

Third harmonic generation in the transition metal trichalcogenides

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The transition metal trichalcogenides (TMTs) are an interesting class of layered 2D materials that have strong anisotropic electrical and optical properties. We report on the polarization-dependent nonlinear optical response of exfoliated crystals at the third harmonic using nonresonant excitation with a 1560 nm femtosecond laser. All members of the TMT crystal family explored (ZrS₃, HfS₃, TiS₃, and NbS₃) display large anisotropy in their polarized third harmonic generation signal, with anisotropy ratios as large as $\chi_{11}/\chi_{22} \approx 6.5$. From the expected nonlinear dependence of these monoclinic and triclinic crystals, we extract the relative nonlinear susceptibility coefficients. We find that the anisotropy ratio is largest for ZrS₃ and decreases across the family, a trend we associate with the proximity of the third harmonic energy to the strongly *b*-polarized absorption edge of each material. NbS₃, the only triclinic crystal, displays a pronounced anisotropy in thick flakes that is strongly reduced in the thinnest flakes, which we attribute to a partial relaxation of the Peierls-type Nb–Nb dimerization that underlies the triclinic distortion. The large anisotropic nonlinear response in this crystal family sets it apart from other 2D materials and makes them particularly attractive for further investigation.

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I. INTRODUCTION

Reduced crystal symmetries often lead to novel phenomena, functionality, and applications. This is exemplified in the layered, van der Waals materials like graphite and the transition metal dichalcogenides (TMDs). These materials are composed of covalently bonded sheets that are stacked through van der Waals forces to create 3D crystals. While the sheets are structurally symmetric in plane, the reduced crystal symmetry in the out-of-plane direction is precisely why these materials can be exfoliated and isolated down to single monolayers. Mono- and few-layer flakes of these materials, and similar layered crystals, have generated a tremendous amount of interest and spawned an entirely new field of research in materials science focused solely on 2D materials.

While most 2D materials to date possess largely isotropic in-plane electrical and optical properties, a few exceptions have emerged. Black phosphorus is perhaps the most well

known of the anisotropic 2D materials [1,2]. Its in-plane puckered crystal structure results in linear, Dirac-like band structure along one direction and quadratic, Schrödinger-like band structure along the other [3]. This leads to anisotropic conductance [1,4], as well as linear dichroism [5], and direction-dependent thermal [6] and mechanical [7–9] properties. This broken in-plane rotational symmetry also has significance in fundamental studies of the fractional quantum Hall effect where anisotropic bubble and stripe phases exist [10,11]. A few other notable anisotropic 2D materials have been (re)discovered including the group IV monochalcogenides (*MX*, *M*: Ge, Sn; *X*: S, Se) [12,13], the 1T' or Td TMD semimetals [14], and the rhenium dichalcogenides [15]. A wandering principal axis was recently discovered in the rhenium dichalcogenides that leads to wavelength-switchable propagation directions of its waveguide modes [16].

The transition metal trichalcogenides (TMTs) are an interesting class of layered materials when compared to the aforementioned 2D materials because the entire family possesses reduced in-plane structural symmetry and the members span a spectrum of electronic phases (metals, superconductors, and semiconductors) [17–19]. Sometimes referred to as “quasi-1D 2D materials,” the TMTs are composed of 1D prismatic chains of transition metal atoms surrounded by chalcogen atoms that are covalently bonded in plane. The transition metal atom distances are slightly smaller along the chains than across leading to anisotropies in electrical and optical properties. Island *et al.* have shown that exfoliated

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TiS₃ displays in-plane mobility ratios as high as 7.6 when comparing electrical transport along the *a* and *b* axes of the crystal and optical transmission ratios up to 30 in the visible wavelengths [20]. This conductance anisotropy in TiS₃ is larger than that found for black phosphorus flakes [20]. Optical measurements of the complex index of refraction of TiS₃ have also shown that the exfoliated crystals are strongly birefringent with magnitudes ($\delta n = +0.30 \pm 0.04$) larger than the well-known birefringent materials TiO₂ and calcite [21].

Polarization-dependent harmonic generation is a powerful tool in the study of 2D materials [22]. It has been used to investigate crystal symmetries, layer number, strain, defects, and stacking orientations in van der Waals heterostructures. Due to its sensitivity to all these aspects of 2D crystals, it also provides an important tool in the careful study of phase transitions. Anisotropic third harmonic generation has been reported in other low-symmetry 2D materials, including GeSe [23] and SnS [24], and strain-tunable THG anisotropy has been demonstrated in Nb₂SiTe₄ [25], placing the trichalcogenides within a broader family of materials with strong nonlinear optical anisotropy. In the TMT family, third harmonic generation has recently been reported in ZrS₃ and TiS₃ [26,27]. Zhu *et al.* found a maximum third-order susceptibility $\chi^{(3)} = 67.9 \times 10^{-18} \text{ m}^2/\text{V}^2$ for a 24.3 nm ZrS₃ flake and an intensity anisotropy ratio as high as 61.5 for a 17.7 nm flake [26]. Zhang *et al.* reported efficient THG in TiS₃, characterizing its intrinsic polarization anisotropy, wavelength dependence, and the strain tuning of that anisotropy [27]. These reports motivate a systematic comparison of the

nonlinear response across the crystal family under identical measurement conditions.

Here we investigate the third-order nonlinear optical properties of four members of the TMTs, ZrS₃, HfS₃, TiS₃, and NbS₃, measured on a single setup. To our knowledge, THG has not previously been reported in HfS₃ or NbS₃. Measuring all four crystals under identical conditions, we identify a systematic ordering of the anisotropy across the family and quantify the overall ratio. In NbS₃ we find a transition from strong anisotropy in thick flakes toward equal-amplitude lobes in the thinnest flakes, in contrast to the other three members, whose extracted susceptibility coefficients are largely thickness independent. We hypothesize that this thickness dependence arises from a partial relaxation of the Peierls-type Nb–Nb dimerization that underlies the triclinic distortion of NbS₃, driving the thinnest flakes toward the undimerized, ZrS₃-like limit.

II. THIRD HARMONIC GENERATION IN MONOCLINIC AND TRICLINIC CRYSTALS

When subjected to intense optical fields, certain materials will present a nonlinear response in their polarization. The third-order nonlinear polarization is written as

$$P_i^{(3\omega)} = \epsilon_0 \sum_{jkl} \chi_{ijkl} E_j E_k E_l, \quad (1)$$

where χ_{ijkl} is the fourth-rank nonlinear susceptibility tensor.

The contracted form of the tensor for monoclinic and triclinic crystals, respectively, is given by [28]

$$\begin{bmatrix} \chi_{11} & 0 & \chi_{13} & \chi_{14} & \chi_{15} \\ 0 & \chi_{22} & 0 & \chi_{24} & 0 \\ \chi_{31} & 0 & \chi_{33} & 0 & \chi_{35} \end{bmatrix} \begin{bmatrix} \chi_{16} & \chi_{17} & \chi_{18} & 0 & 0 \\ 0 & 0 & 0 & \chi_{29} & \chi_{20} \\ \chi_{36} & \chi_{37} & \chi_{38} & 0 & 0 \end{bmatrix}, \quad (2)$$

$$\begin{bmatrix} \chi_{11} & \chi_{12} & \chi_{13} & \chi_{14} & \chi_{15} \\ \chi_{21} & \chi_{22} & \chi_{23} & \chi_{24} & \chi_{25} \\ \chi_{31} & \chi_{32} & \chi_{33} & \chi_{34} & \chi_{35} \end{bmatrix} \begin{bmatrix} \chi_{16} & \chi_{17} & \chi_{18} & \chi_{19} & \chi_{10} \\ \chi_{26} & \chi_{27} & \chi_{28} & \chi_{29} & \chi_{20} \\ \chi_{36} & \chi_{37} & \chi_{38} & \chi_{39} & \chi_{30} \end{bmatrix}. \quad (3)$$

For in-plane excitation, only the first two rows of each tensor are relevant, and the dominant tensor components are

$$\begin{aligned} \chi_{11} &= \chi_{xxxx}^{(3)}, & \chi_{12} &= \chi_{xyyy}^{(3)}, & \chi_{18} &= \chi_{xxyy}^{(3)}, & \chi_{19} &= \chi_{xxxy}^{(3)}, \\ \chi_{21} &= \chi_{yxxx}^{(3)}, & \chi_{22} &= \chi_{yyyy}^{(3)}, & \chi_{28} &= \chi_{yyxy}^{(3)}, & \chi_{29} &= \chi_{yyxy}^{(3)}. \end{aligned} \quad (4)$$

For linearly polarized excitation, the electric field lies in the *x*-*y* plane and is expressed as $\mathbf{E}(\theta) = E_0(\cos \theta \hat{x} + \sin \theta \hat{y})$, where θ is the polarization angle measured from the *x* (*b*) axis.

This leads to the following measurable intensities for monoclinic and triclinic crystals, respectively:

$$I_x^{(3\omega)}(\theta) \propto (\chi_{11} \cos^3(\theta) + 3\chi_{18} \cos(\theta) \sin^2(\theta))^2, \quad (5)$$

$$I_y^{(3\omega)}(\theta) \propto (\chi_{22} \sin^3(\theta) + 3\chi_{29} \sin(\theta) \cos^2(\theta))^2, \quad (6)$$

$$\begin{aligned} I_x^{(3\omega)}(\theta) &\propto (\chi_{11} \cos^3(\theta) + \chi_{12} \sin^3(\theta) \\ &\quad + 3\chi_{18} \cos(\theta) \sin^2(\theta) + 3\chi_{19} \sin(\theta) \cos^2(\theta))^2, \end{aligned} \quad (7)$$

$$\begin{aligned} I_y^{(3\omega)}(\theta) &\propto (\chi_{21} \cos^3(\theta) + \chi_{22} \sin^3(\theta) \\ &\quad + 3\chi_{28} \cos(\theta) \sin^2(\theta) + 3\chi_{29} \sin(\theta) \cos^2(\theta))^2. \end{aligned} \quad (8)$$

We plot I_x , I_y for monoclinic and triclinic crystals in Fig. 1. Figure 1(a) plots the third harmonic intensity for a monoclinic crystal with all susceptibility values equal to 1 ($\chi_{11} = \chi_{18} = \chi_{22} = \chi_{29} = 1$). For these values, sampling the signal at fixed crystallographic axes results in symmetric butterflylike patterns for the *x* and *y* components. Figure 1(b) shows the third harmonic intensity as a function of polarization for a triclinic crystal with all susceptibility coefficients equal to 1 ($\chi_{11} = \chi_{12} = \chi_{18} = \chi_{19} = \chi_{21} = \chi_{22} = \chi_{28} = \chi_{29} = 1$). For this case, the *x* and *y* components are equal for triclinic crystals, Eqs. (7) and (8). A predominantly two-lobe pattern is observed with an angle of 45° relative to the TMT *b* axis (*x* axis) of the crystal. For crystals with strong anisotropies, the susceptibility coefficients will differ greatly. For example, Fig. 1(c) plots the *x* and *y* components for a monoclinic crystal with the following susceptibility coefficients: $\chi_{11} = 1$,

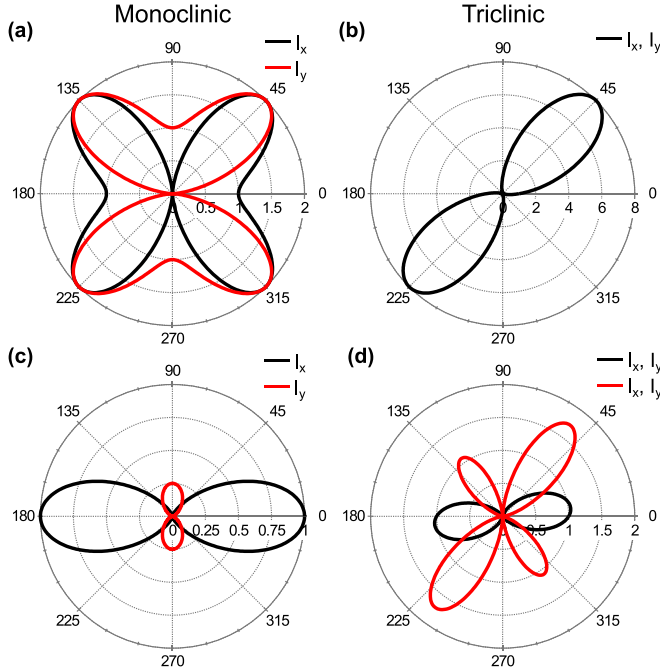


FIG. 1. Expected polarization dependence for monoclinic and triclinic crystals. (a) Third harmonic intensity as a function of polarization for a monoclinic crystal with all susceptibility coefficients equal to 1. (b) Third harmonic intensity as a function of polarization for a triclinic crystal with all susceptibility coefficients equal to 1. For this case, I_x and I_y are equal for triclinic crystals with normal laser incidence. (c) Third harmonic intensity as a function of polarization for a monoclinic crystal with susceptibility coefficients $\chi_{11} = 1$, $\chi_{18} = 0.1$ (black horizontal two-lobe pattern) and $\chi_{22} = 0.5$, $\chi_{29} = 0.1$ (red vertical two-lobe pattern). (d) Third harmonic intensity as a function of polarization for a triclinic crystal with all susceptibility coefficients suppressed (0.1) except one (black two-lobe pattern with $\chi_{11} = \chi_{22} = 1$, red four-lobe pattern with $\chi_{18} = \chi_{28} = 1$).

$\chi_{18} = 0.1$ (black horizontal two-lobe pattern) and $\chi_{22} = 0.5$, $\chi_{29} = 0.1$ (red vertical two-lobe pattern). Anisotropy in the susceptibility coefficients also greatly changes the expected triclinic third harmonic. Figure 1(d) plots the third harmonic intensity for a triclinic crystal with a single susceptibility coefficient of unity for each component and all others suppressed. The black two-lobe pattern is observed for $\chi_{11} = \chi_{22} = 1$ and $\chi_{12} = \chi_{18} = \chi_{19} = \chi_{21} = \chi_{28} = \chi_{29} = 0.1$ while the red four-lobe pattern is observed for $\chi_{18} = \chi_{28} = 1$ and $\chi_{11} = \chi_{12} = \chi_{19} = \chi_{21} = \chi_{22} = \chi_{29} = 0.1$.

III. ISOLATION AND CHARACTERIZATION OF TMTS

Bulk TMT material is obtained through solid-gas reaction between pure metals and sulfur powder sealed in a glass ampule and heated to a temperature of 550 °C for 60 hours [29]. The powders containing bulklike nanowires are characterized using x-ray diffraction (XRD) to determine the crystal structure (see Supplemental Material [30]). ZrS_3 , HfS_3 , and TiS_3 all present XRD patterns that are consistent with monoclinic structures while the NbS_3 crystallizes in the triclinic crystal system. In order to isolate single flakes, the powders are placed on scotch tape or polydimethylsiloxane (PDMS)

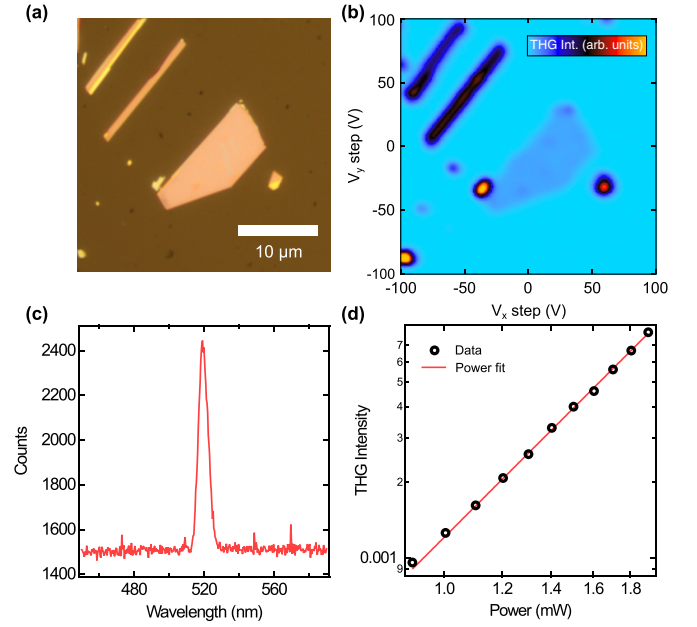


FIG. 2. Third harmonic generation in TMT crystals. (a) Optical microscopy image of exfoliated TiS_3 flakes. (b) THG intensity scan of the third harmonic for the same region shown in panel (a). (c) Spectrum of the third harmonic from a representative TiS_3 flake. (d) THG intensity as a function of laser power for a representative TiS_3 flake.

stamps to facilitate exfoliation onto quartz substrates (0.5 mm thick). Figure 2(a) shows an optical microscopy image of a representative TiS_3 flake on a quartz substrate. Scanning the excitation laser over the surface of the sample and collecting the third harmonic at 520 nm produces a THG intensity map as shown in Fig. 2(b) displaying features that closely match those found in the microscopy image [Fig. 2(a)]. The measured spectrum of the reflected light around the wavelengths expected for the third harmonic shows a narrow peak at 520 nm [Fig. 2(c)]. This signal has a cubic dependence on the incident laser power [Fig. 2(d)] consistent with third harmonic generation. The fit line (red) extracts a power-law exponent of 2.90 ± 0.03 . The cubic power dependence shown in Fig. 2(d) is a representative measurement confirming the third-order nature of the signal; in the remaining materials, the third harmonic was identified by its emission at one-third of the excitation wavelength (520 nm) and its rejection of the fundamental by the bandpass filter. The thickness of the flakes is measured using a Park Instruments atomic force microscope (AFM).

Third harmonic generation in TMT crystals is measured using a custom microscope (see Supplemental Material [30] for details). A femtosecond laser (100 fs pulse width) is directed through a Glan-Taylor polarizer and a half-wave plate to condition and control the polarization of the incident beam. A pair of short-pass dichroic mirrors directs the laser through the objective and toward the sample; the two are oriented so that the polarization-dependent phase and reflectance of the second mirror are compensated by the first, preserving a clean linear polarization state at the sample. The back-scattered light is collected with the same objective, passes back through the

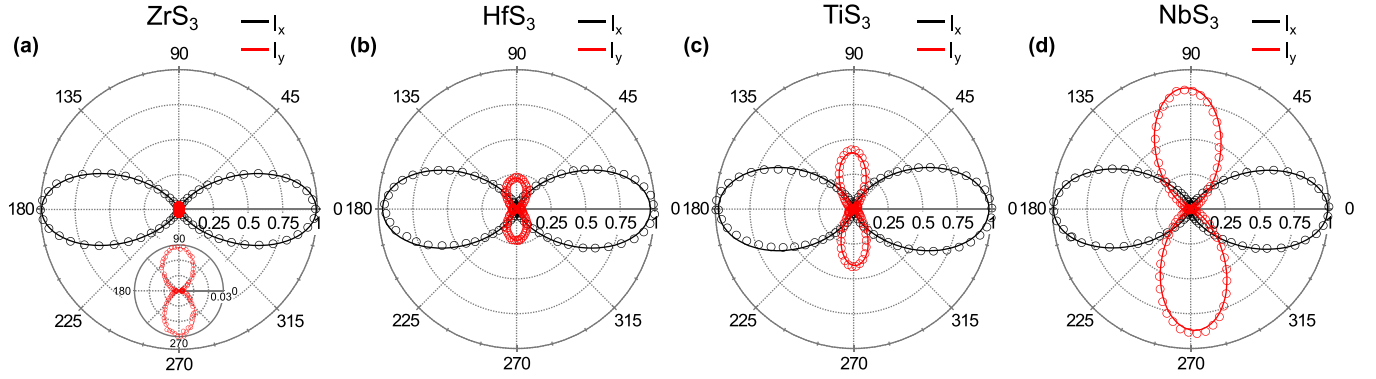


FIG. 3. Polarization-dependent third harmonic generation for selected flakes of each TMT crystal. Each panel shows the normalized THG intensity as a function of excitation polarization angle for the b -axis analyzer (black open circles, I_x) and the a -axis analyzer (red open circles, I_y), along with the corresponding tensor fits (solid lines). Data are normalized to the maximum of the b -axis channel. (a) ZrS_3 (flake 1A), monoclinic, $\chi_{11}/\chi_{22} = 5.82$. Inset shows a zoom of the a -axis data. (b) HfS_3 (flake 3B), monoclinic, $\chi_{11}/\chi_{22} = 2.08$. (c) TiS_3 (flake 2F), monoclinic, $\chi_{11}/\chi_{22} = 1.55$. (d) NbS_3 (flake 1A), triclinic, $\chi_{11}/\chi_{22} = 1.06$.

second dichroic and an analyzer, and is directed through a bandpass filter to an avalanche photodiode.

Figure 3 shows the polarization-dependent THG response for representative flakes of all four TMT crystals. In each panel, the b -axis analyzer signal (I_x , black open circles) and the a -axis analyzer signal (I_y , red open circles) are plotted as a function of excitation polarization angle and overlaid with fits to the symmetry-allowed tensor equations, Eqs. (5)–(8). All datasets are normalized to the maximum of the b -axis channel and rotated so that the dominant χ_{11} lobe is aligned along the $0^\circ/180^\circ$ axis. For the monoclinic crystals, this dominant lobe coincides with the long, needlelike axis of the flake, which is the crystallographic b -axis (chain direction) of the TMTs. We verified this correspondence optically by comparing the flake morphology, imaged *in situ* with the integrated camera, against the known orientation of the incident linear polarization, so that the axis assignment is fixed by the flake morphology rather than inferred from the third harmonic response alone. For thin NbS_3 , the in-plane anisotropy is too weak for the THG lobes to define an axis, and the b axis is taken from the flake morphology. The extracted tensor components are reported normalized to χ_{11} , the dominant component along the b axis, so that all reported coefficients are dimensionless ratios referenced to that flake's own b -axis response; the anisotropy ratio is independent of this choice and serves as our primary, normalization-independent metric for comparison across flakes and materials. These reported ratios are effective values that include linear-optical (Fresnel and dichroic) factors; we estimate these factors in the Supplemental Material [30] and find that they are modest and act to increase the intrinsic anisotropy.

The three monoclinic crystals, ZrS_3 , HfS_3 , and TiS_3 , are each well described by Eqs. (5) and (6). In all three cases the b -axis channel (I_x) exhibits a strongly two-lobe pattern dominated by χ_{11} , while the a -axis channel (I_y) is described primarily by χ_{22} and χ_{29} . ZrS_3 displays the largest anisotropy ratio, $\chi_{11}/\chi_{22} = 5.82$, consistent with the giant anisotropy previously reported for this material [26]. The a -axis signal for ZrS_3 flake 1A is very small and plotted again in the inset of Fig. 3(a). HfS_3 and TiS_3 show progressively reduced anisotropy ratios of 2.08 and 1.55, respectively, with both

analyzer channels cleanly resolved and well described by the monoclinic model.

NbS_3 is the only triclinic member of the family investigated here and is therefore fit using the more general expressions in Eqs. (7) and (8), which include the additional off-diagonal tensor components χ_{12} , χ_{19} , χ_{21} , and χ_{28} . The lower triclinic symmetry of NbS_3 permits additional independent tensor components, and accordingly both the off-diagonal terms and the full pair of channels contribute to the fit. For this representative flake, the measured anisotropy ratio is small ($\chi_{11}/\chi_{22} = 1.06$), with both lobes of comparable amplitude.

The polarization-dependent third harmonic measurements were repeated for multiple exfoliated flakes of each crystal spanning a range of thicknesses, and the in-plane susceptibility tensor components were extracted from fits to Eqs. (5)–(8). See Table S1 in Supplemental Material [30] for a summary of all measured flakes. Figures 4(a)–4(d) show the extracted components as a function of thickness. For the three monoclinic crystals, the response is dominated by the diagonal components χ_{11} and χ_{22} , with the off-diagonal terms χ_{18} and χ_{29} remaining small ($\lesssim 0.2$) across all thicknesses measured. Within the thickness range investigated (~ 19 – 128 nm), the normalized components show no strong systematic thickness dependence for ZrS_3 , HfS_3 , and TiS_3 , indicating that the anisotropic nonlinear response in this regime is governed by the intrinsic crystal symmetry rather than by layer number. NbS_3 , the only triclinic member, requires the additional off-diagonal components χ_{12} , χ_{19} , χ_{21} , and χ_{28} , whose small but nonzero values produce the lobe asymmetry characteristic of the lower crystal symmetry. In contrast to the monoclinic crystals, NbS_3 exhibits a pronounced thickness dependence: χ_{22}/χ_{11} increases toward unity as the flake thickness decreases, so that the two polarization channels become comparable in amplitude and the anisotropy is strongly reduced in the thinnest flakes.

This trend is summarized in Fig. 4(e), which plots the anisotropy ratio χ_{11}/χ_{22} for every flake measured. The ratio is largest for ZrS_3 (reaching $\chi_{11}/\chi_{22} \approx 6.5$) and decreases systematically across the family through HfS_3 ($\chi_{11}/\chi_{22} \approx 2$ – 3) and TiS_3 ($\chi_{11}/\chi_{22} \approx 1.4$ – 1.6). Our largest measured

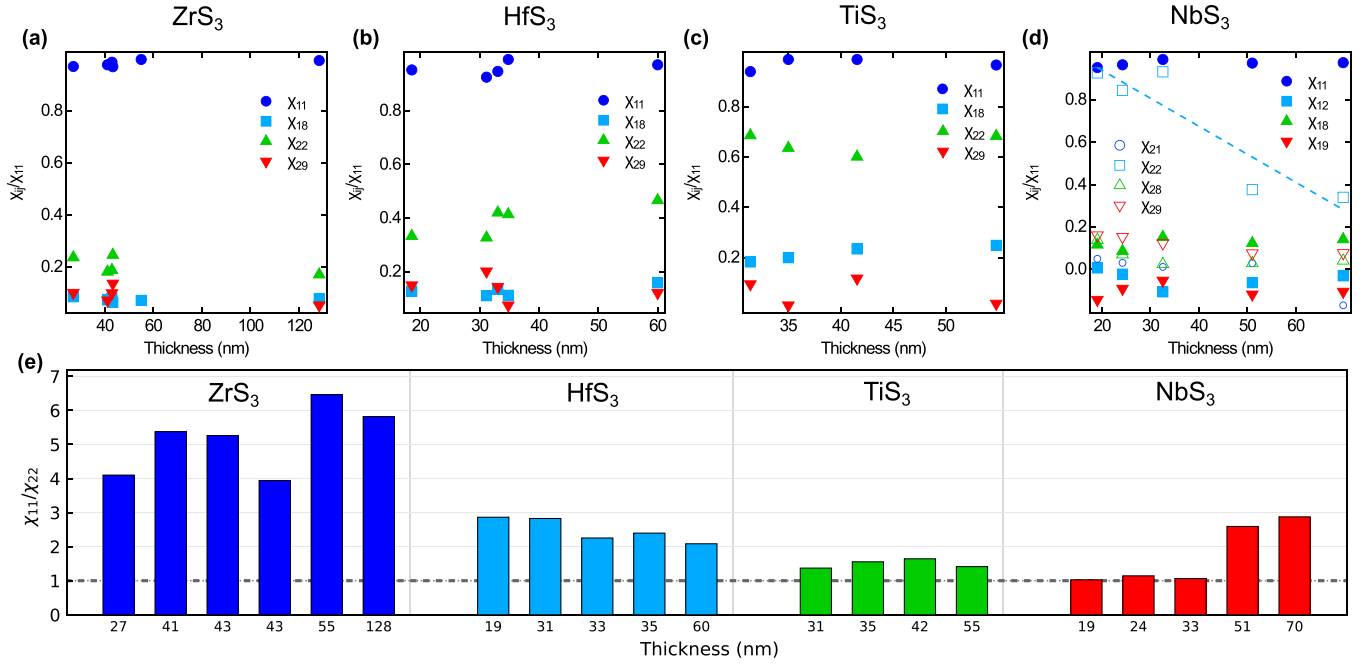


FIG. 4. Extracted third-order nonlinear susceptibility tensor components and anisotropy ratios for all measured flakes of the four TMT crystals. (a)–(d) Normalized tensor components χ_{ij}/χ_{11} as a function of flake thickness for (a) ZrS₃, (b) HfS₃, (c) TiS₃, and (d) NbS₃. Filled symbols denote the dominant in-plane components (χ_{11} , χ_{18} , χ_{22} , χ_{29}) for the monoclinic crystals. In panel (d), filled symbols denote (χ_{11} , χ_{12} , χ_{18} , χ_{19}) and open symbols denote (χ_{21} , χ_{22} , χ_{28} , χ_{29}). All components are normalized to χ_{11} . The dashed line in panel (d) is a linear guide to the eye for χ_{22} , which decreases with increasing thickness. (e) Anisotropy ratio χ_{11}/χ_{22} for every flake, grouped by material and ordered by thickness within each group; the thickness of each flake (in nm) is indicated below each bar. The dotted line marks the equal-amplitude condition $\chi_{11}/\chi_{22} = 1$. The anisotropy ratio decreases systematically across the family, from ZrS₃ through HfS₃ and TiS₃, approaching unity for the thinner NbS₃ flakes.

amplitude ratio, $\chi_{11}/\chi_{22} \approx 6.5$, is in reasonable agreement with the value reported by Zhu *et al.*; once the difference in convention is accounted for, their intensity ratio of 61.5 corresponds to an amplitude ratio of $\sqrt{61.5} \approx 7.8$. Zhu *et al.* further report that this anisotropy varies with flake thickness, in apparent contrast to the thickness-independent ratios we observe for the monoclinic crystals. We attribute this difference to the excitation conditions of the two experiments. Zhu *et al.* excite at 1400–1500 nm, placing the third harmonic at 2.48–2.66 eV, at or above the strongly *b*-polarized absorption edge of ZrS₃, whereas our 1560 nm excitation places the third harmonic at 2.38 eV, nearer the onset of that edge.

We place the third-order response for these materials on an absolute scale by referencing the third harmonic signal of each flake to monolayer WSe₂ and MoS₂ measured under identical conditions. The extracted *b*-axis susceptibilities are of order $1 \times 10^{-19} \text{ m}^2/\text{V}^2$ for TiS₃, ZrS₃, and NbS₃, comparable to those of monolayer transition metal dichalcogenides at the same wavelength; a full account, including the comparison in Table S2 and Figure S3, is given in Supplemental Material [30].

IV. DISCUSSION

The systematic decrease in anisotropy across the monoclinic members is consistent with the proximity of the third harmonic photon energy ($3\hbar\omega \approx 2.4 \text{ eV}$) to each material's strongly *b*-polarized absorption edge (Fig. S3 [30]). For TiS₃,

this picture is supported directly by the recent wavelength-dependent measurements of Zhang *et al.* [27], who observe a *b*-polarized THG resonance near 1585 nm and compute a *b*-polarized absorption that exceeds the *a*-polarized response across 1.80–2.70 eV. Their HSE06 calculation places the indirect gap of TiS₃ at 1.06 eV, so that $3\hbar\omega$ lies well above the edge, in a spectral region where the *a*-polarized absorption has also become appreciable. The activation of this second channel raises χ_{22} relative to the chain-polarized χ_{11} and compresses the anisotropy ratio, accounting for the small χ_{11}/χ_{22} of TiS₃. For ZrS₃ and HfS₃, whose larger gaps ($\sim 1.9 \text{ eV}$) [17] place $3\hbar\omega$ just above the band edge, the *a*-polarized channel remains weak and the chain-polarized response dominates; the wavelength-dependent THG of ZrS₃ reported by Zhu *et al.* [26] shows an analogous resonant enhancement near the band edge. Because the gaps of ZrS₃ and HfS₃ are nearly equal, the larger ratio of ZrS₃ cannot be attributed to resonance proximity alone, and more likely reflects a strongly *b*-polarized band-edge transition governed by the differing 4*d* (Zr) and 5*d* (Hf) metal–sulfur hybridization [39].

NbS₃ stands apart from the monoclinic members. Its anisotropy ratio falls from $\chi_{11}/\chi_{22} \approx 2.6$ –2.9 in the thickest flakes ($\gtrsim 50 \text{ nm}$) toward unity below $\sim 25 \text{ nm}$, opposite to the confinement-driven enhancement of the THG anisotropy reported for monoclinic ZrS₃, whose anisotropy ratio increases as the flakes are thinned [26], pointing to a mechanism specific to this crystal. Unlike the other members, triclinic NbS₃ (NbS₃-I) owes its reduced symmetry to a Peierls-type Nb–Nb dimerization along the *b*-axis chains [40].

Removing this dimerization yields a nondimerized $P2_1/m$ structure essentially identical to ZrS_3 , favored by only ~ 0.18 eV per unit cell [40]. Because such Peierls distortions are strain tunable [41,42] and exfoliated flakes carry inhomogeneous substrate strain that is largest in the thinnest layers, we hypothesize that partial relaxation of the dimerization drives the thinnest flakes toward the undimerized, ZrS_3 -like ($P2_1/m$) limit, consistent with the anisotropic strain response of the related compound ZrSe_3 [43]. We note that the substrate strain in the thinnest flakes could also influence the anisotropy through routes not tied to the dimerization, and we cannot fully separate such a contribution from the partial relaxation proposed here.

V. CONCLUSION

We have investigated the polarization-dependent third harmonic generation of four transition metal trichalcogenides, ZrS_3 , HfS_3 , TiS_3 , and NbS_3 , using nonresonant excitation at 1560 nm. By fitting the polarization dependence along the crystallographic a and b axes to the symmetry-allowed forms of the fourth-rank nonlinear susceptibility tensor, we extracted the dominant in-plane components for multiple flakes of each material and quantified the anisotropy through the ratio χ_{11}/χ_{22} . The ratios are largest for ZrS_3 (reaching ≈ 6.5) and decrease across the family through HfS_3 and TiS_3 . We associate this trend with the proximity of the third harmonic energy ($3\hbar\omega \approx 2.4$ eV) to the strongly b -polarized absorption edge of each material. NbS_3 presents pronounced anisotropy in thick flakes but its anisotropy is strongly reduced in the thinnest flakes, opposite to the confinement-driven trend of the monoclinic crystals, which we attribute to a partial relaxation of the Peierls-type Nb–Nb dimerization that drives the thinnest flakes toward the undimerized, ZrS_3 -like limit.

These results establish the transition metal trichalcogenides as a family of 2D materials with large, symmetry-controlled tunable nonlinear optical anisotropy, making them an attractive platform for polarization-sensitive nonlinear photonic applications such as on-chip frequency conversion, polarization-resolved imaging, and anisotropy-based optical components. Future work combining wavelength-dependent measurements and first-principles calculations of the band-edge transitions would clarify the microscopic origin of the nonlinear anisotropy across the family.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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