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Supplementary Information

First-principles Thermodynamic Calculations and Experimental Investigation of Sr–Si–N–O System—Synthesis of $Sr_2Si_5N_8$:Eu Phosphor

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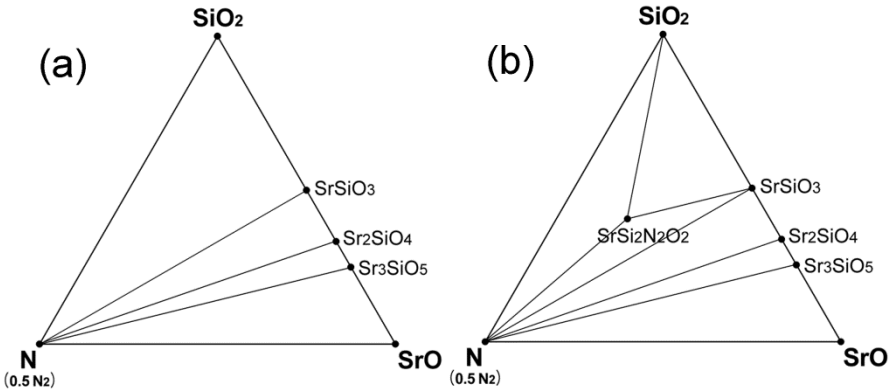
S1. Crystal structure and energy (eV/formula unit) of Sr–Si–N–O system compounds obtained by density functional theory calculation: the energy was used for simulation of phase diagrams.

Compounds	Space group	Energy (eV/fu)	Compounds	Space group	Energy
Sr_5Si_3	$I\,4/mcm$	-27.771	S_2N_2O	$I\,4_1/amd$	-39.705
SrSi	$Cmcm$	-8.096	SiO_2	$P\,6_3/mmc$	-23.691
SrSi	$Immm$	-7.919	SiO_2	$P6_222$	-23.701
$SrSi_2$	$I4_1/amd$	-13.820	SiO_2	$P3_121$	-23.704
$SrSi_2$	$P4_332$	-13.579	SrO_2	$I\,4/mmm$	-17.235
Sr_4Si_7	$I\,4_1/amd$	-48.319	SrO	$Fm\bar{3}m$	-12.093
Sr_2Si_3	$I\,4_1/amd$	-20.991	$SrSiO_3$	$P\bar{1}$	-37.000
SrN	$C\,2/m$	-11.067	$SrSiO_3$	$P\,2_1/c$	-36.913
SrN_2	$I\,4/mmm$	-19.836	$SrSiO_3$	$C\,2/c$	-37.094
Sr_2N	$R\bar{3}m$	-13.339	$Sr2SiO_4$	$Pmnb$	-49.729
SrN_6	$Fddd$	-52.992	Sr_3SiO	$Pbnm$	-22.066
Sr_3N_2	$Ia\bar{3}$	-24.256	SrN_2O_6	$Pa\bar{3}$	-57.976
Si_3N_4	$I\bar{4}3d$	-56.569	$SrSi_2O_5$	$Cmca$	-59.567
Si_3N_4	$P31c$	-57.267	$SrSi_2N_2O_2$	$P1$	-52.326
Si_3N_4	$Fd\bar{3}m$	-56.235	Sr_3SiO_5	$P\,4/ncc$	-61.837
$SrSiN_2$	$P\,2_1/c$	-28.488	$SrSi_6N_8O$	$Imn2$	-126.871
$SrSi_6N_8$	$Imm2$	-117.585			
$Sr_2Si_5N_8$	$Pmn2_1$	-114.978	Sr	$Fm\bar{3}m$	-1.682
$SrSi_7N_{10}$	Pc	-143.193	Si	$Fd\bar{3}m$	-5.425

S2. DFT calculation results of energy of Eu-doped compounds: doping amount of Eu, energy of Eu-doped compounds, and energy change of each compound with Eu-doping relative to those of the undoped.

	Eu/(Eu+Sr)	E (eV/fu)	$(E-E_{undoped})/E_{undoped}$
SrSi	1/16 (6.25 %)	-8.103	-0.093 %
$SrSi_2$	1/16 (6.25 %)	-13.684	+0.983 %
$SrSiO_3$ (Sr1)	1/12 (8.33 %)	-37.172	-0.212 %
$SrSiO_3$ (Sr2)	1/12 (8.33 %)	-37.171	-0.208 %
Sr_2SiO_4 (Sr1)	1/16 (6.25 %)	-49.850	-0.242 %
Sr_2SiO_4 (Sr2)	1/16 (6.25 %)	-49.873	-0.288 %
$SrSiN_2$	1/16 (6.25 %)	-28.545	-0.203 %
SrO	1/32 (3.13 %)	-12.131	-0.312 %
$Sr_2Si_5N_8$ (Sr1)	1/8 (12.5 %)	-115.212	-0.203 %
$Sr_2Si_5N_8$ (Sr2)	1/8 (12.5 %)	-115.208	-0.200 %
$SrSi_6N_8$ (Sr1)	1/4 (25.0 %)	-117.732	-0.125 %
$SrSi_6N_8$ (Sr2)	1/8 (12.5 %)	-117.657	-0.061 %

S3. Change of phase diagrams with different energy values of $SrSi_2N_2O_2$: (a) It is assumed that Sr atoms are not dispersed over different sites but occupies only one type of crystallographic site. This is a simplification for DFT calculation, but it was reported that Sr occupies two sites (with 80:20 ratio). The dispersion may appear because it is energetically more favorable. If we assume actual energy of $SrSi_2N_2O_2$ is about 92% of the calculated energy and simulate phase diagram using this value, $SrSi_2N_2O_2$ appeared as a thermodynamic stable phase, as shown in (b). (both of the diagrams are simulated at 1500K under HRN condition.)



S4. Chemical potential of oxygen: the 0 K chemical potential was determined from combination of formation enthalpies of various metal oxides and DFT-calculated energies, as discussed in the manuscript. The effects of temperature and pressure were reflected based on the data in JANAF thermochemical tables using the following equation:

$$\mu_{O_2}(T,P) = H^o(T) - TS^o(T) + k_B T \ln\frac{P}{P^o}$$

We present chemical potential of oxygen at p_{O_2}= 0.1 MPa and 0.02MPa in the following table as an example.

T (K)	μ_{O_2}(eV)	
	p_{O_2}= 0.1 MPa	p_{O_2}= 0.02 MPa
0	-8.450	-8.450
100	-8.585	-8.599
200	-8.763	-8.790
298	-8.952	-8.993
300	-8.956	-8.997
400	-9.158	-9.214
500	-9.368	-9.437
600	-9.583	-9.666
700	-9.803	-9.900
800	-10.028	-10.138
900	-10.256	-10.381
1000	-10.488	-10.627
1100	-10.724	-10.877
1200	-10.963	-11.130
1300	-11.205	-11.386
1400	-11.450	-11.644
1500	-11.698	-11.906
1600	-11.948	-12.170
1700	-12.200	-12.436
1800	-12.455	-12.704
1900	-12.711	-12.975
2000	-12.970	-13.247

S5. Chemical potential of nitrogen gas, which is calculated in the same manner with that of oxygen shown in S4.

T (K)	μ_{N_2} (eV)	
	p_{N_2} = 0.1 MPa	p_{N_2} = 0.08 MPa
0	-16.050	-16.050
100	-16.186	-16.187
200	-16.363	-16.366
298	-16.552	-16.557
300	-16.556	-16.561
400	-16.759	-16.767
500	-16.970	-16.979
600	-17.187	-17.198
700	-17.409	-17.422
800	-17.636	-17.651
900	-17.867	-17.884
1000	-18.101	-18.121
1100	-18.340	-18.361
1200	-18.581	-18.604
1300	-18.825	-18.850
1400	-19.072	-19.098
1500	-19.321	-19.350
1600	-19.573	-19.603
1700	-19.827	-19.859
1800	-20.083	-20.117
1900	-20.341	-20.378
2000	-20.601	-20.640