論文 / 著書情報
Article / Book Information

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Citation	Applied Physics Express, Vol. 8, Number 11, 115001
Pub. date	2015, 10
DOI	http://dx.doi.org/10.7567/APEX.8.115001
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Note	This file is author (final) version.

Fabrication of nanoscale Ca-α-SiAlON:Eu^{2+} phosphor by laser ablation in water

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Abstract: In this research, nanoscale Ca-α-SiAlON:Eu^{2+} phosphor is formed by pulsed laser ablation (1.27 J/pulse cm^2) in deionized water. Analyses of particle size and composition are accomplished by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS), respectively. High-resolution TEM (HR-TEM) shows that the nanoparticles are highly crystalline and EDS confirms their composition. The emission spectrum of the nanoscale Ca-α-SiAlON:Eu^{2+} shows an obvious blue shift compared with that shown by the target, possibly resulting from changes in the crystal field around Eu^{2+} caused by the enhancement of surface effects due to the nanoscale size.

In recent years, white-light-emitting diodes (WLEDs) have attracted increasing attention as highly efficient, energy-saving, and environment-friendly lighting sources[1)]. In general, phosphor conversion is one of the primary methods of generating WLEDs, with the system phosphor playing a key role in generating the white light. However, the amount of incident light decreases significantly because of backscattering loss caused by micrometer-sized phosphor particles, resulting in poor beam collimation[2)]. For instance, only 30% overall conversion efficiency is obtained from $Y_3Al_5O_{12}:Ce^{3+}$ micrometer-sized particles[3)]. The Rayleigh scattering intensity of one particle, I_S, is determined by the following equation:[4)]

$$I_s = \frac{8\pi^4 N_m a^6}{\lambda^4 r^2}\left|\frac{m^2-1}{m^2+2}\right|\cdot\left(1+\cos^2\theta\right)I_i,$$

where I_i is the intensity of the incident light, N_m is the refractive index of the medium, a is the diameter of the particle, m is N_p/N_m (N_p, refractive index of particle), λ is the wavelength of the incident light, r is the distance between the viewing point and the nanoparticle, and θ is the scattering angle. According to the formula, the scattering efficiency depends on the particle diameter (a) to the sixth power. Accordingly, reducing phosphor particles from micro- to nanoscale size is an effective method of reducing the scattering losses in WLEDs, as recently demonstrated in $Y_3Al_5O_{12}:Ce^{3+}$ phosphor nanoparticles.[2,5)]

α-SiAlON has been established as an excellent host material for the formation of rare-earth doped phosphors owing to its chemical and thermal stabilities derived from the strong covalent bonds of (Si, Al)-(N, O).[1)]. Ca-α-SiAlON:Eu^{2+} phosphor shows an absorption in the range of 280−470 nm, a broad yellow emission between 550 and 600 nm,[1,6)] and is regarded as a potential candidate to replace sulfide and oxide phosphors.[1)] To the best of our knowledge, nanoscale Ca-α-SiAlON:Eu^{2+} has not been reported to date. Owning to the high temperature and gas pressure required to obtain

Ca-α-SiAlON:Eu^{2+}, the ability to control nucleation and grain growth required to obtain nanoscale particles has remained elusive, and we are unaware of any reports of their syntheses. Herein, we offer a new method for the formation of forming nanoscale Ca-α-SiAlON:Eu^{2+} particles and report their optical properties.

In this study, Ca-α-SiAlON:Eu^{2+} nanoparticles are successfully fabricated from a micrometer-sized target by pulsed laser ablation, which is a highly efficient, safe, and clean method.[7-9] In this procedure, nanoparticles are formed in a plasma plume comprising emitted atoms, ions, and clusters ejected from the target during the ablation process. Moreover, laser ablation in liquids results in the formation of nanoparticles with outstanding purity. In addition, the luminescent property of nanoscale Ca-α-SiAlON:Eu^{2+} is also investigated with a view toward their use as a phosphor.

The synthesis of micrometer-sized Ca-α-SiAlON:Eu^{2+} powder was accomplished by the gas-pressure sintering of a mixture of $CaCO_3$, Si_3N_4, AlN, and Eu_2O_3 at 1750 °C for 4h under 0.92MPa of N_2. The powder was then pressed into a laser ablation target pellet and sintered at 1750 °C for 2h under 0.92MPa of N_2. Finally, the target was irradiated in deionized (DI) water with a focused pulsed laser beam (wavelength: 532 nm, repetition rate: 10 Hz, pulse duration: 13 ns.) with an energy density of 1.27 J/pulse cm^2.

The phase analysis of the pellet was performed by X-ray diffraction (XRD, Philips X'Pert-PRO-MRD,) with Cu-K_α radiation and the scanning speed of 1.2°/min at 2θ = 15°–90°. The particle size and the lattice fringe of the nanoparticles were observed by scanning electron microscope (SEM, Hitachi S-5500) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010F), respectively. The elemental composition was measured using an energy-dispersive X-ray spectrometer (EDS) equipped in JEM-2010F. The photoluminescence spectra, under ultraviolet

excitation (365 nm UV-LED), were obtained at room temperature using a multichannel photodetector (Otsuka electronics MCPD7700) with an optical bundle fiber attached to an optical microscope (BX51M).

The structure and crystallinity of the Ca-α-SiAlON:Eu^{2+} target was analyzed by XRD [Fig. 1(a)]. All diffraction peaks for the Ca-α-SiAlON:Eu^{2+} target can be well indexed as the trigonal *P*31/*c* crystal α-$Ca_{0.8}Si_{9.2}Al_{2.8}O_{1.2}N_{14.8}$ (ICDD, No.33-0261), indicating that a highly crystalline structure was formed without any impurity phases [Fig. 1(a)]. The SEM images of the target [Fig. 1(b)] reveal that the Ca-α-SiAlON:Eu^{2+} consists of regularly shaped 0.8−1.2 μm particles that have grown together, ultimately yielding micrometer-sized Ca-α-SiAlON:Eu^{2+} particles.

Nanoparticles of Ca-α-SiAlON:Eu^{2+} were obtained by pulsed laser ablation in DI water of the micrometer-sized Ca-α-SiAlON:Eu^{2+} target. Results of the TEM, EDS, and HR-TEM analyses of the Ca-α-SiAlON:Eu^{2+} nanoparticles are shown in Fig. 2. The highly aggregated nanoparticles are composed of polycrystalline Ca-α-SiAlON:Eu^{2+}. The diameter of the aggregated nanoparticles ranges between 90 and 110nm, whereas the crystalline grain size is less than 20 nm. As shown in Fig. 2(d), the lattice fringe of the crystal is clearly visible with a lattice spacing of 3.37 Å, approximately conforming to the lattice spacing of the (200) plane of Ca-α-SiAlON:Eu^{2+} (JCPDS, No.33-0261). The EDS result shows the elemental composition of the nanocrystalline particles to be Ca, Si, Al, O, N, and Eu [(Fig. 2(c)], indicating that Ca-α-SiAlON: Eu^{2+} has successfully been formed by pulsed laser ablation in water. For a more quantitative analysis, an EDS study of five different zones of nanoparticles and the target was conducted. The mean values with standard deviations of the composition of the nanoparticles and target are presented in Table I. The amount of Si seems to slightly decrease with evaporation in the laser ablation process, while the content decreases from 40.1 ± 2.9 to 33.6 ±

4.3% at.%. The ratio of other elements do not significantly change between the target and the formation of the nanoparticles; however, the O and N elements were not analyzed owing to the inherent inaccuracy of measuring light elements by EDS. A more detailed and accurate composition analysis will be pursued in future research.

The photoluminescence spectra of the Ca-α-SiAlON:Eu^{2+} target and nanoparticles are shown in Fig. 3. The emission spectra of the target and nanoparticles (excited at 450 nm) exhibit a single broad band at 585 nm and 580 nm, respectively, because of the allowed $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+}[10]. As can be seen in Fig. 3, the blue-shift and broadening of Ca-α-SiAlON:Eu^{2+} nanoparticle emission spectrum are obvious compared with those of the target. This phenomenon suggests that the crystal field around Eu^{2+} ions becomes weaker with a wider distribution. The full width at half-maximum (FWHM) of the emission band of nanoparticles is approximately 98 nm, which is wider than that of the target (91 nm). As an important luminescent property, FWHM can represent the color purity of the phosphor emission.

In Ca-α-SiAlON:Eu^{2+}, the broadband emissions are caused by the 5d-4f transitions, according to the knowledge of Eu^{2+} energy level scheme.[11]. The 5d levels are easily affected by the crystal field effect, whereas the 4f energy levels are well protected from the perturbation of the crystal field.[12]. As particle size decreases, the ratio of particle surface area to particle volume increases. It is known that the nanoparticle has a large surface area, which would increase the surface tension. It is possible that the size reduction down to the nanosize range leads to some distortions of crystal lattice owing to the increasing effect of the surface. These distortions of the crystal lattice would affect the crystal field around Eu^{2+} leading to the observed changes in the emission spectra. A similar phenomenon was also reported in the case of the $Y_3Al_5O_{12}$:Ce^{3+},[12-14] Y_2O_3:Eu^{3+},[15] and YVO_4:Eu^{3+} [16] nanophosphors.

However, The detailed mechanism of the changes in luminescence properties and the principle calculation of Ca-α-SiAlON:Eu^{2+} nanoparticles are currently being explored.

In this work, nanoscale Ca-α-SiAlON:Eu^{2+} particles are successfully obtained by the pulsed laser ablation (1.27 J/pulse cm^2) of a micrometer-sized target in DI water. The HR-TEM images clearly display the highly crystalline nanoparticles, and the EDS results show the nanoparticle contents of Ca, Si, Al, O, N, and Eu. Furthermore, we found that the emission spectrum of Ca-α-SiAlON:Eu^{2+} nanoparticles shows an obvious blue shift compared with that of the target, possibly resulting from a change in crystal field around Eu^{2+}caused by the nanometer-size. Continued studies of Ca-α-SiAlON:Eu^{2+} nanoparticles to characterize their optical properties, such as quantum efficiency, and phase purity of powders for WLED application are under way.

Acknowledgements

The authors gratefully thank Prof. K. Nakamura, Mr. Hori, and Mr. H. Iida at Tokyo Tech. This study was supported by JSPS KAKENHI Grant, the Chinese Scholarship Council (CSC), the Collaborative Research Project of Materials & Structures Laboratory (Tokyo Tech.), and the Center for Advanced Materials Analysis (Tokyo Tech.).

References

1) Xie R-J, Hirosaki N, Mitomo M, Yamamoto Y, Suehiro T, Sakuma K, J. Phys. Chem. B. 108, 12027 (2004).

2) Roh H-S, Kim D-H, Park I-J, Song H-J, Hur S, Kim D-W, Hong, K-S, J. Mater. Chem. 22, 12275 (2012).

3) Yamada K, Imai Y and Ishii K. The Abstracts of the Papers. J. Illum. Eng. Inst. Jpn. 2002, 86, 308.

4) C. F. Bohren and D. R. Huffman. *Absorption and Scattering of Light by small particles* (Wiley, New York, 1983) P. 132.

5) Song H-J, Noh J-H, Roh H-S, Kim J-S, Kim D-W, Hong K-S, Curr Appl. Phys.13, S69 (2013).

6) Van Krevel J, Van Rutten J, Mandal H, Hintzen H, Metselaar R, J. Solid State Chem. 165, 19 (2002).

7) Onodera Y, Nunokawa T, Odawara O, Wada H, J. Lumin. 137, 220 (2013).

8) Yoshimura F, Nakamura K, Wakai F, Hara M, Yoshimoto M, Odawara O, Wada. H, Appl. Surf. Sci. 257, 2170 (2011).

9) Takahashi S, Wada H, Noguchi A, Odawara O, Mater Lett. 62, 3407 (2008).

10) Russell H N, Albertson W, Davis DN, Phys. Rev. 60, 641 (1941).

11) Blasse G, Phys. Status Solidi B. 55, K131 (1973).

12) Li Q, Gao L, Yan D, Mater. Chem. Phys. 64, 41 (2000).

13) Kasuya R, Kawano A, Isobe T, Kuma H, Katano J, Appl. Phys. Lett. 91, 111916 (2007).

14) Isobe T, Phys. Status Solidi A. 203, 2686 (2006).

15) Li Q, Gao L, Yan D, Nanostruct. Mater. 8, 825 (1997).

16) Huignard, A.; Buissette, V. Franville, A. C.; Gacoin, T.; Boilot, J. P, J. Phys. Chem. B. 107, 6754 (2003).

Figure captions

Fig. 1. (a) XRD pattern and (b) SEM image of micrometer-sized Ca-α-SiAlON:Eu^{2+} target.

Fig. 2. (a) HR-TEM image of Ca-α-SiAlON:Eu^{2+} nanoparticles; (b)magnified TEM image of (a); (c) EDS results in the encircled area; (d) HR-TEM image of red frame of (b). The inset is selected area electron diffraction pattern of (b).

Fig. 3. Photoluminescence spectra of Ca-α-SiAlON:Eu^{2+} target and nanoparticles.

Table captions

Table I. Atomic percentages of elements from results of EDS analyses of Ca-α-SiAlON:Eu^{2+} target and nanoparticles (average of 5 points).

Fig. 1.

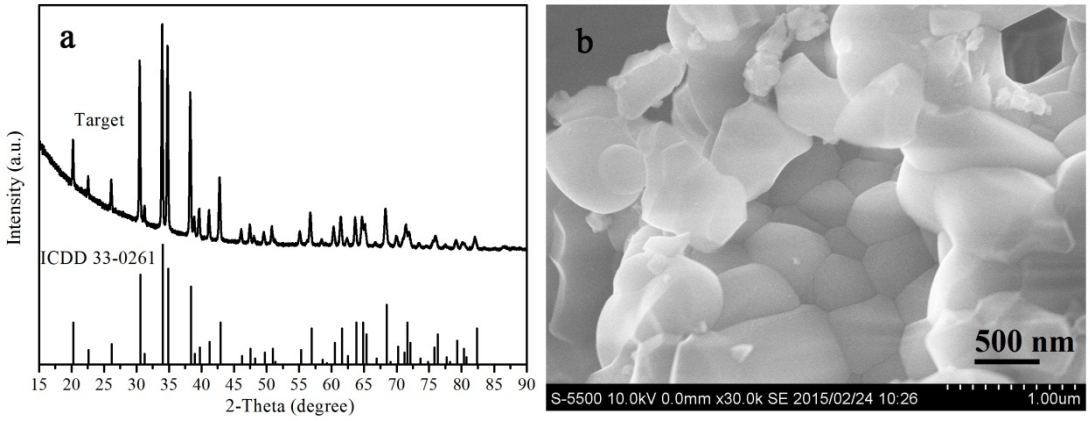
a
Target
ICDD 33-0261
Intensity (a.u.)
15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90
2-Theta (degree)
b
500 nm
S-5500 10.0kV 0.0mm x30.0k SE 2015/02/24 10:26
1.00um

Fig. 2.

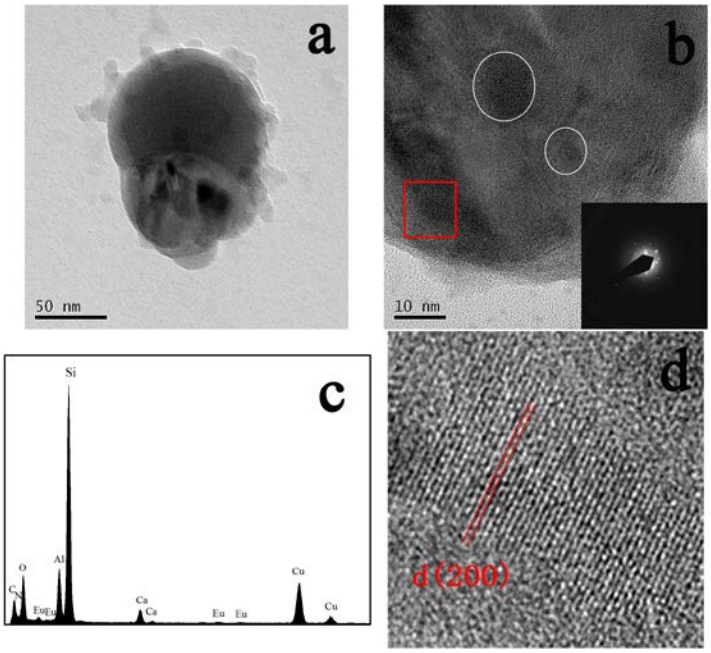
a
50 nm
b
10 nm
c
Si
O
Al
Ca
Ca
Eu
Eu
Cu
Cu
d
d (200)

Fig. 3.

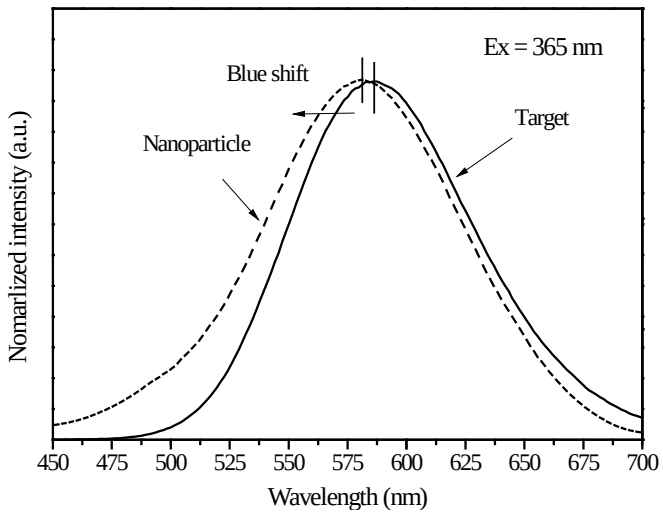

Table I.

	Ca	Si	Al	Eu
Target (Average of 5 points)	4.3±0.9	40.1±2.9	11.1±1.9	0.5±0.2
Nanoparticles (Average of 5 points)	4.3±1.0	33.6±4.3	12.4±2.9	0.6±0.2