



HAL
open science

Enhanced electrical conductivity and photoconductive properties of Sn-doped Sb₂Se₃ crystals

S. Chen, X. Qiao, Z. Zheng, M. Cathelinaud, Hongli Ma, X. Fan, Xianghua Zhang

► **To cite this version:**

S. Chen, X. Qiao, Z. Zheng, M. Cathelinaud, Hongli Ma, et al.. Enhanced electrical conductivity and photoconductive properties of Sn-doped Sb₂Se₃ crystals. *Journal of Materials Chemistry C*, 2018, 6 (24), pp.6465-6470. 10.1039/c8tc01683f . hal-01835068

HAL Id: hal-01835068

<https://univ-rennes.hal.science/hal-01835068v1>

Submitted on 3 Sep 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Enhanced electrical conductivity and photoconductive properties of Sn-doped Sb_2Se_3 crystals†

Shuo Chen,^{ab} Xvsheng Qiao,^a Zhuanghao Zheng,^b Michel Cathelinaud,^b Hongli Ma,^b Xianping Fan^{*a} and Xianghua Zhang^{*b}

Sb_2Se_3 is a highly interesting semiconductor with high absorption coefficient in the visible range and is composed of non-toxic and earth-abundant elements. To overcome the challenge of intrinsic low electrical conductivity of Sb_2Se_3 crystals, tin-doped $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ semiconductors ($x = 0.00, 0.03, 0.05, 0.07$ and 0.10) have been synthesized by a conventional melt-quenching method in a vacuum sealed silica tube. With increasing Sn doping concentration, the $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals exhibited a great improvement in electrical conductivity by several orders of magnitude thanks to the great increase of carrier concentration reaching almost $2 \times 10^{16} \text{ cm}^{-3}$. Compared to undoped Sb_2Se_3 , the dark current density of a representative $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ increased by approximately 10 times and the photocurrent density with essentially visible illumination increased by approximately 14 times. In addition, the doped sample showed a faster, reversible and stable photoresponse. These excellent performances combined with a simple and easily scalable synthesis method pave the way for using this semiconductor for highly efficient photoelectric devices.

Introduction

Antimony selenide (Sb_2Se_3) is an important V–VI binary semiconductor with excellent photovoltaic, photoconducting, photocatalytic and thermoelectric properties.^{1–6} It has a high absorption coefficient higher than 10^5 cm^{-1} in the visible region and an optimum bandgap width of around 1.1 eV for single junction solar cells. In addition, it is stable and nontoxic and composed of earth abundant elements. These properties make it a promising candidate for various important applications in diverse areas such as solar energy conversion, photo-detector technology, thermoelectric power generation, and opto-electronics in the near-infrared region.^{5,7–11}

Despite the important research efforts, the progress in application development is still limited. One major issue with Sb_2Se_3 is its intrinsic low electrical conductivity ($10^{-6} \Omega^{-1} \text{ m}^{-1}$, in the bulk state), which results in low thermoelectric power factor, low spectral response and low external quantum efficiency.^{12,13} A few studies to improve the electrical

conductivity of Sb_2Se_3 have been reported. For example, Choi *et al.* developed Sb_2Se_3 nanowires decorated with Ag_2Se nanoparticles, which increased the electrical conductivity of the Sb_2Se_3 nanowires.¹² Zhang *et al.* explained an interpenetrating iodine-doped- $\text{Sb}_2\text{Se}_3/\text{Cu}_2\text{GeSe}_3$ heterojunction network fabricated by controlling the crystallization of chalcogenide glass which can improve the photoelectric performance.¹⁴ Our previous work including the synthesis of hybrid nanorods with the $\text{Sb}_2\text{Se}_3/\text{AgSbSe}_2$ heterojunction structure also shows a higher electrical conductivity and photodetector performance.¹⁰ Despite these endeavors, the synthesis of Sb_2Se_3 -based crystals with controllable electrical conductivity has been rarely reported and still needs further exploration.

Doping is an efficient way to tune the electrical and photo-electrical performances of semiconductors. It has been widely utilized in the semiconductor industry.^{15–17} For example, S-doped In_2Se_3 nanowires show a much higher conductivity and spectral responsivity to visible light than undoped In_2Se_3 nanowires.¹⁷ A small amount of Sn leads to a significant increase in the electrical conductivity and photoconductivity of the amorphous As_2Se_3 films.¹⁸ Herein, we demonstrate a conventional melt-quenching method to controllably synthesize high-quality and variably doped $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ semiconducting crystals with the Sn ratio x ranging from 0.00 to 0.10. By incorporating additional Sn atoms into the binary Sb_2Se_3 , a significant improvement in the electrical conductivity and

^a State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, P. R. China.

E-mail: fanxp@zju.edu.cn

^b Univ Rennes, CNRS, ISCR UMR6226, 35000 Rennes, France.

E-mail: xzhang@univ-rennes1.fr

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8tc01683f

1 photoconductivity is observed. Moreover, the as-synthesized
 2 bulk samples with easy and relatively large-scale synthesis
 3 features show very interesting properties for fabricating
 4 Sb_2Se_3 -based photoelectric devices.

5 Experimental

Synthesis of $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals

10 A conventional melt-quenching method using high purity tin
 (99.99%), antimony (99.999%) and selenium (99.999%) as raw
 11 materials was used to synthesize $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals.
 A schematic illustration of the preparation process is shown
 12 in Fig. S1 (ESI[†]). At first, a mixture of 12 g of raw materials
 according to the chemical composition $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ (where
 13 $x = 0.00, 0.03, 0.05, 0.07$ and 0.10 , respectively) was loaded into
 a fully cleaned silica tube of 1 cm internal diameter. A vacuum
 trap that was placed in liquid nitrogen was used to condense
 14 any volatile products and also to improve the vacuum. The
 silica tube was sealed under a typical vacuum of around 10^{-5}
 15 mbar and then was placed in a rocking furnace. The mixture
 was heated to 700°C at a rate of $1.5^\circ\text{C min}^{-1}$ and held for
 16 about 8 hours to ensure complete melting and homogeniza-
 tion. Then it was cooled down to 650°C during 2 hours and
 17 subsequent quenching in water at room temperature. Finally,
 in order to reduce the stress generated from the thermal shock
 18 in the quenching process, the as-synthesized crystals were
 annealed at 350°C for 3 hours.

30 Characterization

X-ray diffraction (XRD) analysis was carried out using a PANa-
 31 lytical's X-ray diffractometer with a step width of 0.02° and a
 counting duration of 0.13 s per step. Scanning electron micro-
 32 scopy (SEM) images and the corresponding Energy Dispersive
 Spectrometer (EDS) elemental mappings were obtained using a
 33 JEOL JSM-7100F thermal field emission electron microscope
 equipped with an EDAX instrument. TEM, HRTEM and SAED
 34 images were obtained using a JEOL JEM-2100 field emission
 transmission electron microscope. The bulk sample was milled
 and then dissolved in chloroform before being placed on the
 35 surface of a copper grid for further TEM measurements. The
 quality and composition of the crystals were also analyzed by
 X-ray photoelectron spectroscopy (XPS, ESCALAB). Before elec-
 36 trical conductivity and photoconductivity measurements, the
 as-synthesized $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals were sliced into small
 37 discs with a thickness of about 2 mm also with surface polish-
 ing. Electrical resistivity and bulk carrier density were mea-
 38 sured using a van der Pauw Ecopia HMS-3000 Hall Measure-
 ment System (Ecopia Corporation, Anyang, South
 39 Korea). The temperature-dependent resistivity was measured
 by the conventional four-probe method in the temperature
 40 range of $300\text{--}400\text{ K}$. To characterize the photoelectric per-
 formance, the photo-electro-chemical (PEC) measurement has
 41 been carried out using the classical 3-electrode method, where
 Ag/AgCl in saturated KCl was used as the reference electrode,
 Pt-wire as the counter electrode and our sample as the working

1 electrode. Additionally, to prepare the working electrode, the
 2 as-synthesized bulk $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals were sliced into
 small discs with a diameter of 10 mm and a thickness of about
 3 2 mm, and then the surface was finely polished and cleaned.
 After this, silver paint was homogeneously applied on one face
 4 of the disc-like sample, acting as the back contact, which was
 connected by a copper wire and then covered with a layer of
 5 epoxy resin to be isolated from the electrolyte during the PEC
 test. Then these electrodes were immersed into the electrolyte
 (0.5 mol L^{-1} LiClO_4 solution), and a white light tungsten
 6 halogen lamp with controllable light intensities was used as
 the light source. A mechanical chopper was used to obtain
 7 chopped light and an Autolab Metrohm potentiostat was used
 to record the current-voltage characteristics.

8 Results and discussion

Fig. 1a shows the XRD patterns of the as-synthesized
 9 $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ polycrystalline semiconductors ($x = 0.00, 0.03,$
 $0.05, 0.07$ and 0.10) acquired on sliced and polished disc-like
 10 samples, which all exhibit prominent peaks in agreement with
 the JCPDS standard card (15-0861) of the orthorhombic phase
 11 of Sb_2Se_3 without a second phase, indicating the absence of any
 detectable impurity. The absence of multiple sets of peaks also
 12 indicates that the $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals do not contain a
 second crystalline phase after Sn doping. Then the XRD pat-
 13 terns of the corresponding powdered samples obtained by
 grinding the bulk crystals into fine powders can be indexed
 14 to the same crystalline phase, as shown in Fig. 1b, suggest-
 ing that the crystallization process takes place uniformly inside
 15 the bulk sample and is not restricted to the surface. The rela-
 tive peak intensity is different between the powder and the bulk
 16 because the preferential orientation in the bulk is destroyed
 during the grinding of the powders. It is noted that further

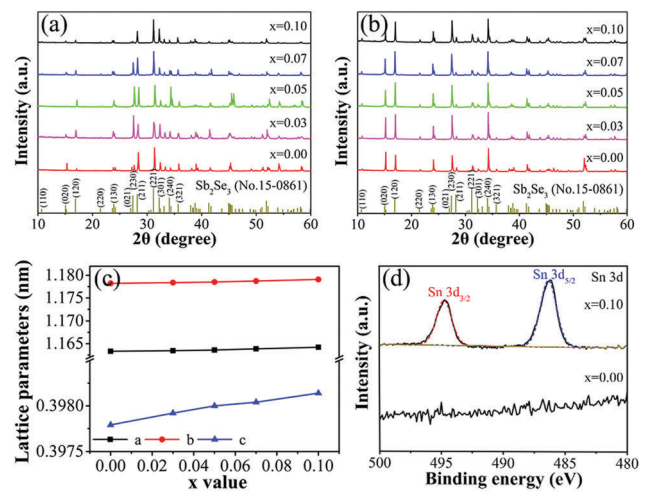


Fig. 1 (a) XRD patterns of the bulk $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals ($x = 0.00, 0.03,$
 0.05, 0.07 and 0.10). (b) XRD patterns of the powdered $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$
 samples. (c) Lattice constants a , b and c derived from powder XRD peaks,
 plotted as a function of Sn doping concentration (x value). (d) XPS
 spectrum of Sn-3d for the $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals ($x = 0.00$ and 0.10).

1 increase of Sn doping concentration will lead to additional
 2 diffraction peaks corresponding to orthorhombic $\text{Sn}_2\text{Sb}_4\text{Se}_8$
 3 (JCPDS Card No. 36-1206), indicating the existence of the
 4 second phase (Fig. S2, ESI[†]). The lattice parameters a , b and c
 5 were determined by refining the diffraction patterns through a
 6 Rietveld method implemented in the FULLPROF program,¹⁹
 7 which show a slight increase upon increasing the Sn doping
 8 concentration (Fig. 1c). This can be attributed to the small
 9 difference in the atomic radius between Sb (0.160 nm) and Sn
 10 (0.158 nm). And this slight difference satisfies the criterion for
 11 substitution solubility proposed by Hume-Rothery who pointed
 12 out that an extensive solid solubility of one metal in another
 13 only occurs if the diameter of the atoms differs by less than
 14 15%.²⁰ Furthermore, the calculated unit cell volume of the
 15 $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals gradually increases from 545.23 \AA^3
 16 ($x = 0.00$) to 546.53 \AA^3 ($x = 0.10$), and this increase is known
 17 to occur due to doping.²¹ Fig. 1d shows the XPS spectrum of Sn-
 18 3d, compared to the pure Sb_2Se_3 . Two obvious peaks located at
 19 494.7 and 486.2 eV from $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ crystals indicate the
 20 existence of Sn, further confirming the successful doping.

21 The $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals' ($x = 0.00, 0.03, 0.05, 0.07$ and 0.10)
 22 morphology of the freshly fractured surface observed by SEM is
 23 shown in Fig. S3 (ESI[†]). All the samples consisted of large crystals
 24 with a layered-like structure and clear strips, indicating a preferential
 25 orientation. According to the theoretical and experimental
 26 studies, bulk Sb_2Se_3 has an orthorhombic crystal structure and is
 27 composed of 1D ribbon-like $(\text{Sb}_4\text{Se}_6)_n$ units stacking together *via*
 28 van der Waals interactions.²² Its preferential growth is indeed
 29 determined intrinsically by the anisotropic Sb-Se atom chain or
 30 the layer structure.^{7,10} To further investigate the doping nature
 31 and also the grain size of the $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals, the finely
 32 polished disk-like samples were etched chemically by 1 mol L^{-1}
 33 NaOH solution for 20 min at room temperature. As shown in
 34 Fig. 2a, the Sb_2Se_3 crystal consists of some big micron-sized
 35 grains. Fig. 2b shows a representative etched microstructure of
 36 the $(\text{Sn}_{0.05}\text{Sb}_{0.95})_2\text{Se}_3$ crystal; the grains are clearly shown with
 37 an average size of approximately 15 μm . In addition, compositional
 38 spatial distribution was determined by EDS elemental mappings
 39 marked with Sn, Sb and Se, which reveals a uniform distribution
 40 of Sb and Se within the crystal. And a few Sn-rich zones between
 41 the grain boundaries can also be observed after chemical etching.
 42 Then for the $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ crystal with a higher Sn doping
 43 concentration, more obvious Sn-rich regions can be observed, as
 44 shown in Fig. 2c. This could be explained by phase separation,
 45 which is reasonable to occur, the minor Sn-rich phase solidifies
 46 first, and then is pushed to the grain boundaries upon freezing of
 47 the major phase. To further reveal the elemental composition of
 48 these Sn-rich regions, EDS analysis has been performed. Fig. 2d
 49 shows the EDS spectra recorded from two different positions
 50 (Point 1 in Fig. 2b and Point 2 in Fig. 2c); the atomic ratio of
 51 Sn:Sb:Se is 14.54:23.74:61.72 and 15.39:22.22:62.39 for Point 1
 52 and Point 2, respectively. It is noted that the composition
 53 analysis of these Sn-rich regions performed on different
 54 $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals show quite similar results, close to the
 55 ratio of 2:4:8 for $\text{Sn}_2\text{Sb}_4\text{Se}_8$, which is also consistent with the
 XRD results.

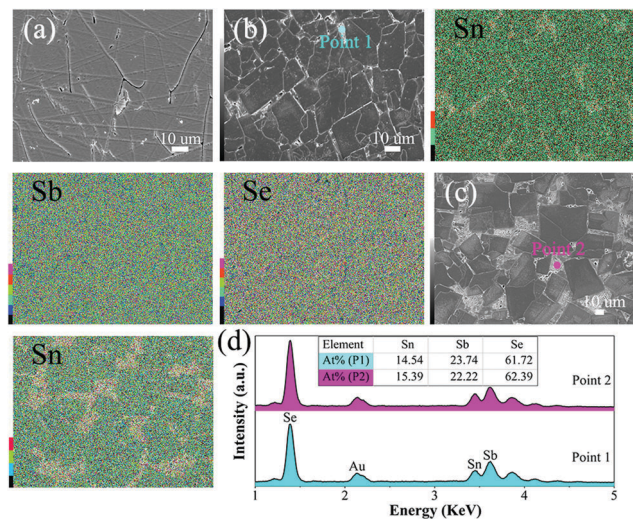


Fig. 2 SEM images of (a) the Sb_2Se_3 crystal, (b) the $(\text{Sn}_{0.05}\text{Sb}_{0.95})_2\text{Se}_3$ crystal and (c) the $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ crystal surface with chemical etching by NaOH solution and following the corresponding EDS elemental mappings of Sn, Sb and Se. (d) EDS spectra recorded from two different positions (Point 1 in (b) and Point 2 in (c)).

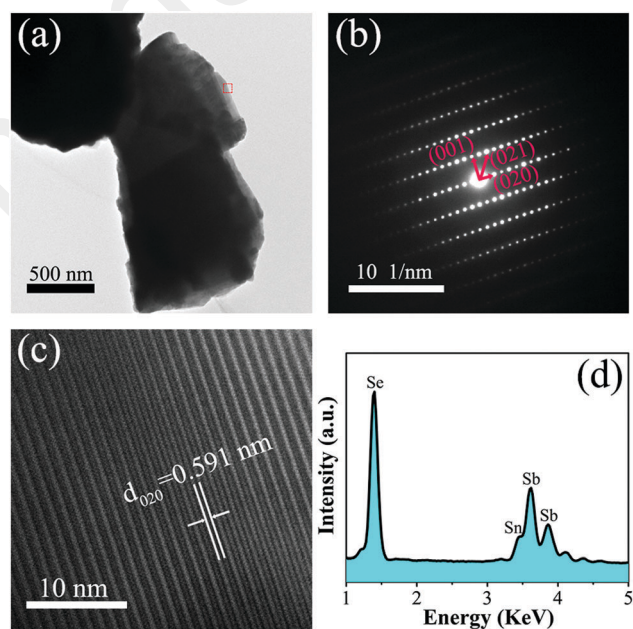


Fig. 3 (a) TEM image of the representative $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ crystal. SAED pattern (b) and the corresponding HRTEM image (c) from the rectangle marked area in (a). (d) EDS spectrum.

Fig. 3a shows the TEM image of an isolated particle milled from the $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ crystal. The selected area electron diffraction (SAED) pattern (Fig. 3b) from the red marked area (in Fig. 3a) is a periodic spot pattern, suggesting its highly crystalline nature. Fig. 3c shows the corresponding HRTEM image with obvious lattice fringes associated with the (020) planes (d -spacing of 0.591 nm) of the orthorhombic phase Sb_2Se_3 . Then the EDS spectrum (Fig. 3d) exhibits strong Sb

1 and Se peaks, and also an observable Sn peak located at 3.44 eV, indicating the successful Sn doping in this crystal.

Fig. 4a shows the electrical resistivity of the as-synthesized $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals with different x values. It can be seen that the pure Sb_2Se_3 exhibits extremely high resistivity. With Sn doping, a significant decrease of resistivity is observed, and the decrease is almost exponential with the x value. The temperature dependent electrical conductivity (σ) in the temperature (T) range of 300–400 K has also been studied. As shown in Fig. 4b, the plots of $\ln \sigma$ versus $1/T$ indicate that the electrical conductivity increases with increasing temperature for all samples, confirming semiconductor characteristics of these samples. Moreover, the conductivity exhibits single activation energy in the temperature range of measurement, according to the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (1)$$

where σ_0 is the pre-exponential factor, ΔE is the activation energy and k is the Boltzmann constant.²³ Thus the thermal activation energy ΔE can be calculated from the slope, while the intercept on the y -axis gives the σ_0 value. Then the bulk carrier density and the doping type were determined by Hall measurements. All the electrical parameters of $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals are summarized in Table 1. It is obvious that the room temperature electrical conductivity shows an increase with several orders of magnitude after Sn doping, accompanied by a synchronous increase of bulk carrier density, which change from $1.44 \times 10^{11} \text{ cm}^{-3}$ ($x = 0.00$) to $1.94 \times 10^{16} \text{ cm}^{-3}$ ($x = 0.10$). Importantly, such a great improvement will provide a bright future for widening applications of Sb_2Se_3 . Since the activation energy varies inversely with the charge carrier density, Sn incorporation in this system should theoretically lead to a decrease of activation energy, which is consistent with the calculated ΔE values. The pre-exponential factor has a close relationship with the defect or impurities in the crystals, Sn doping into Sb_2Se_3 also creates a compositional and configuration disorder, leading to an increase in the localized state density, which is an important factor for the change of σ_0 values. Table 1 also shows the conduction type of $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals; Sn incorporation has been found to result in P-type behavior, suggesting Sn substitution at the Sb site. Sn possesses one fewer valence electron than Sb, thus replacing Sb with Sn constitutes hole doping.²⁴

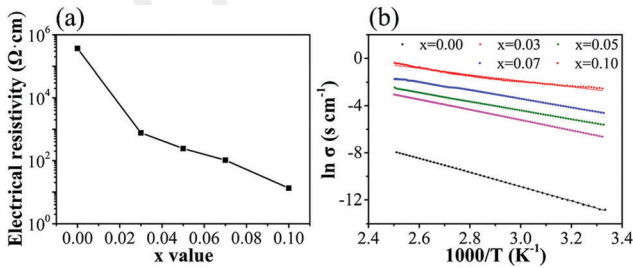


Fig. 4 (a) Electrical resistivity of $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals with different x values. (b) Temperature dependent electrical conductivity (σ) of $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals in the temperature (T) range 300–400 K.

Table 1 A summary of electrical conductivity (σ), bulk carrier density (n), pre-exponential factor (σ_0), activation energy (ΔE) and conduction type of $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals with varied x

x value	σ (S cm^{-1})	n (cm^{-3})	σ_0 (S cm^{-1})	ΔE (eV)	Conduction type
0.00	2.71×10^{-6}	1.44×10^{11}	1.31×10^3	0.52	N
0.03	1.30×10^{-3}	1.52×10^{15}	2.65×10^3	0.38	P
0.05	4.12×10^{-3}	3.59×10^{15}	9.96×10^2	0.32	P
0.07	9.65×10^{-3}	6.90×10^{15}	1.49×10^3	0.30	P
0.10	7.50×10^{-2}	1.94×10^{16}	3.48×10^2	0.22	P

Photoconductivity is a well-known property of semiconductors which describes the electrical conductivity changes with the incident radiation. The photoconductive characteristics of the semiconducting $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals are investigated here by using the classical 3-electrode photo-electro-chemical (PEC) measurements. A schematic illustration of this PEC measurement is shown in Fig. 5a. It is noted that with this 3-electrode technique which measures the generated and separated electron-hole pairs on the surface, it can eliminate the influence of the bulk resistance of the sample, facilitating therefore the comparison between different samples. Fig. 5b shows the current density versus voltage under chopped light using $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ ($x = 0.00, 0.03, 0.05, 0.07$ and 0.10) as the working electrode, respectively. It is obvious that both dark current and photocurrent density of pure Sb_2Se_3 are very weak, which can be explained by its intrinsic low conductivity and low carrier concentration. For Sn-doped crystals, a significant increase of current density is observed, and this increase is proportional to the Sn doping concentration. Up to $x = 0.10$, the dark current density increased approximately 10 times (from $-16 \mu\text{A cm}^{-2}$ to $-160 \mu\text{A cm}^{-2}$ at a bias voltage of -0.6 V) and the photocurrent density increased approximately 14 times

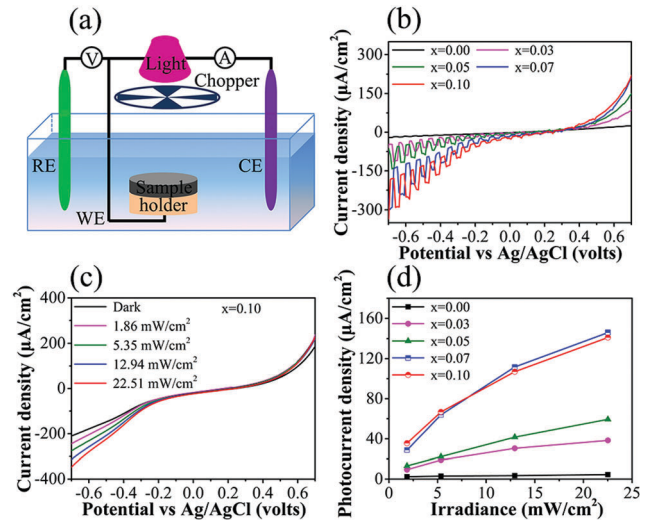


Fig. 5 (a) Schematic diagram of the 3-electrode photo-electro-chemical (PEC) measurement. (b) Current-voltage characteristics using $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals as working electrodes. (c) Dark current density and photocurrent densities at different power densities of the representative $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ crystal. (d) Photocurrent densities measured as a function of incident light density at a bias voltage of -0.7 V .

1 (from $-18 \mu\text{A cm}^{-2}$ to $-250 \mu\text{A cm}^{-2}$ at -0.6 V). This improve-
 2 ment can be considered as an important step to promote
 3 Sb_2Se_3 -based semiconductors for application in high perfor-
 4 mance photoelectric devices. Fig. 5b also shows that the
 5 Sn-doped Sb_2Se_3 crystals are identified as p-type semiconduc-
 6 tors, due to their photocurrent density increase with a negative
 7 bias, which is confirmed by the Hall measurement results.
 8 Then the light intensity dependence of current density is also
 9 investigated. As shown in Fig. 5c, using $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ as an
 10 example, upon illumination, the current density is increased,
 11 and then it increases gradually with increasing light intensity.
 12 Additionally, current-voltage curves of $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ at other
 13 x values (0.00, 0.03, 0.05 and 0.07) are shown in Fig. S4 (ESI[†]),
 14 where similar phenomena were observed. All the samples show
 15 that the photocurrent strongly depends on the light intensity,
 16 which can be attributed to the change in photo-generated
 17 carriers. The corresponding photocurrent density as a function
 18 of light intensity is shown in Fig. 5d, and dependence can be
 19 described by the power law:

$$J_{\text{ph}} = AP^\theta \quad (2)$$

20 where J_{ph} represents the photocurrent density; P is the power
 21 density of the incident light; A is a constant at a specific
 22 wavelength; and θ is an exponent.^{25,26} The fitting curves
 23 showed that $\theta = 0.27, 0.52, 0.65, 0.60$ and 0.54 for x values of
 24 0.00, 0.03, 0.05, 0.07 and 0.10, respectively. All these θ values
 25 are non-unity, indicating that some surface defects and carrier
 26 trapping at the localized states could result in a complex
 27 electron-hole non-radiative recombination process.⁴

28 To evaluate the stability and the response speed of the
 29 photocurrent, chronoamperometry measurements have been
 30 performed. Fig. 6a and b show two plots of the time-resolved
 31 PEC response using Sb_2Se_3 and $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ as the working
 32 electrode, respectively. As shown in Fig. 6a, when the light is
 33

34 on, the current density rapidly increases from $-10.75 \mu\text{A cm}^{-2}$
 35 (dark condition) to $-12.25 \mu\text{A cm}^{-2}$ (with 22.51 mW cm^{-2} light
 36 illumination), and then sharply returns to its initial value as the
 37 light is turned off. This light response remains the same after
 38 multiple cycles, indicating the excellent reversibility and stabi-
 39 lity of this Sb_2Se_3 PEC electrode. Then a similar photoresponse
 40 can be seen for $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$, except for a larger photocur-
 41 rent density in the latter case (Fig. 6b). When using the
 42 $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ crystal as the working electrode, a huge
 43 photocurrent density spike before arriving at a steady value
 44 can also be observed, which was caused by recombination in
 45 the presence of surface states.²⁷ To extract the exact response
 46 time, one of the response periods is magnified, as shown in
 47 Fig. 6c and d, respectively. Under closer examination, the
 48 response time (τ_{on}) and the recovery time (τ_{off}) of the Sb_2Se_3
 49 working electrode are 0.05 s and 0.07 s, respectively. For
 50 $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$, both values show a decrease in value to 0.03
 51 s, which can be attributed to much more surface dangling
 52 bonds, high crystal quality and preferential orientation.^{28,29} It
 53 is worth noting that these short response times are comparable
 54 to the very good results of some reported high performance
 55 photodetectors,^{30,31} further conforming the high potential
 56 application of Sn-doped Sb_2Se_3 crystals as excellent photoelec-
 57 tric devices.

58 The optical absorption spectrum is one of the most effective
 59 tools for understanding and/or engineering the band structures
 60 of semiconductor materials. It is known that an appropriate
 61 band gap of the semiconductor plays a crucial role in fabricat-
 62 ing high performance photoelectric devices. In this work, the
 63 optical absorption spectrum has been employed to characterize
 64 the as-synthesized $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals. And the absorption
 65 data were calculated from diffuse reflectance data using
 66 Kubelka-Munk equations: $F(R) = \alpha/\Lambda = (1 - R)^2/(2R)$, where R
 67 is the reflectance, α and Λ are the absorption and scattering
 68 coefficients, respectively.³² As shown in Fig. 7a, the onset of
 69 the absorption of Sb_2Se_3 crystals starts near 1200 nm, and a
 70 shift toward a longer wavelength is observed after Sn doping.
 71 The higher absorption efficiency for the doped crystals in the
 72 NIR range is interesting for broad spectrum applications. Fig. 7b
 73 shows a plot of $[F(R)h\nu]^2$ versus energy ($h\nu$); the direct band
 74 gap of Sb_2Se_3 is 1.17 eV, and then for the Sn-doped Sb_2Se_3
 75 crystals, the band gap is similar and close to 1.10 eV. The
 76 dwindling band gaps of the doped $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals can
 77 be explained

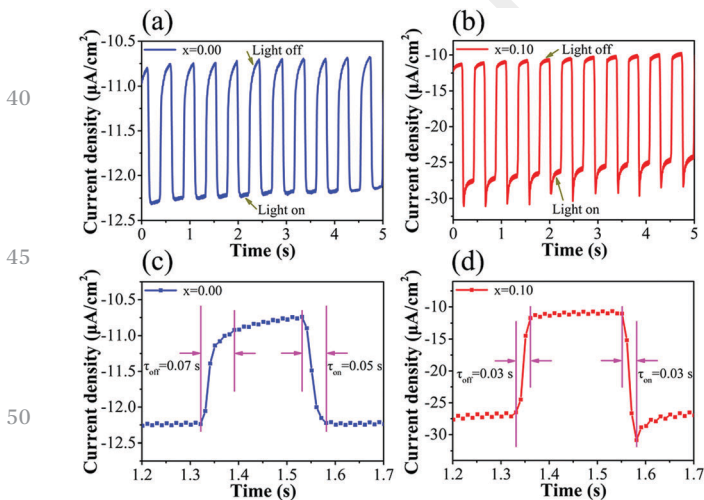


Fig. 6 Time-resolved PEC photoresponse by using Sb_2Se_3 (a) and $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ (b) as the working electrode, respectively. (c) Magnified plot of one response cycle in (a), and (d) one response cycle in (b), used to obtain the response time and the recovery time.

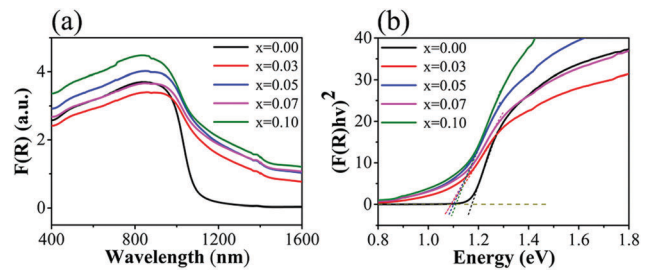


Fig. 7 (a) Optical absorption spectra (calculated from diffuse reflectance data) of the $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals ($x = 0.00, 0.03, 0.05, 0.07$ and 0.10) (b) a plot of $[F(R)h\nu]^2$ vs. energy, from which direct band gap was obtained.

1 by the cooperation of the Burstein–Moss shift and the renormalization effect. This mechanism exists in narrow band gap
 2 semiconductors with a specific doping level.^{33,34} Finally, it is
 3 worth noting that the band gap of the $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals is
 4 close to the best value for absorbing efficiently the solar
 5 spectrum, making them attractive candidates for photovoltaic
 application.

10 Conclusions

11 An effective melt-quenching method has been used to synthesize
 12 high-quality and variably doped $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals
 13 with the dopant Sn ratio x ranging from 0.00 to 0.10. The
 14 successful doping is verified by XRD, XPS and EDS results. With
 15 increasing Sn doping concentration, $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$ crystals
 16 exhibit an improvement of electrical conductivity with several
 17 orders of magnitude due to a much higher charge carrier
 18 concentration. Temperature dependent electrical conductivity
 19 displays a typical semiconductor characteristic and a decrease
 20 of activation energy is also confirmed with Sn incorporation.
 21 Sn-Doped Sb_2Se_3 crystals are identified as p-type semiconduc-
 22 tors according to the photoconductive characteristics. Notably,
 23 compared to pure Sb_2Se_3 , the dark current density of a repre-
 24 sentative $(\text{Sn}_{0.10}\text{Sb}_{0.90})_2\text{Se}_3$ increased approximately 10 times
 25 and the photocurrent density increased approximately 14
 26 times. In addition, it shows a short response/recovery time
 27 (0.03/0.03 s) and a reversible and stable photoresponse. There-
 28 fore, the Sn-doped Sb_2Se_3 crystals have an optimal band gap,
 29 (1.10 eV) which overlaps well with the solar spectrum, and
 30 excellent electrical conductivity and photoconductive prop-
 31 erties, combined with their easy and relatively large-scale syn-
 32 thesis features. These properties confirm the high application
 33 potential of Sn-doped Sb_2Se_3 as highly efficient photoelectric
 34 devices.

35 Conflicts of interest

There are no conflicts to declare.

40 Acknowledgements

41 The authors gratefully acknowledge support for this research
 42 from the Program for Innovative Research Team in the Uni-
 43 versity of Ministry of Education of China (IRT13R54), the
 44 Fundamental Research Funds for the Central Universities
 45 (2016FZA4007) and the Zhejiang Provincial Natural Science
 46 Foundation of China (LY16E020003). We also thank the Chi-
 47 nese Scholarship Council and the Eiffel Excellence Scholarship
 48 Programme for financial support.

50 Notes and references

51 1 L. Wang, D. B. Li, K. Li, C. Chen, H. X. Deng, L. Gao, Y. Zhao,
 52 F. Jiang, L. Li, F. Huang, Y. He, H. Song, G. Niu and J. Tang,
 53 *Nat. Energy*, 2017, 2, 17046.

- 2 G. X. Liang, X. H. Zhang, H. L. Ma, J. G. Hu, B. Fan,
 3 Z. K. Luo, Z. H. Zheng, J. T. Luo and P. Fan, *Sol. Energy*
 4 *Mater. Sol. Cells*, 2017, 160, 257–262.
- 5 3 T. Zhai, M. Ye, L. Li, X. Fang, M. Liao, Y. Li, Y. Koide,
 6 Y. Bando and D. Golberg, *Adv. Mater.*, 2010, 22, 4530–4533.
- 7 4 Y. Q. Liu, M. Zhang, F. X. Wang and G. B. Pan, *J. Mater.*
 8 *Chem. C*, 2014, 2, 240–244.
- 9 5 T. Y. Ko, M. Shellaiah and K. W. Sun, *Sci. Rep.*, 2016,
 10 6, 35086.
- 11 6 N. Hu, M. A. Cheney, Y. Hanifehpour, S. W. Joo and B.-
 12 K. Min, *J. Nanomater.*, 2017, 2017, 1–8.
- 13 7 Y. Zhou, L. Wang, S. Chen, S. Qin, X. Liu, J. Chen, D. J. Xue,
 14 M. Luo, Y. Cao, Y. Cheng, E. H. Sargent and J. Tang, *Nat.*
 15 *Photonics*, 2015, 9, 409–415.
- 16 8 Y. Zhou, M. Leng, Z. Xia, J. Zhong, H. Song, X. Liu, B. Yang,
 17 J. Zhang, J. Chen, K. Zhou, J. Han, Y. Cheng and J. Tang,
 18 *Adv. Energy Mater.*, 2014, 4, 1301846.
- 19 9 R. Huang, J. Zhang, F. Wei, L. Shi, T. Kong and G. Cheng,
 20 *Adv. Funct. Mater.*, 2014, 24, 3581–3586.
- 21 10 S. Chen, X. Qiao, F. Wang, Q. Luo, X. Zhang, X. Wan, Y. Xu
 22 and X. Fan, *Nanoscale*, 2016, 8, 2277–2283.
- 23 11 T. Zhai, L. Li, X. Wang, X. Fang, Y. Bando and D. Golberg,
 24 *Adv. Funct. Mater.*, 2010, 20, 4233–4248.
- 25 12 D. Choi, Y. Jang, J. Lee, G. H. Jeong, D. Whang, S. W. Hwang,
 26 K. S. Cho and S. W. Kim, *Sci. Rep.*, 2014, 4, 6714.
- 27 13 R. J. Mehta, C. Karthik, W. Jiang, B. Singh, Y. Shi,
 28 R. W. Siegel, T. Borca-Tasciuc and G. Ramanath, *Nano Lett.*,
 29 2010, 10, 4417–4422.
- 30 14 X. H. Zhang, Y. Xu, Q. H. Shen, B. Fan, X. S. Qiao, X. P. Fan,
 31 H. Yang, Q. Luo, L. Calvez, H. L. Ma, M. Cathelinaud and
 32 J. J. Simond, *J. Mater. Chem. A*, 2014, 2, 17099–17106.
- 33 15 D. Kong, K. J. Koski, J. J. Cha, S. S. Hong and Y. Cui, *Nano*
 34 *Lett.*, 2013, 13, 632–636.
- 35 16 W. Tian, C. Zhi, T. Zhai, S. Chen, X. Wang, M. Liao,
 36 D. Golberg and Y. Bando, *J. Mater. Chem.*, 2012, 22, 17984.
- 37 17 T. Zhai, Y. Ma, L. Li, X. Fang, M. Liao, Y. Koide, J. Yao,
 38 Y. Bando and D. Golberg, *J. Mater. Chem.*, 2010, 20, 6630.
- 39 18 M. S. Iovu, S. D. Shutov, V. I. Arkhipov and G. J. Adriaenssens,
 40 *J. Non-Cryst. Solids*, 2002, 299, 1008–1012.
- 41 19 P. Barpanda, M. Ati, B. C. Melot, G. Rousse, J. N. Chotard,
 42 M. L. Doublet, M. T. Sougrati, S. A. Corr, J. C. Jumas and
 43 J. M. Tarascon, *Nat. Mater.*, 2011, 10, 772–779.
- 44 20 C. H. Hu, M. H. Chiang, M. S. Hsieh, W. T. Lin, Y. S. Fu and
 45 T. F. Guo, *CrystEngComm*, 2014, 16, 1786–1792.
- 46 21 A. Y. Shenouda and H. K. Liu, *J. Alloys Compd.*, 2009, 477,
 47 498–503.
- 48 22 H. Song, T. Li, J. Zhang, Y. Zhou, J. Luo, C. Chen, B. Yang,
 49 C. Ge, Y. Wu and J. Tang, *Adv. Mater.*, 2017, 29, 1700441.
- 50 23 X. Liu, D. Zhang, H. Li, L. Li and H. Yuan, *Dalton Trans.*,
 51 2017, 46, 2479–2484.
- 52 24 S. R. Culp, J. W. Simonson, S. J. Poon, V. Ponnambalam,
 53 J. Edwards and T. M. Tritt, *Appl. Phys. Lett.*, 2008, 93, 022105.
- 54 25 S. Chen, X. Liu, X. Qiao, X. Wan, K. Shehzad, X. Zhang, Y. Xu
 55 and X. Fan, *Small*, 2017, 13, 1604033.
- 26 H. Zhang, X. Zhang, C. Liu, S. T. Lee and J. Jie, *ACS Nano*,
 2016, 10, 5113–5122.

- 1 27 R. L. Spray, K. J. McDonald and K. S. Choi, *J. Phys. Chem. C*, 2011, **115**, 3497–3506. 31 L. Li, L. Gu, Z. Lou, Z. Fan and G. Shen, *ACS Nano*, 2017, **11**, 4067–4076. 1
- 28 K. Zhang, T. Luo, H. Chen, Z. Lou and G. Shen, *J. Mater. Chem. C*, 2017, **5**, 3330–3335. 32 S. Wang and N. Ye, *J. Am. Chem. Soc.*, 2011, **133**, 11458–11461. 5
- 5 29 W. Zhou, Y. Peng, Y. Yin, Y. Zhou, Y. Zhang and D. Tang, *AIP Adv.*, 2014, **4**, 123005. 33 A. Walsh, J. L. F. Da Silva and S. H. Wei, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 075211. 5
- 30 L. Zheng, K. Hu, F. Teng and X. Fang, *Small*, 2017, **13**, 1602448. 34 Z. M. Gibbs, A. LaLonde and G. J. Snyder, *New J. Phys.*, 2013, **15**, 075020. 5

10

10

15

15

20

20

25

25

30

30

35

35

40

40

45

45

50

50

55

55