Large Second Harmonic Generation in Elemental α -Sb and α -Bi Monolayers

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ABSTRACT: Different from the extensively studied polynary compounds for second-order nonlinear optics (NLO), for the first time, we demonstrate that large intrinsic second harmonic generation (SHG) can also exist in twodimensional (2D) elemental materials such as monolayers α -Sb and α -Bi that have been recently synthesized with large scale and high quality where the Jahn– Teller-like distortions induced by the insufficient sp³ hybridization break the centrosymmetry, thus meeting the requirements for NLO response and leading to huge values of static SHG susceptibilities, which are two orders of magnitude larger than those of hotly studied MoS₂ and *h*-BN. By analyzing the evolution of density matrix, we further show that the major intraband contributions to SHG susceptibilities are from the significant linear dispersions near the band gaps in the two studied systems. Moreover, different from the alternating even–odd behaviors observed in other nonelemental 2D sheets, the SHG response remains in the multilayered α -Sb and α -Bi regardless of their thickness. These findings are



of significance in promoting the applications of 2D α -Sb and α -Bi sheets for future NLO devices.

INTRODUCTION

Nonlinear optics (NLO) has attracted significant interest because of its important role in photonic applications, such as photodetector, frequency conversion, ultrafast pulse generation, optical modulator/switches/memories, structure probing and biological sensing.^{1,2} Recently, large NLO susceptibilities, which are comparable and even 1–3 orders of magnitude larger than those of the commonly used bulk NLO materials, have been predicted and experimentally observed in ultrathin two-dimensional (2D) materials,^{3–6} such as transition-metal dichalcogenides (TMDs),^{7–15} *h*-BN,^{8,16} chromium triiodide,¹⁷ group III selenides,^{18,19} and group IV monochalcogenides.²⁰ Because of the nanoscaled thickness, these 2D materials are promising for on-chip applications without suffering from the integration bottleneck.¹

It is well known that the strength of the NLO response typically decreases with the order n; therefore, the second-order NLO effect, like the second harmonic generation (SHG), is mostly studied as it can be more easily observed in experiments. However, the second-order NLO effect vanishes in centrosymmetric structures. For this reason, all the reported materials with robust second-order NLO response are compounds containing at least two elements. Meanwhile, most known phases for elemental systems, such as graphene and black phosphorus (BP), have an inversion center,²¹ which forbids the even-order terms in electric polarization expansions. Experimentally, the second-order NLO effect in elemental materials can be only observed via special strategies. For example, several techniques have been developed to break

the centrosymmetry of graphene, like doping,^{22–24} multilayer stacking,²⁵ electric/magnetic field dressing,^{26–30} and interface engineering.³¹⁻³³ Thus, an intriguing question arises: is it possible to find a single-element material with an intrinsic second-order NLO effect? In 1964, R.C. Miller proposed a famous empirical rule $\chi^{(2)}_{abc} = \chi^{(1)}_{aa} \cdot \chi^{(1)}_{bb} \cdot \chi^{(2)}_{cc} \cdot \Delta^{(2)}_{abc}$ where $\Delta^{(2)}_{abc}$ is a constant depending on materials.³⁴ He found that the quantities of second-order susceptibilities $\chi^{(2)}$ of different NLO materials can vary by several orders of magnitude, while the variation of $\Delta^{(2)}$ is relatively small.^{34,35} Therefore, $\chi^{(2)}$ is mainly determined by the product of linear susceptibilities $\chi^{(1)}$. Because the ferroelectric (FE) crystal has no inversion center and usually possesses a large $\chi^{(1)}$, it becomes the preferred target for finding the NLO materials. In fact, FE and NLO materials are closely related. For example, conventional bulk ferroelectric KH₂PO₄ (KDP), KNbO₃, and LiNbO₃ are the widely used NLO crystals; recent studies have also showed that the Si surface^{36,37} and 2D group IV monochalcogenides^{20,38} have both good FE and NLO properties. These findings motivate us to explore elemental ferroelectric materials for answering the above question.

Recently, the BP-structured (α -phase) group V (As, Sb, and Bi) monolayers have received considerable attention.³⁹ These

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materials have strain-tunable anisotropic electronic properties,^{40–42} a broad range of band gaps, and large carrier motilities,⁴³ which open up new opportunities for multifunctional applications in optoelectronics, topological spintronics, thermoelectrics, sensors, and batteries.^{39,42,43} Especially, α -Sb and α -Bi monolayers have been found to exhibit spontaneous electric polarization.⁴⁴ Such intrinsic ferroelectricity guarantees the absence of inversion symmetry; thus, in principle, these elemental 2D sheets can have finite second-order NLO responses. More importantly, these 2D materials just have been successfully synthesized with large scale and high quality,^{45–47} making the present study of the NLO effect timely and of significance.

In this work, based on state-of-the-art theoretical calculations, we study the SHG responses in α -Sb and α -Bi monolayers in which the Jahn—Teller-like distortions are found to break the centrosymmetry, leading to large SHG susceptibilities mainly dominated by the intraband transition of electrons, as revealed by correlating the features of frequency-dependent SHG curves to band structures. Our findings not only demonstrate the existence of the secondorder NLO effect in elemental materials but also extend the applications of α -Sb and α -Bi in the NLO field.

COMPUTATIONAL METHODS

First-principle calculations based on density functional theory are performed for the group V monolayers. The DFT method has proven to be one of the most accurate methods for the computation of the electronic structure of solids.⁴⁸⁻⁵⁰ The structural, electronic, and optical properties are calculated by using the Vienna ab initio Simulation Package (VASP)⁵¹ with the projector augmented wave (PAW) method^{52,53} and a plane wave basis. The Perdew-Burke-Ernzerhof (PBE) functional within generalized gradient approximation (GGA)⁵⁴ is used to describe the electronic exchange-correlation interaction. An energy cutoff of 500 eV is applied. The convergence criteria for energy and force are set to be 0.00001 eV and 0.001 eV/Å, respectively. Monkhorst–Pack k-point mesh $(21 \times 19 \times 1)^{55}$ is employed to sample the Brilliouin zone during the structural relaxation. We use a vacuum space of 20 Å in the nonperiodic direction to minimize the interaction between two adjacent layers.

The SHG susceptibility $\chi^{(2)}(-2\omega, \omega, \omega)$ tensor is calculated within the independent particle approximation^{56,57} by using the package⁵⁸ developed by Zhang et al. based on the work of Rashkeev et al.⁵⁹ where the SHG tensor can be expressed as

$$\chi_{\text{total}}^{abc}(-2\omega,\,\omega,\,\omega) = \chi_e^{abc} + \chi_i^{abc} \tag{1}$$

where χ_e^{abc} is the pure interband contribution with the following form

$$\chi_{e}^{abc}(-2\omega, \omega, \omega) = \frac{e^{3}}{\hbar^{2}\Omega} \sum_{nml,k} \frac{r_{nm}^{a} \{r_{ml}^{b} r_{\ln}^{c}\}}{(\omega_{\ln} - \omega_{ml})} \left[\frac{2f_{nn}}{\omega_{mn} - 2\omega} + \frac{f_{\ln}}{\omega_{\ln} - \omega} + \frac{f_{ml}}{\omega_{ml} - \omega} \right]$$

$$(2)$$

and χ_i^{abc} has the form of eq 3, standing for the contribution of the mixed interband and intraband process that includes the

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modulation of linear polarization by the intraband motion (the first three terms), and the intraband motion modified by the polarization energy associated with the interband motion of electrons (the last term)^{56,59}

$$\begin{split} \chi_{i}^{abc}(-2\omega, \omega, \omega) &= \\ \frac{i}{2} \frac{e^{3}}{\hbar^{2} \Omega} \sum_{nm,k} f_{nm} \left[\frac{2}{\omega_{mn}(\omega_{mn} - 2\omega)} r_{nm}^{a} (r_{nm;c}^{b} + r_{mn;b}^{c}) \right. \\ &+ \frac{1}{\omega_{mn}(\omega_{mn} - \omega)} (r_{nm;c}^{a} r_{mn}^{b} + r_{nm;b}^{a} r_{mn}^{c}) \\ &+ \frac{1}{\omega_{mn}^{2}} \left(\frac{1}{\omega_{mn} - \omega} - \frac{4}{\omega_{mn} - 2\omega} \right) r_{nm}^{a} (r_{mn}^{b} \Delta_{mn}^{c} + r_{mn}^{c} \Delta_{mn}^{b}) \\ &- \frac{1}{2\omega_{mn}(\omega_{mn} - 2\omega)} (r_{nm;a}^{b} r_{mn}^{c} + r_{nm;a}^{c} r_{mn}^{b})] \end{split}$$
(3)

where $f_{nm} = f_n - f_{m\nu} \omega_{nm} = \omega_n - \omega_{m\nu}$ and $\Delta_{nm} = v_{nn} - v_{mm}$ are the Fermi distribution function difference, energy difference, and electron group velocity difference between *n*th and *m*th bands, respectively. r_{nm} is the position operator obtained by $\frac{P_{nm}}{im\omega_{nm}}$, Ω is the volume of unit cell, $\{r_{nl}^b r_{lm}^a\}$ is defined as $1/2(r_{nl}^b r_{lm}^a + r_{nl}^a r_{lm}^b)$, and $r_{nm;a}^b$ is the generalized derivative of the coordinate operator in momentum space with the form of

$$r_{nm;a}^{b} = \frac{r_{nm}^{a}\Delta_{mn}^{b} + r_{nm}^{b}\Delta_{mn}^{a}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_{l}\left(\omega_{lm}r_{nl}^{a}r_{lm}^{b} - \omega_{nl}r_{nl}^{b}r_{lm}^{a}\right)$$
(4)

Because optical properties calculations based on these equations require the band structures and momentum matrix elements (p_{nm}), an accurate electronic structure is needed. Therefore, we use a very dense *k*-point mesh of 101 × 97 × 1 to sample the Brilliouin zone for getting the converged SHG susceptibility tensor. Since PBE/GGA underestimates the energy band gap in the calculation of optical properties, the scissor approximation⁶⁰ is applied in which we use the HSE06 functional⁶¹ to obtain a more accurate gap for the correction. Moreover, the SHG susceptibility should be renormalized due to the ill-defined thickness of 2D materials. Similar with 2D piezoelectric coefficients,⁶² we define the sheet susceptibility corresponding to the spacing between 2D layers as $\chi_{\text{sheet}}^{\text{SHG}} = \chi_{\text{bulk}}^{\text{SHG}} \times L_z$. Thus, the unit of sheet SHG susceptibility is in pm²/V.

RESULTS AND DISCUSSION

Structural Distortion in Monolayers α -Sb and α -Bi. The group V monolayers (P, As, Sb, and Bi) have several possible crystal configurations.^{39,63-66} The α phase, also called the BP structure, consists of two flat atomic layers puckered along the x and y directions, which is most stable for phosphorene and arsenene (Figure 1a).³⁹ The space group of both α -P and α -As is *Pmna* with an inversion center, hence forbidding the second-order NLO effect. While for α -Sb and α -Bi, both the monolayers undergo a structural distortion that the flat atomic layers become buckled, as shown in Figure 1b,c (taking Bi as an example), which breaks the centrosymmetry, thus enabling the spontaneous electric polarization⁴⁴ and second-order NLO responses. To understand the origin of this structural distortion, we study the bonding configuration by calculating the charge density difference. Because a group V atom has five valence electrons (s²p³), it prefers to form sp³



Figure 1. Side view and bonding diagram of the (a) α -P, (b) flat α -Bi, and (c) buckled α -Bi monolayer.

configuration with three σ bonds and a lone electron pair. This is the case for α -P and α -As where the charge density distribution around a P (or As) atom has a tetrahedral geometry (Figure 1a), hence ensuring the stability. However, if α -Sb and α -Bi monolayers adopt the BP structure, that is, the two layers are flat, then there exist imaginary optical modes in phonon dispersions (see Figure S1).⁴⁴ This instability comes from the insufficient sp³ hybridization of Sb and Bi atoms, and a representative case of α -Bi is shown in Figure 2b. Different



Figure 2. Imaginary part of the SHG susceptibilities for the (a) α -Sb and (b) α -Bi monolayer.

from the P atom $(3s^23p^3)$, the configuration of valence electrons of Bi is $6s^24f^{14}5d^{10}6p^3$ in which the energy difference between the 6s and 6p orbitals is larger than that of the 3s and 3p orbitals; thus, not all the 6s electrons are excited to form a standard sp³ configuration. Thus, the density of lone electron pair is much lower than that of the σ bonds, which breaks the geometry of the tetrahedron (see Figure 1b).

It is known that the Jahn–Teller distortion occurs to remove the degeneracy and lower the energy when the d bands are partially filled in a certain crystal-field environment.⁶⁷ Here, in a similar way, the buckling in α -Sb and α -Bi monolayers makes one Bi (or Sb) atom more sp²-like in bonding configuration, while its neighboring atom is in sp³-like configuration. From the charge density difference in Figure 1c, it is clear to see that electrons transfer from one site to the other so that both hybridized orbitals on each atom tend to be fully occupied. In this case, the total energy is lowered with enhanced stability due to the splitting of the degenerated energy levels (see Figure 1c), which is similar to that of the T-penta-silicene sheet reported recently.⁶⁸ Second Harmonic Generation (SHG) in Monolayer α -Sb and α -Bi. The SHG susceptibility is described by a thirdrank tensor $\chi^{(2)}_{abc}$ defined as $P^a(2\omega) = \chi^{(2)}_{abc}(-2\omega, \omega, \omega)E^b(\omega)$ $E^c(\omega)$. Because α -Sb and α -Bi belong to the $Pmn2_1$ space group, both monolayers have seven nonzero tensor elements: $\chi^{(2)}_{121} = \chi^{(2)}_{112}, \chi^{(2)}_{221}, \chi^{(2)}_{232}, \chi^{(2)}_{233}$ and $\chi^{(2)}_{323} = \chi^{(2)}_{332}$. Generally, one is interested in the static limit of SHG $\chi^{(2)}(0,0,0)$, usually denoted as $\chi^{(2)}(0)$, because optical absorption can be suppressed in the highly nonresonant region, that is, $\omega \ll \omega_0$, where ω and ω_0 are the frequency of light field and the resonant frequency of a semiconductor ($\omega_0 = E_g/\hbar$), respectively. Besides, the dispersion of SHG susceptibility is very small when the light frequency is close to zero,⁶⁹ thus, $\chi^{(2)}(0)$ can be used to estimate the SHG efficiency in the infrared photon energy ranges. Table 1 lists the calculated

Table 1. Static Value of the SHG Susceptibilities (in pm^2/V) for α -Sb, α -Bi, and Some Previously Studied 2D Sheets

$C_{2\nu}$	$\chi_{12}^{(2)}$	$\chi_{211}^{(0)}(0) = \chi_{112}^{(2)}(0) = \chi_{211}^{(2)}(0)$	$\chi^{(2)}_{222}(0)$	$\begin{array}{l} \chi^{(2)}_{233}(0) = \chi^{(2)}_{323}(0) = \\ \chi^{(2)}_{332}(0) \end{array}$	
α -Sb		1.47×10^{6}	3.05×10^{5}	2.19×10^{5}	
α -Bi		3.43×10^{6}	2.66×10^{6}	1.53×10^{5}	
GeSe		5.45×10^{5}	1.28×10^{5}	4.24×10^{4}	
SnSe		3.51×10^{5}	1.35×10^{5}	3.36×10^4	
	D_{3h}	$\chi_{121}^{(2)}(0) = \chi_{112}^{(2)}(0) = \chi_{211}^{(2)}(0) = \chi_{222}^{(2)}(0)$			
	MoS_2	9.12×10^{4}			
	h-BN		1.26×10^{4}		

values of $\chi^{(2)}(0)$ where it is clear to see that $\chi^{(2)}(0)$ satisfies the full permutation with $\chi^{(2)}_{121}(0) = \chi^{(2)}_{112}(0) = \chi^{(2)}_{211}(0)$ and $\chi^{(2)}_{233}(0) = \chi^{(2)}_{323}(0) = \chi^{(2)}_{332}(0)$ under the Kleinman symmetry. The magnitudes of $\chi^{(2)}(0)$ in α -Sb and α -Bi are much higher than those of 2D MoS₂, *h*-BN, and group IV monochalcogenides. Such large $\chi^{(2)}(0)$ values indicate a strong frequency-doubling effect of both sheets, which are promising for optical device applications.

To understand the origin of the static value of SHG, we now consider the frequency-dependent SHG susceptibility, especially its imaginary part $\text{Im}[\chi^{(2)}(-2\omega, \omega, \omega)]$ from which the $\chi^{(2)}(0)$ value can be obtained by the Kramers–Kronig transformation

$$\chi^{(2)}(0) = \operatorname{Re}[\chi^{(2)}(0, 0, 0)] = \frac{2}{\pi} P \int_0^\infty \{\operatorname{Im}[\chi^{(2)}(-2\omega, \omega, \omega)]/\omega\} d\omega$$
(5)

Figure 2 shows the $\text{Im}[\chi^{(2)}(-2\omega, \omega, \omega)]$ curves of different tensor components for α -Sb and α -Bi (the real part and modulus can be seen Figure S2) where all of the main peaks are located below a photon energy of 1.5 eV, showing good infrared NLO properties. From a mathematic point of view, it can be inferred from eq 5 that $\chi^{(2)}(0)$ is largely determined by the low-energy region of $\text{Im}[\chi^{(2)}(-2\omega, \omega, \omega)]$ due to the existence of denominator ω in integrand. Therefore, only the first several peaks make the major contributions. For MoS₂ and *h*-BN, the main peaks in $\text{Im}[\chi^{(2)}(-2\omega, \omega, \omega)]$ are pushed away from the low-energy range (more than 2.0 eV)²⁰ due to their larger band gaps; thus, the lower weights $(1/\omega)$ lead to smaller $\chi^{(2)}(0)$ values as compared with the two studied sheets. In addition, we can intuitively understand some features of $\chi^{(2)}(0)$ in α -Sb and α -Bi from Figure 2. For example, one can see that the main peaks in $\chi^{(2)}_{121}$ of α -Sb are all with negative

signs; hence, its enclosed area will be added together during integral. However, both positive and negative peaks appear in $\chi^{(2)}_{211}$, so compensation takes place. As a result, although the largest peak in $\chi^{(2)}_{211}$ is higher than that of $\chi^{(2)}_{121}$, $\chi^{(2)}(0)$ of the two components possess the same value. While for α -Bi, we find that $\chi^{(2)}_{222}(0)$ is comparable with $\chi^{(2)}_{121}(0)$ and $\chi^{(2)}_{211}(0)$, differing from the case in α -Sb. From Figure 2, one can see that $\chi^{(2)}_{222}$ curves in two monolayers have the similar features with the appearance of positive peaks followed by negative ones. The only difference is in the low-energy region where the peaks (blue line) in α -Bi are relatively high and significant in weight, thus making more contributions to $\chi^{(2)}_{222}(0)$.

Next, we analyze the Im[$\chi^{(2)}(-2\omega, \omega, \omega)$] curves in terms of the underlying band structure. For the SHG response in a semiconductor, the light-induced electric polarization ($P = \sum_{p + \int_{ij} dt$) includes two main physical contributions (see Figure 3a): one is the electron interband transition, which is similar to



Figure 3. (a) Schematic of interband and intraband transition. (b) Evolution of density matrix in a different optical process for a semiconductor. \vec{r}_e and \vec{r}_i are the interband and intraband parts of the position operator, respectively.

that of the atomic NLO physics, creating a dipole moment (p), and the other is the intraband transition that generates a polarization current (j) as electrons move within their original bands driven by the *E*-field. Theoretically, the SHG effect is treated by solving the dynamical equation of density matrix $i\hbar \cdot d\rho/dt = [H_0 - e\vec{r} \cdot \vec{E}, \rho]$ within the framework of the perturbation theory,^{56,57} where ρ is the probability density, H_0 is the intrinsic Hamiltonian of a semiconductor, and $H' = -e\vec{r}$ $\times \vec{E}$ is the Hamiltonian for light-matter interaction (regarded as the perturbation). The *n*th order of polarization can be represented by $\vec{P}^{(n)} = tr(\rho^{(n)}\hat{P}) + \int_i tr(\rho^{(n)}\hat{J})$ where \hat{P} and \hat{J} denote the dipole moment and current density operators, respectively. One can simply write the expansion of ρ as

$$\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \rho^{(3)} + \dots + \rho^{(n)}$$
(6)

with

$$\frac{\partial \rho^{(n)}}{\partial t} = \frac{1}{i\hbar} \{ [H_0, \rho^{(n)}] + [H', \rho^{(n-1)}] \}$$
(7)

This recursive relation clearly implies that higher order of $\rho^{(n)}$ solely results from the commutation of H' and its lower order $\rho^{(n-1)}$. Figure 3b shows the evolution of density matrix to its second order under the external *E*-field where $\rho^{(2)}$ is composed of $\rho_{ee}^{(2)}$ and $\rho_{ie}^{(2)}$, which corresponds to the perturbation from the pure interband transition and the mixed inter/intraband transition. For a better understanding of the SHG response, one can track how the density matrix is modified in each order of perturbation. Because the density operator ($\hat{\rho} = |\psi\rangle\langle\psi|$) involves the eigen state of H_0 , one can then correlate the features of SHG to the band structure. More detailed illustrations about density matrix can be found in the Supporting Information.

In Figure 4a,b, we plot the different contributions to the imaginary part of SHG in α -Sb. For the tensor elements $\chi^{(2)}_{121}$



Figure 4. Imaginary part of interband, intraband, and modulation contributions to the SHG susceptibility of (a) $\chi_{21}^{(2)}$ and (b) $\chi_{121}^{(2)}$ for α -Sb. (c) Imaginary part of dielectric function $\varepsilon_2(\omega)$ of α -Sb. (d–g) *k*-point-dependent distributions of normalized $\varepsilon_2(\omega)$ for different band pairs.

and $\chi_{211}^{(2)}$ with the largest static values, all of the main peaks are mostly contributed by the intraband term $\chi^{(2)}_{intra}$ for example, the modulation of linear polarization via the electron intraband motion, which means that the second-order polarization originates from $\vec{P}^{(2)} = tr(\rho_{ie}^{(2)}\hat{P})$ where $\rho_{ie}^{(2)}$ is obtained by $[\vec{er}_i \cdot \vec{E}, [\vec{er}_e \cdot \vec{E}, \rho^{(0)}]]$ (see Figure 3b). In this commutation, the evolution of density matrix can be divided into two processes. First, $[\vec{er_e} \cdot \vec{E}, \rho^{(0)}]$ leads to $\rho_e^{(1)}$, creating the first-order polarization. Since $\vec{P}^{(1)} = tr(\hat{\rho}_e^{(1)}\hat{P}) = \sum_m \sum_n \hat{\rho}_{mn}^{(1)} \hat{P}_{nm}$, it in-dicates that the light-induced nonzero off-diagonal elements of $\hat{\rho}_{nm}^{(1)}$ is responsible for the existence of $\vec{P}^{(1)}$. Because $\rho_e^{(1)} \propto [\vec{er}_e \cdot \vec{E}, \rho^{(0)}] = \vec{er}_e \cdot \vec{E} \rho^{(0)} - \rho^{(0)} \vec{er}_e \cdot \vec{E}$, for both terms, one can write their matrix element as $[\vec{er}_e \cdot \vec{E}\rho^{(0)}]_{mn} = \langle m|\vec{P}|n \rangle \langle n|n \rangle \cdot \vec{E} = \langle m|$ $\vec{P}|n\rangle \cdot \vec{E}$ and $[\rho^{(0)}\vec{er_e} \cdot \vec{E}]_{nm} = \langle n|n\rangle \langle n|\vec{P}|m\rangle \cdot \vec{E} = \langle n|\vec{P}|m\rangle \cdot \vec{E}$ in the momentum representation. Therefore, it is useful to show the areas in the Brillouin zone where the dipole transition is allowed between different eigen states of n and m. To this end, one can apply the group theory analysis as did in our previous study⁷⁰ to find the irreducible representations of the dipole moment, initial, and final states under a certain symmetry and to check if Ag is included in their direct product. However, such method is so heavy because of the large number of kpoints and involved bands. Alternatively, we describe the system by calculating the imaginary part of dielectric function $\varepsilon_2(\omega)$ of α -Sb, as plotted in Figure 4c. Here, we focus on the main peaks below 1.5 eV. To shed light on its features, we examine the detailed contributions from band-to-band transitions. Figure 4d-g respectively shows the k-pointdependent distributions of $\varepsilon_2(\omega)$ from four combinations of top two valence bands and bottom two conduction bands. The largest amplitude arises in the area marked by a blue dashed box in the Brillouin zone, and it is governed by the VBM-to-CBM interband transition (see Figure 4d). For clarity, we plot the dispersions of these two bands in Figure 5a,b where two local extreme points (Λ and Λ') connected by a saddle point (D) on the Γ -Y k-path are observed in the above area. The



Figure 5. Projection of band dispersion of (a) VBM and (b) CBM for α -Sb. (c) Band pair energy of VBM and CBM. (d) Band structure of α -Sb along the high-symmetry line.

three specific points are the so-called van Hove singularities, at which the derivative of $\nabla_k[E_c(k) - E_v(k)]$ is close to zero, leading to the divergence in the joint density of states. Therefore, the $\varepsilon_2(\omega)$ value around Λ , Λ' , and D is relatively large as compared with that of other dipole transitions. In Figure 5c, we further show the band-pair energy difference in the whole Brillouin zone. Compared with Figure 4d, it is clear that the positions with large $\varepsilon_2(\omega)$ are with a photon energy less than 0.6 eV (blue line), which corresponds to the first several peaks in Figure 4c.

We then consider the second process in the evolution of density matrix, that is, $[\vec{r_i} \cdot \vec{E}, \rho_e^{(1)}]$, which results in the final $\rho_{ie}^{(2)}$. The matrix element of this commutation can be written as $\rho_{mn}^{(1)} \langle l| \hat{er}_i | m \rangle \vec{E}$. Since \vec{r}_i involves the ill-defined terms of ∇_k and ξ_{nn} (see the Supporting Information),⁵⁷ $\vec{er_i}$ cannot be directly correlated to a classical operator like $\vec{er_e}$. Even so, because the SHG effect is based on the linear process due to the relation $\rho_{ie}^{(2)} \propto [\vec{er}_i \cdot \vec{E}, \rho_e^{(1)}]$, we are still able to link $\text{Im}[\chi^{(2)}(-2\omega, \omega, \omega)]$ ω] to the band structure. In the previous step, we have exhibited all the dipole-transition-allowed areas for the linear optical response (see Figure 4d-g). One can see that the denominator of SHG expression in eq 3 also contains the resonance factors. In this sense, $\text{Im}[\chi_{\text{intra}}^{(2)}(-2\omega, \omega, \omega)]$ should resemble ε_2 (ω). As expected, we find that the positions of main peaks for $\chi_{121}^{(2)}$, $\chi_{112}^{(2)}$, and $\chi_{211}^{(2)}$ are consistent with some of those in the $\varepsilon_2(\omega)$ spectrum (see black dashed lines in Figure 4a,b). Note that the peaks in the $\varepsilon_2(\omega)$ curve are all positive while having different signs in $\text{Im}[\chi^{(2)}]$. This is because the first-order polarization only contains the squared matrix element, while, for the second-order polarization, the matrix elements are more complex and varied.56,57 In addition, we observe that the band edge of α -Sb shows a linear dispersion as marked by a triangle in Figure 5d. Its energy range covers the first three peaks in Figure 4a,b. The large slope in the triangle indicates a higher charge group velocity (defined as $v = \partial \omega /$ ∂k). In Figure S4, we show that the SHG curves originated from VBM-to-CBM transition and find that the total magnitude is almost made up of these two bands, implying that the third term (two-band process) of eq 3 largely determines the SHG coefficients of α -Sb. In this term, $\Delta_{mn} =$ $v_{nn} - v_{mm}$ is involved, which denotes the group velocity difference between nth and mth bands. Because the sign of group velocity is opposite in the valence and conduction bands near the gap, the absolute value of Δ_{mn} will accordingly be large, hence increasing the SHG susceptibilities. A rational understanding is that the significant dispersion results in a

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smaller effective mass; hence, electrons move fast driven by the light field from k to k + dk in the momentum space, generating a large instantaneous polarization current. For a better visualization, we further draw the k-point-dependent distributions of $\chi^{(2)}$ in Figure S5. One can see that the SHG susceptibility is concentrated in the areas that are similar to those of ε_2 (ω) (see Figure 4d), and the surrounding areas of Λ , Λ' , and D points make the major contributions to $\chi^{(2)}$, which confirm that our analysis is reasonable.

Now, we discuss the α -Bi monolayer. The first several peaks of $\chi_{121}^{(2)}$ and $\chi_{211}^{(2)}$ are also found to be from the intraband term (see Figure 6a,b). Because both Sb and Bi are in the same



Figure 6. Imaginary part of interband, intraband, and modulation contributions to the SHG susceptibility of (a) $\chi_{21}^{(2)}$ and (b) $\chi_{121}^{(2)}$ for α -Bi. (c) Imaginary part of dielectric function ε_2 (ω) of α -Bi. (d) *k*-point-dependent distributions of normalized ε_2 (ω) contributed by the VBM-to-CBM transition. (e) Band structure of α -Bi along the high-symmetry line.

group in the periodic table, they share some similar features. For instance, the major contribution to the imaginary part of dielectric function comes from the areas around the extreme and saddle points in the Brillouin zone (see Figure 6d), and the resonance peaks in $\chi_{121}^{(2)}$ and $\chi_{211}^{(2)}$ are consistent with those in the $\varepsilon_2(\omega)$ curve (see dashed lines in Figure 6a–c). Besides, it also shows significant linear dispersion at the band edges, leading to a large difference in group velocity between valence and conduction bands (see Figure 6e), which could generate a large polarization current induced by intraband motion.

Although the intraband term plays a dominant role in the low-energy regions of the SHG susceptibility, we find that the contributions in α -Bi can also come from the interband term that is almost vanished in α -Sb. For the interband transition, the second-order polarization is obtained by $\vec{P}^{(2)} = tr(\rho_{ee}^{(2)}\hat{P})$ where $\rho_{ee}^{(2)}$ comes from the relation $[\vec{er_e} \cdot \vec{E}, [\vec{er_e} \cdot \vec{E}, \rho^{(0)}]]$ (see Figure 3b). The commutation can be also divided into two steps. Compared with the intraband term, the difference between $\rho_{ee}^{(2)}$ and $\rho_{ie}^{(2)}$ is that the second step becomes $[\vec{er}_{e3}, \vec{E}, \vec{E}]$ $\rho_{e}^{(1)}$] with its matrix element of $[\vec{er_e} \cdot \vec{E}, \rho_e^{(1)}]_{ln} = \langle l|\vec{P}|m\rangle \langle m|\vec{P}|n\rangle$ $\cdot \vec{E} \cdot \vec{E}$. This means that dipole transition should be allowed between m and n as well as l and m at the same time. Since it involves three bands, we cannot study the dipole transition between two states with the same electron population via dielectric function. However, we can explore some features on the SHG curve by treating the pure interband transition

analogous to the atomic system where each k-point can act as an atom, while the different bands are like the atomic states. It is known that resonance enhancement in SHG susceptibility happens when a certain combination of light frequency is close to the energy difference between two states. Because secondorder NLO is a two-photon process, the incident light with frequencies of both 2ω and ω can induce resonance for band energy difference of $2\hbar\omega$. Such peaks are observed and marked by the arrows in Figure 6a. The energies of the green pair are 0.52 and 1.04 eV, while the values for the purple pair are 0.55 and 1.10 eV. Both of them correspond to the transition from the band edge next to the gap, as labeled by green dots in Figure 6d,e. For the two-photon process, the electrons first jump to a virtual level in the gap, as shown with the red dashed line in Figure 6e. Note that this is not an eigen level of the intrinsic Hamiltonian of α -Bi but rather represents the combined energy of eigen states and incident photons. One can consider that the origin of this virtual state is due to the interaction between the α -Bi monolayer and the electromagnetic wave; accordingly charge densities are redistributed. Such change modifies the energy of the semiconductor, leading to this intermediate energy level, which couples the initial and final states together.

In experiments, the measured SHG response results from all symmetry-allowed $\chi^{(2)}_{abc}(-2\omega, \omega, \omega)$ tensor elements, which is usually characterized by the SHG intensity as a function of the crystal's azimuthal angle θ . For α -Sb and α -Bi monolayers with point group of $C_{2\nu}$, the angular-dependent SHG susceptibilities under a normal incidence (see Figure S6a) can be represented as

$$\chi_{\parallel}^{(2)}(\theta) = [\chi_{121}^{(2)} + \chi_{211}^{(2)}]\sin\theta\,\cos^2\theta + \chi_{222}^{(2)}\sin^3\theta \tag{8}$$

$$\chi_{\perp}^{(2)}(\theta) = \chi_{211}^{(2)} \cos^3 \theta + [\chi_{222}^{(2)} - \chi_{121}^{(2)}] \cos \theta \sin^2 \theta \tag{9}$$

where the subscripts \parallel and \perp denote the $\chi^{(2)}(\theta)$ parallel and perpendicular to the polarization of incident light with a certain photon energy.²⁰ According to the above equations, we draw the polar plots of SHG intensity for α -Sb and α -Bi in Figure S6b,c. One can see that both their shapes reflect the $C_{2\nu}$ symmetry and exhibit a giant SHG intensity with the maximum value appears at $\theta = 0$. This indicates that SHG polarization anisotropy in α -Sb and α -Bi sheets can be observed by a lowpower pump beam, which could be then applied to precisely determine the orientation of their crystal lattices.

It is worth to note that the bulk counterparts of some 2D materials, such as h-BN, transition metal dichalcogenides, and group IV monochalcogenides, have centrosymmetry, which forbids their second-order NLO responses. Therefore, stacking orders play an important role in determining the breaking of inversion symmetry. For above mentioned 2D sheets, their multilayer structures exhibit alternating even-odd behavior, that is, only the systems with an odd number of layers display the SHG effect, while contributions cancel each other out in the case with an even number of layers. This implies that a good strategy is needed to well-control the thickness for practical applications. For α -Sb and α -Bi, we show the total energy of different stacking sequence up to triple layers in Figure S7 and Table S1, which demonstrates that both sheets prefer the direct AA stacking pattern. Interestingly, the multilayered α -Sb and α -Bi are all noncentrosymmetric regardless of their thickness; thus, the SHG response remains. Different from the bilayer and trilayer α -Bi with metallic

features,⁴⁴ α -Sb is semiconducting in its multilayer configurations. The strength of $\chi^{(2)}(0)$ for the bilayer and trilayer α -Sb (see Table S2) is found to be comparable with that of its monolayer due to the weak van der Waals coupling at the interface. The insensitivity of SHG to thickness exhibits additional advantages of α -Sb as compared with other 2D systems in practical applications.

CONCLUSIONS

In summary, on the basis of first-principle calculations and the independent particle approximation, we have demonstrated the potential of monolayer α -Sb and α -Bi as the promising candidates for nonlinear optical applications. The SHG effect of two studied systems results from the breakage of inversion symmetry because of the structural distortion induced by insufficient sp³ hybridization of Sb and Bi atoms. This is the first report of a robust SHG effect in single-element materials. The static SHG susceptibilities for both two monolayers are much higher than those of many other 2D materials, achieving an order of $10^6 \text{ pm}^2/\text{V}$. The strong SHG response of the α -Sb and α -Bi sheets occurs in the infrared range, showing the potential applications in IR-based devices. The significant linear dispersion near the gap of both two monolayers is responsible for the large intraband contribution to the SHG susceptibility. Moreover, the SHG response remains in the multilayered α -Sb and α -Bi because the inversion centers are absent irrespective of their thickness, providing additional advantage for practical application as compared to other 2D sheets with alternating even-odd behaviors. These intriguing features together with the well-developed techniques for synthesizing α -Sb and α -Bi will stimulate more research efforts in the study of NLO in such materials and developing novel and efficient SHG devices for future applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00898.

Instability in α -Sb and α -Bi monolayers with the flat BP structure, SHG susceptibility of α -Sb and α -Bi, basic description for SHG by density matrix in the framework of perturbation theory, band-to-band contribution to the SHG susceptibility, *k*-point-dependent SHG susceptibility of α -Sb, SHG intensity as a function of crystal's azimuthal angle, and stacking configurations of multilayer structures of α -Sb and α -Bi (PDF)

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Q.W. conceived the idea and supervised the project. Y.G. carried out the simulations. All of the authors analyzed the results and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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