

Most SiAlONs have been prepared by high temperature reaction above 1750 °C in a nitrogen atmosphere [9,17]. β-SiAlON:Eu phosphor have been obtained above 1900 °C [9,14]. These preparations have been done generally in solid state reaction under nitrogen pressure using starting powder mixtures of SiO_2, Si_3N_4, AlN and Al_2O_3. Eu-doped aluminum oxynitride was obtained at 1500 °C using an aluminum glycine gel, although AlON had been crystallized above 1700 °C using a conventional solid state reaction [22,23]. Blue to white luminescence was observed from Eu^{2+} in the aluminum oxynitride with magnetoplumbite structure under an UV excitation. We have obtained new type of gallium oxynitrides by a similar synthesis method using gallium citrate gel instead of glycine [24-26]. These methods are useful to the homogeneous doping of various kinds of cations to the oxynitrides [27,28].

The present preparation method using soft solution route may find out new SiAlON:Eu phosphors containing more aluminum. In this study, β- and 15R-SIAlONs were prepared using nitridation of precursors obtained from a Si_3N_4 dispersed aluminum glycine gel and their post-annealing. The luminescence properties of the Eu^{2+} doped products are discussed in relation to their crystal structure.

2. Experimental Procedure

α-Si_3N_4 (SN-E10, Ube Industries Ltd.), $Al(NO_3)_3 \cdot 9H_2O$ (98%, Wako Pure Chemicals Co.) and AlN (99%, Rare Metallic Co.) were used as starting materials. These powders were mixed in Si/Al molar ratios of 4/1 and 1/1 for z=1.2 and 3 in $Si_{6-z}Al_zO_zN_{8-z}$, and 1/4 and 1/6 for y=4 and 4.6 in $Si_{6-y}Al_{4+y}O_yN_{12-y}$, respectively in distilled water. The aluminum source was either aluminum nitrate or nitride. Glycine (99.0%, Wako Pure Chemicals Co.) was added as a peptizer to the aqueous solution in an equi-molar amount to the total cations. The resultant solutions were heated on a hotplate with stirring to obtain gelatinous products. The gels were prefired in air at 350 °C for 1 h, and were then nitrided under an ammonia flow rate of 50 mL/min at 750 °C for 10 h. After crushing and mixing in an agate mortar, they were post-annealed at 1400-1750 °C for 1-2 h under a nitrogen gas pressure of 0.5 MPa. Similar preparations were performed by adding $Eu(NO_3)_3 \cdot 5H_2O$, (99.9%, Aldrich, St. Louis, MO) either in Eu/(Si+Al) = 5 or 0.5 at% to the starting solution to obtain Eu-doped SiAlON. Crystalline phases were characterized using powder X-ray diffraction (XRD) with monochromatized Cu$K\alpha$ radiation (X'-Pert-MPD, PANalytical Co.). The powder morphology was investigated by scanning electron microscopy (JSM-6390LV, JEOL). Photoluminescence was measured using a fluorescence spectrometer (FP 6500, Jasco)

installed with a Xenon lamp for excitation at 150 W. Emission spectra were measured in the 400-700 nm range with excitation at 254 nm. Excitation spectra were measured in the range of 200-430 nm with an emission at 450 nm.

3. Results and Discussion

3.1. β-SiAlON

The nitrided product prepared from α-Si_3N_4 and $Al(NO_3)_3$•$9H_2O$ at 750 °C was a mixture of α-Si_3N_4 and amorphous AlON. The nitrided product with a starting composition of Si/Al = 4/1 was post-annealed above 1400 °C for several hours under a nitrogen gas pressure of 0.5 MPa. α-Si_3N_4 was present with a small amount of β-Si_3N_4 at 1450 °C. β-SiAlON started to crystallize above 1550 °C as shown in Fig. 1. The amount increased with increase in both the annealing temperature and duration. A small amount of 15R-SiAlON also appeared above 1750 °C. A part of both α- and β-Si_3N_4 may have been changed to these SiAlONs.

β-SiAlON was the major phase in the product post-annealed at 1750 °C (Fig. 1(f)) with small amounts of α-Si_3N_4 and 15R-SiAlON impurities when the composition was changed to Si/Al = 1/1. The 5 at% Eu-doped product annealed at 1750 °C exhibited yellowish emission with two broad maxima at 420 nm and 560 nm under 254 nm radiation

as shown in Fig. 2. The emission at around 560 nm was similar to that reported for Eu^{2+} doped α-SiAlON [5]. Eu-doped Ca-α-SiAlONs prepared by gas-reduction nitridation of citrate precursors had yellow emission spectra with peak at 580-600nm [5]. The variation in the peak position can be understood as the result of differences in composition of the host lattice. The wide change in emission peak between 563-586 nm due to a variation in the chemical composition has been reported on Eu-doped Li-α-SiAlON [29,30]. The shortest position in the emission was observed at the lowest Al/Si ratio and highest O/N ratio in the α-SiAlON. The Eu-doped β-SiAlONs had been prepared in a gas pressure furnace at extremely high temperatures above 1900 °C. They exhibited a green emission at around 530 nm for chemical compositions below z = 2.0 and x = 0.039 in $Eu_xSi_{6-z}Al_zO_zN_{8-z}$ but a violet emission at the higher z– composition [12,13]. The present β-SiAlON obtained with z = 3, i.e. Si/Al = 1/1, and x = 0.3 at 1750 °C for 2 h showed the weakest emission among the products, as shown in Fig. 2, although the amount of β-SiAlON was the largest. In the present products, Eu^{2+} ions might be incorporated into α-SiAlON rather than β-SiAlON, due to relatively low preparation temperature. Even at high temperature above 1900 °C, a part of Eu^{2+} ions remained at amorphous surface layer of the β-SiAlON particles [9]. The emission around 560 nm is generated from the Eu^{2+} doped α-SiAlON that is isostructural to α-Si_3N_4. Another emission at around 420 nm may be assigned to another impurity of 15R-SiAlON

polytypoid in the present products as discussed in the next section.

3.2. 15R-SiAlON polytypoid

15R-SiAlON polytypoid is adjacent to β-SiAlON in the AlN rich side of the quaternary phase diagram [10]. The preparation was performed with an increased aluminum composition of Si/Al = 1/4. The product from α-Si_3N_4 and $Al(NO_3)_3$•$9H_2O$, after post-annealing at 1750 °C for 1 h, was mainly a mixture of α-Al_2O_3 and β-SiAlON contaminated with small amounts of 15R-SiAlON and α-Si_3N_4 impurities, as shown in Fig. 3(a). Shortage of the nitrogen content was expected on the product because the nitrided product from the aluminum glycine gel was spinel-type aluminum oxynitride with a composition of $Al_{2.75}\square_{0.25}O_{3.74}N_{0.26}$ [22]. Aluminum nitride was used as an aluminum source substituting $Al(NO_3)_3$•$9H_2O$ to increase the nitrogen content in the product. Preparation from a mixture of Si_3N_4:$Al(NO_3)_3$•$9H_2O$:AlN = 1:4:8 (Si/Al = 1/4) increased the amount of 15R-SiAlON as represented in Fig. 3(b). The annealed product obtained from only Si_3N_4 and AlN was a mixture of α-Si_3N_4, α-Al_2O_3 and β-SiAlON without any trace of 15R-SiAlON. The use of both AlN and $Al(NO_3)_3$•$9H_2O$ was very important to obtain nitrogen-rich SiAlONs with high aluminum content.

The amount of 15R-SiAlON was further increased by increasing the aluminum ratio

from Si/Al = 1/4 to 1/6 in the starting composition as shown in Fig. 4. The 15R-SiAlON was obtained as a mixture with α-Al_2O_3 from Si_3N_4, $Al(NO_3)_3 \cdot 9H_2O$ and AlN in a compositional ratio of Si/Al = 1/6. Figure 5 shows a SEM image of the Eu-doped product at Si/Al = 1/6. There are agglomerated hexagonal platy grains with a diameter and a thickness of ca 1-3 μm and 0.5 μm, respectively. The hexagonal habit might be related to the 15R polytypoid structure with rhombohedral lattice. The Si_3N_4 starting powder was homogeneously surrounded by the aluminum glycine gel in this preparation route to accelerate their reaction and grain growth.

The Eu-doped products at Si/Al = 1/6 emitted a bluish-white light at around 450 nm for excitation at 254 nm as shown in Fig. 6. They were a mixture of α-Al_2O_3 and 15R-SiAlON although the former has the hexagonal corundum structure with no available sites to locate large cations such as Eu^{2+}. The emission at around 450 nm can be assigned to the Eu-doped 15R-SiAlON. The present product showed an excitation spectrum with maxima at 243 nm and 281 nm for the emission at 450 nm. Eu-doped AlN has been reported to show an excitation maximum at 290 nm and an emission at 495 nm [21]. The wavelength both in the emission and excitation spectra might be shortened, because oxygen substituted a part of the nitrogen in AlN lattice increases the excitation energy of Eu^{2+}. Magnetoplumbite type $EuAl_{12}O_{19}$ was reported to have an excitation peak at 278 nm [23], where the Eu^{2+} ions are

coordinated with twelve oxide anions in the structure. The excitation wavelength is almost the same or slightly shorter than the present larger maxima at 281nm. The present 15R-SiAlON polytypoid may have Eu^{2+} ions located in the cubo-octahedral sites resulting from the reported stacking faults [18]. The sites are surrounded by twelve anions, as reported for the Sr-containing SiAlON polytypoid. This is the first report of photoluminescence for a Eu^{2+} doped 15R-SiAlON polytypoid among the several kinds of SiAlON polytypoids with different chemical compositions and layer stackings. The photoluminescence properties of Eu-doped polytypoids could be modified in another kind of SiAlON polytypoid to be used as a host lattice.

4. Conclusions

Preparation of Eu-doped β- and 15R-SiAlONs was investigated by the ammonia nitridation of precursors obtained from the aluminum glycine gel. Post-annealing in a nitrogen atmosphere at 0.5 MPa above 1750 °C was necessary for their crystallization. Suitable Si/Al atomic ratios for the starting compositions were 1/1 for β- and 1/6 for 15R-SiAlONs to obtain as the major phase in the products. The use of AlN powder as part of the starting aluminum composition was useful in obtaining the 15R-phase after post-annealing, because the aluminum nitrate caused nitrogen deficiency in the as-nitrided

product using a precursor derived from the aluminum glycine gel. The firing temperature could be reduced from 1900 °C, as reported in the literature, to 1750 °C in the present preparation of the β- and 15R-SiAlON. Eu-doped 15R-SiAlON was found to exhibit bluish-white luminescence at around 450 nm under excitation at 254 nm. The luminescence may originate from Eu^{2+} located at cubo-octahedral sites formed by stacking faults in the 15R-SiAlON polytypoid. The emission might shift to 420 nm in the 15R-SiAlON obtained as a mixture with β-SiAlON in the first section because of its larger Si-O composition. This is the first report of 15R polytypoid to be used in phosphor to our knowledge. The yellow luminescence in the present Eu-doped product for Si/Al =1/1 was mainly due to the presence of the Eu doped α-SiAlON impurity.

Acknowledgements

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Figure captions

Fig. 1. XRD patterns for the products of Si/Al = 4/1 post-annealed at 1450 °C (a), 1550 °C (b), 1650 °C (c), 1750 °C (d) for 1 h, and 1750 °C for 2 h (e). The annealed product of Si/Al = 1/1 at 1750 °C for 2 h is shown in (f). Symbols of □, ■, ○ and ● denote diffraction peaks for α-Si_3N_4, β-Si_3N_4, β-SiAlON, and 15R-SiAlON, respectively.

Fig. 2. Emission spectra for the 5 at% Eu-doped SiAlON products with Si/Al = 4/1 (z = 1.2) and 1/1 (z = 3) excited at 254 nm.

Fig. 3. XRD patterns for the products of Si/Al = 1/4 post-annealed at 1750 °C for 1 h. The products were prepared from a mixture of (a) α-Si_3N_4 and $Al(NO_3)_3$•$9H_2O$, and (b) α-Si_3N_4, $Al(NO_3)_3$•$9H_2O$ and AlN. Symbols of □, ○, ● and ♦ denote diffraction peaks for α-Si_3N_4, β-SiAlON, 15R-SiAlON and α-Al_2O_3, respectively.

Fig. 4. XRD patterns for the 0.5 at% Eu-doped SiAlON prepared from a mixture of α-Si_3N_4, $Al(NO_3)_3$•$9H_2O$ and AlN. The Si/Al compositions were Si/Al = 1/4 (a) and 1/6 (b). Symbols of □, ○, ● and ♦ denote diffraction peaks for α-Si_3N_4, β-SiAlON, 15R-SiAlON and α-Al_2O_3, respectively.

Fig. 5. SEM image of the Eu-doped product at Si/Al = 1/6 annealed at 1750 °C for 3h.

Fig. 6. Emission and excitation spectra for the 0.5 at% Eu-doped 15R-SiAlON products with Si/Al = 1/6. Excitation spectrum was monitored at 450nm and emission spectrum was

measured under excitation at 254 nm.

Figure 1

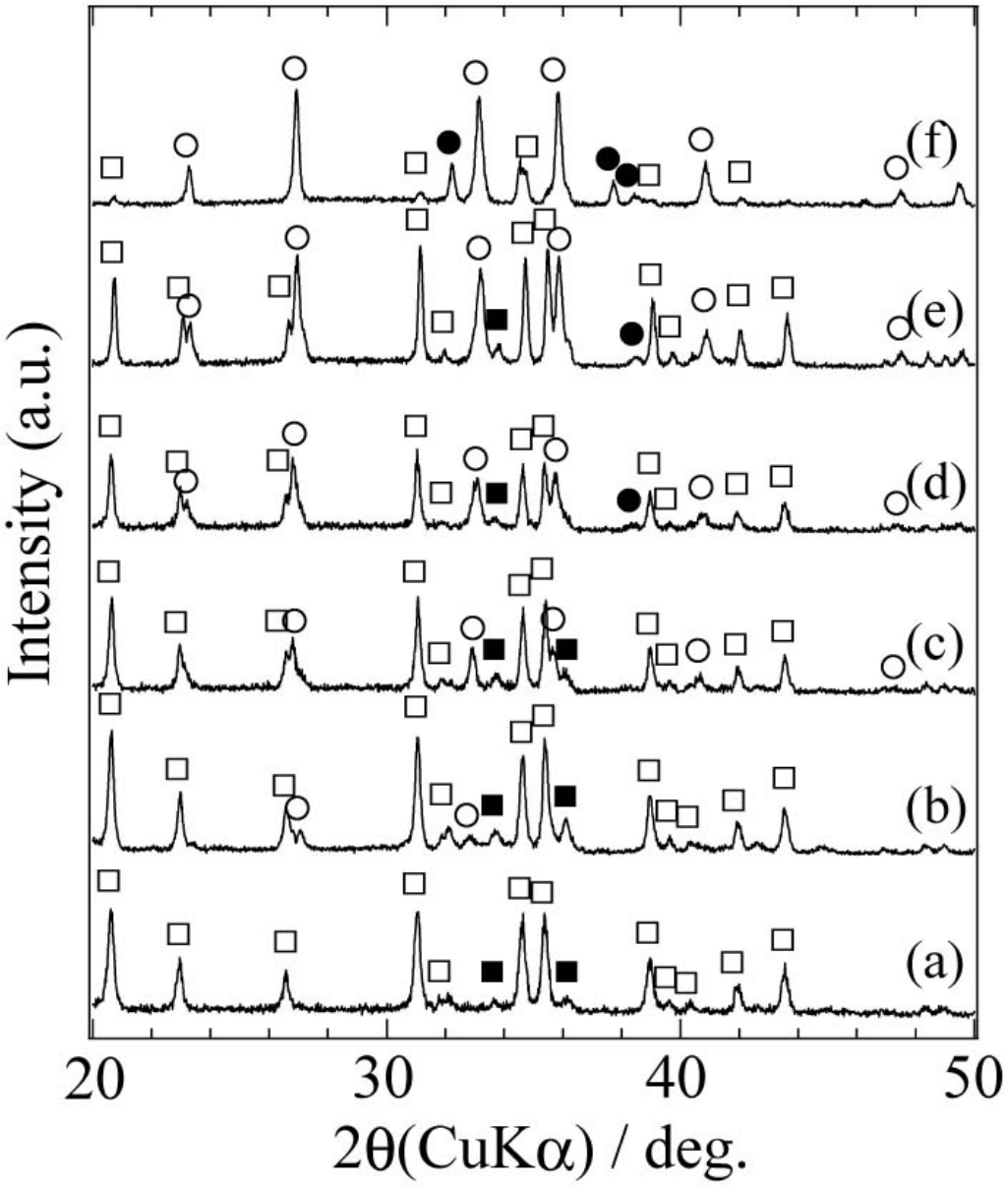


Figure 1 Yuji Masubuchi, et al.

Figure 2

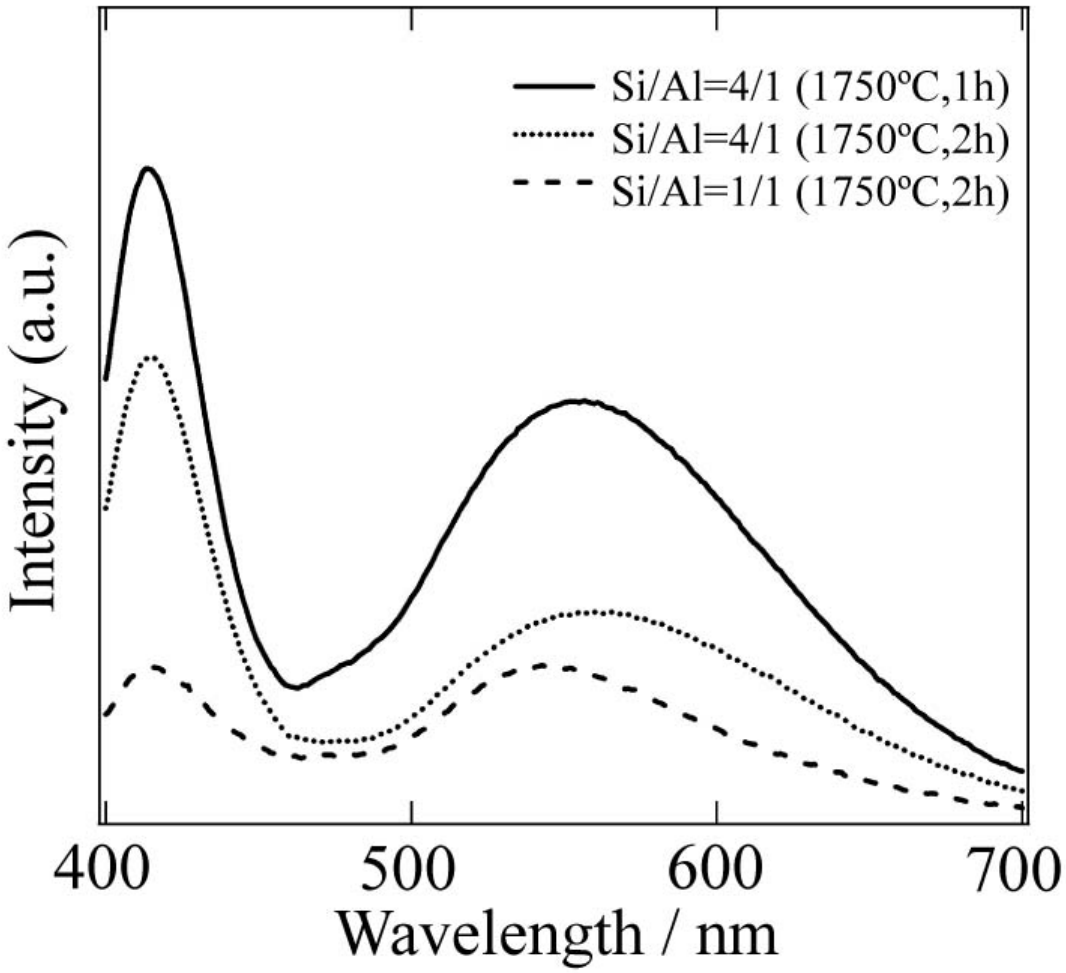


Figure 2 Yuji Masubuchi et al.

Figure 3

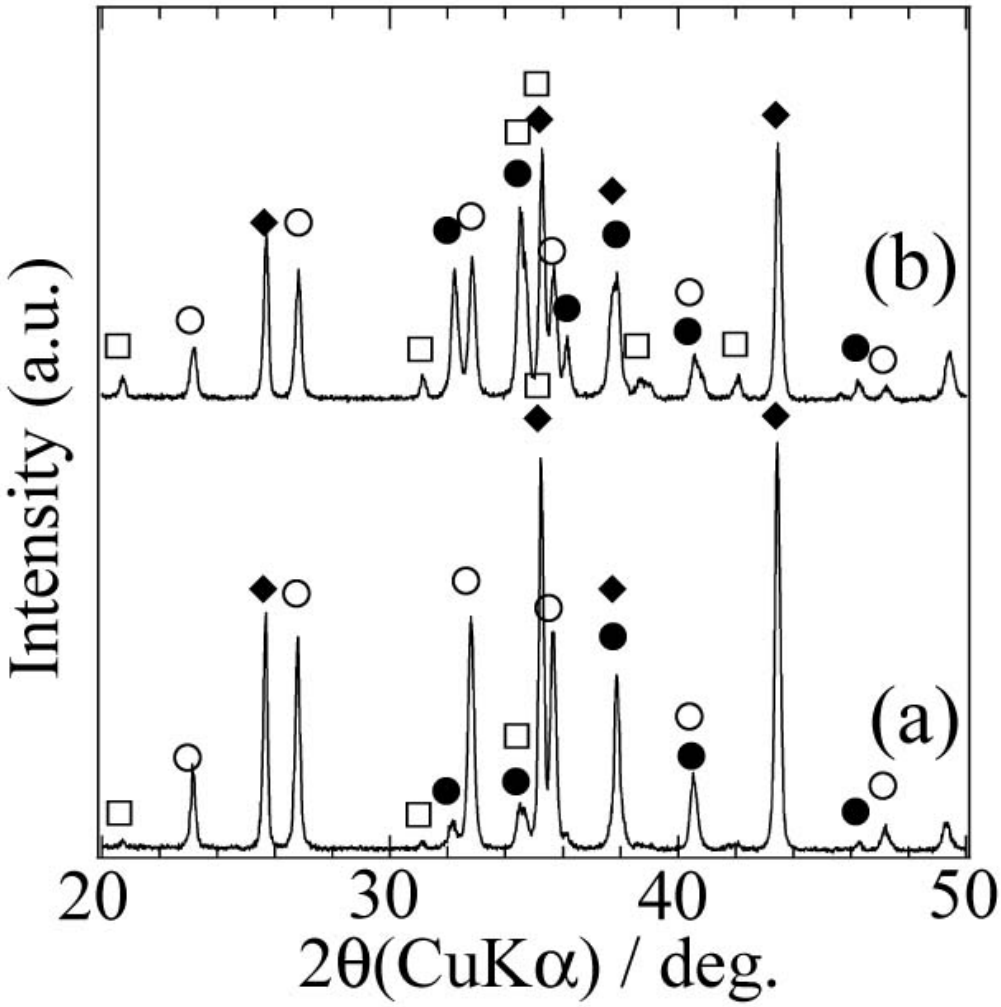


Figure 3 Yuji Masubuchi et al.

Figure 4

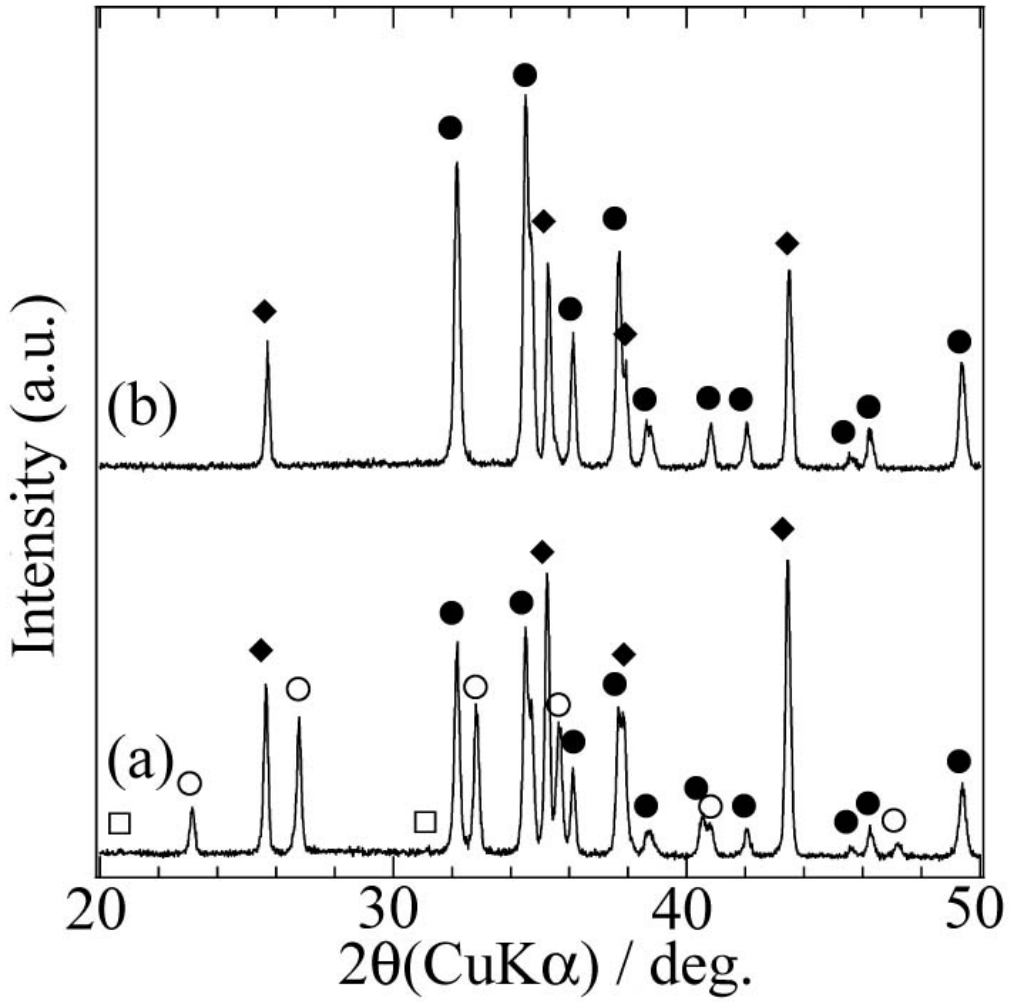


Figure 4 Yuji Masubuchi et al.

Figure 5

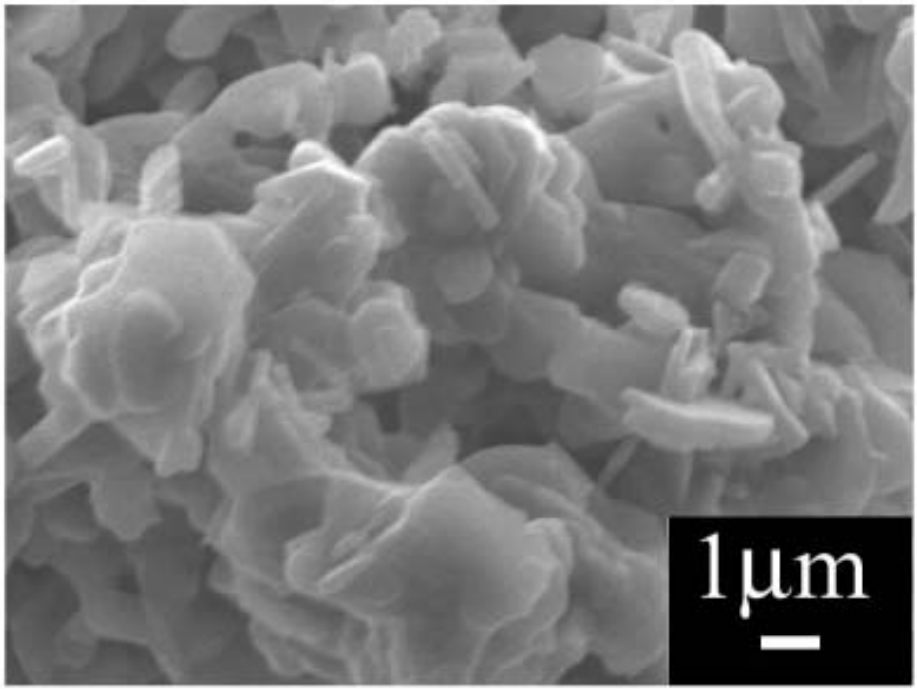


Figure 5 Yuji Masubuchi et al.

Figure 6

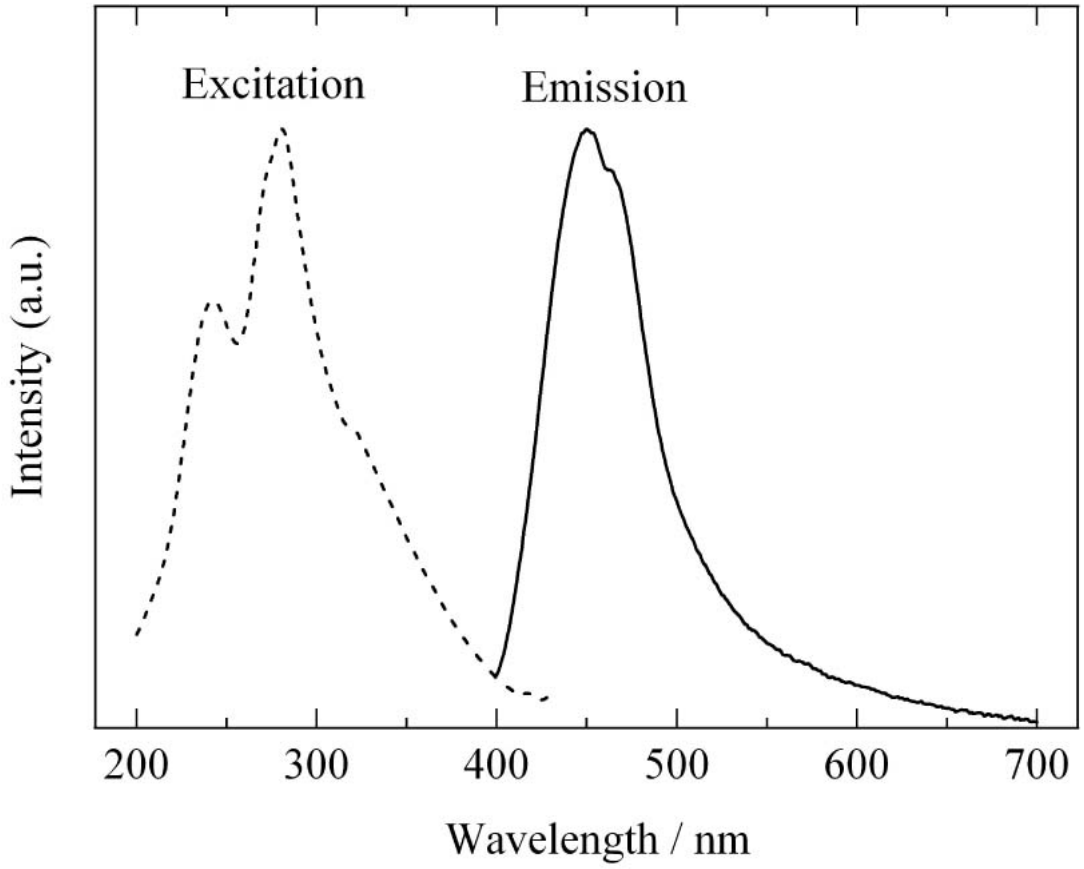


Figure 6 Yuji Masubuchi et al.