Terahertz emission in SnS2 single crystals: ultrafast shift current

Sepideh Khanmohammadi[1]*, Kateryna Kushnir[1]*, Erin M. Morissette[1]&, Curtis W. Doiron[2], Kristie J. Koski[3], Ronald L. Grimm[2], Ashwin Ramasubramamiam[4] and Lyubov V. Titova[1]

[1]Department of Physics, Worcester Polytechnic Institute, Worcester, MA 01609
[2]Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, MA 01609
[3]Department of Chemistry, University of California, Davis, CA, 95616
[4]Department of Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003
*Equal contribution
[&]Currently at Department of Physics, Brown University, Providence, RI 02912

ABSTRACT

We report on THz emission in single-crystalline SnS_2 in response to above bandgap excitation. Symmetry properties of THz generation suggest that its origin is an ultrafast surface shift current, a 2nd order nonlinear effect that can occur as a result of above-gap photoexcitation of a non-centrosymmetric semiconductor.[1-3] Multilayer SnS_2 can exist in several polytypes that differ in the layer stacking. Of those polytypes, 2H and 18R are centrosymmetric while 4H is not. While Raman spectroscopy suggests that the single crystalline SnS_2 in our experiments is 2H, its THz emission has symmetry that are fully consistent with the $P3m1$ phase of 4H polytype. We hypothesize that the stacking disorder, where strain-free stacking faults that interrupt regions of 2H polytype, can break inversion symmetry and result in THz emission. These results lay the foundations for application of SnS_2 as an efficient, stable, flexible THz source material, and highlight the use of THz spectroscopy as a sensitive tool for establishing symmetry properties of materials.

Keywords: SnS2, THz emission, shift current, symmetry breaking

1. INTRODUCTION

Transition metal dichalcogenides (TMD) are layered two-dimensional (2D) materials with van der Waals interaction between the layers. SnS2, a TMD semiconductor with a moderate band gap of ~ 2.3 eV, good environmental stability, and high carrier mobility[4,8] has been reported to be a promising THz emitter material [9,10]. Here, we explore the possibility of THz emission by the shift current, a 2nd order nonlinear optical effect that can occur as a result of above-gap photoexcitation of a non-centrosymmetric semiconductor which give rise to a spatial charge transfer of the order of the bond length [1-3]. Octahedral coordination of S atoms in the unit cell of SnS2 results in monolayers having inversion symmetry, seemingly ruling out second-order nonlinear effects [4-7]. The SnS2 multilayers can exist in different polytypes depending on stacking sequences[11]. Most common polytypes are 2H ($P\bar{3}m1$) which preserves inversion symmetry of the monolayer, 18R which is also centrosymmetric, and 4H that has two non-centrosymmetric polymorphs ($P3m1$) and ($P6_3mc$).[12] The polytype composition for crystals grown by chemical transport is determined by synthesis conditions such as growth temperature and the choice of transporting agent.[12] For growth by carrier agents such I2 or SnI4, the temperatures above 800 ˚C produces predominantly 4H polytype, while at low temperatures (< 600 ˚C) 2H polytype dominates. For the temperatures between 600 ˚C and 800 ˚C, different polytypes are possible, and they can even coexist in single crystals, separated by strain-free stacking faults.[12,13] In this paper, we show that THz emission spectroscopy, which is sensitive to symmetry breaking, can be used as a tool to characterize symmetry properties of SnS2 single crystals, and demonstrate that SnS2 can indeed be used as a THz source material.

2. EXPERIMENTAL RESULTS

2.1 SnS_2 structure

Single-crystalline SnS_2 (few microns-thick, 1-10 mm crystals) was synthesized by chemical vapor transport at ~ 650˚C using I_2 as a transport agent, as described previously.[14] X-ray photoelectron spectroscopy (XPS) spectroscopy

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and X-Ray diffraction analysis XRD confirmed that the resulting crystals were indeed phase-pure SnS_2. We have used Raman spectroscopy to identify the specific polytype 2H polytype, as 2H is known to exhibit a single E_g mode at 205 cm^{-1} while 4H polytype has a doublet at 200 and 214 cm^{-1} due to the E-mode.[15] We find a single mode centered at 206 cm^{-1} which extends from 185 to 220 cm^{-1}.[14] We hypothesize that in this case, the 2H phase is the dominant contribution, while stacking faults may locally create few-layer inclusions that resemble 4H structure.

2.2 THz emission spectroscopy.

We use THz emission spectroscopy (TES) to photoexcite the SnS_2 single crystals as illustrated schematically in Fig. 1a. In the TES experiment, the sample orientation and the linear polarization of the excitation beam can be controlled independently, by rotation of the sample and rotating a half-wave plate placed in the beam path, respectively. The THz pulses are detected by [110] ZnTe crystal where they are focused by parabolic mirrors and are coherently detected by free-space electro-optic sampling. A fixed wire-grid polarizer placed before the detection crystal ensures the detection of one linearly polarized component of the emitted THz pulses. We find that above bandgap excitation with 400 nm (3.1 eV) laser pulses (100fs) at normal incidence results in emission of THz pulses (Fig. 1b). The corresponding bandwidth of the emission which is limited by the bandwidth of the 1 mm thick ZnTe detector crystal (0.2-2.5THz, Fig. 1c). It must be noted that the excitation by 800nm (below the bandgap) did not result in THz emission even with higher fluences.

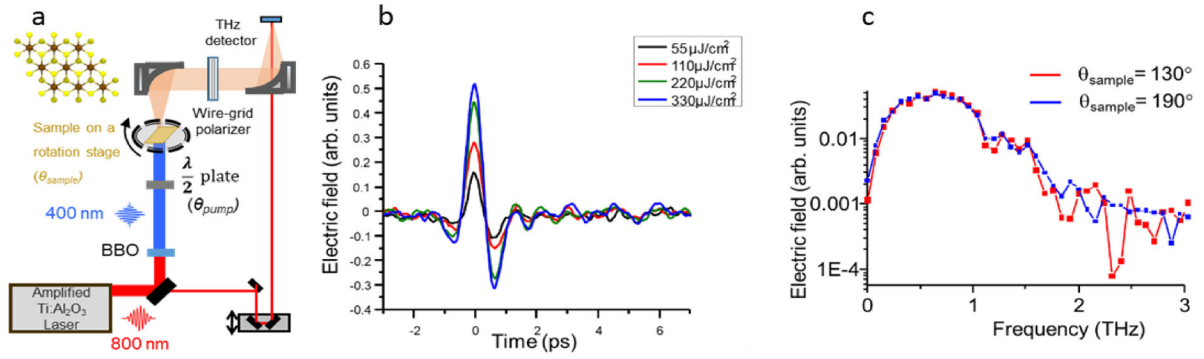

Figure 1.a) Schematic diagram of TES experiment. Inset shows top view of the basal plane of SnS_2. B) THz waveforms emitted by the SnS_2 crystal in response to normal incident photoexcitation with 400 nm, 100 fs pulses with the fluence indicated in the legend. The excitation beam is polarized along the THz detection axis (θ_{pump} =0°). c) The corresponding THz pulses amplitude spectra at 220 mJ/cm^2 pump fluence

The symmetry of the observed THz emission can be seen in the plot of the peak of THz pulse as a function of sample orientation (θ_{sample}) (Fig.2) and of pump polarization (Fig. 3). When the sample is rotated, the peak of the THz emission can be well described by $E_{peak}(\theta_{sample}) = E_0 \cos(3\theta_{sample} - \theta_{0,sample})$, where $\theta_{0,sample} = 6° \pm 1°$ is the offset of the crystal orientation with respect to the THz detection axis, and exhibits a clear six-fold symmetry with respect to sample rotation.

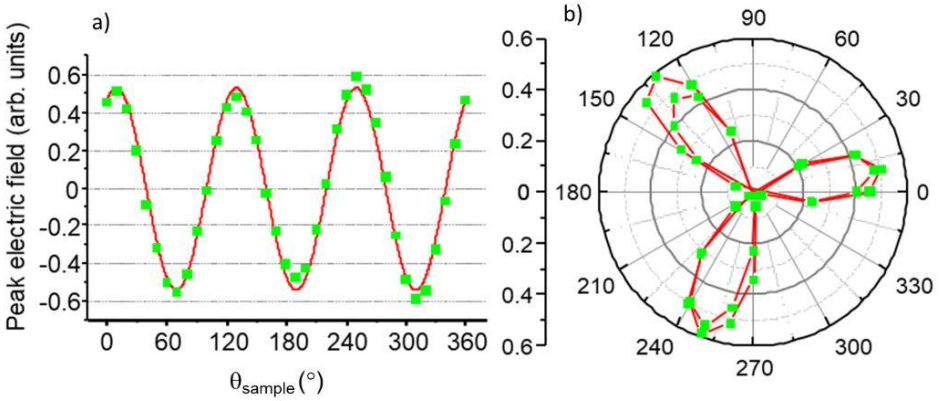

Figure 2. Sample orientation dependence of the THz emission from SnS_2 crystal following optical excitation with 400 nm, 220 μJ/cm^2 pulses with fixed θ_{pump}=0°. a) Peak electric field as a function of θ_{sample}, and b) the corresponding polar plot of emission amplitude.

When the sample orientation is fixed, we find that the dependence of the peak of the electric field on pump polarization angle can be written as $E_{peak}(\theta_{pump}) = E_0 \cos(2\theta_{pump} - \theta_{0,pump})$, with $\theta_{0,pump} = -20° \pm 5°$ which exhibits a four-fold symmetry with respect to pump polarization rotation (Fig. 3).

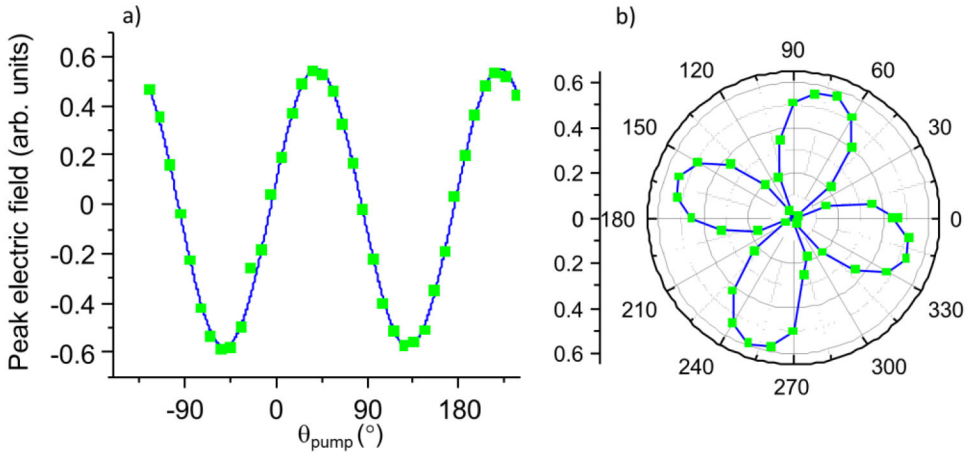

Figure 3. Pump polarization dependence of the THz emission from SnS_2 crystal following optical excitation with 400 nm, 220 μJ/cm^2 pulses, with sample orientation fixed at θ_{sample}=0°. a) Peak electric field as a function of θ_{pump}, and b) the corresponding polar plot of emission amplitude.

3. DISCUSSION

Demonstrated emission of THz pulses in response to photoexcitation at normal incidence unambiguously demonstrates in-plane inversion symmetry breaking in single crystal SnS_2. As above-gap excitation with 400 nm pulses results in THz generation while the below band gap, 800 nm excitation does not, the source of radiation appear to be a transient photocurrent that involves real photoexcited charge carriers, rather than optical rectification or other non-resonant phenomena. In the absence of applied bias and under normal incidence excitation, ultrafast shift current is a likely mechanism. The symmetry properties of the observed emission are consistent with the $P3m1$ phase of 4H polytype (space group 156), while Raman spectroscopy shows instead that the crystal belongs to a centrosymmetric 2H polytype. We hypothesize that the stacking faults that are known to be common in SnS_2,[13] can break inversion symmetry. In the normal incidence geometry, stacking faults that produce the same local symmetry as the $P3m1$ phase of 4H polytype would result in THz emission. This observation highlights the high sensitivity of TES to local symmetry breaking in the materials that are difficult to observe using other techniques. It also demonstrates that SnS_2 is a promising material for THz photonics.

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