

SnP₂S₆: A Promising Infrared Nonlinear Optical Crystal with Strong Nonresonant Second Harmonic Generation and Phase-Matchability

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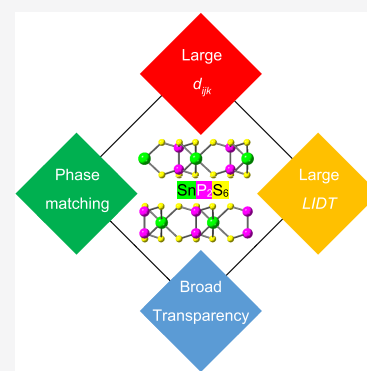
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ABSTRACT: High-power infrared laser systems with broad-band tunability are of great importance due to their wide range of applications in spectroscopy and free-space communications. These systems require nonlinear optical (NLO) crystals for wavelength up/down conversion using sum/difference frequency generation, respectively. NLO crystals need to satisfy many competing criteria, including large nonlinear optical susceptibility, large laser-induced damage threshold (LIDT), wide transparency range, and phase-matchability. Here, we report bulk single crystals of SnP₂S₆ with a large nonresonant SHG coefficient of $d_{33} = 53 \text{ pm V}^{-1}$ at 1550 nm and a large LIDT of 350 GW cm^{-2} for femtosecond laser pulses. It also exhibits a broad transparency range from 0.54 to $8.5 \mu\text{m}$ (bandgap of $\sim 2.3 \text{ eV}$) and can be both Type I and Type II phase-matched. The complete linear and SHG tensors are measured as well as predicted by first-principles calculations, and they are in excellent agreement. Two relatively flat conduction bands in the electronic band structure are shown to enhance the nonresonant SHG response through a double resonance enhancement of the nonresonant optical response. Therefore, SnP₂S₆ is an outstanding candidate for infrared laser applications.

KEYWORDS: second harmonic generation, nonlinear optics, infrared nonlinear optical crystals, metal chalcogenides



INTRODUCTION

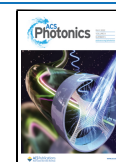
Nonlinear optical (NLO) crystals are essential components in high-power laser systems. They can produce coherent laser radiation at the wavelength of interest by combining or splitting photons, called sum (SFG) and difference (DFG) frequency generation.¹ Second harmonic generation (SHG) is an SFG process by which two identical photons combine into one at twice the frequency.^{1,2} Over the past decades, there has been increasing interest in discovering new infrared NLO crystals because of their scientific and technological applications such as remote sensing,³ biomedical imaging,⁴ and medical surgery.⁵ Traditional NLO materials such as β -BaB₂O₄, LiB₃O₅,⁶ and LiNbO₃⁷ are of limited usage in the mid-infrared regime due to strong multiphonon absorption. Currently, the commercially available infrared NLO crystals are AgGaS₂,⁸ AgGaSe₂,⁹ and ZnGeP₂.^{9,10} They exhibit large NLO coefficients and a broad transmission range; however, they also suffer some intrinsic drawbacks such as a rather low laser induced damage threshold (LIDT)^{11,12} and strong absorption of 1–2 μm ,¹³ limiting the choice of pump lasers.^{10,14} To qualify as a good NLO material, there are several criteria: (1) large SHG coefficients to have efficient NLO conversion; (2) wide transparency window allowing broad-band tunability; (3) large LIDT, and (4) phase-matchability for good SHG efficiency.^{10,15–17} It is well known that the main challenge in

the discovery and optimization of NLO materials is the tradeoff between the bandgap and the magnitude of the NLO coefficients: materials with larger bandgaps typically have lower SHG coefficients but higher LIDTs.^{17,18} Finding new infrared NLO crystals with a superior optimized set of optical properties to the current materials is a grand challenge in this field.

Metal thiophosphates are a promising compound system for NLO applications in the infrared region.¹⁵ The covalent characteristics of the P–S bonds not only give rise to a large NLO response but also lead to larger bandgaps (possibly higher LIDT value),¹⁵ both of which are essential for practical applications. Sn₂P₂S₆ is one of the metal thiophosphates whose linear and nonlinear optical properties are well studied.^{19,20} Though it has a wide transparency window up to $8 \mu\text{m}$ and can be phase-matched, it has a relatively small SHG coefficient of $d_{11} \approx 17 \text{ pm V}^{-1}$.²⁰ SnP₂S₆, closely related to Sn₂P₂S₆, is a

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promising NLO material.²¹ It was first synthesized in 1995 and has been reported to demonstrate excellent SHG response in powder form;^{21,22} however, its detailed optical properties have not been studied due to the lack of large, high-quality single crystals. Recently, Zhang et al. reported the SHG coefficient in two-dimensional SnP_2S_6 at a wavelength of 810 nm,²³ however, since the crystal has a bandgap of ~ 2.3 eV, the measured SHG at 405 nm is resonant in this case. For practical laser applications, the material must demonstrate large nonresonant nonlinearity for all photon energies below the bandgap. To address this question, we studied the experimental and theoretical linear and nonresonant nonlinear optical susceptibilities to evaluate its potential as a future NLO bulk material. We report that bulk single crystals of SnP_2S_6 demonstrate large SHG coefficients of $d_{33} = 53 \text{ pm V}^{-1}$ at 1550 nm, surpassing AgGaS_2 (13.7 pm V^{-1})²⁴ and AgGaSe_2 (33 pm V^{-1}).²⁵ SnP_2S_6 is also determined to be both Type I and Type II phase-matched at 1550 nm with $d_{\text{eff,I}} \approx 20 \text{ pm V}^{-1}$ and $d_{\text{eff,II}} \approx 15 \text{ pm V}^{-1}$. It also exhibits a broad transparency range from $0.54 \mu\text{m}$ to $8.5 \mu\text{m}$ (bandgap of ~ 2.3 eV). First-principles theory sheds light on the crystal chemistry reasons for the superior properties, especially the high nonresonant d_{ij} arising from the two relatively dispersionless conduction bands. Quantitative measurements and theoretical predictions of the complete linear and SHG tensors are in excellent agreement. These superior properties make it an outstanding candidate as a bulk NLO crystal for next-generation infrared laser systems.

RESULTS AND DISCUSSION

The single crystals of SnP_2S_6 were grown by chemical vapor transport using the method reported by Wang et al.²¹ The as-grown SnP_2S_6 crystal demonstrates excellent uniformity, as shown in Figure S1. It crystallizes in the space group of R3 and consists of a chiral and layered atomic arrangement, as shown in Figure 1a. In each layer, the P atoms are bonded covalently with each other and connect the P–S sublayer, in which the P–S bonds exhibit both covalent and ionic characteristics. The crystal structure of SnP_2S_6 is closely related to the parent compound $\text{Sn}_2\text{P}_2\text{S}_6$ except that half of the Sn^{2+} ions are replaced with Sn^{4+} ions, and the other half are vacant. Figure 1b shows the atomic resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image taken along the *a* axis. The STEM image confirmed that the layered structure of the as-grown SnP_2S_6 crystals consisted of the stacking of S–P–P–S layers, which agreed well with structures previously reported (Figure 1a).²¹ X-ray diffraction (XRD) collected on a single crystal SnP_2S_6 indicates its phase purity and high crystallinity, as shown in Figure 1c. The out-of-plane lattice parameter *c* extracted from the XRD (000*l*) pattern is $19.1 \text{ \AA}$, consistent with the previously reported value of $19.424 \text{ \AA}$.²¹

First-principles calculations were additionally performed to characterize the crystal structure of SnP_2S_6 . After structural relaxation with the local density approximation (LDA), the calculated cell parameters are $a = 5.919 \text{ \AA}$ and $c = 18.803 \text{ \AA}$. The former is in very good agreement (difference < 2%) with the previously reported experimental lattice parameter ($a = 5.999 \text{ \AA}$), while the discrepancy is slightly larger for the latter (3.2%). For this reason, the unit cell was also relaxed including van der Waals (vdW) interactions, leading to $a = 5.985 \text{ \AA}$ and $c = 19.460 \text{ \AA}$, in excellent agreement with the experimental values. First-principles calculations were also carried out to determine the band structure of SnP_2S_6 , shown in Figure 1d,

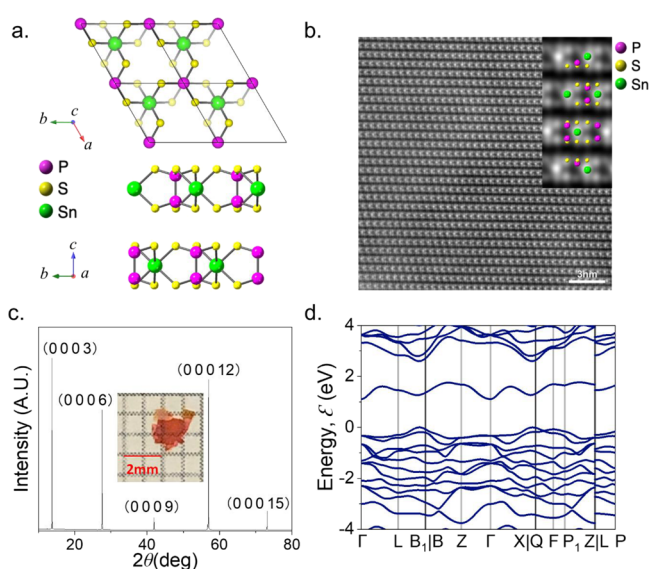


Figure 1. (a) Top view and side view of the SnP_2S_6 layers. (b) STEM image taken from the *a*-axis. Inset: magnified HAADF-STEM image superimposed with a unit cell indicates the layered structure. (c) XRD pattern of a high-quality SnP_2S_6 crystal. All peaks match well with the (000*l*) plane of the bulk crystal, and the *c* lattice constant is calculated to be $\sim 19.1 \text{ \AA}$, which is consistent with the reported value of $c = 19.424 \text{ \AA}$. (d) Computed band structure of SnP_2S_6 for the LDA structure presented here without any scissor shift. Scissor-shifted dielectric function is shown later.

without any scissor shift. As expected within LDA, the bandgap is severely underestimated. For the LDA structure, the fundamental gap is 1.1 eV and the direct gap is 1.3 eV. The first conduction band consists of an isolated electronic band with a bandwidth of 0.7 eV. For the vdW structure, the band structure without scissor shift remains similar (Figure S2), with fundamental and direct gaps of 1 and 1.1 eV, respectively, and the first conduction band has a similar bandwidth. To calculate the optical properties, scissor shifts were applied in the LDA and vdW structures, which will be discussed in the following sections.

We next investigated the linear optical properties of SnP_2S_6 . The transparency window of SnP_2S_6 was measured in transmission through a freestanding sample with the (0001) surfaces by ultraviolet–visible–near-IR spectroscopy (UV–Vis–NIR) (over $0.45 \mu\text{m}$ to $2 \mu\text{m}$) and Fourier transform infrared (FTIR) spectroscopy (over $1 \mu\text{m}$ to $20 \mu\text{m}$). During the FTIR measurements, a $15\times$ objective was used to focus the beam on the area with uniform thickness ($\sim 3.3 \mu\text{m}$). Thus, interference patterns were observed when multiple reflections occurred inside the sample and caused constructive/destructive interference. This was later used to determine the refractive index. No interference was detected in the UV–Vis–NIR data owing to the larger beam size used (beam diameter of 2 mm) and the non-uniform thickness of the sample. The artifacts at $\sim 0.86 \mu\text{m}$ are due to a change in the detector. From the transmittance (*T*) spectrum shown in Figure 2a (red: UV–Vis–NIR, blue: FTIR), SnP_2S_6 was found to be transparent from 0.54 to $8.5 \mu\text{m}$.

To determine the complex refractive index, $\tilde{n} = n + ik$, prism coupling method (performed by Metricon Corp.), spectroscopic ellipsometry, and FTIR spectroscopy were employed. Since SnP_2S_6 belongs to the point group of 3, it is uniaxial with two distinct refractive indices: ordinary refractive index $\tilde{n}_o$ and

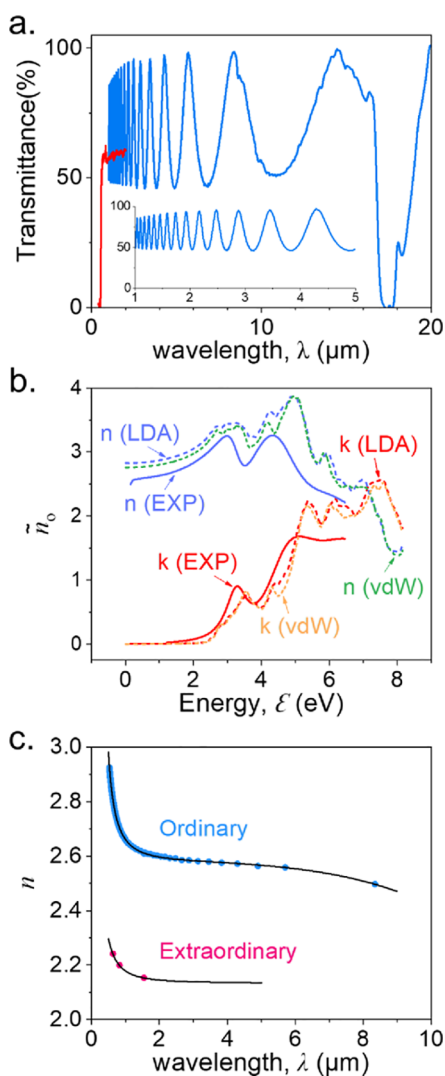


Figure 2. (a) Transmittance spectra of measured from 0.45 to 20 μm using UV-Vis-NIR spectroscopy (red) and FTIR spectroscopy (blue). The inset enlarges the FTIR spectrum from 1 to 5 μm for clarity. (b) Experimental complex ordinary refractive index of SnP_2S_6 compared with results from first-principles calculations using both LDA and vdW structures. (c) Ordinary and extraordinary refractive indices of SnP_2S_6 and the theoretical Sellmeier fit.

extraordinary refractive index $\tilde{n}_e$. A GaP prism was used to measure n_o and n_e at wavelengths of 0.633, 0.827, and 1.55 μm . The ellipsometric spectra collected on the (0001) surface of SnP_2S_6 were fitted to three Tauc Lorentz oscillators to extract $\tilde{n}_o$ from 0.200 to 1.000 μm (see Table S1 and Figure S3). The results agree well with the values measured by the prism coupling method. To obtain the ordinary optical constants in the spectral range of 1 to 8.5 μm , the interferometric method was used.²⁶ Knowing the thickness, $t = 3.3 \mu\text{m}$, of the sample and n_o at the wavelength of the first peak in the transmittance (T) spectrum from Figure 2a, the order of interference, m , can be found using

$$m = \frac{2 \cdot n(\lambda_m) \cdot t}{\lambda_m} \quad (1)$$

The refractive indices at the successive peaks can thus be determined by

$$n(\lambda_{m-i}) = \frac{(m-i) \cdot (\lambda_{m-i})}{2t} \quad (2)$$

Since the energy range is below the bandgap and $n_o \gg k_o$, the reflectance R can be calculated using $R = \frac{(n-1)^2}{(n+1)^2}$. The absorption coefficient α can be estimated using $\alpha = -\frac{1}{t} \ln \frac{T}{(1-R)^2}$,²⁷ and thus k_o can be found since $k_o = \frac{\alpha \lambda}{4\pi}$.

First-principles calculations have also been used to compute the electronic contributions to the frequency-dependent refractive index using the LDA and vdW structures. The experimental and calculated complex ordinary refractive index are shown in Figure 2b, demonstrating a very good agreement.

The experimental n_o and n_e were then fitted to the Sellmeier equation:

$$n^2 = A + \frac{B}{\lambda^2 - C} + D \cdot \lambda^2 + E \cdot \lambda^4 \quad (3)$$

The parameters of the Sellmeier equations are shown in Table 1, and the real ordinary and extraordinary refractive

Table 1. Parameters of the Sellmeier Equation for the Linear Optical Properties of SnP_2S_6

n	A	$B (\mu\text{m}^2)$	$C (\mu\text{m}^2)$	$D (\mu\text{m}^{-2})$	$E (\mu\text{m}^{-4})$
n_o	6.645	0.4121	0.06588	-0.001321	-6.716×10^{-5}
n_e	4.551	0.2003	-0.0268		

indices are shown in Figure 2c. Note that n_e beyond 1.55 μm were obtained by extrapolating the Sellmeier equation to 6 μm based on the fact that it is non-absorbing up to 8.5 μm (Figure 2a).

Next, we studied the second-order NLO susceptibility of SnP_2S_6 . The induced nonlinear polarization $P_{2\omega}$ and the incoming electric field E_ω are related by the second-order optical susceptibility $P_{i,2\omega} \propto d_{ijk} E_{j,\omega} E_{k,\omega}$. The fundamental wavelength used was 1550 nm and the resulting SHG wavelength was thus 775 nm. This ensured that the SHG process occurred within the bandgap of 2.3 eV and only involved virtual transitions²⁸ and therefore minimized absorption and was nonresonant. SHG polarimetry was employed to study the SHG performance of SnP_2S_6 , as shown in Figure 3a. At various incident angles, α , the SHG responses generated from a $\sim 1.2 \mu\text{m}$ -thick SnP_2S_6 single crystal were recorded when the linear polarized fundamental electric field $E_\omega = (E_\omega \cos(\psi), E_\omega \sin(\psi), 0)$, with regard to the laboratory coordinates (X, Y, Z), was rotated by an angle of ψ . By convention, the crystal physics axes (Z_1, Z_2, Z_3) are defined as $Z_1 // [2\bar{1}10]$, $Z_2 // [01\bar{1}0]$, and $Z_3 // [0001]$.²⁹ Two sample orientations were used during the measurement, defined as O1: $X = Z_2, Y = -Z_1, Z = Z_3$, and O2: $X = Z_1, Y = Z_2, Z = Z_3$. The transmitted SHG field was then decomposed into p-polarized ($\parallel$) and s-polarized ($\perp$) by an analyzer and detected by a photo-multiplier tube. Figure 3b shows the quadratic dependence of SHG intensities and the incident power, confirming that the signal measured was generated by the second-order NLO effect.

For point group 3, the d tensor in Voigt notation is

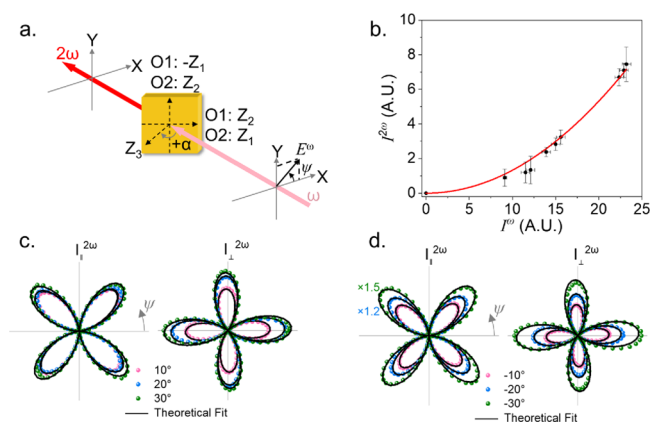


Figure 3. (a) Schematic of the SHG polarimetry geometry. (b) SHG power dependency of SnP_2S_6 crystal, confirming the detected response was from the SHG process. (c) Polar plots of p-polarized and s-polarized intensities for O1 at various incident angles. All sets of data were fit simultaneously to the point group 3.

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}. \quad (4)$$

For O1, the d_{eff} can be expressed as

$$\begin{aligned} d_{\text{eff},\parallel} &= \cos \alpha_{2\omega} (d_{22} t_{\parallel}^2 \cos^2 \psi \cos^2 \alpha_{\omega} - d_{22} t_{\perp}^2 \sin^2 \psi \\ &\quad - d_{14} t_{\perp} t_{\parallel} \sin 2\psi \sin \alpha_{\omega} - d_{15} t_{\parallel}^2 \cos^2 \psi \sin 2\alpha_{\omega} \\ &\quad + d_{11} t_{\perp} t_{\parallel} \sin 2\psi \cos \alpha_{\omega}) \\ &\quad - \sin \alpha_{2\omega} (d_{31} t_{\parallel}^2 \cos^2 \psi \cos^2 \alpha_{\omega} + d_{31} t_{\perp}^2 \sin^2 \psi \\ &\quad + d_{33} t_{\parallel}^2 \cos^2 \psi \sin^2 \alpha_{\omega}) \\ d_{\text{eff},\perp} &= d_{11} t_{\parallel}^2 \cos^2 \psi \cos^2 \alpha_{\omega} - d_{11} t_{\perp}^2 \sin^2 \psi \\ &\quad - d_{15} t_{\perp} t_{\parallel} \sin 2\psi \sin \alpha_{\omega} + d_{14} t_{\parallel}^2 \cos^2 \psi \sin 2\alpha_{\omega} \\ &\quad - d_{22} t_{\perp} t_{\parallel} \sin 2\psi \cos \alpha_{\omega} \end{aligned} \quad (5)$$

where $t_{\parallel}$ and $t_{\perp}$ are the Fresnel transmission coefficients for the p- and s-polarized light, respectively. Expressions of d_{eff} for O2 are provided in the Supporting Information (eq S1). The ratios of the SHG coefficients d_{ij} with respect to d_{22} were extracted by simultaneously fitting the polar plots to an analytical model similar to the one developed by Herman and Hayden,³⁰ with the additional modification that three inhomogeneous waves were considered instead of one. Figure 3c,d and Figure S4 show the SHG polar plots and theoretical fit for O1 and O2, respectively. The theoretical fits yield the following results: $d_{11}/d_{22} = -10.4 \pm 0.4$, $d_{14}/d_{22} = -0.15 \pm 0.04$, $d_{15}/d_{22} = -0.79 \pm 0.1$, $d_{31}/d_{22} = -0.23 \pm 0.1$, and $d_{33}/d_{22} = 25 \pm 3$. By comparing the p-polarized SHG intensities at $\alpha = 0^\circ$ and $\psi = 45^\circ$ of SnP_2S_6 at O1 and a reference z-cut LiNbO_3 crystal (shown in Figure S5), measured under the same experimental conditions, one can find $|d_{11}| = 22 \pm 0.4 \text{ pm V}^{-1}$. The other coefficients can thus be calculated with the known values of ratios. In addition to 1550 nm, we also performed SHG polarimetry at fundamental wavelength of $2 \mu\text{m}$ at $\alpha = 0^\circ$ and extracted $|d_{11}| = 20.2 \pm 3.5 \text{ pm V}^{-1}$ by comparing the p-polarized SHG responses of SnP_2S_6 and a z-cut LiNbO_3 crystal

at $\psi = 45^\circ$ shown in Figure S6. Since the ratios of the SHG coefficients do not change significantly at nonresonant wavelengths, one can calculate the other coefficients with the values shown above. The extracted SHG coefficients at 1550 nm are compared with the first-principles calculation, as listed in Table 2. The results show clear anisotropy and large

Table 2. Second-Order NLO Tensor Elements of SnP_2S_6 from the Experiment and First Principles at 1550 nm^a

d_{ij} at 1550 nm	experiment (pm/V)	first-principles theory (pm/V)
d_{11}	± 22 (0.4)	± 32
d_{15}	± 1.7 (0.2)	± 2.4
d_{31}	± 0.48 (0.2)	± 2.4
d_{22}	∓ 2.1 (0.04)	∓ 3.0
d_{14}	± 0.33 (0.1)	∓ 3.0
d_{33}	∓ 53 (6.4)	∓ 15

^aNumbers within parentheses are error bars.

nonlinear optical susceptibility, especially in one component $|d_{33}| \cong 53 \text{ pm/V}$ at 1550 nm fundamental light, which is higher than the benchmark infrared NLO crystals AgGaS_2 and AgGaSe_2 as shown in Figure S7 and Table S2. The large anisotropy, i.e., a near vanishing d_{22} , can be understood as follows. Each monolayer of the SnP_2S_6 lattice can be considered as applying small distortions to a higher-symmetry D_3 structure. If these distortions are ignored, each monolayer acquires a C_2 rotation axis along the vertical direction in Figure 1a upper panel and Figure S8. Since the distortions are small in the actual lattice, d_{22} is near vanishing. Indeed, a first-principles calculation using a symmetrized D_3 monolayer resulted in zero d_{22} . First-principles calculations were carried out using both the LDA and vdW structures to provide insight into the large SHG coefficients. The static SHG tensor d_{ij} and average $\langle d_{ij} \rangle$ (defined in ref 31) were obtained with the LDA and vdW structures with scissor shifts.³¹ The initial bandgaps are 1.11 and 0.97 eV with the LDA and vdW structures, respectively. Therefore, the applied scissor shifts are different (1.22 and 1.36 eV, respectively), leading to similar results in the end (Table S3). Band diagrams calculated using both LDA and vdW structures including scissor shifts are provided in Figure S9. Even though both structures are similar, using the vdW structure without including a scissor shift leads to a significant increase of $\langle d_{ij} \rangle$, as shown in Table S4. Indeed, a larger scissor shift leads to smaller SHG coefficients. Overall, d_{ij} is very sensitive to both the lattice parameters and the scissor shift.

The frequency dependence of d_{ij} represented in Figure 4 depicts the calculated complex d_{ij} coefficients for both structures at fundamental photon energy, ϵ , from 0 to 1.24 eV, and Figure S10 shows the calculated d_{ij} from 0 to 5.5 eV. Overall, the agreement with the experiment is good, particularly the relative magnitudes of each component and the evolution with ϵ . The d_{33} component shows the largest discrepancy; it is the most prone to being affected by vdW interactions. We find that a mere improvement of the structure (going from LDA to vdW) is, however, not sufficient to reconcile theory and experiment. Therefore, we hypothesize that vdW corrections going beyond the structure (i.e., also acting on the electronic density) are needed to improve d_{33} . We leave such investigation for future work.

In order to theoretically investigate the origin of the good NLO response of SnP_2S_6 , one can first look at the parent structure SnS_2 (both formed of very similar SnS_6 octahedra),

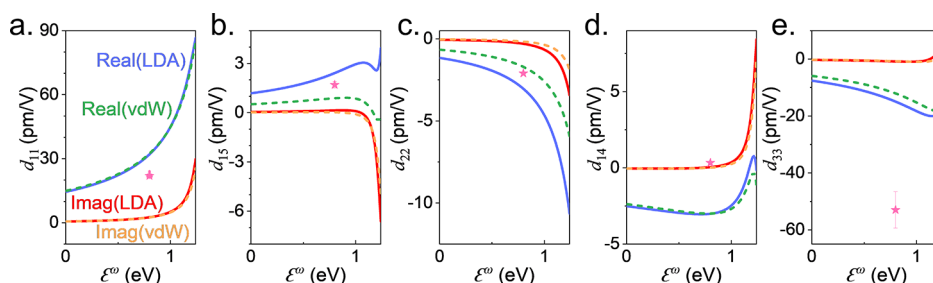


Figure 4. Complex d_{ij} coefficients versus energy calculated from first-principles theory for the LDA (solid line) and vdW (dash line) structures. The real components are labeled in blue (green) and the imaginary components are labeled in red (orange) for the LDA (vdW) structure. The experimental values are highlighted with pink stars for comparison.

depicted in Figure S11. This structure is centrosymmetric and therefore has zero nonlinear response. Yet, the natural centrosymmetry of SnS_2 can easily be artificially broken by rotating one every two layers by 180° around X or Y as shown in Figure S12. This noncentrosymmetric SnS_2 is only 0.5 meV/atom higher in energy than its centrosymmetric counterpart, demonstrating the weakness of the vdW interactions between the layers forming the material. More importantly, it now presents a nonlinear response. Overall, the electronic structures of SnP_2S_6 , centrosymmetric SnS_2 and noncentrosymmetric SnS_2 are very similar (Figure 1 and Figures S2, S9, and S15–S20). The most striking difference is the bandwidth of the conduction band, which is larger in SnS_2 . This can be rationalized by the presence of the P dimers in SnP_2S_6 , creating vacancies (see Figure 1a) that ultimately make the conduction band slightly less dispersive since it is constituted of Sn and S states. Therefore, the joint density of states (JDOS) is similar in all these systems, leading to similar dielectric constants (Table S6).³² Additionally, computing the static SHG tensor d_{ij} and average $\langle d_{ij} \rangle$ for noncentrosymmetric SnS_2 , we obtained a response only slightly smaller than SnP_2S_6 (Table S7), related to the slightly more dispersive conduction band and hence lower JDOS. We concluded that the SnS_6 octahedra present in both SnP_2S_6 and SnS_2 are the origin of the good optical properties of these materials. However, with SnS_2 being centrosymmetric, it simply cannot present a nonlinear response.

The importance of the isolated conduction band can also be verified by examining the calculated d_{ij} spectra. Here, we take the calculated d_{11} as an example (Figure S10a). According to a sum rule,³³

$$\text{Re}\{\chi^{(2)}(0, 0, 0)\} = \frac{2}{\pi} \mathcal{P} \int \frac{\text{Im}\{\chi^{(2)}(-2\omega, \omega, \omega)\}}{\omega} d\omega \quad (6)$$

the majority of the positive contribution to nonresonant d_{11} comes from lower-energy peaks in $\text{Im}[d_{11}]$, e.g., the one near 2.4 eV in Figure S10a. Comparing it with the computed band structure in Figure S9, we find that one-photon vertical transitions at 2.4 eV are only possible between the valence band and the isolated conduction band. The above observation suggests that the large NLO response is due to this intermediate conduction band enabling a double resonance process involving the valence, intermediate, and upper conduction bands, similar to double resonance enhancement mechanisms known in asymmetric quantum wells.³⁴ Double resonances or isolated bands are often discussed in two fields different from (but related to) nonlinear optics. In the

quantum well community, double resonances have often been exploited to maximize second-order nonlinear optical response,^{34,35} more often than in materials discovery literature. This is perhaps due to the relative simplicity of engineering quantum well energy levels compared with engineering dispersive bands in a solid. This observation suggests that double-resonance effects, if present in a periodic solid, may be more dominant when bands with weaker dispersions are present. This is indeed the case for the isolated band in SnP_2S_6 . The utility of isolated bands in solids has also been long embraced by the solar cell community as a means to increase efficiencies above the so-called Shockley–Queisser limit.^{36,37} In the solar cell community, these materials are called intermediate-band materials – they may be good candidates to search for large second-order optical nonlinearities dominated by double-resonance effects. A computational high-throughput search for intermediate-band materials has already been performed recently.³⁸ Future efforts could focus on inversion-asymmetric materials within such catalogs and evaluate whether they have higher nonlinearities in general (than the average nonlinearity in solids of similar band gaps). Quantitative verification of this potential double resonance mechanism will be examined in future work.

We also investigated the phase-matching conditions in SnP_2S_6 . For applications of high-power laser systems, phase-matching is one of the most critical criteria for a practical NLO material to have the most efficient SHG.^{39,40} When an NLO material is phase-matched, the sum of the fundamental wavevectors is equal to the wavevector of the second harmonic radiation, or $n^\omega = n^{2\omega}$. However, due to the dispersion of the refractive indices, this can only be achieved when there is sufficient birefringence in the crystal. Since SnP_2S_6 is a negative uniaxial crystal ($n_o > n_e$), the Type-I phase-matching condition is $n_o^\omega = n_e^{2\omega}(\theta_m)$ and the Type-II phase-matching condition is $n_o^\omega + n_e^\omega(\theta_m) = 2n_e^{2\omega}(\theta_m)$. By calculating the phase-matching angles with the aforementioned Sellmeier equations, SnP_2S_6 was found able to achieve both Type I and Type II phase-matching conditions over a broad spectral range of 1–6 μm , making it an excellent candidate for widely tunable lasers. Figure 5a,b shows the Type I and Type II phase-matching angles (θ_m) at wavelength, λ . The maximum d_{eff} values at 1550 nm wavelength are found to be 20.4 pm/V at $\phi = 1.8^\circ$ and 15.2 pm/V at $\phi = 28.2^\circ$ for Type I and Type II phase-matching, respectively. Here, ϕ is the azimuthal angle. The conversion efficiency for Type I phase-matching of SnP_2S_6 was calculated at 1550 nm, 2 μm , and 3.5 μm , and compared with those of LiNbO_3 and AgGaS_2 using

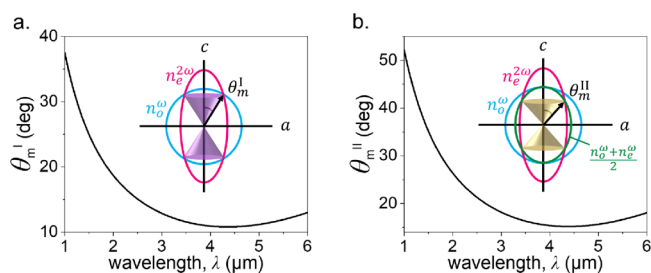


Figure 5. Type I (a) and Type II (b) phase-matching angles of SnP_2S_6 as a function of the fundamental wavelength, λ . The insets depict the relationship of the phase-matching angle and refractive indices.

$$\frac{I_{2\omega}}{I_{\omega}^2} = \frac{2\omega^2}{\varepsilon_0 c^3} \frac{d_{\text{eff}}^2}{n_{2\omega} n_{\omega}^2} t^2 \quad (7)$$

where ω is the angular frequency of light, ε_0 is the vacuum permittivity, c is the speed of light, and t is the thickness of the crystal, which is set to be 100 μm for the three materials as a demonstration. The d_{eff} values at 2 and 3.5 μm were calculated using Miller's rule. As shown in Table S8, SnP_2S_6 has the highest conversion efficiency among the three materials at these wavelengths. In addition, the Type I phase-matching angles and walk-off angles of SnP_2S_6 and LiNbO_3 were also compared at various wavelengths (Figure S21). Compared to LiNbO_3 , SnP_2S_6 has a larger walk-off angle due to its larger birefringence.

To utilize an NLO crystal in actual applications, it is critical for the material to have large LIDT values as LIDT and NLO performance are competing requirements. The LIDT of SnP_2S_6 was assessed using a femtosecond laser system at 1550 nm (1 kHz, 100 fs). The measurement was done on the (0001) plane of the crystal without polishing and coating. The incident power was gradually increased for each trial, and the surface was inspected using an optical microscope until any damage was observed. The LIDT value for SnP_2S_6 was found to be 350 GW cm⁻². This is more than three times greater than that of ZnGeP_2 (100 GW cm⁻² measured with 130 fs pulses),¹³ suggesting that SnP_2S_6 can achieve a large SHG coefficient and laser damage threshold and thus be applied in high-power infrared laser systems.

CONCLUSIONS

The linear and nonlinear optical properties of SnP_2S_6 bulk single crystal have been systematically studied. It exhibits both large nonresonant second-order nonlinear susceptibility of $d_{33} = 53 \text{ pm V}^{-1}$ at a 1550 nm fundamental wavelength and a large LIDT value three times greater than ZnGeP_2 . In addition, it can be both Type I and Type II phase-matched in a broad spectral range, and the effective d coefficients at 1550 nm are comparable to the state-of-the-art infrared NLO crystals AgGaS_2 and AgGaSe_2 . The complete linear and SHG tensors measured experimentally and calculated by first-principles theory are in excellent agreement. These remarkable properties suggest that SnP_2S_6 could be a promising bulk material for next-generation infrared lasers.

EXPERIMENTAL SECTION

Synthesis. A mixture of Sn powder (0.014 mol, 1.7 g), P powder (0.029 mol, 0.89 g), and S powder (0.086 mol, 2.8 g) was ground and sealed in an evacuated quartz tube. The quartz

tube was heated from room temperature to 300 °C in 5 h and held at that temperature for 10 h. After that, the source zone and the growth zone were heated to 400 and 450 °C, respectively, in 5 h and held for 12 h. Then, the temperatures of the two zones were switched within 5 h and maintained at that temperature for 8 days. Then, the growth zone was cooled to 200 °C in 5 h while the source zone was maintained at 450 °C. Finally, both zones were cooled to room temperature in 6 h. The as-grown crystals were characterized by single-crystal X-ray diffraction (XRD) to demonstrate the phase purity and excellent crystallinity.

Spectroscopic Ellipsometry. Spectroscopic ellipsometry was carried out using a Woollam M-2000F spectroscopic ellipsometer with a focused beam. The ellipsometric spectra were collected on the (0001) surface of SnP_2S_6 from 0.200 to 1.000 μm at room temperature and fitted to three Tauc Lorentz oscillators to extract the complex ordinary refractive index. The parameters of each Tauc Lorentz oscillator include an amplitude A , broadening parameter B , central transition energy E_0 , and Tauc gap E_g , as shown in Table S1.

SHG Measurements. The SHG measurements were performed in transmission geometry. The 1550 nm fundamental laser beam was generated by a Coherent Libra Amplified Ti:Sapphire Laser (85 fs, 2 kHz) and focused on the sample surface. The p-polarized and s-polarized SHG intensities were recorded by a photomultiplier tube while the fundamental beam was linearly polarized and rotated by an angle of ψ with a half waveplate with respect to the lab X axis. A z-cut LiNbO_3 (MTI Corporation) was used as a reference.

First-Principles Calculations. First-principles calculations have been performed using density-functional theory (DFT) with ABINIT.^{41–43} The wavefunctions were expanded on a plane-wave basis set with a kinetic energy cutoff of 40 Ha. Only valence electrons were explicitly taken into account adopting optimized norm-conserving Vanderbilt pseudopotentials from the PseudoDojo.^{44,45} The exchange-correlation energy was modeled using the local-density approximation (LDA).⁴⁶ In order to reach accurate and trustworthy results for third-order energy derivatives, ground-state properties have been very precisely determined by sampling the Brillouin zone with a Monkhorst–Pack $16 \times 16 \times 16$ k -point mesh and converging self-consistent field cycles with a criterion of 10^{-22} Ha on the total energy.^{47,48} In all calculations, a scissor shift has been applied to the conduction band to match the experimental band gap of 2.3 eV.

The primitive (trigonal) unit cell, with the same orientation as the experimental one, has been fully relaxed until a maximum force of 2.5 meV/Å on each atom was reached. The unit-cell relaxation has also been performed including van der Waals (vdW) interactions through the DFT-D3 method.⁴⁹ Note that, in that case, the Perdew–Burke–Ernzerhof generalized-gradient approximation⁵⁰ had to be utilized for the exchange-correlation energy, since the implementation of DFT-D3 is not available with LDA. Then, this relaxed cell has also been used to compute NLO coefficients using LDA, as the implementation of static NLO coefficients is limited to LDA. However, since it does not depend explicitly on the electronic density, the DFT-D3 method only induces corrections to the structure or properties related to derivatives of atomic positions such as interatomic force constants. Properties related to electric-field derivatives are not directly affected by such vdW corrections but rather indirectly by the crystal structure change.⁵¹

The static dielectric and SHG tensors have been obtained using density-functional perturbation theory.⁵² Third-order energy derivatives with respect to the electric field are obtained using the $(2n + 1)$ theorem,⁵³ where only the ground-state and first-order wavefunctions are needed. The frequency-dependent dielectric and SHG tensors have been computed within the independent-particle approximation with the Optic utility of ABINIT. Additional empty bands have been included, up to 20 eV above the valence band maximum, leading to a total of 64 empty bands. A broadening of 0.002 Ha (54 meV) has been used to smoothen the spectrum by avoiding divergences in the sum-over-states approach. The refractive index and extinction coefficient can easily be obtained from the dielectric constant following textbook equations. The average of the static SHG tensor, $\langle d_{ij} \rangle$, is obtained with ref 31

$$\langle d_{ij} \rangle^2 = \frac{19}{105} \sum_i d_{iii}^2 + \frac{13}{105} \sum_{i \neq j} d_{iii} d_{ijj} + \frac{44}{105} \sum_{i \neq j} d_{ijj}^2 + \frac{13}{105} \sum_{ijk, \text{cyclic}} \left(d_{ijj} d_{jkk} + \frac{5}{7} d_{ijk}^2 \right),$$

where d_{ijk} is the third rank SHG tensor and d_{ij} is its Voigt notation.⁵⁴

The AbiPy python package has been used to automate the input generation and workflow and analyze the results.⁵⁵

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsp Photonics.2c00131>.

Additional details on the experiment; single crystal, band structure, and complex ordinary dielectric constants of SnP_2S_6 ; polar plots of the p-polarized and s-polarized intensities; comparison of the SHG intensities; and other supporting figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

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