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Low-Temperature Crystallization of Eu-Doped Red-Emitting $CaAlSiN_3$ from Alloy-Derived Ammonometallates

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Recently, some Eu-doped silicon-containing nitrides and oxynitrides have shown very attractive luminescence properties: Ca- and Li-α-sialons (yellow),[1] $M_2Si_5N_8$ (orange-red),[2] $MSi_2O_2N_2$ (M = Ca, Sr, Ba; blue-yellow),[2,3] and $CaAlSiN_3$ (red),[4] indicating their promising applications as phosphors for light-emitting diode (LED) devices. A stable red-light-emitting phosphor has been intensively sought after for the fabrication of LED devices emitting a warm white light. Such devices, because of their high efficiency and long lifetime, are expected to replace the present incandescent and fluorescent lamps. $CaAlSiN_3$ was found to be a very promising material for use as a red phosphor,[4] possessing red light-emitting properties exceeding $M_2Si_5N_8$, and may be commercialized in the near future for the fabrication of warm-white LED devices.

Although there have been a variety of processes for the bulk synthesis of single nitrides at both high (e.g., hexagonal Si_3N_4 at 1300−1500 °C,[5] cubic Si_3N_4 at 2200 K under high pressure,[6] GaN at 1000−1100 °C)[7] and low temperatures (e.g., Si_3N_4 at 450−600 °C,[8] GaN at 280−800 °C),[9] low-temperature approaches for multinary nitride syntheses are rare. Multinary nitrides are generally synthesized via high-temperature solid-state reactions of presynthesized single nitride mixtures. For example, the above-mentioned luminescence sialons and $CaAlSiN_3$ were synthesized at 1600−1800 °C,[1,4] $MSi_2O_2N_2$ (M = Ca, Sr, Ba) at 1100−1400 °C.[3] The more active silicon diimide can be used instead of the very stable silicon nitride (e.g., $M_2Si_5N_8$[10] and $MSi_2O_2N_2$[11] at ∼1550−1650 °C). Solid−gas reactions at high temperatures, which are widely used for the synthesis of single nitrides,[5,7] can also be applied to multinary nitride syntheses, e.g., Ca-sialon[12] and $Sr_2Si_5N_8$[13] at 1400−1500 °C. The requirement of high temperatures in these processes is because of the chemical and thermal inertness of the starting materials and the nonhomogeneity of their mixture. The only reported low-temperature synthesis of multinary nitrides of silicon is via reactions with nitrogen in a sodium flux. This route, known for its ability to grow GaN crystals,[9b,9c] has been successful for the synthesis of some multinary nitride crystals, e.g., $MSiN_2$ (M = Ca, Sr, Ba) crystals at 900−1100 °C.[14] To the best of our knowledge, a solution process for multinary nitride syntheses has not be reported up to now.

High-temperature products are often partially sintered and thus post-synthesis grinding is necessary to obtain micrometer-sized particles. In contrast, low-temperature processes may produce nanostructured materials with a variety of morphologies and may be energy-effective. Low-temperature growth of some nitrides in a flux is a promising method that avoids extremely high pressures (up to several gigapascals) required for high-temperature growth. For example, GaN crystals have been grown in a sodium flux at 600−800 °C in N_2 ($\leq$10 MPa).[9b,9c]

It is a well-known process to synthesize oxide materials in aqueous solutions at low temperatures. This route, referred to as soft solution processing, is environmentally benign, energy-saving, and capable of synthesizing powders, films, and crystals directly without post-firing.[15] One example is the growth of high-quality quartz single crystals in a water solution under hydrothermal conditions.[16] By comparing the water system with the ammonia system (Table 1), one can expect the synthesis of nitrides in solutions of ammonia, the analogue of water for oxide synthesis. In the water solution, hydroxides are converted to oxides by losing water, whereas in the ammonia solution, amides may convert to nitrides by losing ammonia. The conversion may proceed via gradual ammonia loss, first forming imides and then other more polymerized intermediates. (Hereafter, we refer to metal amides and their partially polymerized products as ammonometallates.) The ammonia solution processing may result in

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(1) (a) Xie, R.-J.; Hirosaki, N.; Sakuma, K.; Yamamoto, Y.; Mitomo, M. *Appl. Phys. Lett.* **2004**, *84*, 5404. (b) Xie, R.-J.; Hirosaki, N.; Mitomo, M.; Takahashi, K.; Sakuma, K. *Appl. Phys. Lett.* **2006**, *88*, 101104.

(2) Mueller-Mach, R.; Mueller, G.; Krames, M. R.; Höppe, H. A.; Stadler, F.; Schnick, W.; Juestel, T.; Schmidt, P. *Phys. Status Solidi A* **2005**, *202*, 1727.

(3) Li, Y. Q.; Delsing, A. C. A.; With, G. de; Hintzen, H. T. *Chem. Mater.* **2005**, *17*, 3242.

(4) Uheda, K.; Hirosaki, N.; Yamamoto, Y.; Naito, A.; Nakajima, T.; Yamamoto, H. *Electrochem. Solid-State Lett.* **2006**, *9*, H22.

(5) Riley, F. L. *J. Am. Ceram. Soc.* **2000**, *83*, 245.

(6) Zerr, A.; Miehe, G.; Serghiou, G.; Schwarz, M.; Kroke, E.; Riedel, R.; Fueβ, H.; Kroll, P.; Boehler, R. *Nature* **1999**, *400*, 340.

(7) Schwenzer, B.; Hu, J.; Seshadri, R.; Keller, S.; DenBaars, S. P.; Mishra, U. K. *Chem. Mater.* **2004**, *16*, 5088.

(8) (a) Gu, Y.; Chen, L.; Qian, Y. *J. Am. Ceram. Soc.* **2004**, *87*, 1810. (b) Zou, G.; Hu, B.; Xiong, K.; Li, H.; Dong, C.; Liang, J.; Qian, Y. *Appl. Phys. Lett.* **2005**, *86*, 181901.

(9) (a) Xie, Y.; Qian, Y.; Wang, W.; Zhang, S.; Zhang, Y. *Science* **1996**, *272*, 1926. (b) Yamane, H.; Shimada, M.; Clarke, S. J.; DiSalvo, F. J. *Chem. Mater.* **1997**, *9*, 413. (c) Yamada, T.; Yamane, H.; Iwatac, H.; Sarayama, S. *J. Cryst. Growth* **2006**, *286*, 496. (d) Yoshikawa, A.; Ohshima, E.; Fukuda, T.; Tsujib, H.; Oshima, K. *J. Cryst. Growth* **2004**, *260*, 67.

(10) Schlieper, T.; Milius, W.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1380.

(11) Höppe, H. A.; Stadler, F.; Oeckler, O.; Schnick, W. *Angew. Chem.* **2004**, *116*, 5656; *Angew. Chem., Int. Ed.* **2004**, *43*, 5540.

(12) Suehiro, T.; Hirosaki, N.; Xie, R.-J.; Mitomo, M. *Chem. Mater.* **2005**, *17*, 308.

(13) Piao, X.; Horikawa, T.; Hanzawa, H.; Machida, K. *Appl. Phys. Lett.* **2006**, *88*, 161908.

(14) Gál, Z. A.; Mallinson, P. M.; Orchard, H. J.; Clarke, S. J. *Inorg. Chem.* **2004**, *43*, 3998.

(15) Yoshimura, M. *J. Mater. Sci.* **2006**, *41*, 1299.

(16) Baughman, R. J. U.S. Patent 5 135 603, 1992.

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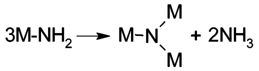
Table 1. Comparison of the Water System for Oxide Synthesis and the Ammonia System for Nitride Synthesis. Here, M Represents a Metal

water system	ammonia system
acids: e.g., HF, HCl	acids: e.g., NH_4F, NH_4Cl
bases: e.g., NaOH, KOH	bases: e.g., $NaNH_2$, KNH_2
hydrolysis forming hydroxide	ammonolysis forming amide
e.g., M-Cl + $H_2O \rightarrow$ M-OH + HCl	e.g., M-Cl + $2NH_3 \rightarrow M\text{-}NH_2 + NH_4Cl$
$M + H_2O \rightarrow M\text{-}OH + 0.5H_2$	$M + NH_3 \rightarrow M\text{-}NH_2 + 0.5H_2$
hydroxide converts to oxide	amide converts to nitride
$2M\text{-}OH \rightarrow M\text{-}O\text{-}M + H_2O$	 $3M\text{-}NH_2 \rightarrow M\text{-}N(M)_2 + 2NH_3$

a variety of material forms (powders, films, single crystals) of binary and multinary compounds, analogous to the water system.

Here, we demonstrate the synthesis of a silicon-containing quaternary nitride, $CaAlSiN_3$, in the ammonia system under supercritical conditions. This nitride was previously produced via solid-state reactions of presynthesized, expensive Ca_3N_2 (very moisture-sensitive), AlN, and Si_3N_4 at 1600−1800 °C.[4] We have been able to synthesize for the first time, to the best of our knowledge, at temperatures up to 800 °C, Eu-doped, well-crystallized products showing a strong red emission. This is also the first synthesis of a multinary nitride via a solution process, to the best of our knowledge.

To realize the synthesis, we first need to obtain ammonometallates of Ca, Al, and Si. The reactions of ammonia or alkali metal amides with halides or some organometallics can be used to obtain many ammonometallates.[5,17] However, the halide-containing system is not preferred for the synthesis of nitrides containing alkaline earth metals, because the halides of the alkaline earth metals are very stable according to our preliminary experiments. On the other hand, the use of organometallics would lead to carbon contamination. Thus, we considered synthesizing them from pure metals. It was found early last century that in a basic alkaline metal amide melt or its ammonia solution, many metals are reactive, forming alkaline metal ammonometallates.[18] Among calcium, aluminum, and silicon, silicon is the most inactive, but it also slowly reacts with molten sodium amide and potassium amide at 350−400 °C.[18a] Alloys may have a higher activity than the constituent elements, e.g., during the nitridation of alkaline earth metal−silicon alloys.[14] We now describe the successful synthesis of our targeted multinary nitride from a Ca−Eu−Al−Si alloy. This metal−ammonometallate−nitride route can be a general "one-pot" method for the synthesis of many multinary nitrides.

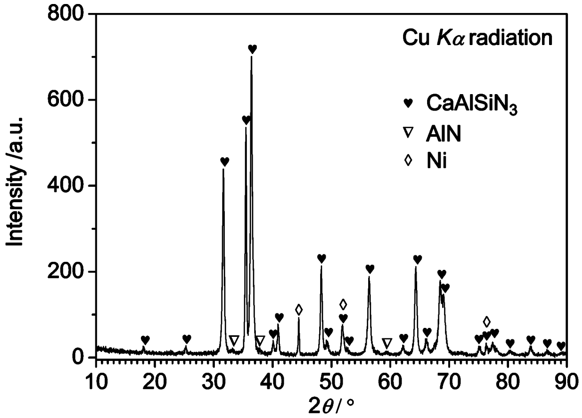


Figure 1. XRD pattern of the product.

In our synthesis, an alloy with the composition $Ca_{0.992}Eu_{0.008}AlSi$ was made by melting the constituent metals (Ca >99.5%, Eu >99.0%, Al 99.999%, Si 99.999%) followed by subsequent quenching in argon. The ground alloy powder (<50 μm) was mixed with sodium amide (95%) at a molar ratio of Na/Ca = 5. The sample was loaded in a nickel tube in a high-pressure autoclave. The synthesis was performed in 100 MPa supercritical ammonia (see the Supporting Information for details). The sample was first allowed to react at 400 °C for a sufficient time (20 h) to complete the conversion of the metals into ammonometalates. Subsequently, it was further slowly heated (0.1 K/min) to 800 °C, during which the ammonometalates decomposed and the $CaAlSiN_3$ crystallized. The nitride product was isolated after first washing with ethanol and then with dilute hydrochloride acid (0.1 M).

At 400 °C, the black alloy powder changed to a white product of ammonometallates. It was extremely sensitive to moisture, releasing ammonia gas and some times sparkling when it was carefully removed from the nickel tube in air. Upon being first washed with ethanol and then with dilute hydrochloride acid, the sample was completely dissolved in the acid. X-ray diffraction (XRD) indicated that the ethanol-washed sample was amorphous. Our present analysis conditions, however, do not allow a detailed analysis of the ammonometalate product without being exposed to air. The alloy−ammonometallates conversion was found to be complete within 20 h even at 300 °C, but the lowest temperature that allows this conversion was not determined.

Upon a further increase in temperature to 800 °C, the ammonometallates decomposed and were converted to $CaAlSiN_3$. The XRD pattern indicated that the final obtained product at 800 °C was crystalline $CaAlSiN_3$ (Figure 1). A tiny amount of AlN was also detected. Also shown in the XRD pattern is the presence of some nickel metal, which was from the sample container (nickel tube). The lattice parameters of our $CaAlSiN_3$ (orthorhombic, *Cmc*21, No. 36) were $a = 9.7813(3)$ Å, $b = 5.6626(3)$ Å, and $c = 5.0570(2)$ Å, which were estimated by applying the program UnitCell.[19] These parameters are close to those of the high-temperature product ($a = 9.8020(4)$ Å, $b = 5.6506(2)$ Å, and $c = 5.0633(2)$ Å).[4] A volume-average particle size of 66(3) nm for our sample was estimated using the Scherrer equation.

Scanning electron microscopy (SEM) observations (Figure 2) indicated that the particles of our $CaAlSiN_3$ product were bar-like, of which the length was up to ~1 μm and the

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(17) (a) Brown, G. M.; Maya, L. *J. Am. Ceram. Soc.* **1988**, *71*, 78. (b) Baxter, D. V.; Chisholm, M. H.; Gama, G. J.; DiStasi, V. F.; Hector, A. L.; Parkin, I. P. *Chem. Mater.* **1996**, *8*, 1222. (c) Li, J.; Dzivenko, D.; Zerr, A.; Fasel, C.; Zhou, Y.; Riedel, R. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1449.

(18) (a) Levine, R.; Fernelius, W. C. *Chem. Rev.* **1954**, *54*, 449. (b) Bergstrom, F. W.; Fernelius, W. C. *Chem. Rev.* **1937**, *20*, 413. (c) Bergstrom, F. W.; Fernelius, W. C. *Chem. Rev.* **1933**, *12*, 43.

(19) Holland, T. J. B.; Redfern, S. A. T. *Mineral. Mag.* **1997**, *61*, 65.

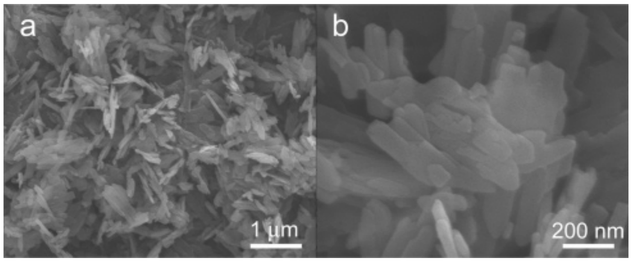

Figure 2. SEM images of the product showing an overview at low magnification (a) and the crystal facets and habits at high magnification (b).

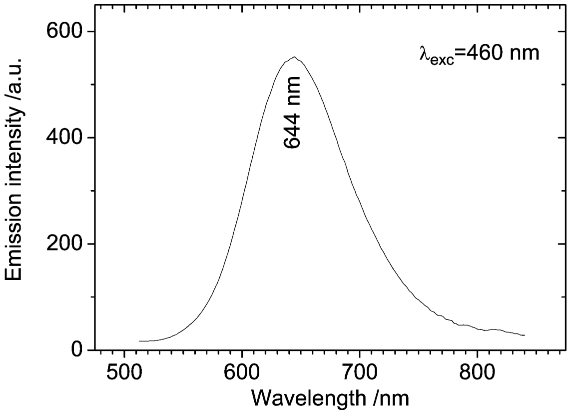

Figure 3. Emission spectrum of the product with the excitation of a blue light ($\lambda = 460$ nm).

thickness was ~50−100 nm, consistent with the value of the size estimated from the XRD pattern. The particles showed clear crystal facets and habits, suggesting that they were single crystals.

Eu-doped $CaAlSiN_3$ is a red phosphor having a broad excitation band ranging from the UV region to 590 nm, with the most prominent excitation peak at 450 nm and another peak at 335 nm.[4] Its ability to be excited by both blue (460 nm) and violet (405 nm) LEDs makes it very promising for the fabrication of warm-white LED devices. A strong red emission of our sample was observed during the photoluminescence analysis. An emission spectrum recorded with the excitation of a blue light (460 nm) is presented in Figure 3. Direct visual observation of the red emission was performed with the illumination of a UV lamp (365 nm), and the photo is shown in Figure 4. The intensity of the emission reached one-third of that of a high-temperature (1800 °C) product (Mitsubishi Chemical, with the same nominal Eu concentration) under the same measurement conditions. This result is significant if one considers that our sample was synthesized up to only 800 °C, i.e., 1000 °C lower than the high-temperature process. Further more, our sample is nanocrystalline, which is not accessible by the high-temperature process.

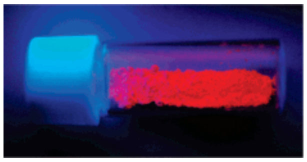

Figure 4. Photo of the sample with the illumination of a UV lamp ($\lambda = 365$ nm).

Our present synthesis is, nevertheless, far from optimized. We have found from the XRD analysis that some calcium oxide was present in the sample before it was washed with acid, indicating considerable oxygen contamination during the synthesis. Oxygen contamination could deteriorate the product via two mechanisms. First, because oxygen is much more affinitive to calcium than to aluminum and silicon, it could extract calcium from the product, resulting in a calcium deficiency, and consequently, a lower crystallinity of the nitride. Second, Eu could enter into the oxide, leading to a lower Eu concentration in the nitride. Either a low crystallinity or low Eu concentration[4] could result in a low emission from the nitride. It has been reported that the emission wavelength increases with the increasing Eu concentration.[4] The emission peak wavelength of our sample, 644 nm (Figure 3), is shorter than the high-temperature product (Mitsubishi Chemical) with the same nominal Eu concentration (655 nm), suggesting a lower dopant level of Eu in our nitride. Further work is now in progress to reduce the oxygen contamination and to improve the quality of the products.

In conclusion, a solution process for multinary nitride syntheses via a metal−ammonometallate−nitride route has been proposed and demonstrated for the synthesis of Eu-doped nanocrystalline $CaAlSiN_3$ in supercritical ammonia at temperatures up to 800 °C, i.e., 1000 °C lower than the previous method. The product showed a strong red emission. This synthetic route may be able to produce a variety of forms (powders, films, single crystals) of multinary nitrides from nanostructures to large crystals. The significantly lower temperatures utilized in this method may allow the synthesis of other various nitrides that are inaccessible via high-temperature processes because of their low decomposition temperatures.

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Supporting Information Available: Experimental details for the synthesis and characterization of the nitride (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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