Enhanced domain wall conductivity in photosensitive ferroelectrics $\text{Sn}_2\text{P}_2\text{S}_6$ with full-visible-spectrum absorption

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ABSTRACT Recent optical stimulation suggests a vital non-contact pathway to manipulate both macroscopic and microscopic ferroelectric properties and paves the foundation for optoelectronics devices. However, up to date, most optical-related manipulation of ferroelectric properties is restricted due to their intrinsic bandgap and limited visible light spectrum absorption. Here, we reveal non-oxide $\text{Sn}_2\text{P}_2\text{S}_6$ single crystal possesses full-visible-spectrum absorption (from 300 to 800 nm) with a unique disproportionation mechanism of photoexcited Sn ions and Urbach tail, which is not contradicting to the intrinsic band gap. Interestingly, we observed the existence of conductive domain walls (c-DW) and the light illumination induced significant enhancement of the domain wall conductivity caused by such disproportionation reaction. In addition, the domains separated by c-DW also exhibited noticeable electrical conductivity difference in the presence of optical illumination owing to the interfacial polarization charge with opposite signs. The result provides a novel opportunity for understanding the electrical conductivity behavior of the domains and domain walls in ferroelectrics with full-visible-spectrum absorption and achieving greatly enhanced performances for optoelectronics.

Keywords: $\text{Sn}_2\text{P}_2\text{S}_6$, ferroelectricity, conductive domain walls, full-visible-spectrum absorption

INTRODUCTION

Ferroelectricity strongly couples with various physical fields such as strain [1,2], temperature [3], electric [4], and magnetic field [5], which has stimulated considerable scientific activities and triggered many technological applications, including telecommunication, medical imaging, ultrasonic, and multiferroic

devices, etc. Recently, the manipulation of ferroelectric functionalities in the presence of optical illumination has attracted strong research interests, leading to a great deal of interesting and unexpected photo-induced phenomena, such as ferroelectric photovoltaic [6,7], ferroelectric photocatalysis [8], photostriction [9], laser-induced ultrafast Terahertz radiation behaviors [10], and organic-inorganic hybrid photosensitive ferroelectrics photodetectors with high-active photoresponse [11]. These results pave the path for utilizing the coupling of light with ferroelectricity and for the development of optoelectronic devices.

Bringing the understanding of the light-triggered macroscopic variations into the micro/nanoscale, the role of the domain and domain wall has to be taken into account. For example, an effective optical tuning of ferroelectric polarization in BaTiO_3 and BiFeO_3 can be attributed to the reversible change of ferroelectric domain configuration [12,13], a unique ferroelectric bifunctional photocatalysis behavior can be achieved due to the existence of charged ferroelectric domain wall in Bi_2WO_6 [14], and the significant enhancement of conductivity is owing to optical-induced conductive ferroelectric domain walls in LiNbO_3 single crystals [15]. What is more important is that light can also induce novel mechanisms for manipulating the ferroelectric behavior such as the light-induced flexoelectric effect, which determines the formation of ordered domains in BiFeO_3 thin films [16]. These new effects potentially suggest remote control of ferroelectric domains and domain walls by light, which opens a framework for micro/nanoscale optoelectronic devices with non-contact external control.

Nonetheless, the all-optical control of both macroscopic and microscopic ferroelectric properties suffers from narrow light absorption range with relatively low absorption efficiency, which drastically limits the range of potential optoelectronic applications. It is known that optical illumination requires the photons

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with an energy $h\nu$ more than the bandgap E_g to achieve the transitions from the valence band to conduction band [17]. Therefore, ferroelectrics generally absorb a limited region of the visible light due to their large bandgap. The conventional ferroelectrics, for instance, BaTiO_3 , LiNbO_3 , and BiFeO_3 , exhibit certain bandgaps (3.2 eV for BaTiO_3 [18], 4.0 eV for LiNbO_3 [15], and 2.67 eV for BiFeO_3 [6]), but they mainly absorb super-bandgap light (300–500 nm), which greatly limits their practical applications under visible light.

Here, we report a photosensitive ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$ (SPS), owning full-visible-spectrum absorption (300–800 nm) and strong absorption ability, which is absent in other ferroelectric systems. We clearly observe the light-induced reduction of the polarization, which is caused by the so-called disproportionation reaction and Urbach tail, giving the dominating Sn^{4+} state for enhancing the full-visible-spectrum absorption. This is confirmed by the XPS measurement and density functional theory (DFT) calculations. More interestingly, by using a combination of various scanning probe techniques, we also find that there exist conductive domain walls (c-DW) in the non-oxide SPS crystal. The light illumination induces significant enhancement of the c-DW conductivity due to the photogenerated charge carriers accumulated on the domain wall caused by such disproportionation reaction of photoexcited Sn ions.

EXPERIMENTAL SECTION

Sample preparation and characterizations

Single crystals of SPS were synthesized by chemical vapor transport (CVT) in a two-zone furnace. Stoichiometric amounts of Sn, P, and S were ground together and then transferred to a quartz tube. The powders were evacuated, sealed, and placed in the two-zone furnace (650–600°C). The pressure inside the tube was pumped down to 3×10^{-4} Pa. After one week of heating, the SPS sample was cooled down to room temperature in the growth zone. The crystals formed as yellowish-brown polyhedra, with irregular shapes up to about 5 mm $\times$ 4 mm $\times$ 4 mm. From the batch, small crystals (orange/yellow, transparent) suitable for single crystal X-ray diffraction (XRD) experiments were selected. To study the crystal structure of the SPS sample, single-crystal XRD were collected on a Rigaku Oxford XtaLAB PRO diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at temperatures above and below the ferroelectric transition temperature. The crystal surface of the SPS crystal was identified by XRD collected from a Bruker D8 Advance X-ray diffractometer using Cu K α radiation at room temperature. Scanning electron microscopy (SEM) photographs were carried out on an FEI Nano 450 microscope at a voltage of 20 kV. The atomic composition of SPS single crystal was checked by energy dispersive X-ray spectroscopy (EDS, Oxford X-Max 50). The X-ray photoelectron spectroscopy (XPS) was recorded from a UK Kratos Axis Ultra spectrometer with an Al K α X-ray source in the dark and illumination conditions. The light source with a wavelength of 532 nm was used to illuminate the sample. The ultraviolet-visible (UV-vis) spectroscopy diffuse reflectance spectra of the sample were measured by UV-3600 (SHIMADZU, Japan) at room temperature. The photocurrent of the SPS crystal was recorded using a semiconductor parameter analyzer (Keithley, 2400) at room temperature. The light source (coherent femtosecond pump-probe system) with different wavelengths

was used to illuminate the sample.

Measurements of dielectric and ferroelectric properties

The dielectric property was measured by a precision impedance analyzer (WK, 6500B, UK) in the temperature range from 300 to 370 K. The dielectric permittivity as a function of frequency was measured with an alternating-current (ac) excitation voltage of 1 V in the dark and illumination conditions. The light source with a wavelength of 532 nm (illumination intensity $I = 0.71 \text{ W cm}^{-2}$) was used to illuminate the sample. Ferroelectric hysteresis loops at room temperature were measured using a standard ferroelectric tester (Radiant Technology, Multiferroic II, USA) at 1 kHz in the dark and illumination conditions. The light sources with a wavelength of 532 nm ($I = 0.71, 1.42$ and 7.1 W cm^{-2}) were focused on the side of the large-sized SPS single crystal, where the power density was calculated to be $\sim 0.71, 1.42$ and 7.1 W cm^{-2} , respectively. The schematic of the experimental set-up for the electric measurements is shown in Fig. S1.

Scanning probe microscope measurements

Piezoresponse force microscopy (PFM) measurement was performed using a commercial atomic force microscope (Asylum Research MFP-3D) with Ti/Ir-coated Si cantilever tips and diamond-coated Si cantilever tips, respectively. In the resonance-enhanced mode, a soft tip with a spring constant of $\sim 2.8 \text{ N m}^{-1}$ was driven with an ac voltage ($V_{ac} = 0.5\text{--}1 \text{ V}$) under the tip-sample contact resonant frequency ($\sim 320 \text{ kHz}$). The out-of-plane (OP) and in-plane (IP) PFM were acquired at the drive frequency of ~ 320 and $\sim 730 \text{ kHz}$ in the Vector PFM mode, respectively. Switching spectroscopy PFM (SS-PFM) was performed by measuring the hysteresis loops in the OP piezoelectric signals using the dual-frequency resonance tracking (DART) mode. Conductive atomic force microscopy (c-AFM) was performed in a contact mode with the c-AFM tip as the top electrode. Since SPS is also a photo-sensitive material, the measurement environment was without light to avoid the additional contributions. Kelvin probe force microscopy (KPFM) and c-AFM measurements were performed in the dark and illumination conditions. The light source with a wavelength of 532 nm was used to illuminate the sample.

Density functional theory calculations

All calculations in this work were carried out using the Vienna *Ab initio* Simulation Package (VASP) [19] based on DFT. For the exchange-correlation functional, the PBEsol functional of generalized gradient approximation [20] was adopted. In the calculation, a kinetic energy cutoff of 500 eV for the plane wave expansion and $6 \times 6 \times 4$ Monkhorst-Pack k -point grids were set for the bulk SPS. The energy and force convergence criteria were 10^{-6} eV and 0.5 meV Å^{-1} during the relaxation, respectively. Additionally, the Berry-phase method was employed to calculate the polarization for bulk SPS.

RESULTS AND DISCUSSION

The grown SPS crystal looks like a truncated prismoid, as shown in the inset of Fig. 1a. The as-grown SPS sample shows good stability against moisture and oxidation at ambient conditions. Based on the XRD measurement, the top facet of the specimen is confirmed as (011) surface, as shown in Fig. S2a. To confirm the homogeneity and the composition of SPS, EDS analysis was

Figure 1 Dielectric and ferroelectric properties of SPS single crystal. (a) Temperature dependence of dielectric permittivity ϵ' for SPS crystal measured at selected frequencies. The inset is a photograph of an SPS crystal. (b) Frequency dependence of ϵ' in dark and illumination conditions ($\lambda = 532$ nm, $I = 0.71$ W cm $^{-2}$) at room temperature. The inset shows the magnified view in the range of low frequencies. (c) Polarization versus electric field hysteresis loops and (d) the corresponding polarization current density versus electric fields at 1 kHz in dark and illumination conditions with $\lambda = 532$ nm ($I = 0.71, 1.42$ and 7.1 W cm $^{-2}$) at 300 K (specimen with thickness = 300 μ m).

Table 1 Temperature-dependent lattice parameters of SPS from the XRD measurement

Temperature (K)	Space group	Lattice parameter			
		a (Å)	b (Å)	c (Å)	β (°)
163	Pn	6.5125(13)	7.4760(15)	9.3801(19)	91.15(3)
300	Pn	6.5297(13)	7.4839(15)	9.3678(19)	91.17(3)
380	$P2_1/n$	6.5382(4)	7.4743(5)	9.3541(5)	91.25(5)

carried out, as shown in Fig. S2b. The structural examinations confirmed the monoclinic Pn symmetry ($T < T_c$, Curie temperature) and $P2_1/n$ symmetry ($T > T_c$) in the SPS single crystal. The detailed atomic structure information can be found in Table 1 and Table S1. The ferroelectric crystal structure of SPS is presented in Fig. S2c. In a conventional unit cell, SPS contains two $(P_2S_6)^{4-}$ anionic units, whereas four Sn^{2+} cations are arranged between these anionic units. Each $(P_2S_6)^{4-}$ unit consists of two distorted trigonal PS_3 pyramids bound by a P–P bond.

The ferroelectricity of the SPS single crystal was confirmed by the temperature-dependent dielectric permittivity and hysteresis loop measurements, as shown in Fig. 1. In Fig. 1a, a prominent dielectric anomaly was observed at 339 K corresponding to T_c , which is consistent with previous work [21]. In the vicinity of T_c , the reciprocal dielectric permittivity ϵ' follows the Curie-Weiss law of ferroelectric materials, $\epsilon' = C/(T - T_0)$, as confirmed by the linear relationship between the reciprocal dielectric permittivity and the temperature, as shown in Fig. S3a. The fitting parameters are Curie-Weiss constant $C = 1.04 \times 10^4$ K and Curie-Weiss temperature $T_0 = 325.8$ K at 1 kHz. Note that the

imaginary part of dielectric permittivity ϵ'' increases with increasing temperature and leads to an increase of ϵ' at low frequencies, which is mainly attributed to the high electrical conductivity (Fig. S3b, c). To study the light illumination effect on the ferroelectric property of SPS single crystal, we performed the frequency dependent dielectric permittivity measurement in dark and illumination conditions at room temperature, as shown in Fig. 1b. Compared with the dark condition, a small enhancement of ϵ' at the low frequency range (<10 kHz) was observed, which is dominated by the light-induced space charge contribution [22]. The change in ϵ' is negligible for high frequencies due to the elimination of several resistive and capacitive effects, such as space-charge depletion and interfacial accumulation [23]. The ferroelectricity of the SPS crystal was further investigated by the polarization-electric (P-E) field hysteresis measurements in the dark and illumination conditions, as shown in Fig. 1c, d. For dark condition, the sample on the (011) surface shows a spontaneous polarization of 4.7 μ C cm $^{-2}$. It is clear that the spontaneous polarization decreases with the increase of laser power, and reaches to 2.5 μ C cm $^{-2}$ under the

illumination with $I = 7.1 \text{ W cm}^{-2}$. The significant reduction in spontaneous polarization can be attributed to the nonequilibrium charge carriers generated under the illumination, which form the screening layer with a high field concentration near the electrodes. This is consistent with the significant reduction of electric resistivity in the illumination condition, as shown in Fig. S3d.

Unlike the traditional ferroelectric perovskite oxides (e.g., BaTiO_3) with a wide bandgap, SPS is a rare ferroelectric sulfide with semiconducting nature. To estimate the optical absorption performance of the SPS crystal, the UV-vis absorption spectrum is shown in Fig. 2a. The intrinsic absorption edge (around 527 nm) of the SPS crystal is observed in the inset of Fig. 2a, corresponding to the direct band gap of about 2.35 eV, which is consistent with previous reports [24,25]. Usually, this band gap will limit the visible-spectrum absorption in the range of 300–527 nm. Interestingly, the spectrum shows a broad absorption band spanning the full-visible-light spectrum (from 300 to 800 nm). Compared with typical ferroelectric photovoltaic BiFeO_3 [26], the UV-vis absorption spectra displays that the SPS crystal possesses full-visible-light spectrum absorption and stronger light-absorption ability, which is consistent with near-infrared-sensitive photorefractive nature due to sulfur vacancies [27–29]. The mechanism of full-visible-spectrum absorption will be discussed later.

The time-dependent photocurrent of the SPS crystal was also recorded with the selected wavelengths, as shown in Fig. 2b. Generally, the higher photocurrent response means the higher charge carrier density. The dark current stability remains before and after illumination, which is only 3.7 nA, whereas the photocurrent rises by more than twice by switching the light on/off.

The photocurrent response properties for SPS with wavelengths in the range of 380–690 nm are shown in Fig. S4. These behaviors also show a reversible light-induced change in the current of SPS sample. Such reversible change in current has a relatively slow response time with a few seconds, possibly due to the low charge carrier mobility in the SPS crystal caused by the formation of small or large polarons by charge carriers [30].

To clearly identify the mechanism of light-enhanced conductivity in the SPS crystal, we further conducted the XPS measurement of the SPS crystal. The Sn 3d core-level spectra for the SPS single crystal in dark and illumination conditions are shown in Fig. 2c, d, respectively. For the dark condition as shown in Fig. 2c, the Sn 3d spectrum of the SPS crystal can be divided into four peaks. The binding energy peaks of Sn $3d_{5/2}$ (485.4 eV) and Sn $3d_{3/2}$ (493.8 eV) are characteristics of Sn^{2+} state, while the two peaks of Sn $3d_{5/2}$ (486.8 eV) and Sn $3d_{3/2}$ (495.3 eV) are characteristics of Sn^{4+} state [31,32]. Note that the presence of Sn^{4+} state originates from the inevitable illumination for the SPS crystal from the sample preparation to characterization. The disproportionation reaction of Sn is responsible for the formation of Sn^{4+} state in the SPS crystal as the following scheme [33]: $\text{Sn}^{2+} + h\nu = \text{Sn}^{3+} + e'$; $2\text{Sn}^{3+} = \text{Sn}^{2+} + \text{Sn}^{4+}$. The obtained ratio of $\text{Sn}^{2+}:\text{Sn}^{4+}$ is 58.48:41.52 by analyzing the XPS spectra. Besides, although Sn^{2+} and Sn^{4+} states both exist in the SPS sample under the illumination condition in Fig. 2d, the four peaks shift to the higher binding energy, indicating the enhancement of total valences of Sn increase. Interestingly, compared with XPS spectra in the dark condition, the content of Sn^{4+} increases while the Sn^{2+} content reduces under the illumination condition. The enhancement of Sn^{4+} content can be ascribed to the disproportionation reaction of photoexcited Sn

Figure 2 Light-induced changes in electronic properties and valence states of Sn. (a) UV-vis absorption spectrum of the SPS crystal. The inset shows the square root of Kubelka-Munk functions $F(R)$ versus photon energy. (b) Photocurrent response of SPS crystal under switching the light on and off with the varying illumination wavelengths at a fixed bias voltage and intensity. (c, d) XPS spectra of Sn 3d in dark and illumination conditions.

ions. In addition, under the illumination condition, it is easy to produce hole-like small polarons at the Sn^{2+} site, and then these polarons can dissociate with formation of two holes [34]: $h^{++} + h\nu = 2h^+$. As a result, the SPS crystal possesses a higher hole carrier density (SPS is a p-type semiconductor) at room temperature in the illumination condition.

The changes of polarization and electrical conductivity in macroscopic observations with light illumination are resultants of the interaction between the bound charges and light-induced charge carriers. This indicates that the light-induced nanoscale changes of charge carriers determine the most significant macroscopic fluctuation in polarization and electrical conductivity. Therefore, the roles of domain and domain wall have to be taken into account in the changes of macroscopic properties under light illumination condition. To further investigate the microscopic mechanism of the light-induced change of the electrical conductivity, we performed a combination of PFM and c-AFM technique study of both domains and domain walls. As shown in Fig. 3a, PFM OP phase mapping shows two distinct regions with 180° phase difference, corresponding to domains with upward (small size domain) and downward (large size domain) polarization components perpendicular to the (011) surface. We define the domains with upward polarization components as up domains, and the domains with downward polarization components as down domains. More details on various OP and IP PFM images, and the corresponding SS-PFM on different locations can be found in Figs S5 and S6.

For the dark condition, the c-AFM mapping is shown in Fig. 3b. Note that the mapping is taken at a sample bias of 2 V, which is 0.133 kV cm^{-1} , smaller than the coercive field. There-

fore, no switching current contributed to the detected current. However, in the presence of light illumination, there are two important features from the c-AFM image in Fig. 3c: (1) the domain wall current remarkably increases from 16.5 pA (dark condition) to 100 pA (light condition); (2) adjacent domains with opposite polarizations separated by the c-DW exhibit distinguishable contrast. Both features are evident from the line profile in Fig. 3e, f. To investigate the origin of the first feature of c-DW, we calculated the polarization from the DFT and found that the net polarization lies in the *ac*-plane (see Fig. S5e and discussion in Supplementary information). The origin of the c-DW in the SPS crystal could result from the inclined ferroelectric domain walls where the tail-to-tail polarization [35,36] leads to the negative bound charges accumulated and attracts the hole carriers (SPS is a p-type semiconductor), as shown in Fig. 3d.

With light illumination, a significant enhancement of the photogenerated charge carriers increases in the electrical conductivity of the SPS crystal due to the disproportionation reaction of photoexcited Sn ions. This leads to more charges accumulated on the domain wall. As a result, the conductivity of domain walls in the illumination condition is significantly higher than that under the dark condition in the SPS crystal. In addition, a lower Schottky barrier height is produced at the tip-down domain interface than at the tip-up domain interface in the illumination condition, leading to higher conductivity for the down domain than the up domain. Therefore, the distinguishable electrical conductivity of up and down domains in the illumination condition in Fig. 3c results from a Schottky-like barrier at the tip-sample interface which is modified by the local

Figure 3 Conduction at domain walls in the SPS single crystal. (a) OP phase of the SPS crystal, where domains with upward (small size domain) and downward (large size domain) polarization components are perpendicular to the (011) surface. (b, c) The corresponding c-AFM images at 2 V in dark and illumination conditions. The scale bar is 3 μm . (d) Schematic illustration of inclined domain walls in the SPS crystal. The net polarization components perpendicular to the (011) plane $P_\perp$ are labeled by white solid arrows, and white and blue dashed arrows mean the parallel and perpendicular components with respect to the domain wall, $\vec{n}$ is the domain wall normal vector. (e, f) The current profiles along the black and red dashed lines in (b) and (c), respectively. The blue arrows in (b, c) and (e, f) represent domain walls (specimen with thickness = 150 μm).

ferroelectric polarization [37–39]. Meanwhile, the electrical conductivity difference between the up and down domains is also verified by KPFM [40] mapping in Fig. S7. The polarization charges are compensated by the intrinsic/extrinsic surface state or the free charges to achieve charge balance [41]. Therefore, the surface of the down domain attracts more hole carriers on the sample surface compared with the up domain, giving rise to higher conductivity. The detailed explanation of the charge distribution and conductive behaviors of two different domains can be found in Figs S7 and S8.

From the above optical absorption measurement, SPS possesses full-visible-spectrum absorption and there exist Sn^{2+} and Sn^{4+} states due to the disproportionation reaction of photo-excited Sn ion. In order to reveal the mechanism of full-visible-spectrum absorption, we calculated the electronic structure and analyzed the optical band structure. Firstly, we calculated the electronic structure and optical absorption of SPS with Sn^{2+} and Sn^{4+} states from first-principles, respectively, as shown in Fig. 4. From Fig. 4a, it shows the semiconductor characteristic with a certain bandgap for SPS with Sn^{2+} state, while the valence band maximum of SPS with Sn^{4+} passes over the Fermi level, forming new empty states. The formation of empty states usually results in the intra-band transition, which indicates that SPS with Sn^{4+} can absorb photons with a very small energy. This is confirmed by the optical absorption coefficient (α) of SPS with Sn^{2+} and Sn^{4+} states, as shown in Fig. 4b. It can be found that SPS with Sn^{4+} state performs excellent absorption in the range of visible-light region (300–800 nm), while SPS with Sn^{2+} state only responds to the short-wavelength region (300–600 nm). This well explains the full spectral absorption observed in the

experimental optical spectra for the SPS single crystal, in which the Sn^{4+} content increases to nearly 50% in the illumination condition. The calculated orbital projected band structure of SPS with Sn^{2+} and Sn^{4+} states are illustrated in Fig. 4c, d. The valence band maximum consists of S-p and Sn-s orbitals, while the conduction band minimum is mainly made up of Sn-p orbital. When the Sn^{2+} state changes to Sn^{4+} state in SPS, the valence band maximum upshifts, causing the valence band to cross the Fermi level. Consequently, the intra-band transition between S-p and Sn-s orbitals will easily occur in its valence band for the SPS crystal with Sn^{4+} state under the illumination condition. The existence of Sn^{4+} state plays an important role in the full-spectrum absorption observed in the experiments. Therefore, the disproportionation reaction is responsible for the valence state change from the Sn^{2+} to Sn^{4+} state under illumination, as shown by the XPS measurement in Fig. 2c, d. The mixing Sn^{2+} and Sn^{4+} states reduce the bandgap of SPS crystal, allowing infrared photons to generate hole-like small polarons and the subsequent charge redistribution under the illumination condition [28]. As a result, the intra-band transition will easily occur in its valence band in the SPS crystal under the illumination condition. However, in the reality, the SPS single crystal has a mixing valence state, containing Sn^{2+} and Sn^{4+} states, as shown by the XPS measurement.

Secondly, the full-spectrum absorption generally exists in the disordered and amorphous materials, which possess an exponential part called Urbach tail near the optical band edge and in the absorption coefficient curve [42,43]. These materials have localized electronic states which extend in the band gap. There are three different contributions to the Urbach absorption edge

Figure 4 The electronic and optical properties of the SPS single crystal with Sn^{2+} and Sn^{4+} states. (a) Total density of states, (b) optical absorption coefficients (α), and (c, d) orbital projected band structures for SPS with Sn^{2+} and Sn^{4+} states. The Fermi level was set as 0 eV in (a, c, d). The orange, red and blue solid lines in (c, d) are Sn-p, Sn-s and S-p orbital projected band structures with their weights, respectively.

[44]: free excitons and momentarily localized self-trapped excitons, thermal and structural disorder, and phonon-induced electric microfields. In our sample, according to the structural and composition measurements, the structural and compositional disorder in SPS pure single crystal should not exist. Hence, the illumination-induced defects and momentarily localized self-trapped excitons are contributing together to the Urbach tail [44], which extends the spectrum absorption range. According to the DFT calculations and Urbach absorption, the observed full-spectrum absorption in the SPS single crystal is attributed to the disproportionation reaction of photoexcited Sn ions and Urbach tail. Therefore, the SPS single crystal exhibits full-visible-spectrum absorption, which is not contradicting to the intrinsic band gap.

CONCLUSIONS

In summary, we revealed that SPS possesses full-visible-light absorption (from 300 to 800 nm) with a unique disproportionation mechanism of photoexcited Sn ions and Urbach tail, which is not contradicting to the intrinsic band gap. Interestingly, we demonstrated the remarkable light-enhanced c-DW in the non-oxide ferroelectric SPS single crystal through a combination of PFM, KPFM, and c-AFM measurements. The enhancement of domain wall conductivity is attributed to the photogenerated charge carriers accumulated on the domain wall caused by such disproportionation reaction. In addition, the two different domains with opposite polarization directions exhibit distinguishable electrical conduction in the presence of optical illumination, which is caused by the different band bending behavior due to the interfacial charge with opposite signs. Our results provide a brand-new platform for the investigation of the coupling of ferroelectricity with optical functionalities and achieving greatly enhanced performances for optoelectronics. Light-enhanced domain wall conductivity is likely to motivate the scientific community for the development of improved next-generation optoelectronics devices.

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Author contributions Wang X and Hong J designed and supervised the experiments; Deng J, Jiang X, Wu M, and Wang X prepared the samples, performed the PFM and c-AFM experiments; Deng J and Zhao W carried out the dielectric and ferroelectric properties characterization; Liu Y performed the DFT calculations; XRD experiments were done by Li Y, Xu S, Wang J, Yao Z, and Xia TL; Zhu C and Chen Q carried out the UV-vis diffuse reflectance spectra measurement and the photocurrent experiments; Tang G and Wang X contributed to the measurements and data analyses; Deng J wrote the manuscript with the support from Wang X and Hong J. All authors discussed the results and commented on the manuscript.

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Supplementary information Supporting data are available in the online version of the paper.

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全可见光吸收的光敏铁电材料Sn₂P₂S₆具有增强的畴壁导电性

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摘要 近年来, 光学调控成为一种重要的操纵宏观和微观铁电性能的非接触调控方式, 为光电子器件的发展奠定了基础。然而, 目前大多数功能铁电材料的光学调控都受到其本征带隙及有限的可见光吸收特性的限制。针对上述铁电材料中光学调控存在的限制, 我们报道了一种全可见光吸收(300–800 nm)的非氧化物铁电单晶材料Sn₂P₂S₆。结合缺陷分析和第一性原理计算方法揭示了光激发Sn²⁺离子的歧化反应和乌尔巴赫带尾增强可见光吸收的机制, 这与Sn₂P₂S₆的本征带隙并不矛盾。有趣的是, 我们在非氧化物铁电体中观测到导电的畴壁, 而且歧化反应引起光致畴壁的导电性显著增强。此外, 光照条件下相反取向的铁电畴展现出明显的导电性差异, 这是由畴壁表面的异号电荷引起界面能带弯曲所致。该工作为全可见光吸收铁电材料中的畴壁和畴壁的导电行为以及改善光电子学性能提供了一个全新的思路。