For systematical first-principles studies and preliminary experiments, a classical and important (Si, Ge)$_2$N$_2$O (or Si$_{2-x}$Ge$_x$N$_2$O, $0 \leq x \leq 2$) system is predicted to have strong nonlinear optical (NLO) performance in a wide spectral region from ultraviolet to infrared. Remarkably, sinoite (i.e., Si$_2$N$_2$O) is reported for the first time to exhibit a wide optical bandgap ($\approx 5$ eV), strong second-harmonic generation (SHG) effect ($\approx 1$ pm/V) and large birefringence ($\approx 0.08$ at 1 $\mu$m). Importantly, by rational doping or solid solution, the alloy system between Si$_2$N$_2$O and Ge$_2$N$_2$O can achieve an adjustable phase-matching harmonic output with high SHG efficiency. Moreover, this alloying is possibly realized from analysis of our first-principles simulations based on the cluster expansion theory. There indeed exists an experimentant mesophase that theoretically exhibits a larger birefringence ($\approx 0.10$ at 1 $\mu$m) and stronger SHG effect ($\approx 5$ pm/V). Therefore, this alloying scheme to regulate NLO performance may get experimentalists to refocus on this classical silicon oxynitride system, and will provide more controls and receive more research interest in the NLO materials field.
Silicon nitride and oxynitrides are very classical materials, which play an important role in many applications in the automobile industry, ceramic bearings, cutting tools, electronics, high-temperature materials, and ultraviolet (UV) light-emitting diodes (LED), due to its hardness, thermal stability, wear resistance and wide bandgap.\(^1\,\,^9\) However, this material family has never been systematically studied for possible nonlinear optical (NLO) effects, which are indispensable in laser technology, optical information, and precision measurements.\(^10\,\,^{14}\) After a thorough analysis, we are aware of that silicon nitride/oxynitrides, as NLO materials, may have the following four advantages: (i) wide optical bandgaps for UV transparency or emission; (ii) variable chemical compositions for proportion-tunable alloy compounds or solid solution phases; (iii) silicon-nitrogen or/and silicon-oxygen tetrahedra as basic components for good mechanical-thermal stability and high laser-induced damage threshold; and (iv) non-toxic and stable optical properties, high optical efficiency, insensitive to temperature and drive current.\(^1\,\,^9\) In view of such superior NLO material properties, therefore, it is highly desirable to evaluate the NLO performance of conventional silicon nitride and especially silicon oxynitride materials.

Due to the tetrahedral (SiN\(_3\))\(^8\) units, silicon nitride compounds usually have small structural and optical anisotropy. As a result, they are difficult to meet the phase-matching conditions for second harmonic generation (SHG) conversion.\(^15\) For example, \(\alpha\)-Si\(_3\)N\(_4\) is the most thermodynamically stable phase of silicon nitride and commercially important. Its structure is constructed by trigonal lattices (symmetry \(P3_1c\)) with corner-shared (SiN\(_3\))\(^8\).\(^16\) Our first-principles calculations (for computational details see the Supporting Information) show that this compound has a strong SHG effect (\(\approx 0.5\) pm/V), larger than the benchmark NLO material K\(_3\)PO\(_4\) (KDP, \(d_{33} = 0.39\) pm/V) and in good agreement with available experimental data (see Table 1).\(^17\) However, its optical birefringence is too small (\(\Delta n < 0.02\) @ 1064 nm by default) to achieve the important UV coherent light output, e.g., third (355 nm) harmonic generation of the practical Nd: YAG 1064 nm lasers, although it has a large energy bandgap (\(\approx 4.6\) eV, corresponding to the UV absorption edge \(\approx 270\) nm).\(^14\) This means that \(\alpha\)-Si\(_3\)N\(_4\) cannot be used to be a UV NLO material. A similar situation also occurs in alkali metal silicon nitride LiSi\(_2\)N\(_3\) (\(\Delta n < 0.03\)),\(^18\,\,\,19\) though it even has larger bandgap (> 5 eV) and stronger SHG effect (\(\approx 5\times\)KDP) as listed in Table S1 of the Supporting Information. Thus, the chemical engineering design should be carried out to enlarge the optical anisotropy in the silicon nitride system.

**Table 1.** NLO Properties of Typical Silicon Nitrides, Silicon Oxynitrides and Germanium Oxynitrides as Found in ICSD.

| Symmetry       | \(\lambda_{UV}\) (nm) | \(E_g\) (eV) | \(d_{ij}\) (pm/V) | \(|d_{33}|_{max/}
\(d_{33}(\text{KDP})\) | \(\Delta n\) at 1064 nm | \(\lambda_{\text{PM}}\) (nm) | Refs | ICSD No. |
|----------------|-----------------------|-------------|-------------------|-----------------------------|-------------------|----------------|-------|---------|
| \(\alpha\)-Si\(_3\)N\(_4\) | \(P3_1c\) Exp. | 249 | 5.0 | \(\sim\) KDP | 1.0 | -- | -- | 4 | 644683 |
| Cal.\(^{a}\) | 270 | 4.6 | \(d_{11}=0.50; \, d_{22}=0.50; \, d_{33}=0.44\) | 1.3 | 0.016 | N/A | This work | -- |
| Si\(_3\)N\(_2\)O | \(CmC2\) Exp. | 230 | 5.4 | \(d_{\text{photon}}\) > KDP | 0.115 | -- | 7 | 34025 |
| Cal.\(^{a}\) | 249 | 5.0 | \(d_{ij}=0.46; \, d_{\text{photon}}=1.00; \, d_{33}=0.86\) | 2.6 | 0.080 | 290 | This work | -- |
| Ge\(_2\)N\(_2\)O | \(CmC2\) Exp. | 444 | 2.8 | \(d_{11}=3.41; \, d_{22}=1.13; \, d_{33}=7.46\) | 19.1 | 0.091 | 444 | 15 | 169121 |
| SiGe\(_2\)N\(_2\)O | \(Cm\) Cal.\(^{a}\) | 345 | 3.6 | \(d_{11}=2.50; \, d_{22}=2.16; \, d_{33}=-4.77\) | 12.2 | 0.103 | 345 | 15 | 169123 |

\(^{a}\) The calculated results are from this work.
Figure 1. Structural evolution from LiSi$_2$N$_3$ to Si$_2$N$_2$O (a), experimental powder XRD result (b), powder and block sample of Si$_2$N$_2$O (c).

In order to expand the optical anisotropy for the phase-matching requirements, we realize that the introduction of some anionic components into the (SiN$_4$)$_8^-$ tetrahedra would effectively enlarge the local structural anisotropy. A feasible way is to replace the bridged nitrogen with oxygen to form the oxynitride structure, as illustrated in Figure 1a from LiSi$_2$N$_3$ to Si$_2$N$_2$O. The crystalline structure of Si$_2$N$_2$O is built by (SiN$_3$O)$_7^-$ tetrahedra connected through oxygen atoms along the c-axis and through nitrogen atoms perpendicular to it. We have obtained the powder sample and charaterized its powder X-ray diffraction (XRD) results in the experiment as shown in Figure 1b and 1c (for details see the Supporting Information).

Figure 2. Calculated bandgaps $E_g$ (a), SHG effects $d_{ij}$ (b) and birefringence $\Delta n$ (c) of typical silicon nitrides, silicon oxynitrides and germanium oxynitrides.

Considering greater electronegativity of oxygen than nitrogen and shorter bond length of Si-O ($\approx$ 1.6 Å) than Si-N ($\approx$ 1.8 Å), silicon oxynitride can exhibit a wider bandgap and a larger structural anisotropy than silicon nitride. As such, the structural anisotropy increases while polar alignment along the $c$-axis does not change. The related NLO results including the bandgaps $E_g$, SHG effects $d_{ij}$ and birefringence $\Delta n$ are listed in Table S1 of the Supporting Information and plotted in Figure 2, well confirming the above analysis. For the typical silicon nitrides and silicon oxynitrides as found in
the inorganic crystal structure database (ICSD), it can be concluded that on average silicon oxynitrides exhibit slightly larger bandgaps, smaller SHG effects but larger birefringence compared with silicon nitrides, which is in good consistent with our proposed design strategy in Figure 1a. As a typical comparison, Si$_3$N$_2$O exhibits a smaller $d_{ij}$ ($\approx 2.6 \times$KDP) but larger $\Delta n$ ($\approx 0.08$) than those of LiSi$_2$N$_3$ ($d_{ij} \approx 5.9 \times$KDP, $\Delta n \approx 0.03$).

In the preliminary experiments, the UV-IR transmission and absorption spectra of Si$_3$N$_2$O sample are obtained as shown in Figure 3a. The results demonstrate that the UV absorption edge is at about 230 nm, corresponding to the optical bandgap $E_g \approx 5.4$ eV, slightly larger than our calculated result and actually greater than that of Si$_3$N$_4$ (exp. $\approx 5$ eV). In fact, Si$_3$N$_2$O, or named sinoite, is a rare mineral, which was first found in chondrite meteorites and can be prepared in the laboratory as silicon oxynitride ceramic. When reported, its structure and property have attracted great attention, published in Nature and Science. The experimental mineral data shows that its biaxial refractive indices include $n_x = 1.740$, $n_y = 1.855$ and $n_z = 1.855$, which are consistent with our calculated results ($n_x \approx 1.777$, $n_y \approx 1.835$ and $n_z \approx 1.856$, relative error < $\pm 2\%$). Accordingly, based on the calculated dispersion curves of refractive indices as plotted in Figure 3b, Si$_3$N$_2$O can achieve the shortest type-I phase-matching output wavelength $\lambda_{PM} \approx 290$ nm, shorter than the important UV 355 nm and most IR harmonic coherent output. Unfortunately, its powder SHG signal is very weak in our preliminary experiment due to the extreme small powder-size (the largest sample size < 10 μm) of our synthetic samples, which maybe too small to be available for the Kurtz-Perry powder SHG technique. Similarly, we also prepared some quartz (SiO$_2$) samples to perform the same powder SHG experiment. There is almost no SHG signal, although the SHG experimental results of quartz crystal have shown that its $d_{11} \approx 0.3$ pm/V, slightly smaller than that of KDP. It notes that our calculated results for quartz crystal, including SHG effect ($\approx 0.32$ pm/V) and bandgap ($\approx 6.1$ eV), are in good agreement with the experimental data. Therefore, if the single crystal of sinoite can be obtained for the SHG measurement, we may get the SHG effect in line with the theoretical prediction.

![Figure 3](image-url)

**Figure 3.** Experimental UV-IR transmission and absorption spectra (a), the calculated dispersion curves of refractive indices (b), PDOS and SHG density analysis of LiSi$_2$N$_3$ (c) and Si$_3$N$_2$O (d).

Furthermore, in order to understand the underlying NLO mechanism, the partial density of states (PDOS) and SHG-weighted density of Si$_3$N$_2$O are plotted in Figure 3d compared with LiSi$_2$N$_3$ in
Figure 3c. Note that (1) as a direct-gap structure, Si$_2$N$_2$O is superior to the indirect-gapped LiSi$_2$N$_3$ in terms of optical transition properties; (2) the 2$p$ orbitals of two-coordinated nitrogen (i.e., bridge-bonded N$^2$) play a more dominate role on the valence band maxima (VBM) than those of three-coordinated nitrogen (i.e., corner-shared N$^3$), so N$^2$ exhibits more SHG density than N$^1$ for LiSi$_2$N$_3$; and (3) the 2$p$ orbitals of oxygen (replace to N$^2$) contribute less to VBM than nitrogen (corresponding to N$^3$), so oxygen atoms exhibit less SHG density than nitrogen atoms for Si$_2$N$_2$O. This shows that Si$_2$N$_2$O has a superior bandgap but smaller SHG effect than LiSi$_2$N$_3$. Considering that 2.6 times of KDP is also a sufficiently large SHG effect for the UV laser, Si$_2$N$_2$O can be applied as a possible UV NLO material candidate.

In addition, the mechanical and thermal properties of Si$_2$N$_2$O and LiSi$_2$N$_3$ are calculated as listed in Table 2. It is revealed that (1) their bulk modulus are 3 times larger than KBe$_2$BO$_3$F$_2$ (KBBF) as a practical NLO material, indicating the stronger mechanical hardness; and (2) the thermal conductivity $\kappa=\nu-C_V\cdot MFP$ ($MFP$ is the phonon main free path, $\nu$ is the sound speed, and $C_V$ is the heat capacity) is larger than that of KBBF, indicating that Si$_2$N$_2$O and LiSi$_2$N$_3$ might possess favorable performances of machining and heat resistance than KBBF, which are important for high-intensity laser applications. In practice, the strong covalent bonding of Si$_2$N$_2$O results in high flexural strength and resistance to heating and oxidation up to temperatures of about 1600 °C. Importantly, Si$_2$N$_2$O can be easily obtained from the combustion synthesis method of $3\text{Si} + 2\text{N}_2 + \text{SiO}_2 \rightarrow 2\text{Si}_2\text{N}_2\text{O}$. There are a large number of studies on the functionalities of Si$_2$N$_2$O, except for the NLO properties that are first presented in this study. As such, we recommend experimentalists to obtain the large-size crystal materials and test the NLO properties in the experiment more practically.

Table 2. Calculated Mechanical and Thermal Properties of Si$_2$N$_2$O and LiSi$_2$N$_3$. The Results of KBBF are Listed for Comparsion.

|          | Bulk Modulus (GPa) | Young Modulus (GPa) | Sound Speed at 300 K (m/s) | Heat Capacity ($C_V$/cell•K) |
|----------|--------------------|---------------------|---------------------------|-----------------------------|
| Si$_2$N$_2$O | 155                | 303 248 329         | 0.40                      | 136                         |
| LiSi$_2$N$_3$ | 154                | 334 290 360         | 0.39                      | 172                         |
| KBBF    | 42                 | 228 228 39          | 0.23                      | 138                         |

exp. ~ 44$^a$)

Based on above calculations and analysis, we did find that the conventional silicon oxynitrides can exhibit promising NLO capabilities due to expected characteristics such as wide band gap and good mechanical-thermal stability. Further considering the practical solid solution characteristics in this kind of system, it may be implemented by alloying to realize the tunable NLO performances. Herein, theoretically, we have also evaluated the strategy of using the alloying of silicon and germanium in the polar oxynitride system to regulate NLO properties from UV to IR region. Based on the structure-property correlation of NLO materials, if germanium can be introduced into Si$_2$N$_2$O to partially replace silicon, the SHG effect will be enhanced while a sufficiently large birefringence can be maintained, because (Ge$_N$O)$^7$ has longer Ge-N/O bond length and larger tetrahedral distortion than (SiN$_2$O)$^7$. In fact, there is an actual mesophase, i.e., SiGeN$_2$O, between Si$_2$N$_2$O and Ge$_2$N$_2$O in...
the ICSD, although it is obtained using molecular synthesis while not solid solution. In order to search for new possible alloy phases, using the cluster expansion method (for details see the Supporting Information), we focus on the typical solid solution property, which is one of the most critical features for all the alloys and can fundamentally determine overall physical properties, e.g., electronic, magnetic, optical, defect, catalytic properties, etc. For example, In$_{1-x}$Ga$_x$N alloys have appeared to be one of the most important monolithic alloys for white LED. Moreover, the possible solid solution have been actually realized in some silicon oxynitride compounds such as in the Al-Si-N-O system.

Note that (Si, Ge)$_2$N$_2$O system can be effectively considered as a quasi-binary system in the present study, so that the cluster expansion theory based on first-principles calculations can be applied to calculate the formation energies of a large number of Si$_{2-x}$Ge$_x$N$_2$O alloy phases. From the simulated results as listed in Figure 4a, it can be found that there are several ordered alloy phases, e.g., with $Cc$ and $P2_1$ symmetry as shown in Figure S1 of the Supporting Information, having lower energies than the experimental SiGeN$_2$O phase with $Cm$ symmetry. Then, the NLO properties of the alloying Si$_{2-x}$Ge$_x$N$_2$O ($x = 0 ~ 2$) system can be theoretically obtained based on the ordered structures with the lowest energies, which are listed in Table S2 of the Supporting Information and plotted in Figure 4b.

![Figure 4](image.png)

**Figure 4.** Calculated formation energies (a), bandgaps and SHG effects of Si$_{2-x}$Ge$_x$N$_2$O with respect to the alloy proportion $x$ from 0 to 2 (b), and balanced area of IR NLO materials (c). The green star represents that the alloy phase is an experimentally synthetic compound.

It is demonstrated that with $x$ varies from 0 to 2, the SHG effect is indeed gradually enhanced from 2.6 to 19 times of KDP. Meanwhile, the birefringence is still maintained in a large level (0.07 ~ 0.10) for most of phase-matching processes. However, the bandgap $E_g$ is decreased as the proportion of germanium increases due to the bandgap bowing effect in alloy system, so the type-I phase-matching output wavelength $\lambda_{PM}$ is red-shifted from 290 nm to 444 nm. In principle, the experimental Ge$_2$N$_2$O compound cannot achieve the UV light generation, despite it exhibits much larger SHG effect than that of KTiOPO$_4$ (KTP), a widely-used all-round NLO crystal. As for SiGeN$_2$O, it can also achieve the important UV 355 nm output. Importantly, SiGeN$_2$O exhibits a much larger SHG effect ($\approx 12 \times$KDP) than some practical UV NLO materials (e.g., $\approx 3 \times$KDP for $\beta$-BaB$_2$O$_4$). In addition, when $x$ is located in the range of 0.5~0.75, Si$_{2-x}$Ge$_x$N$_2$O can exhibit relatively large bandgap (> 3 eV) and strong SHG effect (> 10×KDP), satisfying the balanced IR NLO requirement as shown in Figure 4c, which
indicates that they could be available for possible IR frequency conversion.\textsuperscript{39}

On the other hand, since Si\textsubscript{2}xGe\textsubscript{1-x}N\textsubscript{2}O can achieve possible third harmonic generation (355 nm) in the UV region when \(x \geq 1\), the question is if there exists a silicon nitride compound that can output the shorter UV coherent light (e.g., 266 nm), which is very important for fourth harmonic generation of Nd: YAG lasers. Note that Si\textsubscript{2}N\textsubscript{2}O is in fact transparent for 266 nm (\(\lambda_{\text{UV}} \approx 230\) nm). However, its insufficient refractive dispersion causes its shortest phase-matching SHG output \(\lambda_{\text{PM}} \approx 290\) nm (> 266 nm). Based on the proposed design strategy from (SiN\textsubscript{2})\textsuperscript{6} to (SiN\textsubscript{3}O)\textsuperscript{7} as illustrated in Figure 1a, we can further introduce halogen atoms (e.g., fluorine to form (SiN\textsubscript{3}F)) to continue to expand the structural anisotropy and simultaneously enlarge the bandgap. Unfortunately, there is no such a compound in the ICSD. In order to evaluate the potential of silicon fluoronitrides for UV 266 nm or even deep-UV (< 200 nm) output, we have designed a novel SiNF structure by removing Li\textsuperscript{+} and replacing O\textsuperscript{2-} with F\textsuperscript{−} based on an experimental LiSiNO compound.\textsuperscript{40} Based on the NLO materials modeling and ab initio simulations, SiNF is predicted to exhibit a wider UV bandgap (\(E_{\text{g}} \approx 6.2\) eV, close to the deep-UV edge), smaller SHG effect (\(d_{15} \approx 1.5\times K\text{DP}\), close to \(d_{22}=1.2\times K\text{DP}\) of KBBF) and larger birefringence (\(A_n \approx 0.13\), close to that of BBO) than Si\textsubscript{2}N\textsubscript{2}O. Accordingly, it can achieve the phase-matching SHG output above 202 nm and be available for the practical UV 266 nm output. The first-principles molecular dynamics (MD) simulations are performed to further confirm that the lattice structure of SiNF is stable at room temperature.\textsuperscript{41} As shown in Figure 2b, the volume of SiNF with respect to time oscillates in an average level and the structure can be maintained after a long-time MD simulation (~ 2 ps). The phonon property is further calculated to verify the dynamical stability.\textsuperscript{42} The phonon spectrum of SiNF in Figure 2e shows that there is not any imaginary phonon mode, indicating that it is dynamically stable as in the cases of LiSi\textsubscript{2}N\textsubscript{3} and Si\textsubscript{2}N\textsubscript{2}O (see Figure S2c and S2d).

Finally, we will give an outlook of possible NLO applications of the polar (Si, Ge)\textsubscript{2}N\textsubscript{2}O system. First, as large-size crystalline materials, it can be used in traditional laser frequency doubling devices to achieve tunable SHG phase-matching output. Even if large-size (Si, Ge)\textsubscript{2}N\textsubscript{2}O crystal may be difficult to be grown out under current technical conditions, it can also be made into pole glass as in the case of SiO\textsubscript{2} for noncrystalline state electro-optic uses. Note that SiO\textsubscript{2} can be used as a crystal for piezoelectric devices and as a polar glass for second-order NLO effects. For example, the thermal poling, which was actually electrothermal in nature, has been demonstrated in bulk SiO\textsubscript{2} samples by Myers et al.\textsuperscript{43} The nonlinearity induced, which was evaluated from the SHG signals of 1064 nm laser, is of a similar magnitude to that in quartz. Analysis indicates that in so-called glass ceramics, embedded crystals seem to be responsible for prominent SHG effect.\textsuperscript{44} Thus, we encourage experimentalists to conduct NLO studies of polar (Si, Ge)\textsubscript{2}N\textsubscript{2}O glass states.

In conclusion, from systematical analysis of the NLO properties in silicon and germanium oxynitrides, for the first time we have predicted that the classical Si\textsubscript{2-x}Ge\textsubscript{x}N\textsubscript{2}O (\(x = 0, 1, 2\)) system exhibits promising NLO capability and can be alloyed to achieve the adjustable NLO applications. In particular, Si\textsubscript{2}N\textsubscript{2}O as an important ceramic material can realize the phase-matching harmonic generation with high SHG efficiency in the UV region. Also, our preliminary and available experimental data have confirmed our calculated results. Moreover, by rational doping or solid solution, the alloying Si\textsubscript{2-x}Ge\textsubscript{x}N\textsubscript{2}O (\(x = 0\) to 2) system can achieve tunable phase-matching SHG output from UV to IR region. Many of them can further meet the requirement of balanced IR NLO performance. As a representative, SiGeN\textsubscript{2}O is predicted to exhibit sufficiently large SHG effect and
birefringence for UV, visible and IR NLO crystals. Finally, we have also designed a novel SiNF structure to achieve an available UV 266 nm output. Based on the discovery, we believe that our research of this alloying scheme to regulate NLO performance may re-arouse the interests to theorists and experimentalists in the classical silicon oxynitride system, and provide more control means for the NLO materials.

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