



Electronic, optical and mechanical properties of SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ via first-principles

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The different properties of two structurally similar nitridosilicates, SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$, are attributed to the oxygen atom. To explore the effects of the O atom on the properties, structural, electronic, optical and mechanical properties of SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$ and O-doped SrSi_6N_8 have been simulated via first-principles in this work. The results indicate the Si–O–Si bond is stronger than the Si–Si bond, resulting in a more stable crystal structure of $\text{SrSi}_6\text{N}_8\text{O}$ compared with SrSi_6N_8 . The calculated bandgaps (E_g) of SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ are 3.10 and 3.97 eV, respectively. The lower E_g of SrSi_6N_8 originates from the Si–Si σ^* bond, however, the E_g can be enlarged through introducing the O atom into the Si–Si bond. The optical properties illustrate that the refractive peaks are blue-shifted with O doping into the lattice of SrSi_6N_8 . Furthermore, the elastic properties show that SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ are comparable to traditional mechanical ceramics such as sialons. This work not only expounds the difference between SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$, but also gives theoretical foundation for their potential applications as optical and mechanical materials.

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1. Introduction

Nitridosilicates doped with active ions (such as Eu^{2+} and Ce^{3+}) have been widely used as phosphors in phosphor-converted light emitting diodes (pc-LEDs) in consideration of their high chemical and thermal stability in combination with low thermal quenching and high conversion efficiencies.^{1–3} Compared to traditional phosphors such as orthosilicates (*e.g.* $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$)⁴ or alkaline earth sulfides (*e.g.* $\text{SrCa}_2\text{S}_4:\text{Eu}^{2+}$),⁵ nitridosilicates have more diversiform crystal structures owing to their more varied crosslinking patterns.⁶ In nitridosilicates, the N can connect up to four neighboring Si tetrahedral centers, causing a higher degree of lattice condensation to improve the chemical stability of nitride phosphors, preventing the hydrolysis reaction which often happens in phosphors with terminal or ionic O or S atoms over time.^{7,8}

In the last few years, research into rare earth metals activating alkaline-earth-metal nitridosilicates-based phosphors has become increasingly important, such as MSi_6N_8 ($\text{M} = \text{Sr}$ and Ba),^{9,10} $\text{MSi}_7\text{N}_{10}$ ($\text{M} = \text{Sr}$, Ba),^{11,12} $\text{M}_2\text{Si}_5\text{N}_8$ ($\text{M} = \text{Ca}$, Sr and Ba),^{13–15} MSiN_2 ($\text{M} = \text{Sr}$, Ba),¹⁶ and $\text{Ba}_3\text{Si}_2\text{N}_6$.¹⁷ Among the available alkaline earth nitridosilicates-based phosphors, SrSi_6N_8 is very different from the others. For example, the oxidation states of Si are +III and +IV in SrSi_6N_8 , and the framework contains single Si–Si bonds in $\text{N}_3\text{Si–SiN}_3$,⁹ as seen in Fig. 1(a). Also, $\text{SrSi}_6\text{N}_8:\text{Eu}^{2+}$ was reported to have blue

luminescent property of 450–455 nm,^{18,19} while most of nitridosilicates-based phosphors emitted yellow to red wavelengths. Besides, because of the structural similarity compared with MSi_6N_8 , $\text{MSi}_6\text{N}_8\text{O}$ ($\text{M} = \text{Ca}$ and Ba) based material has also been reported to have excellent luminescent properties. Fig. 1(b) shows the crystal structure of $\text{SrSi}_6\text{N}_8\text{O}$, which can be gained by inserting one O atom into the single Si–Si bond in SrSi_6N_8 .⁹ Although there is no experimental report of the preparation of pure $\text{SrSi}_6\text{N}_8\text{O}$, the compound of $\text{Sr}_2\text{Si}_{12-x}\text{Al}_x\text{N}_{16-x}\text{O}_{2+x}:\text{Eu}^{2+}$ ($x \approx 2$) has been synthesized by Z Shen.²⁰ $\text{Sr}_2\text{Si}_{12-x}\text{Al}_x\text{N}_{16-x}\text{O}_{2+x}$ exhibits an isotypic structure compared with $\text{SrSi}_6\text{N}_8\text{O}$, therefore the analogous silicon atoms are also bridged by oxygen atoms. Also, the photoluminescence properties of Eu activating $\text{CaSi}_6\text{N}_8\text{O}$ and $\text{BaSi}_6\text{N}_8\text{O}$ have been studied experimentally. The reported main photoluminescent peaks are at about 500 nm for $\text{BaSi}_6\text{N}_8\text{O}:\text{Eu}^{2+}$,^{21,22} 614 and 587 nm for $\text{BaSi}_6\text{N}_8\text{O}:\text{Eu}^{3+}$,²³ and 405 nm for $\text{CaSi}_6\text{N}_8\text{O}:\text{Eu}^{2+}$.²⁴ Furthermore, some alkaline-earth-metal nitridosilicates have been reported to have excellent mechanical properties. For instance, $\text{SrSi}_7\text{N}_{10}$ has a yield hardness of 16.1(5) GPa,¹¹ and CaAlSiN_3 has been considered as a relatively hard materials from first-principles simulation.²⁵ However, even SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ have been investigated a lot in previous works, there is almost no paper having reported their basic characteristics such as electronic, optical and mechanical properties. In order to take full advantage of the properties of SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ for eventual technological applications, a better understanding of their electronic, optical and mechanical properties is required. What's more, the photoluminescence peaks of intrinsic and O-replacement defective SrSi_6N_8 have been reported by Wen Yeh *et al.* to locate at 452 and 652 nm,

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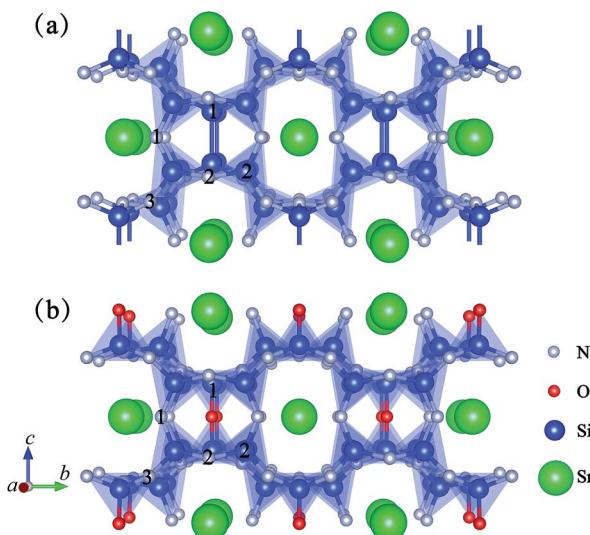


Fig. 1 Projective representation of $2 \times 2 \times 1$ supercells of (a) SrSi_6N_8 and (b) $\text{SrSi}_6\text{N}_8\text{O}$.

respectively.²⁶ The results show that the oxygen atom has significant effect on electronic and optical properties of SrSi_6N_8 . Actually, nitrogen-rich sialon materials, with partial substitutions of Si by Al and N by O, have attracted great interest owing to their excellent optical and mechanical performance.³ The ratio of O : N has the significant effect on the properties of sialon materials. So introducing the O atom into the lattice of SrSi_6N_8 may generate positive effects on electronic, optical and mechanical properties. Considering that the big difference between SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ is the O atom, investigating the effect of O atom on SrSi_6N_8 may also give some ideas to understand the difference in their properties.

Herein, in this work, first-principles calculations^{27–29} have been used to investigate the electronic, optical and mechanical properties of SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$, and O-doped SrSi_6N_8 . On the one hand, this work has given the comparison and explanation of the difference between SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ in electronic, optical and mechanical properties. On the other hand, the effects of O atom on SrSi_6N_8 have also been investigated through introducing O atoms to replace different N atoms and to insert into the single Si–Si bond. This work not only explains the difference between SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$, but also gives the theoretical foundation for their potential applications.

2. Theoretical and computational methods

Fig. 1 shows the crystal structures of $2 \times 2 \times 1$ SrSi_6N_8 and $2 \times 2 \times 1$ $\text{SrSi}_6\text{N}_8\text{O}$ supercells. As seen in Fig. 1(a), there are two types of connectivity models of N atoms, which are bonded with two Si atoms (marked as $\text{N}^{[2]}$) and three Si atoms (marked as $\text{N}^{[3]}$). And the spatial locations of Si–N^[3]–Si bonds are vertical and with a certain angle to the b axis.⁹ So, we marked the $\text{N}^{[2]}$ as N_1 , the two N atoms in the different Si–N^[3]–Si bonds as N_2 and N_3 , the Si atoms in the Si–Si bonds as Si_1 , and the other Si atoms as

Si_2 , as seen in Fig. 1(a). Herein, four types of O-doped $2 \times 2 \times 1$ SrSi_6N_8 supercells were considered in our work, which were O_i substituting to N_i ($i = 1, 2$ and 3) and O_4 inserting into the Si–Si bond, and marked as $\text{O}_i\text{–SrSi}_6\text{N}_8$ ($i = 1, 2, 3$ and 4), respectively.

All first principle calculations were performed using Cambridge Serial Total Energy Package (CASTEP) code.²⁹ The electronic exchange–correlation function was Perdew Burke Ernzerhof (PBE) of generalized gradient approximation (GGA).³⁰ Ultrasoft pseudopotentials were used with $5s^2\ 5p^0, 3s^2\ 3p^2, 2s^2\ 2p^3$ and $2s^2\ 2p^4$ as the valence-electron configurations for Sr, Si, N and O atoms, respectively, to describe the interactions between ions and electrons.³¹ With convergence testing, the plane-wave cutoff energy of 400 eV and k -point meshes of $3 \times 2 \times 3$ were used to ensure the accuracy and efficiency of calculations. The threshold for self-consistent field iterations was 5.0×10^{-7} eV per atom. The convergence tolerance parameters of optimized calculation were the energy of 1.0×10^{-5} eV per atom, the maximum force of 0.03 eV \AA^{-1} , the maximum inner stress of 0.05 GPa and the maximum displacement of 1.0×10^{-4} nm. After finishing geometry optimizations, electronic, optical and mechanical properties of all models were calculated. The lattice stabilities of all the optimized structures were evaluated by the phonon dispersions, where the imaginary frequency was the sign of lattice instability.^{32,33}

Considering no experimental report of the preparation of pure $\text{SrSi}_6\text{N}_8\text{O}$, we used the acid–base idea as mentioned by M. Mikami³⁴ to assume the solid-state reaction for production of $\text{SrSi}_6\text{N}_8\text{O}$. The binary oxide is generally considered as acid while binary nitride as base. So the reaction for production of $\text{SrSi}_6\text{N}_8\text{O}$ should be defined as following:



The formation energy (E_{form}) of reaction [1] was calculated as following equation:

$$E_{\text{form}} = E_{\text{SrSi}_6\text{N}_8\text{O}} - E_{\text{SrO}} - 2E_{\text{Si}_3\text{N}_4} \quad (1)$$

where the $E_{\text{SrSi}_6\text{N}_8\text{O}}$, E_{SrO} and $E_{\text{Si}_3\text{N}_4}$ were the total energies of $\text{SrSi}_6\text{N}_8\text{O}$, SrO and $\alpha\text{-Si}_3\text{N}_4$, respectively. A negative value of formation energy indicates the reaction is exothermic and the production is stable.

The binding energy (E_b) can be used to investigate the relative stability of the model. The value of binding energies of all models were calculated by the following formula:³⁵

$$E_b = \frac{E_{\text{tot}} - (n_{\text{Si}}\mu_{\text{Si}} + n_{\text{N}}\mu_{\text{N}} + n_{\text{O}}\mu_{\text{O}})}{n_{\text{Si}} + n_{\text{N}} + n_{\text{O}}} \quad (2)$$

where the E_{tot} was the total energy of the considered model, and the chemical potentials of Si, N and O were defined as $\mu_{\text{Si}} = \mu_{\text{bulk-Si}}$, $\mu_{\text{N}} = \mu_{\text{N}_2}/2$ and $\mu_{\text{O}} = \mu_{\text{O}_2}/2$, respectively.^{36,37} The coefficients n_{Si} , n_{N} and n_{O} were the numbers of the Si, N and O atoms in each model. For O-doped SrSi_6N_8 models, the values of bonding energies were used to predict the preferential position for O doping in the lattice of SrSi_6N_8 .

Understanding elastic properties of nitridosilicates is very important for their application and improvement. For



orthorhombic crystals, it is known that the mechanical stability requires elastic constants satisfying the following conditions:^{38,39}

$$\begin{aligned} c_{ij} &> 0 \quad (i=1\sim 6), \\ c_{11} + c_{22} + c_{33} + 2c_{12} + 2c_{13} + 2c_{23} &> 0, \\ c_{11} + c_{22} - 2c_{12} &> 0, \\ c_{11} + c_{33} - 2c_{13} &> 0, \\ c_{22} + c_{33} - 2c_{23} &> 0 \end{aligned} \quad (3)$$

The mechanical constants: bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) have been calculated using the following equations:^{38,39}

$$B = (1/9)(c_{11} + c_{22} + c_{33} + 2c_{12} + 2c_{13} + 2c_{23}) \quad (4)$$

$$G = (1/15)[(c_{11} + c_{22} + c_{33} + 3(c_{44} + c_{55} + c_{66}) - c_{12} - c_{13} - c_{23})] \quad (5)$$

$$E = 9BG/(3B + G) \quad (6)$$

$$\nu = (1/2)(3B - 2G)/(3B + G) \quad (7)$$

3. Results and discussion

3.1 Geometry optimization results

Table 1 lists the calculated lattice parameters, average bond lengths and binding energies of all models. The lattice parameters of $2 \times 2 \times 1$ SrSi_6N_8 and $2 \times 2 \times 1$ $\text{SrSi}_6\text{N}_8\text{O}$ supercells are well agreement with previous results.^{9,24} There is no big change in the lattice parameters after O doping into SrSi_6N_8 . The slight volume expansions come from the changes of local bond lengths. The average bond lengths of $\text{Si}-\text{O}^{[2]}$ and $\text{Si}-\text{O}^{[3]}$ are larger than the $\text{Si}-\text{N}^{[2]}$ and $\text{Si}-\text{N}^{[3]}$ in $\text{O}_i\text{-SrSi}_6\text{N}_8$ ($i = 1, 2$ and 3), while the average bond length of $\text{Si}-\text{O}^{[2]}$ is smaller than the $\text{Si}-\text{N}^{[2]}$ in $\text{O}_4\text{-SrSi}_6\text{N}_8$. The results indicate that different coordination environments of O atom has different effects on the

$\text{Si}-\text{O}$ bond lengths. The E_{form} of pure $\text{SrSi}_6\text{N}_8\text{O}$ calculated by eqn (1) is -0.37 eV, which indicates that the reaction [1] is somewhat exothermic and $\text{SrSi}_6\text{N}_8\text{O}$ is stable. The lower value of E_b indicates the more stable degree of the model. The E_b (-1.71 eV) of $\text{SrSi}_6\text{N}_8\text{O}$ means that it has the more stable crystal structure and can be easier to synthesis compared with SrSi_6N_8 (-1.40 eV). These phenomenon is corresponding to the fact that SrSi_6N_8 is a kind of reduced nitridosilicate and must be synthesized under the condition of extreme lack of oxygen.⁹ The E_b of $\text{O}_4\text{-SrSi}_6\text{N}_8$ (-1.45 eV) is the lowest one among all O-doped SrSi_6N_8 models, meaning that O atom prefers to insert into the single Si-Si bond to stabilize the crystal structure of SrSi_6N_8 .

Furthermore, phonon dispersions of all optimized models have been calculated to evaluate the structural stability, as seen in Fig. 2. The results shows that there is no imaginary frequency of pure SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$, which means that SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ are structurally stable. The lowest frequencies of $\text{O}_i\text{-SrSi}_6\text{N}_8$ ($i = 1, 2, 3$ and 4) are $-0.20, -0.81, -0.53$ and -0.05 THz, respectively. According to the previous works, the small negative frequencies of $\text{O}_1\text{-SrSi}_6\text{N}_8$ and $\text{O}_4\text{-SrSi}_6\text{N}_8$ could be ignored because the small negative frequencies may be caused by the relatively smaller supercells and lower computational accuracies.^{32,33} However, the calculation of phonon dispersion is time consuming with a bigger supercell and higher computational accuracy. So we think it is reasonable to consider $\text{O}_1\text{-SrSi}_6\text{N}_8$ and $\text{O}_4\text{-SrSi}_6\text{N}_8$ as structurally stable models based on the calculated phonon dispersions. While, the structures of $\text{O}_2\text{-SrSi}_6\text{N}_8$ and $\text{O}_3\text{-SrSi}_6\text{N}_8$ are metastable or unstable according to their obvious imaginary frequencies as seen in Fig. 2(d) and (e). The results of phonon dispersions are well agreement with the results of bonding energies (E_b), which means that the structures of $\text{O}_1\text{-SrSi}_6\text{N}_8$ and $\text{O}_4\text{-SrSi}_6\text{N}_8$ are more stable than $\text{O}_2\text{-SrSi}_6\text{N}_8$ and $\text{O}_3\text{-SrSi}_6\text{N}_8$.

3.2 Electronic properties

Fig. 3 shows the band structures and partial density of states (PDOS) of SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$. The calculated bandgaps (E_g) of SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ are 3.10 and 3.97 eV, respectively. Although, there is no experimentally reported the E_g of SrSi_6N_8

Table 1 Optimized lattice parameters, bond lengths and binding energies of all models

Models	Lattice parameters (Å)			Volume (Å ³)	Average bond length (Å)					E_b (eV)
	a	b	c		Si-N ^[2]	Si-N ^[3]	Si-Si	Si-O ^[2]	Si-O ^[3]	
SrSi_6N_8	9.664	15.854	9.331	1429.56	1.679	1.755	2.379			-1.40
$\text{SrSi}_6\text{N}_8^a$	4.801	7.855	9.260	349.21			2.352			
$\text{SrSi}_6\text{N}_8^b$	4.803	7.836	9.261	350.93						
$\text{O}_1\text{-SrSi}_6\text{N}_8$	9.682	15.897	9.302	1431.80	1.680	1.757	2.367	1.688		-1.43
$\text{O}_2\text{-SrSi}_6\text{N}_8$	9.679	15.869	9.331	1433.13	1.678	1.757	2.370		1.850	-1.42
$\text{O}_3\text{-SrSi}_6\text{N}_8$	9.670	15.890	9.320	1432.10	1.679	1.757	2.370		1.811	-1.42
$\text{O}_4\text{-SrSi}_6\text{N}_8$	9.673	15.939	9.400	1449.29	1.681	1.756	2.406	1.589		-1.45
$\text{SrSi}_6\text{N}_8\text{O}$	9.722	16.400	9.706	1547.62	1.683	1.752		1.620		-1.71
$\text{SrSi}_6\text{N}_8\text{O}^a$	4.865	8.206	9.721							

^a Ref. 9. ^b Ref. 19.



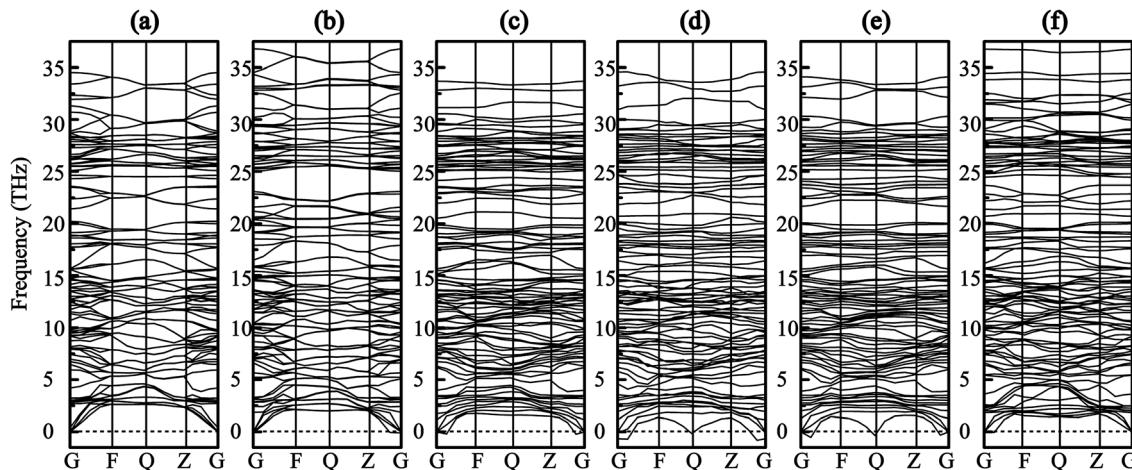


Fig. 2 Phonon dispersion curves (a) SrSi_6N_8 , (b) $\text{SrSi}_6\text{N}_8\text{O}$, (c) $\text{O}_1\text{-SrSi}_6\text{N}_8$, (d) $\text{O}_2\text{-SrSi}_6\text{N}_8$, (e) $\text{O}_3\text{-SrSi}_6\text{N}_8$ and (f) $\text{O}_4\text{-SrSi}_6\text{N}_8$.

or $\text{SrSi}_6\text{N}_8\text{O}$, our GGA calculated E_g are expected to be smaller than experimental values since the underestimation of GGA calculation.³⁹ While the effects of oxygen on electronic

properties of SrSi_6N_8 can be expounded through the relative changes. The top of valence bands of SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ are occupied by N 2p states. Differing in band structures from the other alkaline-earth-metal nitridosilicates,⁶ there are some energy levels below the conduction bands of SrSi_6N_8 , which are mainly constituted of Si 3p states as seen from the PDOS. Furthermore, the 3p states of Si_1 contribute the more parts of the bottom of conduction bands compared to Si_2 , which indicates that the energy levels below the conduction bands are attributed to the single Si–Si bond. The previous works reported that Si–Si bond forms an empty σ^* state under the bottom of conduction bands in some nitrides.^{40,41} Therefore, the Si–Si σ^* state is the main reason for the lower bandgap of SrSi_6N_8 compared to $\text{SrSi}_6\text{N}_8\text{O}$.

Furthermore, the electron density distribution (EDD) plots are calculated to investigate the difference between Si–Si and Si–O–Si bonds. Fig. 4(a) and (b) illustrate the partial atom distributions and corresponding EDD plots on the (010) plane of SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$, respectively. We can find that there is

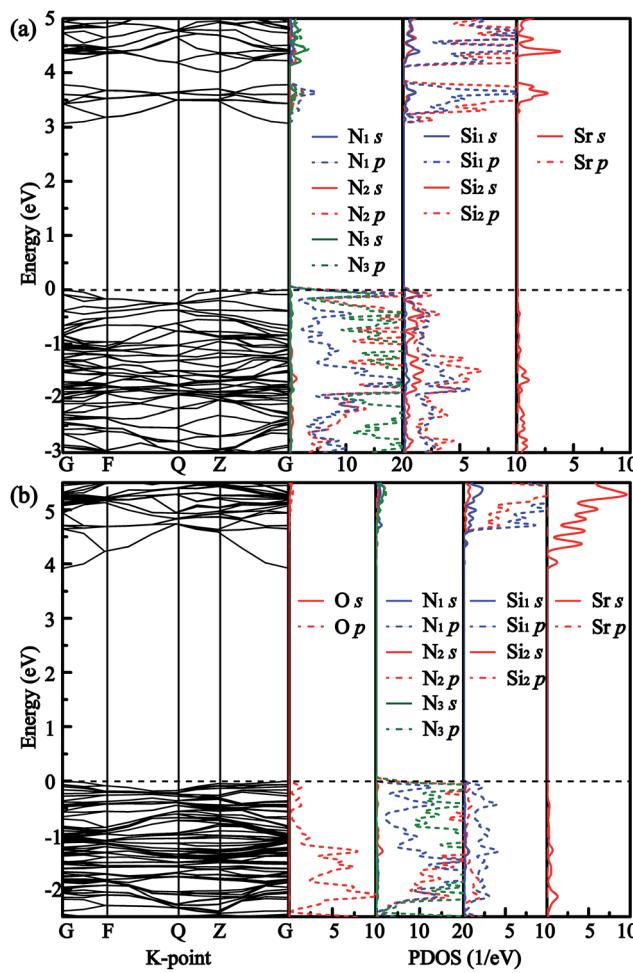


Fig. 3 Band structures and partial density of states (PDOS) of (a) SrSi_6N_8 and (b) $\text{SrSi}_6\text{N}_8\text{O}$.

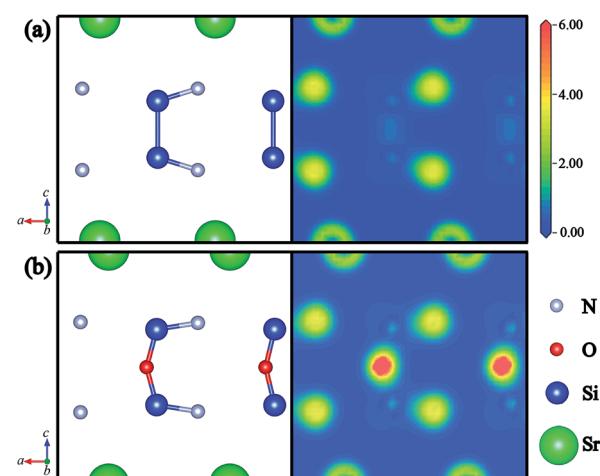


Fig. 4 Partial atom distributions and corresponding electron density distribution plots of (a) SrSi_6N_8 and (b) $\text{SrSi}_6\text{N}_8\text{O}$ on the (010) plane.

a small amount of electron density distributing in the center of Si–Si bond in SrSi_6N_8 , while a high density of electron gathers on the O atoms in $\text{SrSi}_6\text{N}_8\text{O}$. The stronger electronic interaction of Si–O–Si bond gives the more stable crystal structure for $\text{SrSi}_6\text{N}_8\text{O}$, which is consistent with results of the calculated E_b . Besides, the electron densities of O atoms are obviously higher than that of N atoms in $\text{SrSi}_6\text{N}_8\text{O}$, which is attributed to the stronger electronegativity of O atom.

The calculated band structures and PDOS of the O atoms and its adjacent Si atoms for all O-doped SrSi_6N_8 models are plotted in Fig. 5. The calculated bandgaps (E_g) of $\text{O}_i\text{-SrSi}_6\text{N}_8$ ($i = 1, 2, 3$ and 4) are 3.17, 2.84, 3.09 and 3.33 eV, respectively. For $\text{O}_1\text{-SrSi}_6\text{N}_8$, as seen in Fig. 5(a), the band structure of $\text{O}_1\text{-SrSi}_6\text{N}_8$ is very close to that of undoped SrSi_6N_8 , which indicates that the O^[2] has the similar properties of N^[2]. As seen in Fig. 5(b) and (c), the reason of the E_g decreasing for $\text{O}_2\text{-SrSi}_6\text{N}_8$ and $\text{O}_3\text{-SrSi}_6\text{N}_8$ is that the hybrid Si–O bonds generate energy levels under the conduction bands. For $\text{O}_4\text{-SrSi}_6\text{N}_8$, the distribution of O 2p states are very similar to that of $\text{SrSi}_6\text{N}_8\text{O}$, showing that the O₄ atom has the same character to the O atoms in $\text{SrSi}_6\text{N}_8\text{O}$. The E_g of $\text{O}_4\text{-SrSi}_6\text{N}_8$ is larger than that of SrSi_6N_8 , which indicates that inserting O atom into the single Si–Si bond to decrease the concentration of Si–Si bonds can increase the E_g .

3.3 Optical properties

The absorption coefficient is one of key parameters to evaluate the performance for phosphors. The absorption spectra can be described in terms of time-dependent perturbations of the ground-state electronic states, which has always been investigated combined the electron transition between valance bonds

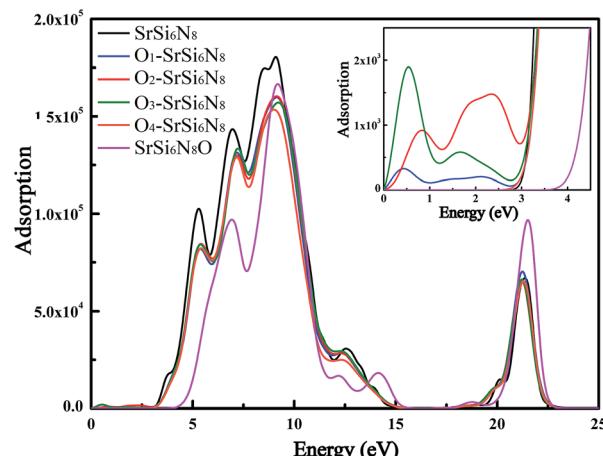


Fig. 6 Calculated absorption spectra of SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$ and O-doped SrSi_6N_8 models.

and conduction bonds.⁴² Fig. 6 shows the calculated absorption spectra of all models. The absorption peak for undoped SrSi_6N_8 is located at about 3.0–15.0 eV, which are corresponding to the electron transitions from N 2p states in the valence bands to Si 3p and Sr 5s states in the conduction bands as shown from PDOS in Fig. 3(a). The absorption edge of $\text{SrSi}_6\text{N}_8\text{O}$ starts at 3.9 eV, with a large blue shift compared to that of SrSi_6N_8 at 2.9 eV. The positions of the main absorption peaks for $\text{O}_i\text{-SrSi}_6\text{N}_8$ ($i = 1, 2, 3$ and 4) are almost the same as SrSi_6N_8 , while the absorption intensities become lower. Besides, as shown in the enlarged view in Fig. 5, the weak peaks located around 0–3.0 eV of the $\text{O}_2\text{-SrSi}_6\text{N}_8$ and $\text{O}_3\text{-SrSi}_6\text{N}_8$ derive from the electron

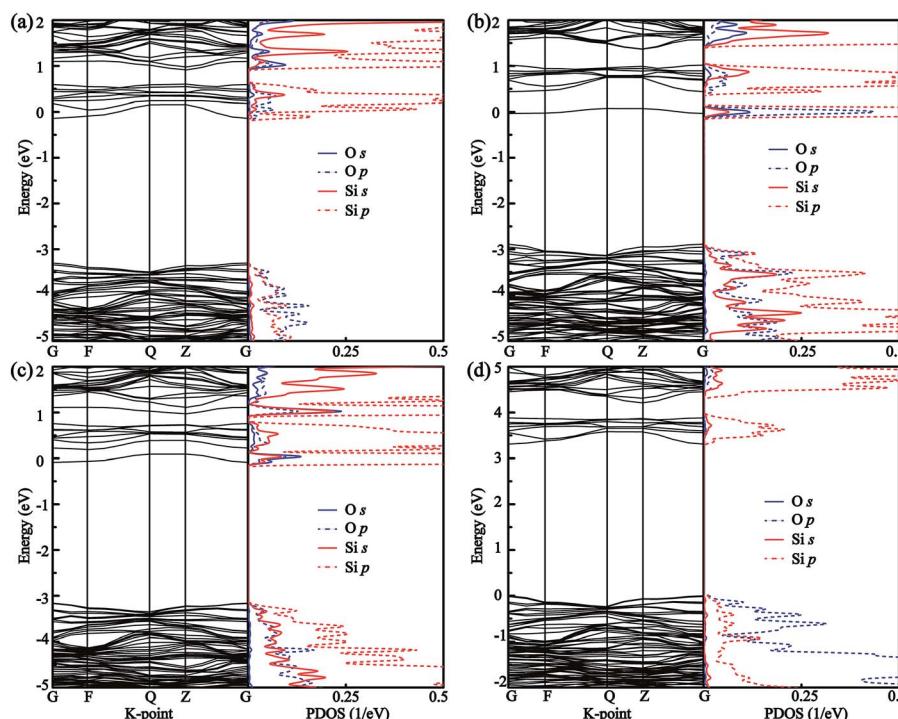


Fig. 5 Band structures and PDOS of (a) $\text{O}_1\text{-SrSi}_6\text{N}_8$, (b) $\text{O}_2\text{-SrSi}_6\text{N}_8$, (c) $\text{O}_3\text{-SrSi}_6\text{N}_8$, and (d) $\text{O}_4\text{-SrSi}_6\text{N}_8$.



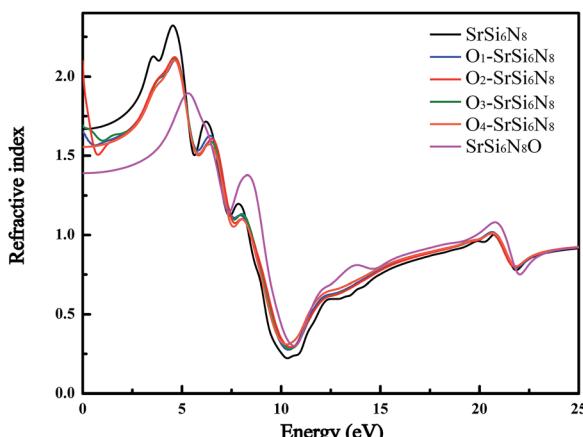


Fig. 7 Calculated refractive spectra of SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$ and O-doped SrSi_6N_8 models.

transitions between Si–O hybrid states under the bottom of conduction bands and conduction bands, as shown in Fig. 5(b) and (c).

Fig. 7 shows the refractive spectra of SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$ and O-doped SrSi_6N_8 models. Although, there is no experimentally reported refractive index (n) of SrSi_6N_8 or $\text{SrSi}_6\text{N}_8\text{O}$, the static refractive indexes (n_0) of SrSi_6N_8 (1.67) and $\text{SrSi}_6\text{N}_8\text{O}$ (1.39) are expected to be lower than the experimental value due to the underestimated calculation of GGA-PBE.³⁹ Nevertheless, the relative changes can reflect the effects of O atoms on SrSi_6N_8 . The calculated static refractive indexes of $\text{O}_i\text{-SrSi}_6\text{N}_8$ ($i = 1, 2$ and 3 and 4) are 1.65, 2.08, 1.69 and 1.56, respectively, which are well corresponding to Moss rule that the static refractive index is inversely proportional to the E_g .⁴³ Except for the static refractive indexes, the main peaks of refractive indexes of all O-doped SrSi_6N_8 models are lower than that of SrSi_6N_8 . Furthermore, compared with SrSi_6N_8 , the locations of main peaks for $\text{SrSi}_6\text{N}_8\text{O}$ are significantly blue-shift. The results of optical properties show that different doping sites of O atoms in SrSi_6N_8 have different effects on its basic absorption and refractive spectra.

3.4 Mechanical properties

The optimized structures of all models have been applied to calculate the elastic tensors which consist of nine independent components, as tabulated in Table 2. It can be seen that the relationships of elastic constants satisfy the conditions as shown in eqn (3), which indicates that SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$ and O-doped SrSi_6N_8 are mechanically stable.

Table 2 Calculated elastic tensor C_{ij} (GPa) for all models

Models	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
SrSi_6N_8	380.08	308.27	341.91	94.79	81.51	131.64	91.21	84.21	101.08
$\text{O}_1\text{-SrSi}_6\text{N}_8$	272.6	288.96	349.77	76.14	120.84	85.98	88.23	68.13	65.22
$\text{O}_2\text{-SrSi}_6\text{N}_8$	326.66	320.01	376.75	89.42	148.04	96.83	102.69	95.72	77.35
$\text{O}_3\text{-SrSi}_6\text{N}_8$	308.17	332.72	378.19	83.16	133.37	96.20	100.24	94.78	79.93
$\text{O}_4\text{-SrSi}_6\text{N}_8$	299.77	320.38	371.85	81.32	135.48	96.61	99.14	96.71	77.35
$\text{SrSi}_6\text{N}_8\text{O}$	324.25	377.85	374.25	92.30	67.54	142.86	85.77	71.16	119.8

Table 3 Calculated bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa) and Poisson's ratio ν for all models

Models	B	G	E	ν
SrSi_6N_8	175.92	111.84	276.85	0.24
$\text{O}_1\text{-SrSi}_6\text{N}_8$	150.5	102.58	250.77	0.22
$\text{O}_2\text{-SrSi}_6\text{N}_8$	174.99	116.7	286.43	0.23
$\text{O}_3\text{-SrSi}_6\text{N}_8$	174.33	112.15	277.04	0.24
$\text{O}_4\text{-SrSi}_6\text{N}_8$	170.93	100.6	252.30	0.25
$\text{SrSi}_6\text{N}_8\text{O}$	181.09	113.85	282.37	0.24

Furthermore, the mechanical constants: bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) for all models are listed in Table 3. The mechanical constants: B , G and E of $\text{SrSi}_6\text{N}_8\text{O}$ are larger than that of SrSi_6N_8 , which mainly attributes to the more stable Si–O–Si bond than Si–Si bond. Though introducing O atom produces a certain degree of lattice distortion in SrSi_6N_8 , there is no obvious deterioration on mechanical properties of O-doped SrSi_6N_8 compared to undoped SrSi_6N_8 , even some mechanical constants are improved. Besides, with the comparison of traditionally mechanical ceramics such as sialons ($B = 170\text{--}240$ GPa, $G = 118.84$ GPa and $E = 197\text{--}283$ GPa),^{44,45} the mechanical properties of all models considered in this work indicate that they have the application prospect for mechanical ceramics.

4. Conclusions

In this work, first-principles simulation has been performed to investigate the structural, electronic, optical and mechanical properties of SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$ and O-doped SrSi_6N_8 . Firstly, this work has given the comparison and explanation of the difference between the two structurally similar nitridosilicates SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$. The results show that $\text{SrSi}_6\text{N}_8\text{O}$ is more stable than SrSi_6N_8 , and the E_g of $\text{SrSi}_6\text{N}_8\text{O}$ is larger than that of SrSi_6N_8 . The key factor of the difference between SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$ is the O atom. Namely, the Si–O–Si bond is stronger than the single Si–Si bond, which contributes to the more stable crystal structure of $\text{SrSi}_6\text{N}_8\text{O}$. And the Si–Si σ^* states under the conduction bonds are the main reason for the smaller E_g of SrSi_6N_8 compared to $\text{SrSi}_6\text{N}_8\text{O}$.

Secondly, the effects of O on electronic, optical and mechanical properties of SrSi_6N_8 have been investigated systematically. The crystal structure of SrSi_6N_8 can be stabilized with doping O into the lattice and the most preferential doping position of O is



insertion between the single Si-Si bonds. And introducing O into the Si-Si bond can significantly increase the E_g of SrSi_6N_8 . The static refractive indexes become larger for O substituting to N models while become smaller for the O insert into the Si-Si bond. Besides, the calculated mechanical constants are comparable to traditionally mechanical ceramics such as sialons, which indicates SrSi_6N_8 , $\text{SrSi}_6\text{N}_8\text{O}$ and O-doped SrSi_6N_8 have potential applications as mechanical materials. This work is helpful to understand the difference between SrSi_6N_8 and $\text{SrSi}_6\text{N}_8\text{O}$, and opens up their possibility of new application.

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