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ARTICLE

Low temperature synthesis of barium oxynitridosilicates using $BaCN_2$ and SiO_2

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Barium oxynitridosilicates, $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$, were obtained from a mixture of $BaCN_2$ and SiO_2 at 800 °C, which is several hundred degrees lower than that required in solid state reactions using $BaCO_3$, SiO_2 and Si_3N_4. The low-temperature formation mechanism was investigated by thermogravimetry analysis in conjunction with gas chromatography and mass spectroscopy. The phase ratio between the oxynitridosilicates was controlled by tuning the reaction temperature, duration, and atmosphere. Almost single-phase $Ba_3Si_6O_{12}N_2$ was obtained by reaction at 800 °C for 15 h under a N_2 atmosphere, but the product changed to $Ba_3Si_6O_9N_4$ after 50 h at 800 °C or by heating at 950 °C for 15 h. The photoluminescence properties of Eu-doped products obtained at 800 °C using a mixture of $BaCN_2$:Eu and SiO_2 were investigated.

Introduction

Metal oxynitrides containing both oxide and nitride anions have a wide range of applications such as phosphors, dielectric materials, and non-toxic pigments.[1-7] Many of them are prepared via solid state reactions (SSR) between metal oxides and nitrides. Silicon nitride, Si_3N_4, is generally used as a nitrogen source for the preparation of oxynitridosilicate phosphors together with SiO_2. In the SSR, a high reaction temperature is inherently required to enhance the diffusion of elements, especially covalent nitrogen atoms. Perovskite-type $SrTaO_2N$ has also been prepared from a mixture of SrO and TaON at a high temperature of 1500 °C.[8] The ammonolysis reaction is extensively used as a preparation method to obtain many perovskite-type transition metal oxynitrides from their respective oxide precursors.[3,4,9] The reaction temperature is around 1000 °C and ammonia gas is applied as a nitrogen source. Alkaline earth oxynitridosilicates have various chemical compositions and promising photoluminescence properties.[10-13] Their preparation method is a SSR using $AECO_3$ (AE = Ca, Sr, and Ba), SiO_2 and Si_3N_4 as the starting powders with a reaction temperature that is generally higher than 1300 °C. Several approaches to lower the reaction temperature have focused on the use of a flux, such as NH_4Cl and AEF_2, and polymer-derived precursors.[14-16] For example, $BaSi_2O_2N_2$:Eu was generally obtained at 1350 °C in a SSR using $BaCO_3$ and Si_3N_4.[17] (Ba,Eu)CO_3/SiO_2 core-shell oxides were applied as a precursor for direct gas reduction nitridation to form a $BaSi_2O_2N_2$:Eu phosphor at relatively low temperatures of around 1100-1200 °C.[18] $Ba_3Si_6O_9N_4$:Eu was prepared from high-energy ball milled precursors of $BaCO_3$, SiO_2, and Si_3N_4 at 1200 °C.[19] A pure $Ba_3Si_6O_{12}N_2$:Eu phase was obtained at 1300 °C via a spray pyrolysis route using tetraethylorthosilicate and Si_3N_4 nanopowder.[20] Both Eu-doped $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$ were also synthesized using Si_2N_2O as the starting powder with the assistance of a NH_4Cl flux at 1250 and 1350 °C, respectively.[15] Amorphous silicon carbodiimide, $Si(CN_2)_2$ and silicon diimide, $Si(NH)_2$ have been investigated as precursors to synthesize (oxxy)nitridosilicates instead of Si_3N_4.[21,22] Formation of Li_2CN_2 intermediate has been suggested during a synthesis of Li_2SiN_2 below 1000 °C from the amorphous $Si(CN_2)_2$.[21] High-temperature synthesis methods involve large energy consumption and a post-milling process to reduce the particle size. Therefore, novel synthesis methods that lower the formation temperature are still desired.

Recently, low-temperature synthesis methods have been proposed for the preparation of oxynitride compounds. Perovskite-type $SrTaO_2N$ and $SrNbO_2N$ were obtained from the respective oxide precursors and carbon nitride with the assistance of a strontium carbodiimide, $SrCN_2$, intermediate.[23,24] Carbon nitride was used as both nitrogen and reduction sources and $SrTaO_2N$ was formed from a $Sr_2Ta_2O_7$ precursor at 800 °C, which was 200 °C lower than that required for the ammonolysis reaction of $Sr_2Ta_2O_7$. $SrCN_2$ and Ta_3N_5 intermediates on the residual $Sr_2Ta_2O_7$ surface played a vital role in achieving the low-temperature reaction. A wurtzite-type $Ga_{1-x}Zn_xN_{1-x}O_x$ photocatalyst was prepared by a reaction between a Ga-Zn double layered hydroxide and urea at 700 °C.[25] The low-temperature reaction was attributed to the formation of intermediate $ZnCN_2$, which was confirmed by in-situ X-ray absorption spectroscopy. Urea as a nitrogen source has also been applied to the synthesis of perovskite-type

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$LaTiO_2N$ and $SrTaO_2N$ via formation of $La_2O_2CN_2$ and $SrCN_2$ intermediates, respectively.[26,27]

Tetragonal, barium carbodiimide, $BaCN_2$ was first prepared by an ammonolysis reaction of $BaCO_3$.[26] It has been used as the host crystal for divalent Eu doping. The Eu-doped tetragonal $BaCN_2$ showed intense red luminescence at room temperature, peaking at 660 nm. The peak wavelength varied widely depending on both the temperature and applied pressure.[28,29] Metal carbodiimide is thought to be a potential agent to lower the formation temperature of the oxynitride. In this study, $BaCN_2$ was used as both a Ba and nitrogen source to form barium oxynitridosilicate phosphors doped with divalent Eu at lower temperature than that required for a conventional SSR using $BaCO_3$, SiO_2 and Si_3N_4. The low-temperature formation mechanism for barium oxynitridosilicate was investigated by thermogravimetry-differential thermal analysis (TG-DTA) and mass spectroscopy (MS) of the gas released during the reaction.

Experimental

Tetragonal $BaCN_2$ powder was synthesized by ammonia nitridation of $BaCO_3$ (99.9%, FUJIFILM Wako Pure Chemical) on an alumina boat under a 100 mL/min flow of ammonia at 900 °C for 15 h, similar to our previously reported method.[26] The obtained $BaCN_2$ was wet mixed with SiO_2 (99.9%, FUJIFILM Wako Pure Chemical) using hexane in a glove box under a dry N_2 atmosphere. The Ba:Si ratio of the mixture was fixed at 1:2. TG-DTA (STA2500, Netzsch) was conducted on approximately 10 mg of the mixture to investigate the reaction temperature under 200 mL/min of Ar flow. The mixed powder was transferred into an alumina crucible and the sample chamber was evacuated to below 3 Pa prior to introducing Ar gas. The sample was subsequently heated at a rate of 10 °C/min up to 950 °C and then maintained at that temperature for 1 h. Quadrupole MS (Q-MS; Transpector CPM, INFICON) was used for analysis of the gas released during the heating of the $BaCN_2/2SiO_2$ mixture. About 20 mg of the mixture was heated for MS analysis under the same heating conditions as in the TG-DTA measurements in a silica tube furnace under a 10 mL/min flow of Ar. Gas chromatography (GC; Micro GC fusion, INFICON) combined with TG (Thermo Plus Evo2, RIGAKU) was also performed using 35 mg of the mixture in an alumina crucible under the same heating conditions used for MS.

The powder mixture was placed in an alumina boat and then heated in an alumina tube furnace under a 50 or 100 mL/min of Ar flow at 800 and 950 °C, for durations of 15 or 50 h. The mixture was also placed in an alumina crucible enclosed in a container prepared using a tantalum sheet. The encapsulation was carried out in an Ar filled glove box and the container was loosely sealed without welding. The tantalum container including the powder mixture was heated at 800 and 950 °C for 15 or 50 h under an Ar flow 50 mL/min. The encapsulation and heating were also conducted under a N_2 atmosphere. Divalent Eu-doped products were prepared using $BaCN_2:Eu^{2+}$ instead of $BaCN_2$ in the abovementioned procedure. A mixture of $BaCO_3$ and Eu acetylacetonate hydrate (99.9%, Aldrich) with a Ba:Eu ratio of 0.96:0.04 was nitrided under an ammonia flow.[28]

Caution: C_2N_2 gas can be released during the heating of the $BaCN_2/2SiO_2$ mixture; thus, the preparation process should be performed in a fume hood.

Crystalline phases of the products were characterized using powder X-ray diffraction (XRD; Ultima-IV, Rigaku) with Cu-Kα radiation. The oxygen and nitrogen contents were measured using a combustion analyser (EMGA-620, Horiba). Si_3N_4 (Ceramic Society of Japan) and Gd_2O_3 (99.9%, FUJIFILM Wako Pure Chemical) were used as the nitrogen and oxygen references, respectively. The latter reference was calcined at 1000 °C to remove adsorbates. The microstructures of the products were examined using field-emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL). Photoluminescence spectra were acquired at room temperature with a fluorescence spectrometer (FP-6500, Jasco) equipped with a 150 W Xe lamp as an excitation source.

Results and discussion

Figure 1 shows TG-DTA curves for the $BaCN_2$-SiO_2 mixture with Ba:Si = 1:2 under flowing Ar gas. A small weight loss of approximately 0.5 wt% was observed below 600 °C, which was attributed to the release of adsorbates from the precursor powders. Above 800 °C, a steep weight loss appeared together with a sharp endothermic peak in the DTA curve at 800 °C. The weight loss was almost completed after holding the temperature at 950 °C for 60 min. The weight loss from 800 °C to the end of the measurement was 12.2 wt%. There were several small endothermic peaks below 800 °C in the DTA curve. Although the origin of the reactions is not clear, similar endothermic peaks also appeared in a preliminary TG-DTA measurement of $BaCN_2$.

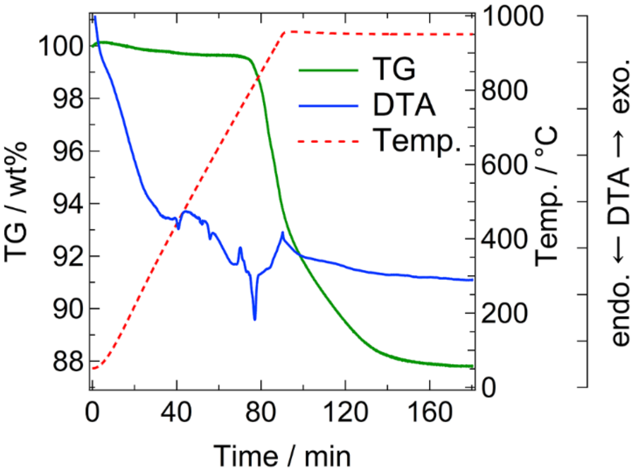

Figure 1 TG-DTA curves obtained from $BaCN_2/2SiO_2$ mixture under Ar flow.

The XRD pattern for the sample after the TG-DTA measurement is shown in Fig. 2. $Ba_3Si_6O_9N_4$ oxynitride appears as the main crystalline phase together with minor $Ba_3Si_6O_{12}N_2$ and SiO_2 phases. The chemical reaction from a mixture of $BaCN_2/2SiO_2$ to $Ba_3Si_6O_9N_4$ is considered to be:

$$3BaCN_2 + 6SiO_2 \rightarrow Ba_3Si_6O_9N_4 + N_2\uparrow + 3CO\uparrow \quad (1)$$

The weight loss expected for reaction (1) is 12.5 wt%, which agrees well with the weight loss measured in the TG-DTA analysis of the $BaCN_2/2SiO_2$ mixture.

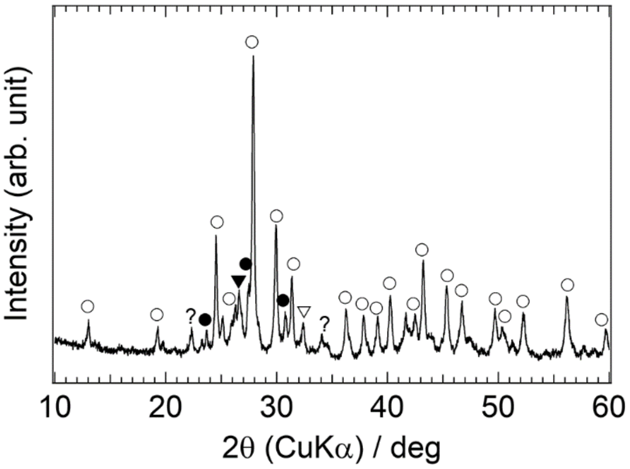

Figure 2 XRD pattern for the product after TG-DTA measurement with heating to 950 °C after duration of 1 h in an Ar flow. The filled and open circles, and filled and open triangles indicate peaks attributed to $Ba_3Si_6O_{12}N_2$, $Ba_3Si_6O_9N_4$, SiO_2, and $BaCO_3$, respectively. Unknown peaks are marked with "?".

To investigate the reaction mechanism, MS of the gas released during heating of the $BaCN_2/2SiO_2$ mixture under an Ar gas flow of 50 mL/min was performed and the data is shown in Fig. 3. A small amount of gas molecules with MS of 44 (CO_2) and 52 (C_2N_2) appeared around 800 °C (at 75 min), followed by large emission peaks due to molecules with MS of 28 (N_2, CO), 44 (CO_2) and 52 (C_2N_2). During the measurement period at 950 °C, release of gas with a MS of 28 continued. The crystalline phase of the sample after the Q-MS analysis was a mixture of $Ba_3Si_6O_9N_4$ and $Ba_3Si_6O_{12}N_2$ similar to the product after TG-DTA measurement as shown in Fig. S1 in the electronic supplementary information (ESI). Gas chromatography (GC) of the emissions was also performed to distinguish N_2 from CO, which have the same molecular weight. The results are shown in Fig. S2 in the ESI. CO_2 was first released, and then CO was detected, similar to the results of the MS measurements. The small amount of CO_2 gas generated at 600 °C might be related to the decomposition of minor $BaCO_3$ impurity in the $BaCN_2$ precursor. The large amount of N_2 gas detected throughout the GC measurements is perhaps due to a N_2 purge gas before an introduction of the powder mixture to the TG-GC sample chamber. Regardless of the large N_2 background, a small hump due to N_2 was clearly observed at around 800 °C together with CO and CO_2. During the reaction, both N_2 and CO were released from the mixture to form $Ba_3Si_6O_9N_4$ as expressed in equation (1).

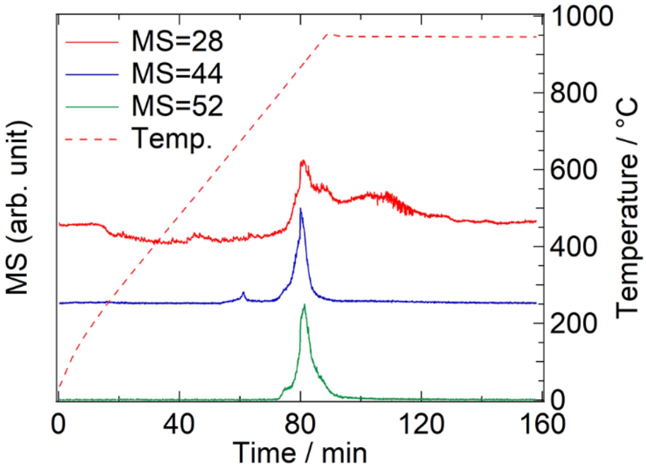

Figure 3 Q-MS obtained from $BaCN_2/2SiO_2$ mixture under Ar flow. The heating rate was 10 °C/min, which was the same as that for the TG-DTA measurement.

Figure 4 shows XRD patterns for the products obtained after firing at 800 and 950 °C for 15 h under 100 mL/min of Ar flow in the alumina tube furnace. The main crystalline phase changed from $Ba_3Si_6O_{12}N_2$ at 800 °C to $Ba_3Si_6O_9N_4$ at 950 °C. From the $BaCN_2/2SiO_2$ mixture, $Ba_3Si_6O_{12}N_2$ oxynitride appeared as the first oxynitride phase and then the main oxynitride phase changed to the nitrogen-rich $Ba_3Si_6O_9N_4$. The effect of the Ar flow rate on the phase ratio was investigated in mixtures fired at 800 °C or 950 °C. The $Ba_3Si_6O_9N_4$ content increased with decreasing Ar flow rate from 100 to 50 mL/min in the products heated at both 800 °C and 950 °C, as shown in Fig. S3. The nitridation reaction of $Ba_3Si_6O_{12}N_2$ to $Ba_3Si_6O_9N_4$ was enhanced under low gas-flow conditions. Released gases from the starting mixture are expected to be important for the nitridation reaction from $Ba_3Si_6O_{12}N_2$ to $Ba_3Si_6O_9N_4$ to proceed, because a higher Ar gas flow rate removes the released gases from the reaction area. An alumina crucible containing the $BaCN_2/2SiO_2$ mixture was loosely encapsulated in a Ta container under a dry Ar atmosphere. The Ta container was heated in an alumina tube furnace at 800 °C for 15 h under an Ar flow of 50 mL/min. Almost single-phase $Ba_3Si_6O_9N_4$ together with a small amount of $BaCO_3$ and SiO_2 was obtained in the product, as shown in Fig. 5. In a nearly static Ar atmosphere, the $Ba_3Si_6O_9N_4$ content was increased even at a low temperature of 800 °C and a short duration of 15 h.

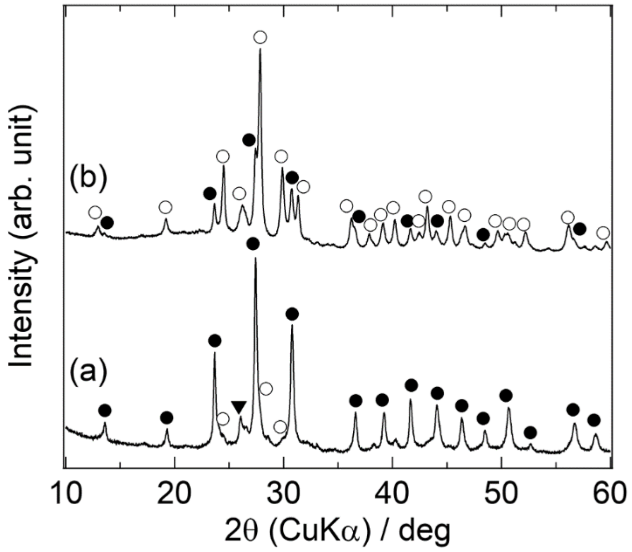

Figure 4 XRD patterns for products obtained at (a) 800 °C and (b) 950 °C for 15 h in Ar flow of 100 mL/min. The filled and open circles and filled triangles indicate peaks attributed to $Ba_3Si_6O_{12}N_2$, $Ba_3Si_6O_9N_4$ and SiO_2, respectively.

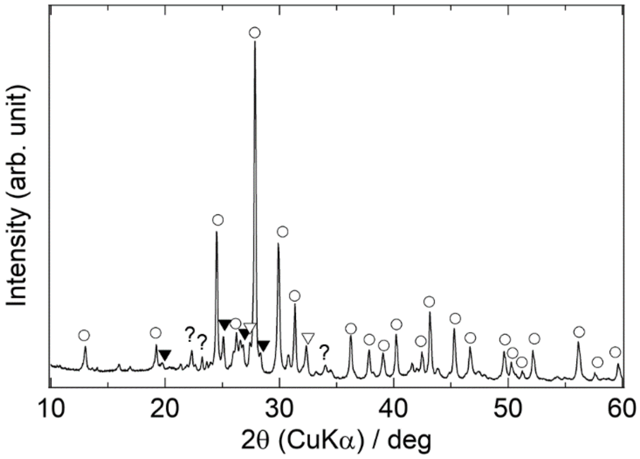

Figure 5 XRD pattern for the product obtained at 800 °C for 15 h in a loosely sealed Ta container under Ar atmosphere. The open circles and filled and open triangles indicate peaks attributed to $Ba_3Si_6O_9N_4$, SiO_2 and $BaCO_3$, respectively. Unknown peaks are marked with "?".

Table 1 Phase ratio between $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$ in the products obtained from the $BaCN_2/2SiO_2$ mixture. The phase ratio was calculated from their XRD peak intensity ratio regardless of impurity phases.

Temp. / °C	Ar flow rate / mL/min	Duration / h	Phase ratio / mol %	
			$Ba_3Si_6O_{12}N_2$	$Ba_3Si_6O_9N_4$
800	100	15	99.5	0.5
950			39.6	60.4
800	50		74.0	26.0
950			-	100
800	Static (in Ta)		-	100

These results indicate that $Ba_3Si_6O_{12}N_2$ forms from the mixture of $BaCN_2$ and SiO_2 in the first stage and then the crystalline phase changes into the nitrogen-rich $Ba_3Si_6O_9N_4$ via a nitridation reaction. The phase ratio in the products calculated from their XRD patterns are summarized in Table 1. The $Ba_3Si_6O_9N_4$ content in the product increases as the Ar gas flow rate decreases from 100 to 50 mL/min or under a nearly static Ar atmosphere in a Ta container. Nitrogen related C_2N_2 and N_2 gases were observed by MS at the beginning of the reaction between $BaCN_2$ and SiO_2 at around 800 °C (Fig. 2). The formation of the $Ba_3Si_6O_{12}N_2$ phase together with the generation of C_2N_2 and N_2 gases from the mixture of $BaCN_2$ and SiO_2 is expected to occur as follows:

$$3BaCN_2 + 6SiO_2 \rightarrow Ba_3Si_6O_{12}N_2 + 3/2C_2N_2\uparrow + 1/2N_2\uparrow \quad (2)$$

By decreasing the Ar gas flow rate or encapsulation in a Ta container, the $Ba_3Si_6O_9N_4$ content increased. The released C_2N_2 gas remained around the sample powder for a long time under a low gas-flow rate or in a nearly static atmosphere in the Ta container. The reaction between $Ba_3Si_6O_{12}N_2$ and C_2N_2 gas is expected to occur as follows:

$$Ba_3Si_6O_{12}N_2 + C_2N_2 \rightarrow Ba_3Si_6O_9N_4 + CO_{2\uparrow} + CO\uparrow \quad (3)$$

The CO_2 and CO byproducts were detected by both the MS and GC analyses. Figure 6 shows a possible reaction mechanism. The retention time of the released gases affects the crystalline phase of the barium oxynitridosilicate. SSR between $BaCN_2$ and SiO_2 forms $Ba_3Si_6O_{12}N_2$, which is a nitrogen-poor oxynitridosililcate, at 800 °C and releases C_2N_2 gas. This temperature is much lower than that required for the SSR using Si_3N_4 as a nitrogen source. Nitrogen-rich oxynitride $Ba_3Si_6O_9N_4$ can be formed by a reaction between $Ba_3Si_6O_{12}N_2$ and C_2N_2 gas with the phase ratio depending on the gas-flow rate. For a low Ar gas-flow rate or in a Ta container, the reaction between $Ba_3Si_6O_{12}N_2$ and C_2N_2 gas is accelerated and nitrogen-rich $Ba_3Si_6O_9N_4$ is obtained as the main crystalline phase.

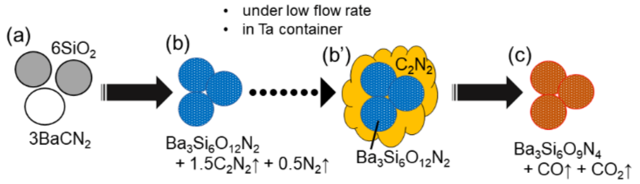

Figure 6 Formation mechanism of $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$: (a) starting $BaCN_2/2SiO_2$ mixture, (b) product heated at 800 °C, (b') product heated at 800 °C in Ta container or under low flow rate of Ar gas, and (c) product heated at 950 °C.

The phase purity of the barium oxynitridosilicates was improved when the precursor mixture in the Ta container was heated under a nitrogen flow. The $BaCN_2/2SiO_2$ mixture was encapsulated in a Ta container under a dry N_2 atmosphere and heated. Almost single-phase $Ba_3Si_6O_{12}N_2$ was obtained by heating at 800 °C for 15 h as shown in Fig. S4. Heating at 800 °C for 50 h or at 950 °C for 15 h in the loosely sealed Ta container under N_2 atmosphere formed nitrogen-rich $Ba_3Si_6O_9N_4$. The oxygen and nitrogen contents of products heated at 800 and 950 °C for 15 h in the N_2-filled Ta container were analyzed after washing with nitric acid and distilled water, followed by drying. A total of 27.0(4) wt% of oxygen and 4.0(1) wt% of nitrogen were observed for $Ba_3Si_6O_{12}N_2$ prepared at 800 °C, which agree well with the theoretical values for the oxynitridosilicate. The nitrogen content increased to 7.0(2) wt% for the $Ba_3Si_6O_9N_4$ obtained at 950 °C for 15 h. The reactivity of the $Ba_3Si_6O_{12}N_2$ with C_2N_2 might be suppressed in a N_2 atmosphere compared with the case for an Ar atmosphere due to a different stability of the C_2N_2 gas in different atmosphere.

Divalent Eu-doped $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$ were prepared using $BaCN_2$:Eu as the starting material instead of $BaCN_2$, in a Ta container loosely-sealed under an N_2 atmosphere. SEM images of the products are shown in Fig. S5. The particle size for the $Ba_3Si_6O_{12}N_2$:Eu is below 2 µm, which is smaller than that for the $Ba_3Si_6O_9N_4$:Eu obtained at 950 °C. There was no significant sintering between the grains due to the low reaction temperature. Photoluminescence spectra for both oxynitride phosphors are depicted in Fig. 7. Both phosphors show broad green photoluminescence under UV and blue light irradiation at wavelengths ranging from 250 nm to 400 nm. The broad photoluminescence peaks at 528 nm and 507 nm associated with the 4f-5d transition of divalent Eu-doped $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$, respectively, agree well with those for the oxynitrides prepared by a SSR between $BaCO_3$ and Si_3N_4 at high temperature.[12,13] Additional thermal annealing of the products or the low temperature reaction of $BaCN_2/2SiO_2$ coexisting with flux should be considered to improve the crystallinity and photoluminescence properties. Using $BaCN_2$ as the nitrogen source instead of Si_3N_4, which is widely used in high-temperature SSR for oxynitride phosphors, significantly reduces the formation temperature. Low-temperature synthesis of oxynitrides has also been proposed for perovskite oxynitrides and zinc-blende gallium-zinc oxynitrides. They are prepared using C_3N_4 or urea as the nitrogen source instead of NH_3. Their low-temperature formation has been attributed to the formation of metal carbodiimide intermediates. By comparison with $BaCO_3$, $BaCN_2$ reacts with SiO_2 to release C_2N_2 and N_2 as observed by MS analysis of the released gases, together with the formation of $Ba_3Si_6O_{12}N_2$. The gas release reaction shown in equation (2) implies that the free energy of the formation is expected to be negative due to the increase in entropy, as has been previously reported[30] for Sr-Nb oxynitride formation with NH_3 gas generation. Reduction and nitridation of $Ba_3Si_6O_{12}N_2$ to $Ba_3Si_6O_9N_4$ occur by reaction with C_2N_2 at very low temperature. The high-temperature SSR using BaO decomposed from $BaCO_3$, SiO_2, and Si_3N_4 is entirely a solid-state reaction without benefit from the generation of byproduct gas. The low-temperature reaction procedure suggested in this research can be applied to the synthesis of other oxynitrides by using metal carbodiimides such as $CaCN_2$ or $SrCN_2$ as a solid nitrogen source instead of the highly stable Si_3N_4.

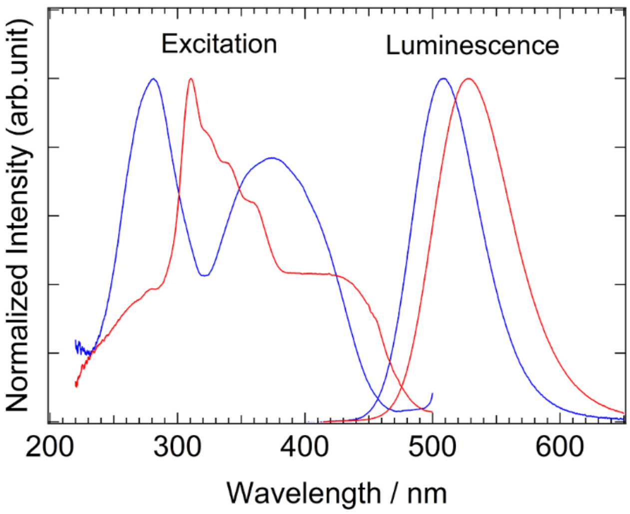

Figure 7 Photoluminescence and excitation spectra of Eu doped $Ba_3Si_6O_{12}N_2$ (red) and $Ba_3Si_6O_9N_4$ (blue) obtained at 800 °C and 950 °C, respectively under a nitrogen atmosphere in a Ta container.

Conclusions

Barium oxynitridosilicates, $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$, were prepared from a mixture of $BaCN_2$ and SiO_2 at 800 °C, which is the lowest temperature reported for a formation of the oxynitrides. Almost single-phase oxynitridosilicates were obtained by tuning the gas-flow rate and heating atmosphere. The low-temperature reaction was promoted by the generation of byproduct gases and the C_2N_2 gas increased the nitridation reaction rate to give the nitrogen-rich product. Alkaline earth carbodiimide is a potential nitrogen source for achieving a low-temperature and energy-efficient process for the formation of oxynitride compounds.

Author Contributions

YM: Conceptualization, writing – original draft. NS: Conceptualization, Investigation. YK, KA, and TM: MS and GC analysis. MH: Conceptualization

Conflicts of interest

There are no conflicts of interest to declare.

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