First-principles thermodynamic calculations and experimental investigation of Sr–Si–N–O system—synthesis of Sr$_2$Si$_5$N$_8$:Eu phosphor†

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Thermodynamic stabilities of the phases of Sr–Si–N–O system were evaluated by simulating phase diagrams at various conditions based on first-principles density functional theory calculations. Synthesis conditions and stability of the compounds belonging to the system, in which oxidation and nitridation reactions are involved complicatedly, could be interpreted through this first systematic investigation on the two-gas system. Practical synthetic methods of nitrides, such as hydrogen-reduction and nitridation or carbothermal reduction and nitridation reactions, were studied with special attention. This study enabled us to calculate proper conditions for synthesis of the Sr$_2$Si$_5$N$_8$ phase, which is drawing attention as a new phosphor material for light emitting diodes. The types of impurities appearing with deviation from the proper synthetic conditions were also investigated, which may provide information about optimizing synthesis conditions. Synthesis of Sr$_2$Si$_5$N$_8$:Eu phosphor using SiO$_2$ instead of conventionally used Si$_3$N$_4$, was predicted by first-principles calculations, and we succeeded in synthesizing Sr$_2$Si$_5$N$_8$:Eu phosphor for the first time using all oxide raw materials under normal pressure on this basis. The results of this study are expected to provide useful guidelines for synthesis of nitrides and the established simulation method may effectively be applied to other multi-gas systems.

1 Introduction

Non-oxide solids have recently attracted great interest as they are expected to show novel properties that cannot be provided by conventional oxide materials. Owing to their thermal, chemical, and mechanical stabilities, nitridosilicates, oxonitridosilicates, or oxonitridialuminosilicates have been actively investigated. They are also known to exhibit more variety of structural features than silicates. Typical building units of silicates are SiO$_4$ tetrahedra and the oxygen atoms are connected to only one or two Si atoms; whereas, it was reported that nitrogen atoms can have more connections, even to four silicon atoms, thus, the crystals including nitrogen atoms have a high structural diversity.

Considering this point, many researchers have been focusing on the preparation and characterization of new nitrido- or oxonitridosilicates, especially in the systems containing the Si–N–O framework and countercations, such as Ca, Sr, or Ba. These compounds have been studied as hosts for rare earths (RE) because the higher covalent character of nitrogen than that of oxygen bonding can induce photoluminescent excitation and emission in the much longer wavelength range than oxide materials, and the cations can provide a site for RE activators.

Sr$_2$Si$_5$N$_8$ may be one of the most successful outcomes of the research efforts. This material has emerged as a host for RE doped phosphor materials applied in light emitting diodes (LEDs). In phosphor converted LEDs, blue light generated from a semiconductor source is used to excite luminescent materials that emit a longer wavelength of light. YAl$_2$O$_3$:Ce$^{3+}$ is widely used for white LEDs because the yellow emission of the phosphor can make white light, combined with the blue light from the GaN-based semiconductor. However, this combination is insufficient in terms of color rendering property because of the lack of red emission. Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ is an excellent supplementation to this problem because it shows orange-red emission with high quantum efficiency and low thermal quenching under excitation with blue light, this makes it an encouraging red phosphor to improve the color rendering of white LEDs.

Various synthetic routes were tried for the synthesis of M–Si–N system compounds. It was reported that nitride phases, such as SrSiN$_2$, Sr$_2$Si$_3$N$_8$, SrSi$_6$N$_8$, and SrSi$_3$N$_{10}$ were
synthesized through a high temperature reaction of stoichiometric amounts of metals with silicon diimide,\textsuperscript{11,23–28} or reaction of all nitride materials under a nitrogen atmosphere.\textsuperscript{16,27} Recently, the carbothermal reduction and nitridation (CRN) method was used to produce the Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ phosphor using SrCO$_3$, Eu$_2$O$_3$, and Si$_3$N$_4$ as starting materials. Xie et al.\textsuperscript{11} reported that Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ could be synthesized by firing SrCO$_3$, Eu$_2$O$_3$, and Si$_3$N$_4$ mixtures under high N$_2$ pressure. The resultant compound contained some amount of Sr$_2$SiO$_4$ as an impurity phase.

Although researchers have tried various methods and some of them were successful, difficulty in synthesis still seems to be the main obstacle for the investigation of compounds containing nitrogen. Unlike oxide materials whose synthesis is mainly controlled by the heating temperature, nitride or oxo-nitride preparation requires precise control of temperature, and nitrogen and oxygen partial pressures. The situation becomes more complicated by interactions of these conditions. Thus, it is necessary to investigate the synthesis conditions and their effects on the stability of phases in terms of a systematic thermochemical approach. Yet, to the best of our knowledge, there have been few attempts on this subject.

In this study, we investigated phase equilibria of the Sr–Si–N–O system by a first-principles thermodynamic calculation method. Energies of the compounds that belong to the system were calculated using density functional theory (DFT) and the enthalpies of nitrogen and oxygen molecules were determined through the combination of the first-principles calculation and experimental data. Through simulating phase stability of the compounds at various conditions, phase diagrams of the Sr–Si–N–O system were constructed. Phase equilibria under thermochemical conditions of hydrogen-thermal reduction and nitridation (HRN) and CRN reactions—the methods that are generally used for commercial production—were especially deeply investigated. The calculations’ results showed excellent agreement with experimental data that supports the validity of our simulation model and methods, thus this first attempt of a systematic study is expected to provide a useful reference for synthesis and thermodynamic stabilities of the phases containing nitrogen.

## 2 Methods

Phase diagrams are formed with thermodynamically stable compounds at given conditions, thus comparison of the Gibbs free energies among the phases is necessary. To construct the ternary phase diagram of the Sr–Si–N–O quaternary system, the fourth element going in and out of the planar ternary diagram should be considered in comparing the phase stability. That is, for compounds with a general chemical formula of Sr$_a$Si$_b$N$_c$O$_d$, the grand potential, which is expressed as follows, should be used as a measure of thermodynamic stability:

$$
\mathcal{G}(\text{Sr}_a\text{Si}_b\text{N}_c\text{O}_d) = G(T, P, \text{Sr}_a\text{Si}_b\text{N}_c\text{O}_d) - \frac{d}{2}\mu_{O_2}
$$

For solid state compounds, it can be approximated as:\textsuperscript{28,29}

$$
\mathcal{G}(\text{Sr}_a\text{Si}_b\text{N}_c\text{O}_d) = \frac{G(T, P, \text{Sr}_a\text{Si}_b\text{N}_c\text{O}_d)}{a + b + c} - \frac{d}{2}\mu_{O_2}
$$

$$
\approx \frac{E^0(0 \text{ K, Sr}_a\text{Si}_b\text{N}_c\text{O}_d)}{a + b + c} - \frac{d}{2}\mu_{O_2}
$$

$$
\left\{ \begin{array}{l}
\left( G = E + PV - TS = E^0(0 \text{ K}) + P^0V(0 \text{ K}) \\
+ \int_0^T C_v dT + \int_p^P \{V(1 - \alpha T)\} dP - TS \approx E^0(0 \text{ K})
\end{array} \right.
\right.
$$

where $\mu$ is chemical potential, $C_p$ is specific heat at constant pressure, and $\alpha$ is the thermal expansion coefficient. Binary and ternary compounds of the system were treated in the same manner, that is, one or two of $a$–$d$ in the equations was set to be zero. As provided in the equations, the free energy is approximated to the internal energy at 0 K. This is a potential source of error, but it does not seem to be significant for solid phases. In addition, the error related to the approximation would affect little on the change of phase diagrams because the stability of each phase on the phase diagram at a given condition is determined by the relative free energy of the phases.

Nitrogen exists in the gas state, thus $1/2\mu_{O_2}$ is used for the comparison of stability. Changes of $\mu_{O_2}$ and $\mu_{O_2}$ with temperature and pressure were reflected according to the data of JANAF thermochemical table\textsuperscript{30} because the effects of volume and entropy of gases cannot be neglected. For each phase, the position on a ternary diagram ($x$ and $y$) and the grand potential value ($z$) can make a unique coordination in a 3-D space. Taking vertices and edges, which form a convex hull,\textsuperscript{31} to the $-z$ direction and projecting them on a 2-D plane, ternary phase diagrams could be constructed.

The energy of each compound was calculated using DFT based on the generalized gradient approximation of Perdew–Burke–Ernzerhof and projector-augmented plane wave (PAW) pseudopotentials implemented in the Vienna \textit{ab initio} simulation package (VASP),\textsuperscript{32–34} with an energy cutoff of 500 eV, $3 \times 3 \times 1$ k-mesh points, and self consistency field (SCF) convergence of $10^{-5}$ eV. We allowed full relaxation of atomic positions and lattice vectors of the crystal models composed of one unit cell, for the structure optimization and calculation of energy. Compounds of Sr–Si–N–O system registered in the international crystal structure database (ICSD) were calculated,\textsuperscript{35} and new phases that have been reported recently were added.\textsuperscript{10,23–27,36–38} Because gas phases are difficult to calculate accurately, the room-temperature enthalpies of nitrogen and oxygen molecules were determined so that energies of nitride or oxide crystals calculated by DFT may agree with experimental data (section 3.1). All the calculated energies are presented in the ESI.\textsuperscript{†}

The first-principles study was examined experimentally: synthesis of Sr$_2$Si$_5$N$_8$, which draws interest for its potential application in LEDs, was tried under various conditions, and
phases of the resulting powder samples were observed. SrCO₃ (Sigma-Aldrich, 99.9%) and SiO₂ (Alfa Aesar, 99.9%) were used as starting materials, and Eu₂O₃ (Sigma-Aldrich, 99.9%) was added for synthesis of the Eu-doped phosphor material. Si₃N₄ was also tested as a Si source instead of SiO₂ and the results were compared. The raw materials were dry-mixed, ground, and embedded in graphite crucibles. The mixtures were fired in a tube furnace of 60 mm diameter and 700 mm length. Two types of reduction process, HRN and CRN reactions, were tested. For HRN reactions, a flow of 100 sccm of mixed gas H₂–N₂ 5/95 was used. Active carbon granules were mixed with the raw powders and 100 sccm gas flow of pure N₂ was used for CRN reactions. The amount of carbon was changed to examine the effect of change in oxygen partial pressure. The powder samples after firing were analyzed using X-ray diffraction (XRD, Rigaku D-max 2500). The photoluminescent property of Sr₂Si₅N₈:Eu phosphor was measured using a spectrofluorometer (Jasco FP-5600) with Xe-lamp as a light source.

3 Calculation results and discussion

3.1 Determination of enthalpies of O₂ and N₂

For a thermochemical interpretation of a system that contains nitrides or oxides, the energy change of the nitridation or oxidation reaction must be calculated with accuracy. However, first-principles calculation often shows considerable errors because gaseous phases are difficult to make a proper structure model for, and calculation of binding energies between the atoms is often incorrect. It was also reported that GGA error occurs for oxygen when O²⁻ is formed from O₂ by adding electrons to p orbitals. Yet the overall errors related to the oxidation reactions can be corrected just by determining the proper enthalpy value of O₂ molecules so that it may include all the errors, because they usually show a similar amount irrespective of the cations involved. Thus, determination of proper chemical potential values of N₂ and O₂ can compensate DFT errors conveniently and improve the accuracy of calculations for nitridation or oxidation reactions.

We calculated the energies of nitrides or oxides of metals of various oxidation numbers (Mg, Ca, Al, Si, Zr, Nb) and compared them with the reported experimental standard formation enthalpy values, and then determined enthalpies of nitrogen and oxygen molecules so that the DFT calculations may agree with experimental data. That is, enthalpies of gas phases, which form the results of the following equation, dovetail into the existing data:

\[ \Delta H_{\text{calc}}(M,G_2) = H_{\text{calc}}(M_2G_2) - xH_{\text{calc}}(M) - H(G_2) \]

\[ = \{E_{\text{calc}}(M_2G_2) + PV(M_2G_2)\} - x\{E_{\text{calc}}(M) + PV(M)\} - H(G_2) \]

\[ \approx E_{\text{calc}}(M_2G_2) - xE_{\text{calc}}(M) - H(G_2) \]

where, \( M = \text{Mg, Ca, Al, Si, Zr, Nb} \) and \( G_2 = \text{N}_2, \text{O}_2 \)

Energies of nitrides and oxides calculated by DFT are shown in Fig. 1. The enthalpies of \( \text{N}_2 \) and \( \text{O}_2 \) \( (H(G_2)) \) of above equations obtained by the method mentioned above are also presented in the figure. Although energies of nitrides \( \{\text{Mg}_3\text{N}_2, \text{Ca}_3\text{N}_2, 2\text{AlN}, 1/2\text{Si}_3\text{N}_4, 2\text{ZrN}, 2\text{NbN}\} \) and oxides \( \{2\text{MgO}, 2\text{CaO}, 2/3\text{Al}_2\text{O}_3, \text{SiO}_2, 2\text{ZrO}_2, 2/\text{5Nb}_2\text{O}_3\} \) are different depending on the cations involved, the enthalpies of \( \text{N}_2 \) and \( \text{O}_2 \) determined appeared nearly identical. This again indicates that a consistent thermodynamic calculation is possible regardless of the cations, just by determining the enthalpies of the gas phases to include all the error terms occurring with DFT calculations of nitridation or oxidation reactions.

Another error factor that should be considered is that DFT calculation assumes 0 K while standard formation enthalpies are obtained at 298 K. Integration of the difference of heat capacities between metals and their nitrides or oxides from 0 K to 298 K should be corrected in principle. However, this error was reported to be negligible and of affects little, thus can be dispensed with. As a result, the room-temperature chemical potentials of 1 atm \( \text{N}_2 \) and \( \text{O}_2 \) were determined to be \(-16.05 \text{ eV per fu}\) and \(-8.95 \text{ eV per fu}\), respectively \((\text{fu} = \text{formula unit})\). These values were used for all the nitridation and oxidation reactions in this study, with a modification of the effects of temperature and pressure based on the JANAF thermochemical table.
3.2 Sr–Si–N system and formation of Si₃N₄

Fig. 2 shows the room-temperature phase diagram of Sr–Si–N system, which was calculated excluding oxygen. The phase diagram shows that SrSi3, SrSi, and Sr₂Si exist as stable phases on the Sr–Si line, and this result agrees well with experimental reports. Sr₂Si₃, which is reported to exist at room temperature, did not appear stable in the diagram, which is the only disagreement. Close examination revealed that the Gibbs free energy of Sr₂Si₃ was located just above the calculated convex hull, which indicates that the disagreement originates from a minute error of first-principles calculations. The phases on the Si–N and Sr–N lines also showed good agreement with previous reports.

Nitrides of ternary components, such as SrSiN₂, Sr₂Si₅N₈, Sr₅Si₃N₁₀, and Sr₂Si₅N₈ are known to exist for the Sr–Si–N system, but SrSi₅N₁₀ did not appear to be stable in our simulation. Pilet et al. synthesized this phase for the time, but they reported that it was not a single phase and considerable amounts of Sr₂Si₅N₈ and Si₃N₄ were mixed together. Further investigation may be necessary to verify whether SrSi₅N₁₀ is a thermodynamically stable phase or just a metastable compound that appears by kinetic reasons. Altogether, our simulation model seems to give an exact reflection of experimental results.

Fig. 3 shows the phase diagrams of Sr–Si–N system simulated for the conditions just before (Fig. 3a) and after (Fig. 3b) the appearance of Si₃N₄ as oxygen partial pressure was reduced. When O₂ partial pressure is not sufficiently low, only oxides (Sr₂SiO₅, Sr₂SiO₄, and Sr₂SiO₃) existed as stable phases (Fig. 3a). As the partial pressure of oxygen becomes smaller, the Si₃N₄ phase appeared at certain points (Fig. 3b) which were reported to be P₀₂ = 10⁻¹⁸.7 MPa at 1623 K and 10⁻²¹ MPa at 1473 K. The O₂ partial pressure of the points calculated in this study were 10⁻¹⁸.¹ MPa and 10⁻²⁰.⁷ MPa, respectively, for the same conditions, which shows excellent agreement with the experimental data. This observation again shows that the first-principles model of this study was well designed for precise simulation of the real situation.

3.3 Hydrogen-thermal and carbothermal reduction and nitridation (HRN and CRN)

HRN and CRN reactions are widely used for thermal reduction or synthesis of nitride materials. These methods reduce oxygen partial pressure by oxidation of hydrogen or carbon, and the equilibrium partial pressure changes with temperature. Equilibrium oxygen partial pressures of HRN and CRN reactions were read from the Ellingham diagram and presented with respect to temperature in Fig. 4 (empty symbols). Combining them with the room-temperature enthalpies obtained in section 3.1 and thermochemical data (H°₂ – H°₂985, S°) of the JANAF table, the chemical potential of O₂ can be calculated for both of the reactions. They are presented in Fig. 4 (solid symbols).

Under a normal N₂ flow condition without pressurizing, the N₂ partial pressure was assumed to be 0.1 MPa (normal pressure). Then the N₂ chemical potential at given temperatures could also be calculated from the room-temperature enthalpies.
calculated in section 3.1 and the data of the JANAF table, in the same way as the oxygen chemical potential mentioned above. Using the calculated N₂ and O₂ chemical potentials, the Sr–Si–N–O phase diagram under HRN condition was simulated (Fig. 5). Six phases—SrO, SiO₂, N₂, SrSiO₃, Sr₂SiO₄, and Sr₃SiO₅—existed as thermodynamically stable forms that compose the convex hull. This did not change in the range of 1000–2300 K. It seems that the oxygen chemical potential is too high because of the high oxygen partial pressure for HRN conditions, making nitride phases unstable.

Phase diagrams for the CRN reaction were also simulated in the same way as that of HRN. Oxygen chemical potential under CRN conditions changed over a wider range with temperature, and therefore many phases emerged or disappeared with temperature change. The phase diagram of CRN at 1400 and 1500 K is given in Fig. 6a, which shows that only oxide compounds, such as SrSiO₃, Sr₂SiO₄, and Sr₃SiO₅, are stable, probably because the O₂ chemical potential is not low enough in the temperature range. In the diagram of 1600 K, Si₃N₄, the first nitride phase appeared (Fig. 6b).

Si₃N₄ is generally used as a starting material for the synthesis of nitrido- or oxonitridosilicates because of the intuitive expectation that starting with Si₃N₄ would be more advantageous to the formation of the compounds than using SiO₂. However, our simulation result gives an expectation that nitrides can be synthesized with SiO₂ as a starting raw material instead of Si₃N₄ in CRN reactions. Fig. 6 shows that Si₃N₄ appears at a lower temperature than any other nitride compounds even if we start with oxide raw materials, which indicates that SiO₂ raw material makes thermodynamically the same results as starting with Si₃N₄ for CRN reactions above 1600 K. Using SiO₂ has great merit over Si₃N₄ in terms of cost.

Sr₂Si₅N₈ appeared on the phase diagram of CRN at 1900 K and stayed stable until 2100 K (Fig. 6c–e). Other ternary nitride compounds, SrSi₃N₈ and SrSiN₂ also appeared in this temperature range. They were stable over a narrower temperature range than Sr₂Si₅N₈, which implies that synthesis of Sr₂Si₅N₈ and SrSiN₂ requires precise control of the reaction temperature and sustenance of the reducing atmosphere during the cooling process. Above 2200 K (Fig. 6f), all the nitride phases disappeared from the phase diagram of Sr–Si–N–O system and only compounds of the Sr–Si system remained. This is because both

Fig. 5 Phase diagram of Sr–Si–N–O system simulated for HRN conditions (T = 1000–2300 K).

Fig. 6 Phase diagrams of Sr–Si–N–O system simulated for CRN conditions: (a) at 1400–1500 K, (b) 1600–1800 K, (c) 1900 K, (d) 2000 K, (e) 2100 K, and (f) 2200 K.
oxygen and nitrogen chemical potentials decrease as temperature increases, resulting in no more thermodynamic preference for formation of nitride phases.

3.4 Synthesis of Sr$_2$Si$_3$N$_8$

Sr$_2$Si$_3$N$_8$ is attracting special attention among the compounds of the Sr–Si–N–O system as the next generation of phosphor materials for fabrication of LEDs. Based on the simulation results, it seems that Sr$_2$Si$_3$N$_8$ cannot be prepared by HRN reaction. But, we expected it could be synthesized via CRN reaction even under normal pressure of N$_2$ atmosphere between 1850 and 2150 K (Fig. 6). It was also predicted that the synthesis becomes easier with high N$_2$ pressure, a method which is frequently used for the synthesis of nitride compounds. The simulation of N$_2$ pressure conditions under 100 MPa showed that the lowest limit of synthesis temperature was lowered by ~100 K and the compound remained stable up to 2300 K, indicating that the possible temperature range of synthesis is widened. The temperature range for Sr$_2$Si$_3$N$_8$ synthesis under 0.1 and 100 MPa of N$_2$ pressure is presented in the bottom of Fig. 4.

Some researchers reported that impurity phases existed together with their Sr$_2$Si$_3$N$_8$ compounds.[11,16,20] SrSiO$_3$ and Sr$_2$SiO$_4$ commonly appeared, which was exactly predicted from our calculation; we mentioned that Sr$_2$Si$_3$N$_8$ could be formed by CRN reaction at 1900 K. Two types of fluctuation in this synthesis condition—decrease of temperature (Fig. 7a) and increase of O$_2$ partial pressure (Fig. 7b)—were simulated. The phase diagrams of both cases are presented in Fig. 7.

The equilibrium partial pressure and chemical potential of oxygen in CRN reaction at 1900 K are 7.943 × 10$^{-18}$ MPa and −18.78 eV per fu, respectively, and the phase diagram simulated for the condition shows that formation of Sr$_2$SiO$_4$ is thermodynamically more favorable and thus reaction (b) would be dominant with increasing oxygen partial pressure.

$$\text{Sr}_2\text{Si}_3\text{N}_8 + 3\text{O}_2 = 2\text{SrSiO}_3 + \text{Si}_3\text{N}_4 + 2\text{N}_2 \quad (a)$$

$$\text{Sr}_2\text{Si}_3\text{N}_8 + 2\text{O}_2 = \frac{4}{3}\text{Si}_3\text{N}_4 + \frac{4}{3}\text{N}_2 \quad (b)$$

From the above results, it is deduced that SrSiO$_3$ appears as an impurity phase when the temperature is not high enough, or that it is formed during the cooling process, thus our simulation results suggest that in order to remove SrSiO$_3$ secondary phase, Sr$_2$Si$_3$N$_8$ should be synthesized at a high enough temperature and fast cooling after the synthesis seems to be desirable. Whereas, Sr$_2$SiO$_4$ is expected to be formed by increasing of O$_2$ partial pressure at a high enough synthesis temperature, therefore momentary fluctuation of O$_2$ partial pressure by leak-in of air should be avoided, and the carbon should be able to be fully oxidized so that the equilibrium atmosphere of the CRN reaction may be maintained at the given temperatures. We believe that these measures derived from the first-principles simulation of this study would be essential for synthesis of a uniform Sr$_2$Si$_3$N$_8$ compound.

3.5 Application of the simulation to synthesis of Sr$_2$Si$_3$N$_8$:Eu phosphor

The results so far have not considered doping of europium, but phase diagrams with Eu-doping are necessary to get information on the synthesis of Sr$_2$Si$_3$N$_8$:Eu phosphor. However, DFT calculation of 4f rare earths with GGA-PBE often lacks accuracy. Moreover, to make a crystal model that contains ~3 atom% of dopants, the size of the supercell becomes too large because it should include more than 30 Sr atoms. These limitations make it difficult to simulate phase diagrams of the Eu-doped

![Fig. 7](https://example.com/fig7.jpg)

Fig. 7 Prediction of impurity phases in the synthesis of Sr$_2$Si$_3$N$_8$ phase by CRN reactions: (a) at the equilibrium CRN condition of 1800 K (p$_{O_2}$ = 2.512 × 10$^{-18}$ MPa), whose temperature is not high enough for stable existence of Sr$_2$Si$_3$N$_8$, and (b) at 1900 K, a high enough temperature, but oxygen partial pressure is assumed to have increased to 2.397 × 10$^{-17}$ MPa from the equilibrium pressure of 7.943 × 10$^{-18}$ MPa for some reason.)
Sr–Si–N–O system; therefore, validity of our first-principles investigation should be indirectly checked.

We substituted part of the Sr atoms with Eu for the compounds that appear on the simulated phase diagrams, and calculated their energies (ESI†). Because of the constraints of supercell size, the doping amount of Eu was in the range of 6.25−12.5 atom%, much larger than that of Sr2Si2N8:Eu phosphors in practical use (about 3 atom%). The results showed that change of energy with doping was under −0.3%. Considering the large doping amount of Eu in our crystal models, the actual energy change with doping was under a practical use (about 3 atom%). The results showed that change of energy with doping was under −0.3%. Considering the large doping amount of Eu in our crystal models, the actual energy with doping was under a practical amount (of Eu in our crystal models, the actual energy change with a conventional doping amount (−3 atom%) of Eu is expected to be much smaller. With an assumption that energy change with doping is proportional to Eu-doping amount, we estimated the difference in energy between the compounds containing a practical amount of Eu (3 atom%) and those without doping, which turned out to be very small, within 0.1%.

For all the phases considered, Eu-doping changed the energy of the compounds in the same direction (all the energies decreased) and the change was very small, indicating that phase diagrams of Sr–Si–N–O system would be affected little with Eu-doping. The only exception was SrSi2N8, whose energy increased with doping and the amount of change was somewhat larger. Therefore, Eu-doped SrSi2N8, which is a little more unstable than the undoped, may not be able to exist as a stable phase in some cases. For Sr2Si5N8, it was predicted that the energy decreases by about 0.015%, and the lattice parameter change is −0.085 to −0.127% with 3 atom% of Eu-doping.

### 3.6 Limitation and corrections

In this section, we discuss several factors that were omitted to avoid making the simulation too complicated. First, melting of the solids was not considered. Compounds on the Sr–Si line, which are stable at elevated temperatures but have relatively low melting points,49 would appear as liquid phases. This would apply to Si (Tm = 1687 K), SrSi2 (Tm = 1393 K), and SrSi (Tm = 1468 K) in Fig. 6. Over the melting points, heats of melting should be added to the energy of the crystals and this modified energy (DFT-calculated crystal energy + melting heat) should be used for the simulation of phase diagrams. Unfortunately, the exact melting heats have not been reported, except for Si (Tm = 1687 K and ΔHm = 0.520 eV per fu).

For a rough examination of the effect of melting, we assumed the melting heats of SrSi2 and SrSi to be similar to that of Si and then simulated phase diagrams of the CRN reaction (Fig. 8). Compared with Fig. 6, which did not consider melting, the phase diagrams with melting of the compounds were identical below 1800 K but showed differences at elevated temperatures. At 1900 K, SiO2 instead of Si appears stable presumably because melted Si is higher in energy than in the solid state by the heat of melting, and thus the energy of SiO2 lies between that of the solid and liquid phases of Si. At 2000–2100 K, oxide phases, such as SrSiO3, Sr2SiO4, and Sr3SiO5, were stable on the Sr–Si line because of the increased energies of SrSi and SrSi2 with consideration of melting. Silicides appeared above 2200 K, and the ternary nitrides (Sr2SiN8, SrSi2N8, SrSiN2) were still stable at these temperatures. Thus, by including the melting, the stability of compounds on the Sr–Si line changed. However, this change did not affect the types of secondary phases formed with change of temperature and O2 partial pressure for Sr2Si2N8 synthesis described in section 3.4.

The SrSi2N2O2 phase also should be examined, which was not stable in our simulated phase diagrams but frequently appeared in actual experiments as is shown in the next section. This compound is attracting interest for its application as a green-yellow phosphor for LEDs, and is known to be easily synthesized if Si3N4 is used as a starting raw material even under a hydrogen atmosphere.37,43–46 However, this phase did not appear on the phase diagrams of this study. Two possible interpretations may explain this disagreement. The first hypothesis is that SrSi2N2O2 exists as a metastable phase, which appears by some kinetic reason, although it is not a thermodynamically stable phase. This interpretation seems plausible in that Sr2Si2N2O2 has been synthesized from Si3N4 and there is no report of synthesis with SiO2 as a Si source.

Another interpretation is the possibility of an error in the DFT calculation of energy of SrSi2N2O2. According to Oeckler et al., SrSi2N2O2 belongs to the space group of P1 and there are four Sr atoms in a unit cell. Site occupancies of Sr are not one in the crystal, four Sr atoms are dispersed in eight sites—half of the sites have site occupancy of 0.8, and others have 0.2. This type of crystal is hard to calculate accurately because a large size supercell should be constructed to disperse Sr atoms in accordance with the actual distribution ratio. In addition, there are a numbers of possible configurations for placing Sr atoms at the sites and this requires determination of the minimum energy configuration as a prerequisite.

For these reasons, the structure was simplified so that in our simulations four major sites had 100% occupancy of Sr. If dispersion of Sr atoms, as in the real structure, lowers energy of the crystal, SrSi2N2O2 may be able to appear as a stable phase. We assumed that the energy of the real structure was less than that of the imaginary crystal used for the DFT calculation by ~2.5% and simulated the phase diagrams of CRN reactions at 1500 K (Fig. 8). SrSi2N2O2 appeared as a stable phase with this modification of energy (Fig. 8a−c). The new stability lines formed with appearance of SrSi2N2O2 are shown as dotted lines in Fig. 8. If the assumption reflects the actual situation, the original lines crossing with the new dotted lines must be eliminated from the phase diagrams. This simulation implies the possibility that a dispersed distribution of Sr atoms in the real structure makes the phase more stable than the imaginary structure used for the simulation. More investigation of crystal structure and energy calculation of SrSi2N2O2 would be necessary for the exact interpretation of SrSi2N2O2:Eu phosphor synthesis.

### 4 Experimental results and discussion

To confirm the simulation results experimentally, we prepared a mixed powder of SiO2 and SrCO3 in the molar ratio of Sr : Si = 2 : 3, which is the stoichiometric composition for synthesis of SrSi2N8, and examined the phases after firing at various conditions of atmosphere and temperature. Fig. 9a shows the XRD pattern of the powder fired at 1773 K under H2/N2 flow. The
Diffraction peaks were addressed to SiO$_2$, SrSiO$_3$, Sr$_2$SiO$_4$, and Sr$_2$Si$_2$N$_2$O$_2$ phases. This result agrees with the simulations presented in section 3.3 and the discussion of section 3.6 about Sr$_2$Si$_2$N$_2$O$_2$, which predicted SiO$_2$, and SrSiO$_3$, with or without Sr$_2$Si$_2$N$_2$O$_2$, may appear with HRN reactions. Detection of the Sr$_2$SiO$_4$ phase, which was the only disagreement, may be caused by regional nonhomogeneity of the composition with formation of Sr$_2$Si$_2$N$_2$O$_2$.

Fig. 8 Phase diagrams of Sr–Si–N–O system simulated for CRN conditions considering melting of Sr–Si compounds. Imaginary point and lines from the simulation assuming that energy of SrSi$_2$N$_2$O$_2$ is less than that of the calculated are also added as dotted lines. (a) 1400–1500 K, (b) 1600–1800 K, (c) 1900 K, (d) 2000 K, (e) 2100 K, and (f) 2200–2300 K.

Fig. 9b–d show XRD patterns of CRN reactions at 1673, 1773, and 1873 K, respectively. Diffraction peaks of SrSiO$_3$, SrSi$_2$N$_2$O$_2$, Si$_3$N$_4$, and SiO$_2$ were detected with firing at 1673 K (Fig. 9b). The simulated phase diagram (Fig. 8b) predicted Si$_3$N$_4$ and SrSiO$_3$ phases would appear stable for this condition because the temperature is not high enough to synthesize the nitride phase of Sr$_2$Si$_5$N$_8$. Except detection of a small amount of SiO$_2$, this remained supposedly because of partial incompleteness of the reaction, the XRD pattern in Fig. 9b shows good agreement with the previous calculations.

In the CRN reaction at 1773 K (Fig. 9c) mainly Sr$_2$Si$_5$N$_8$ was produced, with weak peaks from SrSiO$_3$ and a trace of Si$_3$N$_4$. This seems to be an intermediate state between Fig. 8b and c and thus shows good agreement with the simulations. In the previous sections we deferred the decision whether SrSi$_2$N$_2$O$_2$ is thermodynamically a stable phase or not. If it is, the broken lines in Fig. 8 would form a convex hull of stable phases, then Si$_3$N$_4$ and SrSi$_2$N$_2$O$_2$ would appear as the main impurity phases in CRN reaction at 1773 K because the composition of powder (Sr : Si = 2 : 5) becomes located in the area of Si$_3$N$_4$–SrSi$_2$N$_2$O$_2$–N. However, this did not happen, rather diffraction peaks from SrSiO$_3$ were observed in reality. Thus, SrSi$_2$N$_2$O$_2$ is not supposed to be a thermodynamically stable phase in the system.

Pure Sr$_2$Si$_3$N$_6$ phase could be obtained with firing at 1873 K (Fig. 9d), agreeing with the simulation, which predicted Sr$_2$Si$_3$N$_6$ stably exists on the phase diagram above 1850 K. Thus, all the experimental results of HRN and CRN reactions showed excellent agreement with the calculations with temperature.
errors of less than 100 K. Considering that general errors related to measurement of temperatures and deviations of temperature with positions in the furnace are dozens of K, it can be concluded that the simulation of this study provides useful information about the synthesis of Sr$_2$Si$_5$N$_8$ with good accuracy.

The type of impurity phases appearing with firing conditions also supported the reliability of our simulation. It was discussed from the simulation in section 3.5 that SrSiO$_3$ would appear as an impurity if the temperature of CRN reaction is not high enough, whereas Sr$_2$SiO$_4$ appears if the oxygen partial pressure is not sufficiently low even at high enough temperatures (Fig. 7). We reduced the amount of carbon for CRN reactions; the XRD patterns of the products are presented in Fig. 10. With a smaller amount of carbon, the Sr$_3$SiO$_9$ phase appeared mixed with Sr$_2$Si$_3$N$_8$ (Fig. 10b) because of the increased oxygen pressure as predicted from the calculations. Interestingly, when we used a cracked tube of the furnace accidentally, we also obtained Sr$_2$Si$_3$N$_8$ containing Sr$_2$SiO$_4$ impurity (Fig. 10c). The oxygen partial pressure may have increased with an inflow of outer air through the crevices. Fig. 9e shows an example of low temperature synthesis, in which SrSiO$_3$ appeared as an impurity. All these results again support the reliability of our simulation models and method.

Lastly, based on the simulation results we predicted that the Sr$_2$Si$_3$N$_8$:Eu phosphor could be synthesized via a CRN reaction using SiO$_2$ as a starting material instead of Si$_3$N$_4$, which is conventionally used (section 3.3). The experimental results are briefly presented in Fig. 11, and the details of synthetic conditions, optical properties, and other characteristics will be reported in a separate paper. Fig. 11a and b are photos of as-sintered Sr$_2$Si$_3$N$_8$:Eu powders from Si$_3$N$_4$ and SiO$_2$, respectively, both of them show the typical red body color of the Sr$_2$Si$_3$N$_8$:Eu phosphor. XRD patterns of products exactly matched with that of Sr$_2$Si$_3$N$_8$ phase, and the photoluminescent property of a strong red emission indicated that a Sr$_2$Si$_3$N$_8$:Eu phosphor of good quality was obtained (Fig. 11c). Thus, synthesis of Sr$_2$Si$_3$N$_8$:Eu phosphor using SiO$_2$ was predicted by first-principles calculations, and the possibility was confirmed through experiments. This is a good model which indicates that the simulation method of this study can be applied to nitride systems and be utilized as a useful tool for cost reduction by examining the potential application of cheap oxide raw materials.

5 Conclusion

Thermodynamic stabilities and phase diagrams of Sr-Si-N-O system compounds were simulated using a first-principles method based on DFT calculations. The system includes two kinds of gas species, nitrogen and oxygen, whose chemical potentials were determined from comparison between DFT calculations and thermochemical data reported by experiments so that they agree with each other. The chemical potentials were adjusted to reflect enthalpy and entropy changes with temperature and pressure for higher accuracy of simulations. We constructed phase diagrams for HRN and CRN conditions through the simulations and predicted synthetic conditions of nitride or oxonitride compounds.

The results implied that nitridosilicates appear as stable phases under CRN reaction conditions at elevated temperatures above 1800 K, while the HRN reaction is not suitable for the synthesis because of the high equilibrium partial pressure of oxygen. It was found that impurity phases appearing with Sr$_2$Si$_3$N$_8$ differ with synthetic conditions: a shortfall in reaction temperature generates SrSiO$_3$, while Sr$_2$SiO$_4$ appears with an increase in oxygen partial pressure. Si$_3$N$_4$ appeared stable at a
lower temperature than any other nitrides in our simulation, raising the possibility that nitride compounds, including Sr₂Si₂N₆:Eu phosphor, could be synthesized using SiO₂ as a starting raw material instead of costly Si₃N₄. We examined the expectations of these nitridation and oxidation reactions are involved complicatedly. These can be useful guidelines for the synthesis of compounds of this system. We expect that the first-principles methodology for a two-gas system established in our investigation may be effectively applied to other multi-gas systems.

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