NLO Materials

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Unbiased Screening of Novel Infrared Nonlinear Optical Materials with High Thermal Conductivity: Long-neglected Nitrides and Popular Chalcogenides

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Abstract: Traditional infrared (IR) nonlinear optical (NLO) materials such as AgGaS₂ are crucial to key devices for solid-state lasers, however, low laser damage thresholds intrinsically hinder their practical application. Here, a robust strategy is proposed for unbiased highthroughput screening of more than 140000 materials to explore novel IR NLO materials with high thermal conductivity and wide band gap which are crucial to intrinsic laser damage threshold. Via our strategy, 106 compounds with desired band gaps, NLO coefficients and thermal conductivity are screened out, including 8 nitrides, 68 chalcogenides, in which Sr₂SnS₄ is synthesized to verify the reliability of our process. Remarkably, thermal conductivity of nitrides is much higher than that of chalcogenides, e.g., $5 \times AgGaS_2$ (5.13 W/mK) for ZrZnN₂, indicating that nitrides could be a longneglected system for IR NLO materials. This strategy provides a powerful tool for searching NLO compounds with high thermal conductivity.

Introduction

Frequency conversion via nonlinear optical (NLO) material is a convenient and highly efficient approach to generating laser beams.^[1] At present, β -BaB₂O₄ (β -BBO),^[2] LiB₃O₅ (LBO),^[3] KH₂PO₄ (KDP),^[4] KTiOPO₄ (KTP),^[5] and KBe₂B₂O₆F₂(KBBF)^[6] are used or potential as NLO materials in the ultraviolet (UV) /deep-UV region.^[7] In the infrared (IR) region, the exploration of new NLO crystals is still challenging.^[8] After decades of intensive effort, metal

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chalcogenides,^[9] such as the benchmark IR NLO materials $AgGaS_2$ and $AgGaSe_2^{[10]}$ become the preferred source owing to their wide transmission ranges in the IR region and large second harmonic generation (SHG) responses but suffer from the drawbacks such as low laser-induced damage thresholds (LDTs) that hinder their high-power applications.[11] Electron absorption causes thermal and electronic effects, thereby leading to laser damage. A wide band gap corresponding to good electronic effects and high thermal conductivity corresponding to good thermal effects are beneficial for high LDTs,^[12] however, the intrinsic contradiction between the band gap and SHG coefficient renders the difficulty in balancing the NLO performances in one compound. In addition, the thermal conductivity decreases with the increasing band gap,^[13] which leads to the challenge of searching for IR NLO materials with high thermal conductivity.

Beyond the traditional experimental trial and error attempts, computational tools have been utilized in the pursuit of discovering new NLO materials.^[14] For example, crystal structure prediction combined with electronic-structure methods is proved as a powerful technique to speed up materials discovery.^[15] Also, with the development of massive material databases such as the Inorganic Crystal Structure Database (ICSD)^[16] and Materials Project,^[17] screening and predicting potential materials has already applied been successfully in thermoelectrics.^[18] superconductivity,^[19] ion batteries^[20] and photovoltaic fields.^[21] For NLO materials, some germanates from ICSD database were screened in terms of band gaps and NLO coefficients.^[22] More recently, combined with machinelearning methods, a multi-level data-driven approach has also been proposed to realize fast and efficient structure prediction.^[23] However, high-throughput screening is generally applied to specific systems, a more systematic search based on a wider chemical space is very necessary to explore the novel system for IR NLO materials. In addition, the screening or designing condition mainly focuses on large SHG coefficients and wide band gaps, while the role of thermal properties in LDTs is neglected because thermal conductivity is difficult to evaluate due to the limited computational resources.

In this work, we designed a robust high-throughput computational strategy to search for excellent NLO materials with balanced optical properties and high thermal conductivities. We first extracted 1925 thermodynamically

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stable/meta-stable compounds with suitable band gaps from 144595 materials in the Material Project database. And then a total number of 106 candidates as very promising IR materials were successfully identified. The thermodynamically and dynamically stable compounds with balanced NLO properties of large E_g (2.59–4.09 eV), strong SHG efficiency (6.2–39.7 pm/V), and good thermal conductivity (\geq 1 W/(mK)) were screened out, among which we successfully synthesized Sr₂SnS₄ and measured its SHG intensity, the results verify the reliability of our process. We further analyzed the structure-property relationship of NLO-related properties and high thermal conductivity. The result indicates that nitrides could be novel materials with high thermal conductivity and potential ability in the IR NLO field. In the meanwhile, the exploration of new NLO-active units in nitrides and the mechanistic analysis of high thermal conductivity may provide new prospects for the discovery of new NLO materials with high thermal conductivity.

Results and Discussion

Unbiased high-throughput screening framework

Figure 1 shows the workflow of high-throughput screening process in detail, to make our screening results objective and unbiased, we systematically extract 144595 inorganic compounds from the Material Project. For this large number of potential compounds in the Material Project, a rapid estimation of the thermodynamic stability is important to evaluate the possibility of the experiment, all compounds with $E_{\rm hull} \leq 50$ meV/atom are selected as experimentally synthesizable candidates. In addition, the number of atoms in the unit cell of a structure is limited to no more than 30 atoms in order to conserve computational resources. To further narrow down the search range, the band gaps provided by Material Project are limited between 2 eV and 4 eV to accelerate the discovery of targeted candidate crystals considering the opposite trend between band gaps



Figure 1. The targeted workflow of high-throughput screening process.

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and SHG response. In total, 1925 compounds are screened, among which 601 compounds are non-centrosymmetric and extracted for next step of high-throughput calculations for band gaps and SHG coefficients. Then, 106 compounds with required band gaps and SHG coefficient are discovered, among them, 66 compounds have been reported as promising NLO materials before, which verifies the efficiency of our high-throughput screening framework.

Except for NLO-related optical properties, thermal properties also play an important role in further applications. Higher thermal conductivities can reduce the thermal effect and decrease the thermal damage of the crystal, which is beneficial to improving the service life of the NLO device and the efficiency of the optical device. However, to date, thermal conductivity has been barely considered in highthroughput screening for NLO materials, because calculating thermal conductivities is usually expensive and timeconsuming by first-principles calculation. To solve this problem, a rapid and rough screening method based on slack model^[24] was proposed to estimate the thermal conductivity. In this step, compounds with thermal conductivity calculated by slack model $(k_{\rm L}^{\rm Slack})$ larger than 1 W/(mK) were retained, 38 compounds were screened out with unreported NLO properties and good thermal conductivity. Then, the dynamical stability calculation was performed by calculating their phonon dispersion, 17 compounds were highlighted as final candidates due to the absence of imaginary phonon modes as shown in Figure S1.

Figure 2(a) shows the system distribution of 601 noncentrosymmetric structures, containing 117 chalcogenides, 46 nitrides, 349 oxides, 83 halides and 6 other compounds, illustrating the inhomogeneity of data distribution in Material Project and proving the unbiasedness of our process. High-throughput computing for NLO performance is conducted to these materials, the results show that their band gaps span widely from 1.80 to 5.99 eV, and the maximum SHG coefficient $|d_{ij}|^{\text{max}}$ spans from 0 to 36.06 pm/V. Especially, in 106 compounds which satisfy the balance between large band gap (\geq 2.5 eV) and SHG coefficients (\geq 6 pm/V) (Figure 2(b)), there are 68 chalcogenides, 8 nitrides, 20 oxides, 6 halides and 4 other compounds like AlP and SiC, covering a wide range of compounds from binary to pentanary compounds, as shown in Figure 2(c). The distribution of the band gap and SHG coefficient respective to chalcogenides, nitrides, oxides, halides and other compounds are shown in Figure 2(d). Among 106 compounds, chalcogenides show an overwhelming advantage in NLO materials with high SHG coefficient, but with relatively smaller band gaps compared with nitrides. Nitrides exhibit large band gaps and large SHG coefficients. Oxides have large band gaps but lower SHG coefficients and narrow transparency ranges originated from the intrinsic vibration absorption of metal-O bonds.^[25] Halides, which mainly include iodinecontaining halides and chalcohalides, show enhanced SHG response but much smaller band gaps and birefringence.^[26]

By using a preliminary screening method implemented based on slack model, thermal conductivities are further evaluated. There are 81 compounds with k_L^{Slack} values larger than 1 W/(mK), considered as materials with potential high

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Figure 2. Schematic diagram of high-throughput screening process. (a) Data distribution of 601 compounds through preliminary screening. (b) Calculated HSE06 band gaps (E_g^{HSE06}) and the maximum SHG coefficients ($|d_{ij}|^{max}$) by high-throughput method. 106 compounds with E_g^{HSE06} values larger than 2.5 eV and $|d_{ij}|^{max}$ larger than 6 pm/V were screened out. (c) Data distribution of screened 106 compounds. (d) NLO-related properties classified by chalcogenides, nitrides, oxides, halides and others. (e) Calculated thermal conductivity based on slack model (k_L^{Slack}), compounds with k_L^{Slack} values larger than 1 W/(m K) were retained. (f) Average value of $|d_{ij}|^{max}$, E_g^{HSE06} , birefringence (Δn) and k_L^{Slack} for nitrides, chalcogenides, oxides and halides, respectively.

thermal conductivity (Figure 2(e)). For instance, SiC with $k_{\rm L}^{\rm Slack}$ value of 138 W/(mK), is screened out, which has already been reported as a good NLO crystal with high thermal conductivity to generate IR radiation,^[27] further verifying the efficiency of our evaluation. Surprisingly, apart from extensively explored chalcogenides, several novel nitrides are screened out. After systematic investigation, it is found that nitrides are often regarded as promising photovoltaic materials,^[28] only a few of them have been studied as NLO materials^[29] such as SrSiN₂ (4.15 eV, 8.66 pm/V), BaGeN₂ (3.30 eV, 12.61 pm/V),^[30] NaSnN (1.34 eV, 27.0 pm/ V),^[31] etc. Figure 2(f) exhibits the average value of $|d_{ii}|^{\text{max}}$, E_{g}^{HSE06} , birefringence (Δn), and thermal conductivities, illustrating that nitrides possess much higher thermal conductivities compared with chalcogenides.^[32] The systematic data analysis indicates that nitrides could be a novel system for NLO materials with excellent performance. The unexplored structure-property relationship of the longneglected nitrides and popular chalcogenides is worth studying.

NLO Performance of Dynamically Stable Structures

Through the screening method, we obtained 38 unreported NLO materials with good thermal conductivity, 17 of them are dynamically stable with balanced NLO properties, including 11 chalcogenides and 6 nitrides.

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For the 11 chalcogenides, they can be classified according to the composition (Table 1): (i) the structures containing lone-pair cations: Li₃SbS₃, Na₄Si₂PbSe₆, Li₂PbGeS₄ with the band gap of 2.59-3.38 eV, the maximum SHG coefficient value of 9.88-15.17 pm/V, birefringence of 0.100-0.243; (ii) the structures containing d^0 transition metal cations (Ti^{4+}) : Li₄TiS₄, Li₈TiS₆ with the band gap of 3.42–3.52 eV, the maximum SHG coefficient of 8.12-16.25 pm/V, birefringence of 0.004–0.024; (iii) the structures containing d^{10} transition metal cations $(Zn^{2+} \text{ and } Cd^{2+})$: ZnCdGa₄S₈, MgZn₃S₄, Al₂Zn₂S₅ with the band gap of 3.02-4.09 eV, the max SHG coefficient of 9.08-17.34 pm/V, birefringence of 0-0.033; (iv) other structures with main group elements: Li_3SbS_4 , InGaS₃, Sr₂SnS₄ with the band gap of 2.80–3.67 eV, the maximum SHG coefficient of 6.21-9.71 pm/V, birefringence of 0.014-0.064. It is worth noting that structures containing lone-pair cations usually exhibit larger birefringence, while the structures with main group elements usually exhibit larger band gaps. A more detailed description of the crystal structure and properties are provided in the Supporting Information. Herein, we choose Sr₂SnS₄ for case study as it perfectly meets the most balanced properties: a wide band gap of 3.67 eV, a strong SHG response $d_{24} = -6.21$ pm/V and a moderate birefringence of 0.064. Sr₂SnS₄ (Ama2, No. 40) has two crystallographic Sr atoms, one Sn atom and three S atoms as shown in Figure 3(a). [SrS₈] dodecahedra and [SnS₄] connected with each other by edge-sharing or cornersharing. The calculated thermal conductivity based on the slack model is 1.06 W/(mK). Further, we successfully **Table 1:** Calculated E_{g} , Δn and d_{ij} of 11 chalcogenides.

Formula	Space Group	E _g [eV]		Δn	d _{ij} [pm/V]
		GGA	HSE06	[@ 1064 nm]	
Li₃SbS₃	R3m	2.59	3.38	0.243	$d_{15} = 5.43;$
Na4Si2PbSe6	C2	2.32	2.59	0.150	$d_{33} = 15.17$ $d_{16} = -9.88;$ $d_{14} = -2.71;$ $d_{14} = -2.71;$
		2 1 2	2 77	0 100	$d_{22} = 9.21,$ $d_{23} = -1.55$ $d_{23} = -15.08$
	142m	2.13	2.77	0.100	$d_{14} = -15.08$
Li ₈ TiS ₆ ZnCdGa ₄ S ₈	I42m P6₃cm P4	2.32 2.40 2.12	3.42 3.02	0.024 0.000	$d_{14} = -8.12$ $d_{15} = -8.12$ $d_{15} = -1.55;$
$MgZn_3S_4$	Pm	2.04	3.32	0.030	$d_{14} = 17.34$ $d_{11} = 11.23;$ $d_{12} = -6.22;$ $d_{13} = -6.10;$ $d_{14} = -6.10;$ $d_{15} = -6.10;$
$Al_2Zn_2S_5$	P 2 ₁	2.75	4.09	0.033	$d_{24} = 3.22, \\ d_{33} = -3.58 \\ d_{16} = -4.44; \\ d_{14} = -0.15; \\ d_{22} = 9.08;$
Li₃SbS₄	l42m	2.84	3.50	0.038	$d_{23} = -4.39$ $d_{14} = 6.98$
InGaS₃	P6 ₁	2.54	2.80	0.014	$d_{15} = 6.10;$
Sr_2SnS_4	Ama2	2.97	3.67	0.064	$d_{33} = -9.71$ $d_{15} = 5.75;$ $d_{24} = -6.21;$ $d_{33} = -1.84$



Figure 3. (a) Structure of screened chalcogenide: Sr_2SnS_4 . (b) Strucctures for nitrides $ZrZnN_2$; (c) $TiZnN_2$; (d) $CaGeN_2$.

synthesize powder sample of Sr₂SnS₄ (Figure S3), it exhibits the SHG intensity of $0.5 \times \text{AgGaS}_2$ at 2.09 µm fundamental wave laser radiation (particle size range: 105–150 µm), which serves as a good verification of the effectiveness of our screening process.

Six non-centrosymmetric nitrides are screened out including $AZnN_2$ (A = Ti, Zr), Mg₃MoN₄, Zn₃BN₄ (B = W,

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Mo), and CaGeN₂. Except for ZrZnN₂ (Figure 3(b)), others are all diamond-like structures (Figures 3(c-d) and S4). Mg_3MoN_4 and Zn_3BN_4 (B = W, Mo) have similar structures, crystalizing in *Pmn2*₁ (*No.* 31), TiZnN₂ (Figure 3(c)) crystalizes in the same space group as LiGaS₂ (Pna2₁, No. 33), these four structures can be considered as derived from hexagonal forms of diamond with wurtzite structures. $CaGeN_2$ (Figure 3(d)) crystalizes in the same space group as $AgGaS_2(I\overline{4}2d, No. 122)$, which can be considered to be derived from tetragonal form of diamond with sphalerite structures. Each cation is coordinated with four N atoms to form distorted [MN₄] (M=Mg, Mo, Zn, W, Ti, Ca, Ge) tetrahedra, these tetrahedra are linked together by sharing the N atom to form three-dimensional structures. ZrZnN₂ crystalizes in P3m1, in the structure one crystallographically unique Zr atom is octahedrally coordinated with N atoms to form [ZrN₆], [ZrN₆] connects with each other by edgesharing to build octahedral layers, one unique Zn connects with four N atoms to form [ZnN₄] which connects with each other to form tetrahedral layers. The two layers are stacked in the c direction.

The band gaps based on the HSE06 hybrid functional in Table 2 (3.06-4.09 eV) show a great promotion compared to AgGaS₂ (2.73 eV), and comparable to LiGaS₂ (4.15 eV).^[33] Owing to a positive correlation between a large band gap and a large LDTs,^[34] these six nitrides may have a higher LDTs compared to chalcogenides for subsequent applications. Further, as the high-energy end of the transparency window of a crystal is approximately determined by the electronic structure band gap (E_g) , the corresponding lowenergy end is approximately dependent on the band localized at the largest vibration frequency.[35] Herein, phonon dispersion spectra (Figure S1) and the infrared spectra (Figures S5-S6) illustrate that infrared transmission range of the nitrides is slightly smaller than that of chalcogenides, which mainly results from the intrinsic vibration of N atoms, but it can also achieve preferable transmission in the $3-5 \mu m$ region, making them a promising alternative system for infrared NLO materials.

Table 2: Calculated E_{g} , Δn and d_{ij} of six nitrides.

Formula	Space Group	E _g [eV]		Δn [@	d _{ij} [pm/V]
		GGA	HSE06	- 1064 nmj	
TiZnN ₂	Pna2 ₁	2.67	3.70	0.072	$d_{15} = 18.87;$ $d_{24} = 21.55;$ $d_{33} = -39.72$
$Mg_{3}MoN_{4}$	Pmn2 ₁	3.00	4.09	0.030	$d_{15} = -12.50$ $d_{24} = 12.22;$ $d_{33} = 24.95$
$ZrZnN_2$	P3m1	1.98	3.11	0.276	$d_{15} = 10.06;$ $d_{33} = 2.15$
Zn_3WN_4	Pmn2 ₁	2.12	3.60	0.069	$d_{15} = 9.86;$ $d_{24} = 10.56;$ $d_{33} = -18.71$
Zn₃MoN₄	Pmn2 ₁	1.73	3.06	0.094	$d_{15} = 18.26;$ $d_{24} = 19.42;$ $d_{33} = -34.57$
$CaGeN_2$	I42d	2.82	3.95	0.064	$d_{14} = 7.23$

More interestingly, nitrides show a better balanced optical performance with the SHG coefficient around 0.5–2.9×AGS and the birefringence about 0.030–0.276. The results are comparable to or larger than some known compounds in the nitride system, e.g., NaSnN^[31] (1.34 eV, 2.0×AGS, Δn =0.629), Zn₂NCl (3.21 eV, 0.9×AGS, Δn =0.060), and Zn₂NBr^[29b](3.28 eV, 0.8×AGS, Δn =0.063). Especially, TiZnN₂ exhibits the most balanced NLO-related properties with the maximum value of the SHG coefficients in the effective SHG formula d_{24} =21.55 pm/V (1.6 times that of AGS), the band gap of 3.7 eV.

New NLO active motifs

Based on the robust high-throughput screening strategies, we have successfully screened out compounds with the balanced NLO performance in nitrides and chalcogenides system. However, unlike popular and well-studied chalcogenides, the underlying mechanisms of the large band gap and strong SHG response in nitrides system remain unknown. What is the difference in NLO active motifs between nitrides and chalcogenides? In terms of chalcogenides, as shown in Figure 4(a), taking Sr_2SnS_4 for example, the total and partial density of states (PDOS) show that the valance bands (VBs) mainly originate from S-s/p, Sn-s, and Sr-p, conduction bands (CBs) are mainly composed of S-s/p, Sn-p, and Sr-s/p orbitals, indicating that SnS_4 contributes the most to the optical properties, which is also verified by bandresolved NLO coefficients and SHG density result (Figure S8). Similarly, for other chalcogenides, covalent groups such as Zn/Ti/Sb-S motifs make the main contribution to the SHG response (Figure S9), while the group with alkaline earth metals such as Sr/Mg–S contributes a little to it.

For nitrides, the electronic structures of six nitrides exhibit similar features, as shown in Figure 4(b) and Figure S10, the VB top for A_3MN_4 (A = Mg, Zn; M = W, Mo) is occupied with N-*p*, A-*p*, M-*d* orbitals, while the difference



Figure 4. Total and partial density of states (PDOS) and band-resolved NLO coefficients of (a) Sr_2SnS_4 , (b) $TiZnN_2$; (c) SHG-weighted densities of Mg₃MoN₄. Here, $\chi_{223} = 2 d_{24}$; $\chi_{113} = 2 d_{15}$.

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mainly appears at the CB bottom which is mainly occupied by *M*-*d*, N-*p*, and *A*-*s* orbitals. For AMN_2 (*A* = Ti, Zr, Ca; M = Zn, Ge), the VB top mainly contributes from N-p, A-d, and M-p orbitals, and the CB bottom is mainly occupied by A-d and N-p. As for band-resolved SHG, the NLO-related VB at -2 eV and -1 eV come from N-p orbitals with a positive contribution. For NLO-related CB, MoN₄ with *d-p* hybridization and MgN₄ units located near the Fermi level make a positive contribution for Mg₃MoN₄, similar effects occur in [MoN₄] for Zn₃MoN₄; [TiN₄] for TiZnN₂; [WN₄], and [ZnN₄] or Zn₃WN₄; [ZrN₆] for ZrZnN₂; [CaN₄] and [GeN₄] for CaGeN₂. SHG-weighted densities as shown in Figures 4(c) and S11 also reveal the novel NLO active motifs in nitrides, namely, $[MN_4]$ (M = Mg, Zn, Mo, Ti, W, Ca, Ge) and [ZrN₆]. It is worth noting that different from the wellknown NLO-active motifs in chalcogenides system, the group with alkaline earth metals [MgN₄]/[CaN₄] have significant contributes to the NLO effects (Figure 4(c)). To further analyze the micro mechanism for this difference, electronic density is analyzed as taking MgZn₃S₄ and Mg₃MoN₄ for comparison: the aspherical charge distribution of [MgN₄] is more apparent as compared to [MgS₄], which indicates [MgN₄] with more covalent interaction and stronger bond strength under the non-centrosymmetric sublattice is the major reason for the difference in NLO functional motifs between nitrides and chalcogenides (Figure S12).^[36]

Harmonic and anharmonic vibration of the lattice and thermal conductivity

A great advantage of nitrides over chalcogenides lies in high thermal conductivity as illustrated by preliminary screening. To further analyze the difference and mechanism of thermal conductivity in these two systems, herein we further calculated the temperature-dependent lattice thermal conductivity by first-principles method. Since ZrZnN₂ exhibits the largest k_1^{slack} among all compounds, it is highlighted for thermal conductivity analysis. The temperature-dependent lattice thermal conductivity values of ZrZnN₂ by firstprinciple (Figure 5(a)) shows that the thermal conductivity in the *ab* plane and along the *c*-axis is 5.13 and 2.07 W/(mK) at 300 K, both larger than that of $AgGaS_2$ (0.88 W/(mK)). Table S2 shows the calculated and experimental thermal conductivity $(k_{\rm L})$ at 300 K for some well-known IR NLO materials, among which ZrZnN₂ shows an overwhelming superiority in thermal conductivity, which further verifies the effectiveness of our strategy.

To explain the high thermal conductivity of ZrZnN₂, the intrinsic mechanisms of phonon scattering and phonon anharmonicity are elaborated. According to $k_{\rm L} = (1/vN_0)\Sigma_{\lambda}C_{\lambda}v_{\lambda} \otimes v_{\lambda}\tau_{\lambda}^{\rm SMRT}$, phonon group velocity and phonon lifetime are the key factors of lattice thermal conductivity. ZrZnN₂ exhibits a larger outer products of the group velocities $v_{\lambda} \otimes v_{\lambda}$ compared to AgGaS₂ in both acoustic and low-frequency (4–8 THz) optical phonon modes, reaching 17103 THz²Å² compared to 13524 THz²Å² of AgGaS₂ (Figure 5(b–c)). Furthermore, to effectively evaluate the degree of phonon anharmonicity of two compounds, the frequency-dependent



Figure 5. (a) Temperature-dependent lattice thermal conductivity of ZrZnN₂ and AgGaS₂. (b–c) Outer products of the group velocities $v_{\lambda} \otimes v_{\lambda}$ for AgGaS₂ and ZrZnN₂, respectively. (d–e) Phonon lifetime for ZrZnN₂ and AgGaS₂ respectively in the frequency domain. (f) Distribution of ELF for AgGaS₂ (up) and ZrZnN₂ (down).

phonon lifetime is discussed (Figure 5(d–e)), the results demonstrate that $ZrZnN_2$ exhibits an obviously higher value for optical phonons in 4–10 THz than that for AgGaS₂, which can be considered as the main cause for the high thermal conductivity of $ZrZnN_2$.

As for the macroscopic and chemical bonding, apparently, ZrZnN₂ possesses an ordered layered crystal structure with high symmetry. This structure leads to a small-cell volume (53.09 $Å^3$), which is considerably smaller than AgGaS₂. Furthermore, the electronic localization function (ELF) values of different chemical bonds are shown in Figure 5(f), the small value in Zr-N bonding areas demonstrates the high covalent bonding nature for Zr-N bond, leading to a strong directivity and lower possibilities of atomic slides. The density of phonon states also confirms the high covalent bonding of Zr-N and Zn-N in the range of 2-10 THz. Less magnitude of lattice vibration of ZrZnN₂ can be deduced, resulting in the weak phonon anharmonicity which may lead to a high phonon lifetime, thus a high thermal conductivity. The result also indicates that compounds with strong bonding, ordered crystal structure with high symmetry and low anharmonicity are more likely to exhibit high thermal conductivity.

Conclusion

In conclusion, an efficient and unbiased high-throughput screening method combined with an accelerated thermal conductivity evaluation is proposed to search IR NLO material with high thermal conductivity. The stages of

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screening based on band gaps, SHG coefficients and thermal conductivity evaluation are conducted to more than 10^5 -level compounds from the Material Project database, and compounds with E_g^{HSE06} values larger than 2.5 eV, $|d_{ij}|^{\text{max}}$ values larger than 6.0 pm/V, k_L^{Slack} larger than 1 W/(mK) are screened out. Especially, the synthesizable nitrides as well as chalcogenides are highlighted which shows superiority in optical performances: SHG responses of 0.5–1.3×AGS and band gaps of 2.59–4.09 eV for chalcogenides, 0.7–2.9×AGS and 3.06–4.09 eV for nitrides. One compound Sr₂SnS₄ is synthesized and measured with SHG intensity as verification.

Several new NLO-active units are discovered, namely $[MN_4]$ (M=Mg, Zn, Mo, Ti, W, Ca, Ge) and $[ZrN_6]$, different from the well-known NLO-active motifs in chalcogenides system, the group with alkaline earth metals $[MgN_4]/[CaN_4]$ have significant contributions to the NLO effect due to the strong bonding of M-N bonds under noncentrosymmetric sublattice. In addition, nitrides exhibit much higher thermal conductivity compared to chalcogenides, for example, ZrZnN₂ shows 5.13 W/(mK) at 300 K in the *ab* plane, which is almost five times that of $AgGaS_2$. Further analysis reveals that highly symmetrical and ordered structure, strong bonding, high phonon velocity and long phonon lifetime induce a high thermal conductivity of ZrZnN₂. The high-throughput method provides a powerful tool that allows us to screen NLO compounds with balanced properties and high thermal conductivity, search for novel NLO-active genes, which is promising for the discovery of novel materials.



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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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