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Alloy Engineering of a Polar (Si,Ge)₂N₂O System for Controllable Second Harmonic Performance

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ABSTRACT: Although silicon oxynitrides are important semiconductors for many practical applications, their second-order nonlinear optical (NLO) properties have never been systemically explored. Using the first-principles calculations, in this article, we discover that the sinoite (e.g., silicon oxynitride Si_2N_2O) can simultaneously exhibit wide optical band gap, strong secondharmonic generation (SHG) effect, and large birefringence, which are further confirmed by our preliminary experimental measurement. Importantly, we propose that alloying engineering can be further applied to control the balanced NLO properties in the Si_2N_2O system. Based on first-principles cluster expansion theory, we demonstrate that alloying Ge into Si_2N_2O can form low



formation-energy $Si_{2(1-x)}Ge_{2x}N_2O$ alloys, which can in turn achieve controllable phase-matching harmonic output with high SHG efficiency at different energy ranges. Therefore, alloy engineering could provide a unique approach to effectively control the NLO performance of $Si_{2(1-x)}Ge_{2x}N_2O$, making this polar alloy system hold potential applications in tunable laser conversion and controllable optical devices.

1. INTRODUCTION

Silicon nitrides and oxynitrides are well-known multifunctional material systems that play an important role in a wide range of applications, for example, ceramic bearings, cutting tools, electronics, high-temperature materials, and ultraviolet (UV) light-emitting diodes, due to their good performance in hardness, thermal stability, wear resistance, and optical band gap.^{1–9} To further extend their applications to laser technology, optical precision measurement, quantum information, and computing,^{10–13} it is highly desirable to realize nonlinear optical (NLO) frequency conversion in these systems. Unfortunately, to best of our knowledge, the feasibility of NLO properties in these systems, for example, second harmonic performance, remains unclear due to the lack of a systematic understanding.

In general, for a NLO system (here, it mainly refers to the second-order nonlinearity), the ideal situation is to simultaneously realize wide energy band gap (E_g) , strong second harmonic generation (SHG) effect (d_{ij}) , and large optical birefringence (Δn) , which are three critical but competing factors in a NLO system.¹⁴ It is known that these three factors are difficult to be achieved in one single material system. For example, a larger E_g is usually accompanied by a smaller first-order (e.g., refractive indices n_i) and second-order (e.g., d_{ij}) optical susceptibility; a smaller n_i and lower optical anisotropy can result in a smaller Δn . In practice, the UV NLO materials, for example, β -BaB₂O₄ (BBO) and LiB₃O₅ (LBO),^{15,16} usually have relatively larger E_g but smaller d_{ij} than those of infrared

(IR) NLO materials, for example, AgGaS₂ and ZnGeP₂.^{17,18} Although they can meet the basic requirements of NLO application in the UV region (e.g., 355 nm for third harmonic generation of the practical Nd: YAG 1064 nm lasers), they cannot realize efficient NLO conversion in the IR region (e.g., $4 \mu m$ for the practical atmospheric transparent window) due to the strong IR absorption and small d_{ij} . In comparison, although the IR NLO materials can meet the IR NLO conversion with high efficiency (large d_{ij}), they are opaque to the UV light due to the small E_g . Therefore, a good balance among the E_g , d_{ij} , and Δn (for phase-matching condition) is critical for achieving the balanced NLO performance in different energy regions,¹⁰ which, however, is challenging to be realized due to the lack of a general design principle.

We expect that the silicon nitride/oxynitride may be ideal material platforms that can achieve balanced NLO performance in wide spectra from UV to IR in terms of their following advantages: (i) wide E_g for UV optical transparency, (ii) high mechanical-thermal stability and laser-induced damage threshold due to the existence of Si-N or/and Si-O

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tetrahedra, (iii) nontoxic, and (iv) stable electronic property, high optical efficiency, insensitivity to temperature, and drive current.^{1–9} More importantly, the silicon nitride/oxynitride may form solid solutions with their germanium (Ge) analogue due to their similar structural and chemical properties. Therefore, alloy engineering may provide a unique approach to tune their overall linear and NLO properties, for example, E_g , Δn , and d_{ij} , which can have various important applications, especially in terms of performance regulation.^{19–25} In view of these superior properties, it is highly desirable to evaluate the potential linear and NLO performance in the silicon nitrides/ oxynitrides and their potential alloys, for example, for the SHG process applied to practical frequency conversion.

In this article, we propose a general design principle for achieving the good balance of NLO performance by alloy engineering, which is successfully demonstrated in the silicon oxynitride system. First, using the first-principles calculations, we discover that the Si₂N₂O can simultaneously exhibit wide optical E_{g} (~5 eV), strong SHG d_{ii} effect (~2.6 × KDP), and large Δn (~0.08), which are further confirmed by our preliminary experimental measurements. Second, based on first-principles cluster expansion theory, we demonstrate that alloying Ge into Si₂N₂O can easily form low-formation-energy $Si_{2(1-r)}Ge_{2r}N_2O_r$, which can in turn achieve controllable phasematching harmonic output with high SHG efficiency at different energy ranges. Therefore, alloy engineering can provide a unique approach to effectively control the overall NLO performance of $Si_{2(1-x)}Ge_{2x}N_2O$, making it useful for different energy-range applications with well-balanced NLO performance.

2. DESIGN PRINCIPLE AND METHODS

2.1. Design Principle of Alloy Engineering for Balanced NLO Performance. As an important criterion for practical NLO materials, the NLO conversion efficiency in a phase-matchable SHG process can be evaluated according to the following formula under the nondepletion approximation

$$\eta = \frac{8\pi^2 d_{\text{eff}}^2 \cdot L^2 \cdot I_{\omega}}{\varepsilon_0 c \cdot n_{\omega}^2 n_{2\omega} \lambda_{\omega}^2} \tag{1}$$

where η is the conversion efficiency, d_{eff} is the effective SHG coefficient (generally proportional to d_{ij} along the PM direction), *L* is the length of a crystal, I_{ω} is the peak power density of the input beam, ε_0 is the vacuum permittivity, n_{ω} and $n_{2\omega}$ are the refractive indices at the fundamental λ_{ω} and the second harmonic $\lambda_{2\omega}$ along the PM direction, and *c* the light speed in vacuum.

According to eq 1, in order to achieve a similar efficiency η , the NLO materials at different energy regions should exhibit λ_{ω} dependent d_{eff} . For example, for the 4 μ m IR light, in order to achieve the same efficiency η as the 400 nm UV light, under the same conditions, the d_{eff} of an IR NLO material, for example, the widely used all-round NLO crystal KTiOPO₄ (KTP) with $d_{\text{eff}} = 3.2 \text{ pm/V}$, needs to be ~ 10 times larger than that of an UV NLO material, for example, the important benchmark NLO material KH₂PO₄ (KDP) with $d_{36} = 0.39 \text{ pm/V}$. Therefore, we can understand that even if BBO or LBO can transmit IR light, their SHG conversion efficiency is relatively low because their SHG effects are around $3-5 \times \text{KDP}$. although they have a high laser-induced damage threshold (assuming that the crystal is not damaged).¹⁰ One thing to note here is that the UV conversion is achieved through sum frequency generation (e.g., SHG), while the IR conversion is usually achieved through difference frequency generation. Generally, the IR conversion efficiency is also related to the SHG effect. The simple comparison based on the SHG conversion efficiency formula could still provide a reasonable reference.

Accordingly, a good UV NLO material should satisfy the following balanced linear and NLO performance, including an energy band gap $E_g \geq 4.7$ eV for short UV absorption edge $\lambda_{\rm UV} \geq 266$ nm, an SHG coefficient $d_{ij} \geq 1 \times$ KDP, and a birefringence $\Delta n \geq 0.08$ (approximately) to realize moderate PM output of 355 and 266 nm, respectively, corresponding to the third and fourth harmonic generation of the practical Nd: YAG 1064 nm lasers. Correspondingly, a good IR NLO material needs a $E_g \geq 3$ eV (mainly to avoid multiphoton absorption damage for the μ m-lasers), a $d_{ij} \geq 10 \times$ KDP (or 1 × KTP), and a $\Delta n \geq 0.05$ (approximately).

To achieve the balanced requirements for potential NLO applications in both UV and IR (near-IR) regions, we take the silicon nitride/oxynitride system as an example to illustrate our design principles by alloy engineering, which is generally applicable to other similar systems. Note that, for most of silicon nitride compounds, based on their basic $(SiN_4)^{8-}$ tetrahedral motifs as schematically shown in Figure 1a, they usually have large E_g due to strong sp³-



Figure 1. Design principle for a good balance between the three key NLO parameters. Structural evolution from (a) $SiN_3-N-SiN_3$ tetrahedra to (b) $SiN_3-O-SiN_3$ tetrahedra and to (c) $SiN_3-O-GeN_3$ tetrahedra. Corresponding radar charts of band gap $E_{g'}$ SHG effect d_{ij} and birefringence Δn are shown in the bottom panels.

hybrid Si–N bonds but small structural and optical anisotropy (i.e., small Δn and d_{ij}) due to regular tetrahedral coordination. As a result, the balance between these three key NLO parameters (i.e., E_{g} , Δn , and d_{ij}) cannot be achieved, preventing them to meet the PM requirements for the SHG conversion, especially in the UV region.²⁷

Here, we propose two feasible steps to enhance the Δn and d_{ij} . First, to enhance the Δn , based on the anionic group theory,¹⁰ one can introduce some anionic components into the $(SiN_4)^{8-}$ tetrahedra to enlarge the structural anisotropy. As shown in Figure 1b, an effective way is to replace the bridge-site nitrogen with oxygen forming the oxynitride structure. In this case, the $SiN_3-O-SiN_3$ structure is built by distorted $(SiN_3O)^{7-}$ tetrahedra connected through O atoms along the polar axis, which may exhibit similar E_g and d_{ij} but larger Δn as compared with $(SiN_4)^{8-}$ in Figure 1a. Second, in order to further enhance the d_{ij} alloying Ge into $(SiN_3O)^{7-}$ forming ordered $[(Si,Ge)N_3O]^{7-}$ solid solution, as illustrated in Figure 1c, could lower the structural symmetry and enhance the NLO response. Meanwhile, alloy engineering may also be used to tune the E_g for various NLO applications in different energy ranges due to the different E_g of $(SiN_3O)^{7-}$ and $(GeN_3O)^{7-}$ hosts, providing an effective way to control the overall linear and NLO performance.

2.2. Computational and Experimental Methods. To verify the design principle shown in Figure 1, based on the first-principles calculations, we have evaluated the linear and NLO properties of the corresponding material systems, including typical silicon nitrides, silicon oxynitrides, and germanium oxynitrides, as listed in Table 1. The first-principles calculations are performed by the plane-wave pseudopotential method using CASTEP based on the density

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:	symmetry		NLO-active unit	$\lambda_{\rm UV}~({\rm nm})$	$E_{\rm g}~({\rm eV})$	$d_{ij} (pm/V)$	$ d_{ij} _{\max}/d_{36} (\text{KDP})^c$	Δn at 1 μ m
α -Si ₃ N ₄	P3 ₁ c	exp.	(SiN ₃) ₃ -N	249	5.0	~KDP	1.0	
		cal. ^a		270	4.6	$d_{15} = 0.50; d_{24} = 0.50; d_{33} = -0.44$	1.3	0.016
$LiSi_2N_3$	$CmC2_1$	cal. ^a	$(SiN_3)_2 - N$	249	5.0	$d_{15} = 2.30; \ d_{24} = 0.91; \ d_{33} = -0.21$	5.9	0.029
Si_2N_2O	$CmC2_1$	exp.	$(SiN_3)_2 - O$	230	5.4	$d_{\text{powder}} > \text{KDP}$	0.115	
		cal. ^a		249	5.0	$d_{15} = 0.46; d_{24} = 1.00; d_{33} = -0.86$	2.6	0.080
LiSiNO	$Pca2_1$	cal. ^a	$(SiN_2O)_3-N$	230	5.4	$d_{15} = 0.37; \ d_{24} = 0.56; \ d_{33} = 0.10$	1.4	0.040
Ge_2N_2O	$CmC2_1$	cal. ^{a,b}	$(GeN_3)_2 - O$	444	2.8	$d_{15} = 3.41; d_{24} = 1.13; d_{33} = -7.46$	19.1	0.091
KGeNO	$Pca2_1$	cal. ^a	$(GeN_2O)_3-N$	444	2.8	$d_{15} = 0.72; d_{24} = 1.27; d_{33} = -3.68$	9.4	0.048
SiGeN ₂ O	Ст	cal. ^a	$(Si/GeN_3)_2$ –O	345	3.6	$d_{11} = 2.50; \ d_{24} = 2.16; \ d_{33} = -4.77$	12.2	0.103

Table 1. Linear and NLO Properties of Typical Silicon Nitrides, Silicon Oxynitrides, and Germanium Oxynitrides

^{*a*}Calculated results from this work. ^{*b*}Related data; also see refs 50 and 51. ^{*c*} d_{36} (KDP) = 0.39 pm/V.



Figure 2. Crystal structures (left panels) and corresponding radar charts (right panels) of calculated band gaps E_g , SHG effects d_{ij} , and birefringence Δn in (a) silicon nitride α -Si₃N₄, (b) silicon oxynitride Si₂N₂O, (c) germanium oxynitride Ge₂N₂O, and (d) silicon–germanium oxynitride SiGeN₃O.

functional theory (DFT).²⁸ The norm-conserving pseudopotentials and Perdew–Burke–Ernzerhof functional in generalized gradient approximation are employed.^{29,30} The lattice constants and atomic positions are optimized using the quasi-Newton method.³¹ The electronic structures, linear and NLO properties are obtained according to our proposed methods.^{32,33} In order to effectively study the (Si,Ge)₂N₂O binary alloy systems, the first-principles based cluster expansion (CE) approach, as implemented in the ATAT code,³⁴ is employed to generate the random Si_{2(1-x)}Ge_{2x}N₂O alloy structures at different *x* and simulate the formation energies of Si_{2(1-x)}Ge_{2x}N₂O systems.

In addition, the powder X-ray diffraction (XRD), UV–visible-IR absorption spectrum, and Kurtz-Perry powder SHG measurements are used to characterize the fundamental properties of synthetic Si_2N_2O samples in the experiments, with the main purpose of confirming the accuracy of our computational methods. For more computational and experimental details, see Methods in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. NLO Properties of Silicon Nitrides and Oxy**nitrides.** Silicon nitride α -Si₃N₄, an important semiconductor system,³⁵ is constructed by the trigonal lattice ($P3_1c$ symmetry) with corner-shared $(SiN_3)_3$ -N tetrahedral motifs, as shown in Figure 2a, same as the SiN_3 –N– SiN_3 units shown in Figure 1a. The first-principles results show that α -Si₃N₄ has a suitable (but not strong) SHG effect (~0.5 pm/V, see Table 1), in good agreement with the experimental data ($\sim 1 \times \text{KDP}$ for thin film).³⁶ However, its Δn is too small (<0.02 at 1 μ m) to achieve the important UV coherent output, for example, 355 nm, although it has a large $E_{\rm g} \approx 4.6$ eV ($\lambda_{\rm UV} \approx 270$ nm). It clearly indicates that α -Si₃N₄ cannot achieve a good NLO balance among E_{g} , d_{ij} , and Δn for UV SHG. Similarly, the alkali—metal silicon nitride LiSi $_2N_3$ also has a small Δn (<0.03),³⁷ and even its E_g (>5 eV) and d_{ii} (cal. $\approx 5 \times \text{KDP}$) are relatively large (Table 1).



Figure 3. Experimental measurements of (a) powder XRD, (b) UV–visible-IR spectra, (c) powder SHG effect (in comparison with KDP), and (d) calculated refractive indices of Si_2N_2O as a function of the wavelength.

As proposed in Figure 1b, the oxygen doping of silicon nitride forming distorted silicon oxynitride tetrahedra may enlarge the optical anisotropy of Si_3N_4 . To confirm this, we select the Si₂N₂O structure as the typical example to investigate its linear and NLO properties. As shown in Figure 2b, Si_2N_2O is composed by the $(SiN_3O)^{7-}$ tetrahedra connected through oxygen atoms along the c-axis, same as the case in Figure 1b.38-40 Considering the larger electronegativity of O than N and the shorter bond length of Si-O (~1.6 Å) than Si–N (~1.8 Å), Si₂N₂O can exhibit a wider E_{σ} (due to stronger bonding-antibonding separation) and a larger structural anisotropy (due to the tetrahedral distortion) than α -Si₃N₄. Indeed, the calculated E_{g} , d_{ii} , and Δn shown in Table 1 confirm our physical intuition. Comparing Figures 2a,b, it is seen that the Si₂N₂O exhibits a stronger d_{ii} (~2.6 × KDP) and a larger Δn (~0.08) than those of Si₃N₄. Similar trends of enhanced d_{ii} and Δn are also observed in our study for the alkali-metal silicon oxynitride LiSiNO ($d_{ii} \approx 1.4 \times \text{KDP}, \Delta n \approx$ 0.04; see Table 1) compared to those of LiSi₂N₃.⁴¹

3.2. Experimental Measurements on Silicon Oxynitride of Si₂N₂O. To further confirm our design strategy and theoretical prediction, we have performed the experimental measurements for the Si₂N₂O system. The powder XRD results of synthetic Si₂N₂O samples are shown in Figure 3a, which is consistent with the existing XRD data of Si₂N₂O. The UV-visible-IR transmission and absorption spectra are measured as shown in Figure 3b, indicating that the UV absorption edge $\lambda_{\rm UV}$ is at ~230 nm, corresponding to the $E_{\sigma} \approx$ 5.4 eV, which is slightly larger than α -Si₃N₄ ($E_g \approx 5$ eV). The Kurtz-Perry powder SHG measurement of Si₂N₂O samples is shown in Figure 3c.⁴² Due to the extremely small powder-size (<10 μ m, see Figure S1) of our synthetic samples, the powder SHG signal with respect to the particle size cannot be characterized experimentally. However, compared with the SHG signal and trend of KDP benchmark, it is reasonable to believe that the SHG intensity of Si₂N₂O should be larger than that of KDP ($d_{36} = 0.39 \text{ pm/V}$), which is qualitatively consistent with our theoretical prediction (~1 pm/V in Table

1).⁴² Meanwhile, according to the Kurtz–Perry derivation, the powder SHG effect can be obtained from the SHG coefficients;⁴² the simulated d_{powder} of Si₂N₂O is 0.95 pm/V (2.4 × KDP), comparable as the maximum SHG coefficient $d_{24} \sim 1 \text{ pm/V}$.

Although it is difficult to measure the refractive indices directly due to the limited size of Si₂N₂O samples, its structural properties have been measured in other experiments.^{38,39} The experimental mineral data shows that its biaxial refractive indices $n_x = 1.740$, $n_y = 1.855$, and $n_z = 1.855$, which are in good agreement with our calculated results ($n_x \approx 1.777$, $n_y \approx 1.835$, and $n_z \approx 1.856$, relative error $<\pm 2\%$). Based on the calculated dispersion curves of refractive indices, as plotted in Figure 3d, the Si₂N₂O can achieve the shortest type-I PM output wavelength $\lambda_{\rm PM} \approx 285$ nm, shorter than the important 355 nm in the UV region.

3.3. Tunable NLO Properties in Alloying (Si,Ge)₂N₂O. As proposed in Figure 1c, it is highly possible to further enhance the SHG effects in the silicon oxynitride system by alloying to form $(Si,Ge)_2N_2O$ solid solution.^{25,43} Since $(GeN_3O)^{7-}$ has longer Ge–N/O bond length and larger tetrahedral distortion than those of Si–N/O in $(SiN_3O)^{7-}$, the structural anisotropy would be enlarged so that a sufficiently large birefringence can be maintained (see Figure 2c). In addition, it is expected that the E_g of $(Si,Ge)_2N_2O$ can be tuned in a wide range, depending on the Ge concentration due to large E_g difference between Si_2N_2O (~5 eV) and Ge_2N_2O (~2.8 eV). Therefore, it is expected that the $Si_{2(1-x)}Ge_{2x}N_2O$ can be applied to realize the NLO applications in different energy ranges.

In order to examine the feasibility of forming $(Si,Ge)_2N_2O$ alloys, based on the first-principles based CE approach,³⁴ we have systemically investigated the formation energies (E_f) of $Si_{2(1-x)}Ge_{2x}N_2O$ ($0 \le x \le 1$) binary alloys. Here, the E_f is defined as

$$E_{\rm f} = E[{\rm Si}_{2(1-x)}{\rm Ge}_{2x}{\rm N}_2{\rm O}] - (1-x)\mu_{{\rm Si}_2{\rm N}_2{\rm O}} - x\mu_{{\rm Ge}_2{\rm N}_2{\rm O}}$$
(2)

where μ Si₂N₂O (μ Ge₂N₂O) is the total energy of Si₂N₂O (Ge₂N₂O) unit cell (see Methods in the Supporting Information for more details). The basic idea of CE is to expand the energies of a Si_{2(1-x)}Ge_{2x}N₂O configuration into energy contributions of cluster figures (single atoms, pairs, triples, etc.) based on a generalized Ising Hamiltonian

$$E(\sigma) = J_0 + \sum_i J_i \hat{S}_i(\sigma) + \sum_{i < j} J_{ij} \hat{S}_i(\sigma) \hat{S}_j(\sigma) + \sum_{i < j < k} J_{ijk} \hat{S}_i(\sigma) \hat{S}_j(\sigma) \hat{S}_k(\sigma) + \dots$$
(3)

In eq 3, the index *i*, *j*, and *k* run over all the alloy sites, and $S_m(\sigma)$ is set to +1 (-1) when it is occupied by the Si₂N₂O (Ge₂N₂O) dimer. Ideally, the CE can represent any Si_{2(1-x)}Ge_{2x}N₂O alloy energy $E(\sigma)$ by the appropriate selection of *J*, which can be fitted from the first-principles total energy calculations based on a sufficient number of random alloy configurations. To calculate the binary phase diagram of Si_{2(1-x)}Ge_{2x}N₂O, the Monte Carlo simulations, which sample a semigrand-canonical ensemble, are carried out, in which the energetics of Si_{2(1-x)}Ge_{2x}N₂O are specified by the CE Hamiltonian.

First, we have calculated the E_f of 119 Si_{2(1-x)}Ge_{2x}N₂O alloys (<20 atoms/supercell) with different structural symmetries at different Ge concentrations (*x*) based on the first-principles methods. Second, the self-consistent CE fitting is employed to fit the DFT-calculated E_f to obtain the most important effective cluster interactions *J*. Our calculations confirm that these 119 alloy structures are sufficient to obtain the converged *J* for the CE Hamiltonian. Therefore, the CE Hamiltonian of the binary alloy Si_{2(1-x)}Ge_{2x}N₂O can be well obtained. Third, we can use this Hamiltonian to quickly predict the E_f of all the nonequivalent alloy configurations. The DFT-calculated, CE-fit, and CE-predicted E_f are shown in Figure 4a. Interestingly, it is found that the E_f of all the Si_{2(1-x})Ge_{2x}N₂O alloys are rather



Figure 4. Calculated (a) formation energies E_{b} (b) E_{g} and d_{ij} of $Si_{2(1-x)}Ge_{2x}N_{2}O$ with respect to the Ge concentration x from 0 to 1, and (c) IR NLO balanced area. Red star marked in (a) represents the calculated E_{f} of experimentally synthesized SiGeN₂O. Inset in (a): Monte Carlo-simulated T-x phase diagram of $Si_{2(1-x)}Ge_{2x}N_{2}O$.

low, mostly in the range between 0 and 40 meV, indicating that they are easily formed at finite temperature. Indeed, by employing the CE-based MC simulations, we further obtained the T-x phase diagram of $\text{Si}_{2(1-x)}\text{Ge}_{2x}\text{N}_2\text{O}$ as a function of x. As shown in the inset of Figure 4a, the miscibility gap of $\text{Si}_{2(1-x)}\text{Ge}_{2x}\text{N}_2\text{O}$ is ~155 K, which is even below the room temperature. Note that this miscibility gap is obtained based on the thermal equilibrium conditions, assuming that the alloyed atoms are free to move to reach their equilibrium positions. In practice, the sizable diffusion barriers need to be overcome for the atoms to move in $\text{Si}_{2(1-x)}\text{Ge}_{2x}\text{N}_2\text{O}$.

Interestingly, we notice that there is an existing ordered SiGeN₂O phase with the *Cm* symmetry in the crystal structure database (see Figure 2d).^{44,45} For comparison, its calculated $E_{\rm f}$ (marked as red star) is also shown in Figure 4a. Obviously, there are a couple of SiGeN₂O structures predicted by our CE calculations that can have even lower $E_{\rm f}$ than that of the Cmphase of SiGeN₂O, for example, the Cc- and P21-phase SiGeN₂O (for details, see Figure S2), indicating that many SiGeN₂O structures may also be able to be synthesized in the experiments. To show the influence of random occupancy structures on the NLO properties, we have further selected four random alloy structures of SiGeN₂O (Figure S2) to simulate their optical properties. As listed in Table S1, the calculations clearly demonstrate that their linear and NLO properties are basically comparable as the SiGeN₂O ground state.

Taking the Si_{2(1-x)}Ge_{2x}N₂O ($0 \le x \le 1$) structures with lowest $E_{\rm f}$ in Figure 4a at different x as examples, their linear and NLO properties can be calculated, as shown in Figure 4b (for details, see Table S1). Again, the calculated linear and NLO properties of the *Cm*-phase of SiGeN₂O are also listed in Table 1 for comparison. It is seen that when x increases from 0 to 1, the SHG intensity d_{ij} of Si_{2(1-x)}Ge_{2x}N₂O gradually increases from ~2.6 × KDP to ~19 × KDP, which validates our alloy design principle shown in Figure 1c. Meanwhile, the Δn can maintain sufficiently large values between 0.07 and 0.10, which are good enough for most PM processes from UV to IR. However, $E_{\rm g}$ smoothly decreases as x increases, as expected (Table 1). Therefore, the PM wavelength $\lambda_{\rm PM}$ is redshifted from 285 to 444 nm.

In principle, Ge₂N₂O cannot achieve the UV laser generation due to its $\lambda_{\rm PM} \approx 444$ nm, although it exhibits larger SHG effect than KTP.²⁶ In contrast, the SiGeN₂O has a larger $E_{\rm g} \approx 3.6$ eV that can achieve the 355 nm output ($\lambda_{\rm PM} \approx$ 345 nm), satisfying a good balance of UV NLO performance (Figure 2d). Importantly, in this region, SiGeN₂O exhibits stronger SHG effect ($\approx 12 \times \text{KDP}$, Table 1) than many practical UV NLO materials (e.g., ~3–5×KDP for LBO and BBO). Furthermore, when x is tuned in the range of 0.5-0.75, the Si_{2(1-x)}Ge_{2x}N₂O can exhibit relatively large E_g (>3 eV) and strong SHG d_{ii} (>10 × KDP), satisfying the balanced IR NLO requirement,⁴⁶ as shown in Figure 4c. This indicates that they could be available for possible IR (near-IR) NLO conversion. All the results demonstrate that the polar (Si,Ge)N₂O system can have strong NLO effects in wide energy regions, exhibiting either higher d_{ij} (e.g., than BBO at 355 nm) or higher E_g (e.g., than AgGaS₂ at 1 μ m), respectively, for UV or IR SHG conversion. In addition, IR transparency is a particularly important condition for IR NLO materials, which generally requires large-size crystal measurement for relative accuracy. Although the experimental powder transmission spectrum is given in Figure 2b, it only shows that it is transparent in the



Figure 5. (a) Calculated band structure, (b) projected density of states, and (c) band-resolved SHG (d_{33}) analysis for Si₂N₂O. (d-f) are same as (a-c) but for SiGeN₂O. Insets are the corresponding SHG density projection for Si₂N₂O and SiGeN₂O.

range from 0.3–2 μ m (UV to near-IR). As preliminary evaluation, this study only shows its SHG capability in the IR/ near-IR region and does not strictly evaluate its IR transparency capability. Considering the IR absorption edge of traditional oxides, it is probably suitable for near-IR rather than the mid-IR region.

3.4. SHG Origin in Si₂N₂O and SiGeN₂O. To further understand the underlying NLO mechanism, the electronic band structures, partial density of states (PDOS), bandresolved SHG analysis, and SHG weighted density of Si₂N₂O and SiGeN₂O are calculated and plotted in Figure 5 (see Methods for more details). Because of the direct E_g shown in Figure 5a,d, Si₂N₂O and SiGeN₂O are superior to the semiconductors with indirect E_g in terms of the optical transition properties. These optical transitions mainly originate between the p orbitals of N/O and s orbitals of Si/Ge around the band edges (Figure 5b,e). Since the 2p orbitals of N/O contribute significantly to the valence band maximum (VBM), these N/O orbitals can contribute dominantly to the SHG effects, exhibiting strong SHG densities in Si₂N₂O and SiGeN₂O, as shown in Figure 5c,f.⁴⁷

Furthermore, compared to Si_2N_2O , due to the inclusion of Ge, the conduction band minimum (CBM) of $SiGeN_2O$ is mainly contributed by the 4s orbitals of Ge due to the lower orbital energy of Ge 4s than Si 3s. Meanwhile, the VBM maintains to be contributed by the orbitals of N/O (Figure 5e). Consequently, the electronic states on the Ge site exhibit more dominant SHG contribution and densities than those on the Si site (Figure 5f). Consequently, SiGeN₂O can exhibit a stronger SHG effect (~12 × KDP) than Si₂N₂O (~2.6 × KDP). The results are overall consistent with our design principle explained in Figure 1.

4. OUTLOOK AND CONCLUSIONS

On the one hand, if the large-size crystals of $(Si,Ge)_2N_2O$ can be obtained, they can be directly used in traditional NLO devices to achieve tunable SHG PM output. In addition, they might possess favorable machining performance due to good mechanical properties (e.g., large bulk modulus ~155 GPa for Si_2N_2O). In practice, the strong covalent bonding of Si_2N_2O results in high flexural strength and resistance to heating and oxidation up to temperatures of around 1350 °C.⁴⁸ Moreover, Si_2N_2O can be easily obtained from the combustion synthesis method of $3Si + 2N_2 + SiO_2 \rightarrow 2Si_2N_2O$. Although there are many studies on the functionalities of Si_2N_2O ,¹⁻⁹ its NLO properties are presented for the first time in this study. Therefore, the further experimental synthesis of large-size crystal is of great importance to evaluate its NLO performance.

On the other hand, if the large-size $(Si,Ge)_2N_2O$ crystals are difficult to be obtained in the experiments, they can also be made into the pole glass, similar to the pole SiO₂ glass for possible electro-optic applications. For example, thermal poling, which was electrothermal in nature, has been demonstrated in bulk SiO₂ samples by Myers et al.⁴⁹ The nonlinearity induced, which was evaluated from the SHG signals of 1064 nm laser, is of a similar magnitude to that in quartz. The related analysis indicates that in so-called glass ceramics, embedded crystals seem to be responsible for prominent SHG effect. Therefore, further investigation of the NLO properties of the pole $(Si,Ge)_2N_2O$ glass states by both theories and experiments is highly desired.

In conclusion, we have proposed a general proposal to realize the balanced and tunable NLO properties of semiconductors by alloy engineering, which has been well demonstrated in the $(Si,Ge)N_2O$ system. The polar $(Si,Ge)-N_2O$ system can achieve tunable-energy band gaps and PM SHG outputs from the UV to IR region. As a representative, SiGeN₂O is predicted to exhibit sufficiently large SHG effect and birefringence for NLO crystals. We believe that this study may rearouse the interests to theorists and experimentalists in the classical silicon oxynitride system for broad NLO applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00590.

Methods, crystal size and pictures of experimental Si_2N_2O samples, crystal structures of several $SiGeN_2O$ phases, band gaps, and SHG coefficients of $Si_{2(2-x)}Ge_{2x}N_2O$ (x = 0 to 1) (PDF)

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Notes

The authors declare no competing financial interest.

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