Powder Synthesis of Ca-α′-SiAlON as a Host Material for Phosphors

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Fine powders of Ca-α′-SiAlON have been synthesized from the system $CaO-Al_2O_3-SiO_2$, by using an NH_3-CH_4 gas mixture as a reduction−nitridation agent. Completion of the reduction−nitridation was achieved at low temperatures of 1400−1500 °C without unfavorable particle coarsening or carbon contamination, while the phase purity and crystallinity of the powders were markedly improved by a postsynthesis heat treatment. The resulting fine Ca-α′-SiAlON powders possessed high purity and uniform discrete particle morphology, which meet the requirements for the new application of SiAlON ceramics as a host material for phosphors. The reduction−nitridation synthesis of the yellow-emitting Ca-α′-SiAlON:Eu powder phosphor was also performed for the first time, and better photoluminescence property was demonstrated compared to that of the conventionally prepared powder.

Introduction

α′-SiAlONs are solid solutions of the M−Si−Al−O−N system, which have a structure derived from α-Si_3N_4 with the general formula $M_x^{v+}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where $x = m/v$ and M is one of the cations Li, Mg, Ca, Y, and some rare earths.[1] In contrast to the purely substitutional solubility in β′-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$), there are two interstitial sites per unit cell in the α-Si_3N_4 structure that can be partially occupied by modifying cations M (Figure 1). α′-SiAlON ceramics have been developed for structural engineering applications for years[2−6] because of their excellent mechanical and thermal properties. Recently, in the course of fundamental studies on rare-earth-doped systems, a new potential application of α′-SiAlONs as luminescent materials has emerged.[7−10] Among them, Eu-doped Ca-α′-SiAlON, which exhibits yellow emission (ca. 570−600 nm) by excitation in UV to blue spectral region (ca. 300−460 nm), is attracting considerable attention in the electronic industry for use as a wavelength-conversion phosphor for white light-emitting diodes (LEDs).

At present, the only established synthesis route for producing α′-SiAlON is the reaction sintering of the system MO_y-AlN-Si_3N_4, which requires high-purity nitride starting materials and a postsynthesis grinding step to pulverize a dense sintered body or hard agglomerates into fine powder. Direct synthesis of α′-SiAlON powders by carbothermal reduction−nitridation (CRN) of oxide precursors has also been attempted,[11−14] but the process may cause carbon contamination and concurrent formation of SiC. These conventional processes are thus disadvantageous from the viewpoint of the optical use and industrial development, triggering the search for sophisticated processes to synthesize fine α′-SiAlON powders.

In the current work, the gas-reduction−nitridation method (called GRN hereafter), which has been developed recently

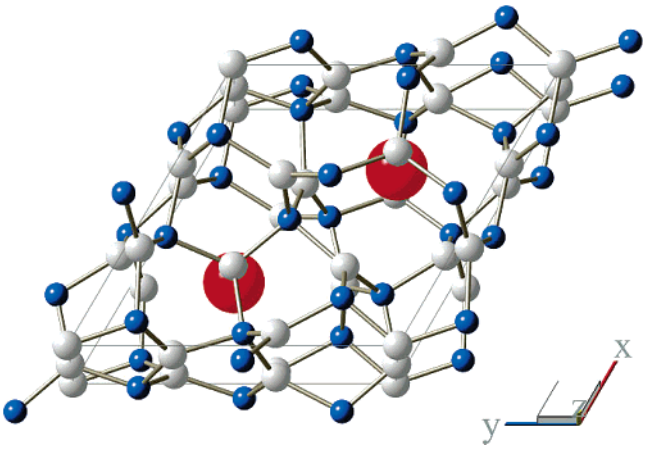

Figure 1. Structure of α′-SiAlON viewed along a direction nearly parallel to the *c* axis. Modifying cations (Ca and a luminescent ion) are represented by red spheres, (Si,Al) atoms and (N,O) atoms are shown as blue and white spheres, respectively.

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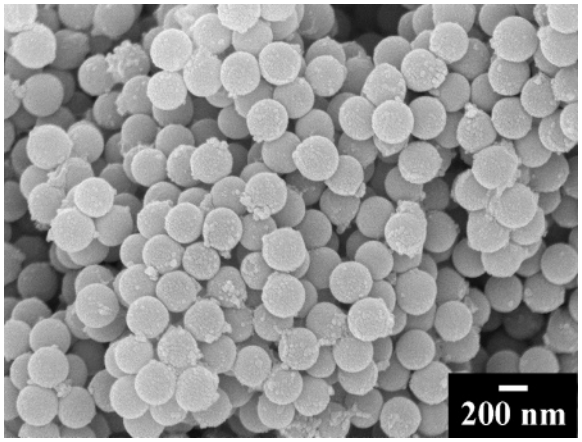

Figure 2. FESEM micrograph of the raw Ca−Si−Al−O powder.

as a method for producing fine aluminum nitride powders,[15−18] was applied to the multicomponent oxide system $CaO-Al_2O_3-SiO_2$ as a new synthesis route for α′-SiAlON powders. Highly phase-pure, fine Ca-α′-SiAlON powders consisting of uniform submicrometer-sized particles were successfully prepared at processing temperatures of 1400−1500 °C in a soaking time of 4 h. The effects of process parameters and an additional heat-treatment step on powder characteristics were discussed with regard to the results of X-ray diffraction, electron microscopy, surface area measurements, and UV−vis spectroscopy. Finally, the photoluminescence properties of the Ca-α′-SiAlON:Eu^{2+} powder phosphors synthesized by the GRN process were reported and compared with the specimen prepared by using reaction sintering.

Experimental Procedure

An amorphous SiO_2 powder (SP-03B, Fuso Chemical Co., $D_{BET} = 0.23\ \mu m$) was used as a starting material. Homogeneous mixture of the system Ca−Si−Al−O was prepared by coprecipitation method using citric acid, for obtaining the target composition of $Ca_{0.80}Si_{9.60}Al_{2.40}O_{0.80}N_{15.20}$ ($m = 1.6$, $n = 0.8$). The organic components of the citrate precursor were burnt off by calcination at 700 °C in air, giving the SiO_2 particles uniformly coated with amorphous CaO and Al_2O_3 (Figure 2). The starting powder thus-obtained was contained in a high-purity alumina boat and set in a horizontal alumina tube furnace (inner diameter of 24 mm). The furnace was subsequently heated to the experimental reaction temperature (1350−1500 °C) at various heating rates in an NH_3−1.5 vol % CH_4 gas mixture (each >99.999% purity), introduced from the extremity of the reactor at a constant flow rate of 1.3 L/min. After the predetermined reaction time, the sample was furnace cooled in an NH_3 atmosphere. The fraction of observed and theoretical weight loss ($\Delta W_{obs}/\Delta W_{theor}$) resulting from the reduction−nitridation reaction was calculated for each run, which corresponds to the extent of nitridation. The loss on ignition of the starting powder was predetermined and was taken into account. An additional postsynthesis heat treatment was conducted for the selected samples. The as-synthesized powder was transferred to a high-purity BN crucible, and an alumina tube furnace equipped with molybdenum silicide heating elements was used for heating the samples at 1700 °C with a soaking time of 4 h in a N_2 atmosphere.

Table 1. Characteristics of the Product Powders Obtained by Heating at 1500 °C for 2 h with Various Heating Rates

sample	heating rate (°C/h)	phase assemblage	$\Delta W_{obs}/\Delta W_{theor}$	S_{BET} (m^2/g)	D_{BET} (μm)
C1	500	α′ (70.7%), β′ (29.3%)	1.01	4.61	0.46
C2	750	α′ (69.8%), β′ (30.2%)	1.05	1.63	1.14
C3	300	α′ (85.4%), β′ (14.6%)	1.03	5.89	0.32
C4	200	α′ (91.7%), AlN (4.7%), β′ (3.6%)	1.04	8.84	0.21

Phase assemblage of the product powders was analyzed by X-ray diffractometry using Cu Kα radiation (RINT2200, Rigaku). The multiphase Rietveld analysis was conducted to determine the mass fraction of each phase using the program RIETAN-2000.[19] The actual solubility of the Ca ion (x value) in the α′-SiAlON matrix was also determined by the refinement of the site occupancy factor of the Ca ion, with the isotropic displacement parameter fixed to the literature value.[20] Specific surface areas of powders were measured by the multi-point Brunauer−Emmett−Teller (BET) method (Autosorb, Quantachrome). Nitrogen and impurity carbon contents of the selected samples were analyzed by the selective hot-gas extraction method (TC-436, CS-444LS, LECO Co.). Electron micrographs of platinum-coated samples were obtained using a field-emission scanning electron microscope (FESEM; JSM-6340F, JEOL). Diffuse reflectance of the undoped powders was measured with a spectrometer equipped with an integrating sphere (Ubest V-560, JASCO), by referring to the Spectralon reflectance standard. Photoluminescence properties of the Eu-activated powders were studied on a fluorescence spectrophotometer (F-4500, Hitachi) at room temperature.

Results and Discussion

Powder Preparation of Ca-α′-SiAlON by GRN. Table 1 summarizes the result of GRN experiments carried out by heating at 1500 °C for 2 h with the ramping rates ranging from 200 to 750 °C/h. The reaction was first conducted with a heating rate of 500 °C/h, and the sample thus-obtained exhibited almost complete nitridation while containing a considerable amount of β′-SiAlON (∼29%). The sample prepared with a higher heating rate (750 °C/h) showed severe agglomeration and a markedly lower specific surface area, suggesting increased liquid phase formation during the reaction. In contrast, slower heating (300 °C/h) resulted in markedly higher α′ content and finer particle size, and the product powder possessing an α′ content as high as ∼92% and a mean particle size of 0.21 μm was successfully obtained with the heating rate of 200 °C/h.

With the objective of revealing the difference in the phase evolutions during the reduction−nitridation, several partly reacted samples were prepared for both fast (500 °C/h) and slow (200 °C/h) heating systems. Figure 3 shows the XRD patterns of the samples synthesized at temperatures in the range of 1200−1500 °C without isothermal holding (0 h soaking). The phase assemblages of both samples were not very different up to 1300 °C, with the crystalline phases

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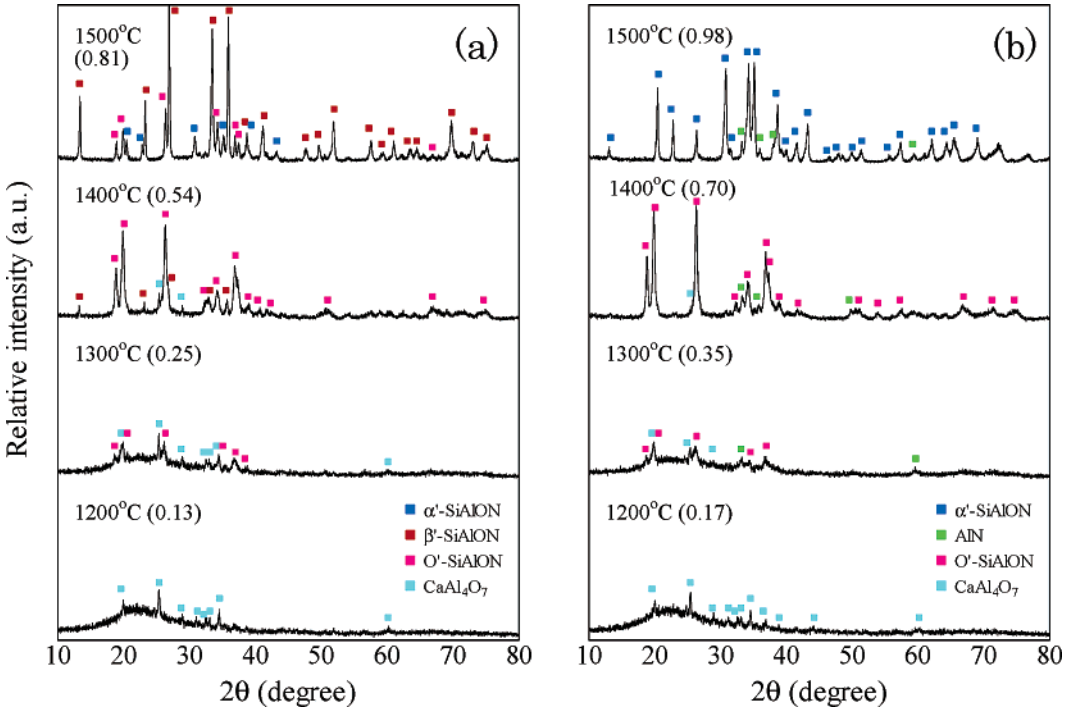

Figure 3. X-ray diffraction patterns of the powders heated to temperatures in the range 1200−1500 °C with a ramping rate of (a) 500 °C/h and (b) 200 °C/h in an NH_3−1.5 vol % CH_4 atmosphere. The number in parentheses denotes the nitridation extent of each sample.

Table 2. Characteristics of the Product Powders Obtained at Optimized Reaction Conditions with a Heating Rate of 200 °C/h

sample	reaction conditions	α′ content (wt%)	x	$\Delta W_{obs}/\Delta W_{theor}$	S_{BET} (m^2/g)	D_{BET} (μm)	carbon content (wt%)
C5	1400 °C, 4 h	89.6	0.57(1)	0.96	6.50	0.28	0.06(1)
C6	1425 °C, 4 h	89.6	0.47(1)	1.00	5.35	0.35	0.09(1)
C7	1450 °C, 1 h	90.7	0.44(1)	0.98	10.23	0.18	0.11(1)
C8	1500 °C, 0.5 h	91.9	0.50(1)	1.03	9.57	0.19	0.53(1)

detected being $CaAl_4O_7$, O′-SiAlON ($Si_{2-z}Al_zN_{2-z}O_{1+z}$)[21] and AlN. A small hump on the backgrounds at $2\theta \approx 22°$ suggests that a large part of the starting SiO_2 is unreacted and still in amorphous state, as indicated by the low values of the nitridation extent. At 1400 °C, the major crystalline phases were O′-SiAlON for both systems, while the sample prepared by slower heating exhibited much higher nitridation extent of 0.70, as compared to 0.54 in the sample with fast heating. Also at this temperature, formation of β' phase was detected for the fast heating sample. The difference becomes more evident at the soaking temperature of 1500 °C, at which the sample with slower heating consisted exclusively of α′-SiAlON and AlN, while the fast heating sample consisted mainly of β'-SiAlON; the formation of β' phase during the heating was completely suppressed in the former system.

These results clearly indicate that the fast heating, by which the reaction system reaches the soaking temperature in more oxygen-rich composition, leads to excess formation of liquid phases, and this in turn promotes the formation of β-Si_3N_4/ β'-SiAlON.

The reacted powders were homogeneous throughout the sample bulk, and whiskerlike products, frequently observed in the conventional carbothermal synthesis, were not formed in the powder bed. The product powders were essentially white, except the sample C4 synthesized with the longest soaking due to the slower heating rate of 200 °C/h, which exhibited slightly grayish coloration. This result suggests that the excess soaking after completion of the reaction leads to the decomposition of CH_4 and to the consequent carbon contamination.

On the basis of these experimental findings, optimization of the processing conditions was attempted with a fixed heating rate of 200 °C/h, varying the processing temperatures from 1400 to 1500 °C. The characteristics of the product powders are summarized in Table 2. Under these conditions, formation of β' phase and particle coarsening were suppressed in every case, and fine α′-SiAlON powders possessing a phase purity of ∼90% and a mean particle size of 0.19−0.35 μm were prepared. The soaking time required for completion of the reaction decreased markedly with the increase of the processing temperature, from 4 h at 1425 °C to 0.5 h at 1500 °C. The shorter soaking at higher reaction temperature seemed to be also beneficial for obtaining finer particles, while the increase of the processing temperature led to the increase of carbon content of the final products. The latter observation might result from the favored decomposition of CH_4 at higher temperatures, as expected from the thermodynamic considerations.[15] The x values determined by the Rietveld analysis were found to be ∼0.5, meaning that the actual solubility of Ca in the as-prepared α′-SiAlON powders was about 63% of the target composition of $x = 0.8$.

The typical XRD pattern of the as-prepared powder is shown in Figure 4, and the SEM micrographs of the samples

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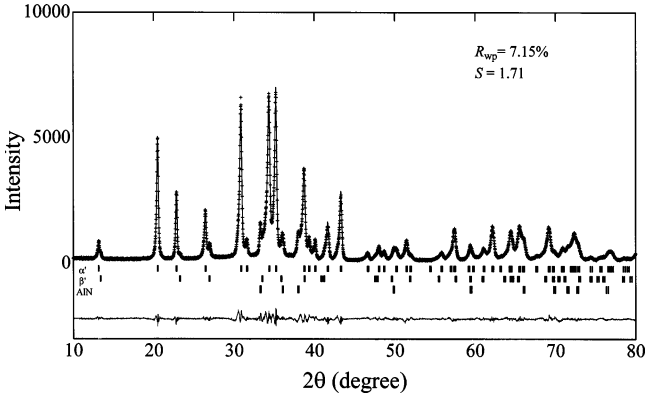

Figure 4. X-ray Rietveld refinement pattern of the as-prepared powder synthesized at 1425 °C with a soaking time of 4 h.

Table 3. Characteristics of the Product Powders Processed with the Post-Synthesis Heat Treatment (1700 °C, 4 h in N_2)

sample	phase assemblage	x	S_{BET} (m^2/g)	D_{BET} (μm)
C6R	α′ (single phase)	0.816 (10)	0.712	2.59
C8R	α′ (99.1%), AlN (0.9%)	0.797 (9)	0.999	1.84

C6 and C8 are shown in Figure 5. Both product powders consisted of well-dispersed, uniform primary particles of ∼0.2−0.3 μm, consistent with the values estimated from the BET analyses. The particle sizes of the product powders were also comparable to the size of the starting SiO_2 (0.23 μm), while the microstructures were completely altered from the initial spherical morphology, indicating that the reduction−nitridation in the current system proceeded predominantly through the liquid-assisted solid-state reactions.

Effects of Postsynthesis Heat Treatment on Powder Characteristics. To reveal the effects of high-temperature heat treatment on powder characteristics, the postsynthesis annealing was conducted for two different batches of powders (samples C6 and C8) at 1700 °C for 4 h in a N_2 atmosphere. The resulting data are summarized in Table 3. Both of the heat-treated powders were composed of nearly single-phase α′-SiAlON, possessing the refined x values of ∼0.8. This result indicates that the small amount of unreacted AlN and Ca-containing noncrystalline phases remaining in the as-prepared samples were almost completely dissolved into α′-SiAlON, giving the compositions very close to the target value. The nitrogen contents of the heat-treated powders determined by the hot-gas extraction method were found to be 35.7(1) wt % for the sample C6R and 35.8(2) wt % for the sample C8R, which also prove the achievements of near complete nitridation (35.95 wt %). Figure 6 shows

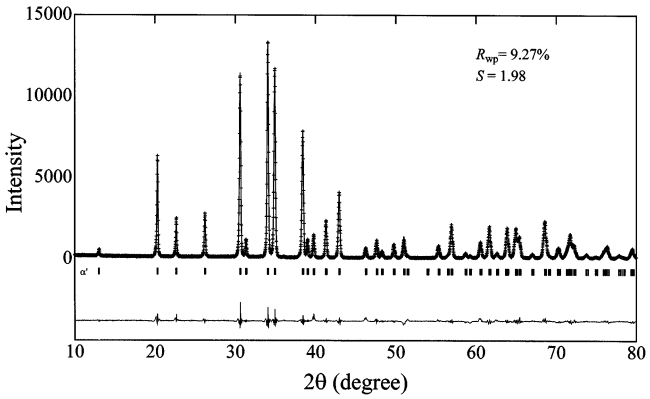

Figure 6. X-ray Rietveld refinement pattern of the powder prepared at 1425 °C with a soaking time of 4 h and subsequently heat-treated at 1700 °C for 4 h in N_2 (sample C6R).

the XRD pattern of the sample C6R, revealing the absence of any secondary phases. The narrower and intense diffraction profiles also indicate the improved crystallinity compared to the as-prepared powder. Figure 7 shows the morphologies of the powders after the heat treatment. The particle size of the heat-treated powders increased significantly to ∼1.8−2.6 μm, while the particles maintained the nonaggregated character.

These results show that the processing temperatures of <1500 °C are sufficient for the completion of the reduction−nitridation, and for synthesizing a very fine powder with high α′ content, while the higher temperatures are still required for obtaining a highly crystalline, homogeneously dissolved α′-phase powder, which is expected to possess more suitable characteristics for the phosphor applications.

Diffuse Reflectance of Synthesized Ca-α′-SiAlON Powders. The UV−visible diffuse-reflectance spectra of the powders synthesized at the optimized conditions (samples C5−C8) are shown in Figure 8. The results are also compared with reference samples prepared by reaction sintering at 1700 °C for 4 h (sample R1) and by carbothermal reduction at 1450 °C for 4 h (sample R2). The impurity carbon contents of the reference samples were measured to be 0.01(1) and 1.00(1) wt %, respectively. In every sample, the diffuse-reflectance spectrum was almost flat in the visible wavelength region, whereas the absolute value of reflectance varied from sample to sample. The spectra exhibited the absorption edge in the UV part ∼250 nm, in conformity with

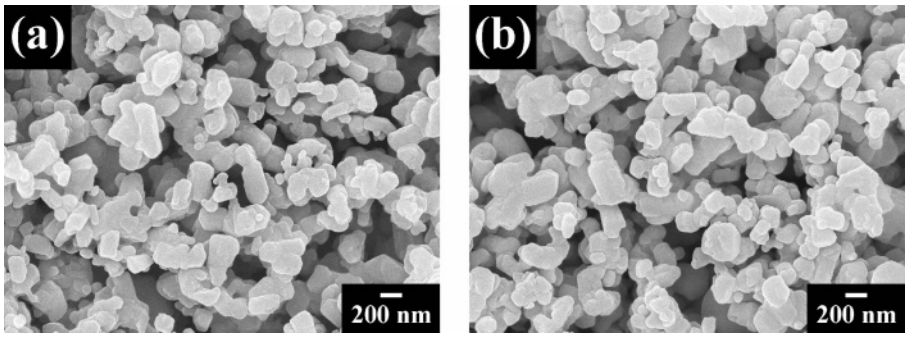

Figure 5. FESEM micrographs of the as-prepared powders synthesized by heating at (a) 1425 °C for 4 h (sample C6) and (b) 1500 °C for 0.5 h (sample C8).

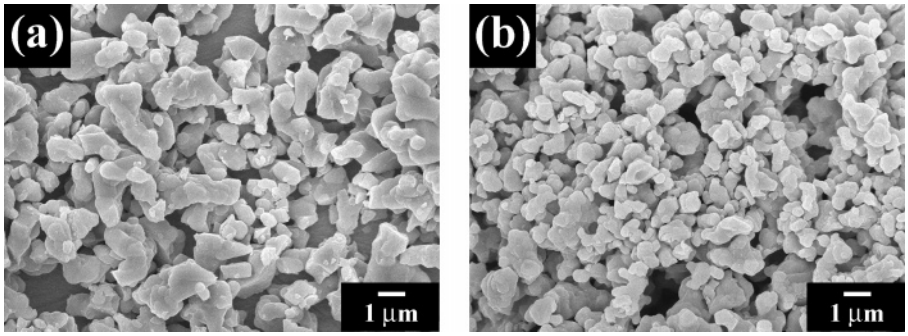

Figure 7. FESEM micrographs of the heat-treated powders: (a) sample C6R, and (b) sample C8R.

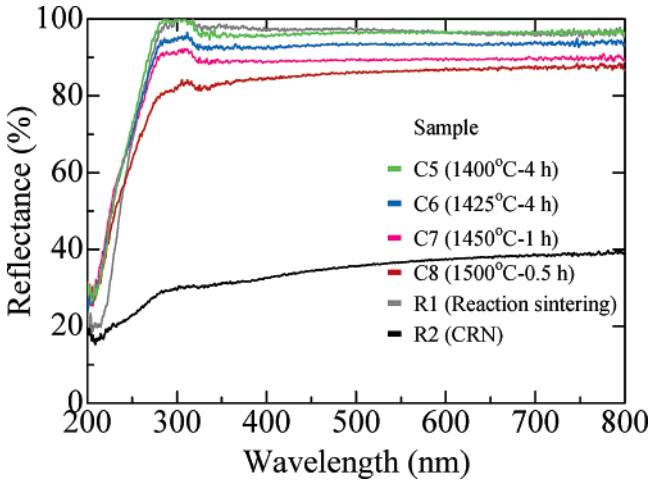

Figure 8. UV-vis diffuse-reflectance spectra of the synthesized Ca-α′-SiAlON powders.

the observation reported earlier.[9] As expected from their white color, the diffuse reflectance of the powders produced by GRN is high (~85−96%) over the whole visible spectral range, which is comparable to that of the conventional reaction-sintered powder.[9] It is obvious that the reflectance of the product powders is directly related to their impurity carbon content, for both GRN powders (see Table 2) and reference samples; the sample R1 prepared under carbon-free conditions exhibited the highest value of ~97%, while the sample R2, which showed grayish coloration even after carbon removal at 700 °C in air, exhibited much lower reflectance of ~32−40%, due to the considerable absorption by the residual carbon.

The above results conclusively show that for the powders synthesized by reduction−nitridation, the impurity carbon content must be kept as low as ~0.5 wt % to maintain the minimal absorptance in the visible spectral region, and this could not be attained by the conventional carbothermal reduction process without some particular treatment for carbon removal. The characteristic feature of the current process, i.e., in situ supply of the gas-phase reducing agent, suppressed the carbon contamination effectively, enabling the preparation of intrinsically white Ca-α′-SiAlON powders, appropriate for a phosphor host.

Photoluminescence Property of Ca-α′-SiAlON:Eu Prepared by GRN. On the basis of the results of synthesis experiments for undoped Ca-α′-SiAlON powder, the preparation of Eu^{2+}-activated samples with a target composition of $Eu_{0.250}Ca_{0.750}Si_{8.625}Al_{3.375}O_{1.375}N_{14.625}$ was attempted under tentatively optimized processing conditions. The three different product powders (samples E1−E3) were obtained and their main characteristics are summarized in Table 4. In the Eu-doped system, the reduction−nitridation was achieved at a considerably lower temperature of 1350 °C, presumably due to the lower eutectic point of the Eu-containing quaternary system. Also, formation of AlN tended to be promoted with the heating rate of 200 °C/h, and thus the faster heating rate of 300 °C/h was adopted and the final phase assemblage resulted in predominant α′ phase with some β′-SiAlON and less amount of AlN.

Table 4. Characteristics of the As-Prepared Ca-α′-SiAlON:Eu Powders

sample	reaction conditions	heating rate (°C/h)	phase assemblage	x	$\Delta W_{obs}/\Delta W_{theor}$
E1	1350 °C, 2 h	300	α′ (80.4%), AlN (12.3%), β′ (7.3%)	0.68(1)	0.98
E2	1450 °C, 1 h	300	α′ (83.8%), β′ (12.4%), AlN (3.8%)	0.87(1)	1.00
E3	1500 °C, 0.5 h	300	α′ (83.3%), β′ (11.1%), AlN (5.6%)	0.94(1)	1.04

The photoluminescence spectra of the as-prepared Ca-α′-SiAlON:Eu powders are shown in Figure 9. The excitation spectra are characterized by two broad bands; the first peak is attributed to the host-lattice absorption, and the second one corresponds to $4f^7 \rightarrow 4f^6 5d$ absorption of Eu^{2+} ion. The broad emission band, characteristic of $5d-4f$ transition in Eu^{2+}, is located in the range of ~500−700 nm resulting in a yellow emission. These emission characteristics of Eu-doped Ca-α′-SiAlON coincide well with the results reported in the earlier works.[9,10] The emission intensity of the as-prepared powder increased with the increase of the processing temperature, which may reflect the difference in composition of the host lattice, unlike the situation encountered with the undoped system where the processing temperature scarcely affected the x value of the α′-SiAlON matrix. The emission peak intensity of the powder synthesized at 1500 °C for 0.5 h (sample E3) reaches ~89% of that of the reaction-sintered powder prepared at 1700 °C with 4 h soaking.

Figure 10 shows the photoluminescence spectra of the powders heat-treated at 1700 °C for 4 h in N_2 (samples E1R−E3R). All samples after the heat treatment consisted exclusively of α′-SiAlON and a minor amount (~3%) of Eu-JEM ($EuAl(Si_{6-z}Al_z)N_{10-z}O_z$)[8,22] phase, and the difference of the emission intensities among samples prepared by different

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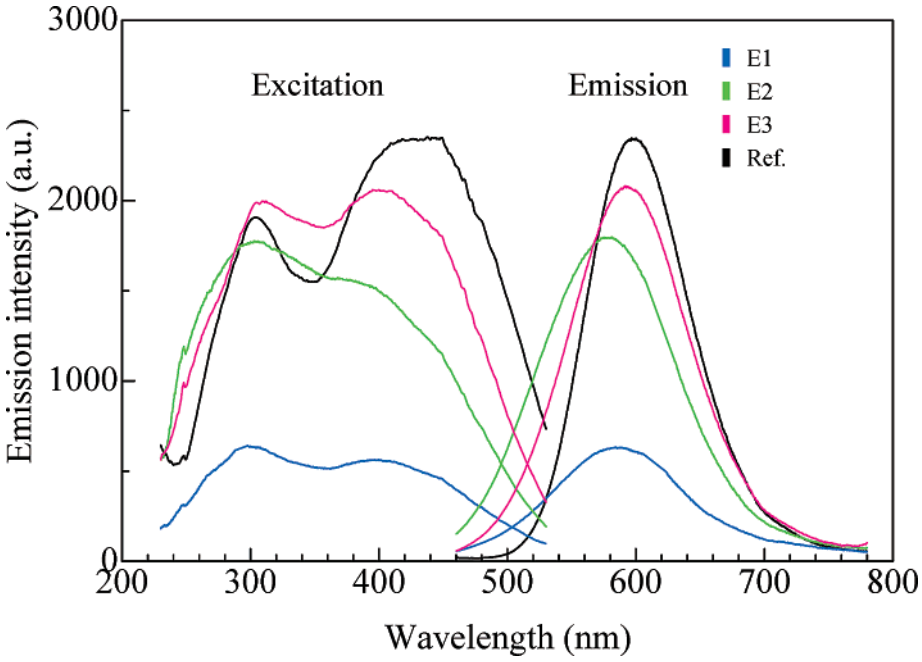

Figure 9. Photoluminescence spectra of the as-prepared Ca-α′-SiAlON:Eu powders synthesized at various processing temperatures.

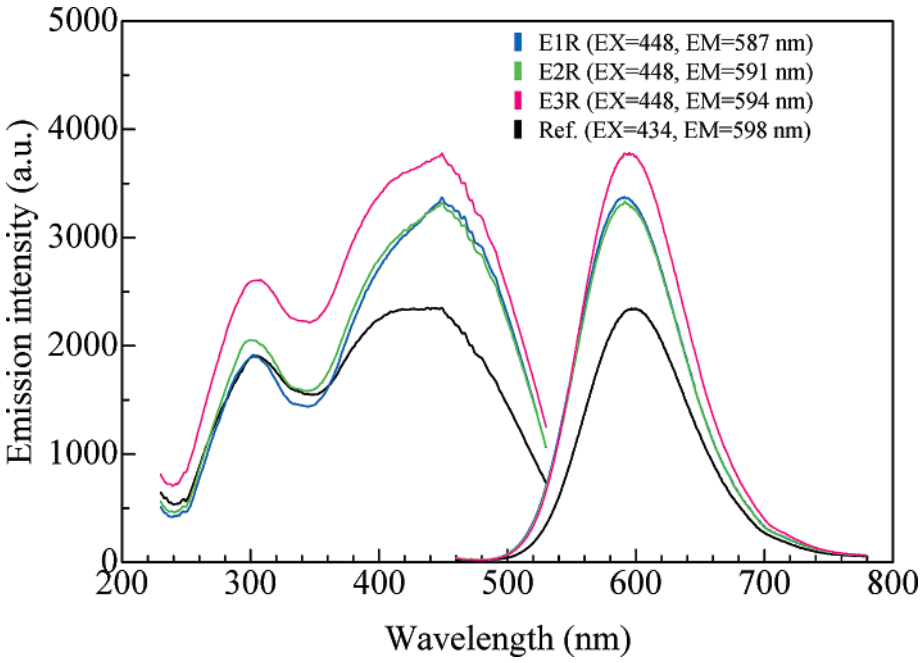

Figure 10. Photoluminescence spectra of the Ca-α′-SiAlON:Eu powders after the postsynthesis heat treatment. The values of wavelength at the excitation and the emission maxima are also indicated.

conditions became less significant compared to the case for as-prepared powders. It is noticeable that the broad excitation band centered at ∼450 nm became more intense, which provides promising applicability to the wavelength-conversion phosphor with the use of blue InGaN-based LEDs. The emission intensity increased markedly after the heat treatment, with the peak intensities being ∼142−162% of that of the reference sample.

As indicated by the results for the undoped system, the observed improvement of photoluminescence property might result from the higher phase purity and the better crystallinity in the heat-treated samples. In addition, the favorable discrete particle morphology and the minimal possibility of introducing defects at particle surface (generally through the mechanical grinding), attained by the one-step synthesis in the current process, would provide the better photoluminescence properties compared to reaction-sintered powders. The detailed mechanisms of the improvement of photoluminescence properties are to be further explored in our future studies.

Conclusions

The direct synthesis of Ca-α′-SiAlON powders from the multicomponent oxide system $CaO-Al_2O_3-SiO_2$ was performed using the GRN process to establish an advanced powder synthesis method for newly developed α′-SiAlON phosphors. The precise control of the processing conditions suppressed effectively the competing formation of β'-SiAlON

phase and carbon contamination, enabling the preparation of very fine Ca-α′-SiAlON powders possessing the favorable characteristics for the phosphor applications: phase purity of ∼90%, nonaggregated particle morphology, and a high reflectance of ∼85−96% in the visible spectral region. Further improvement of the powder characteristics was attained by the postsynthesis heat treatment at 1700 °C, and the highly crystalline, completely dissolved Ca-α′-SiAlON powders consisting of discrete micrometer-sized particles were obtained. The GRN synthesis of the yellow-emitting Ca-α′-SiAlON:Eu powder phosphor was also demonstrated by the current study, and the better photoluminescence property compared to the conventional reaction-sintered powder was proven.

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