Electronic Supplementary Information

A hetero-phase growth method to control the crystal growth of β-antimony single crystals with high quality and large sizes

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Experimental section

Synthesis of antimony single crystals:

A mixture of antimony (120mg, Aladdin, 99.999 % metals basis), red phosphorus (470 mg, Aladdin, 99.999 % metals basis), Sn (10 mg, Alfa Aesar, 99.995% metals basis), and SnI_4 (18 mg, Alfa Aesar, 99.998% metals basis) were sealed in a 15 cm long quartz tube with an inner diameter of 10 mm and a thickness of 2 mm under a vacuum of 10^{-4} pa. The quartz tube was placed horizontally in a three-zone OTF-1200X- III muffle furnace. The quartz tube was heated up where one end of the quartz tube with antimony source (source zone) to 650 °C and the other empty end (reaction zone) to 630 °C for 8h. The sample was kept at these temperatures for 5h and then cooled 100 °C down for 10h. The source zone was then kept at 550 °C with the reaction zone at 530 °C for 30h. The quartz tube was then slowly cooled to 250°C and 230 °C for 100h. The antimony single crystals were then obtained.

Single Crystal X-ray Diffraction

A representative crystal was selected and the diffraction data were collected from a Bruker APEX-II CCD diffractometer. The crystal was kept at 150.0 K during data collection. Using Olex2,[1] the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [2] refinement package using Least Squares minimization.

Crystal data and structure refinement for Antimony single crystal:

Crystal Data for Sb (M =121.75 g/mol): trigonal, space group R-3m (no. 166), a = b = 4.2851(3) Å, c = 11.3128(12) Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$. V = 179.90(3) $Å^3$, Z = 6, T = 150.0 K, μ(MoKα) = 22.079 mm^{-1}, Dcalc = 6.743 g/cm^3, 457 reflections measured ($11.568° \leq 2\theta \leq 52.42°$), 58 unique (Rint = 0.0590, Rsigma = 0.0528) which were used in all calculations. The final R_1 = 0.0525 ($I > 2\sigma(I)$) and wR_2 = 0.1186. CSD-2160361 contains the supplementary crystallographic data in this paper. These data can be

obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

SEM and EDS Characterization

The SEM and EDS analysis were carried out with a GeminiSEM 500 instrument equipped with an electronic differential system.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Agilent 7700x spectrometer was used in semiquantitative mode, involving 15 mg of antimony single crystals previously dissolved in 10 mL of aqua regia.

HRTEM and SAED measurements

HRTEM images and SAED patterns were acquired using an FEI Titan G260-300 transition electron microscope equipped with a field-emission gun (acceleration voltage: 300 kV).

X-ray Diffraction Characterization

X-ray diffraction patterns were obtained from a Bruker D2 PHASER using Cu/Kα radiation (λ = 1.5418 Å) at 40 kV and 30 mA. And the fwhm of the X-ray rocking curve was carried out by using SmartLab (Japan).

Raman Characterization

Raman spectroscopy was taken in a backscattering geometry using a single monochromator with a microscope (Reinishaw inVia) equipped with a CCD array detector (1024 × 256 pixels, cooled to −70 °C) and an edge filter. The spectral resolution and reproducibility were determined to be better than 0.1 cm^{-1}.

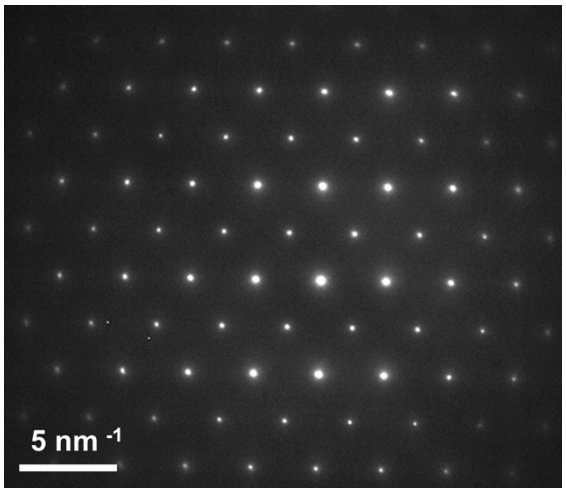

Figure S1. SAED pattern of a β-antimony single crystal.

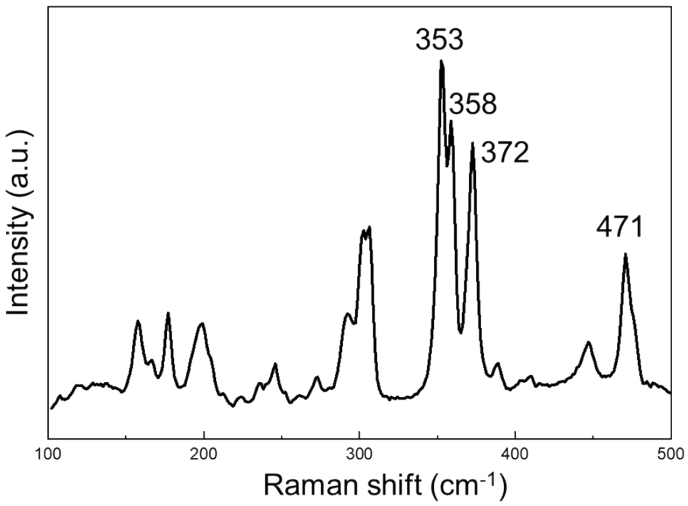

Figure S2. Raman spectrum of phosphorus crystals connected to antimony crystals

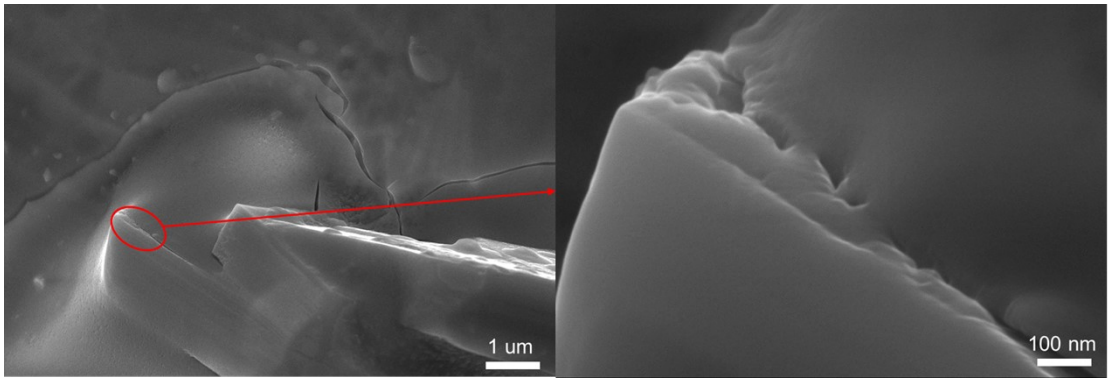

Figure S3. Magnified SEM images of the junction between a β-phase antimony single crystal and violet phosphorus.

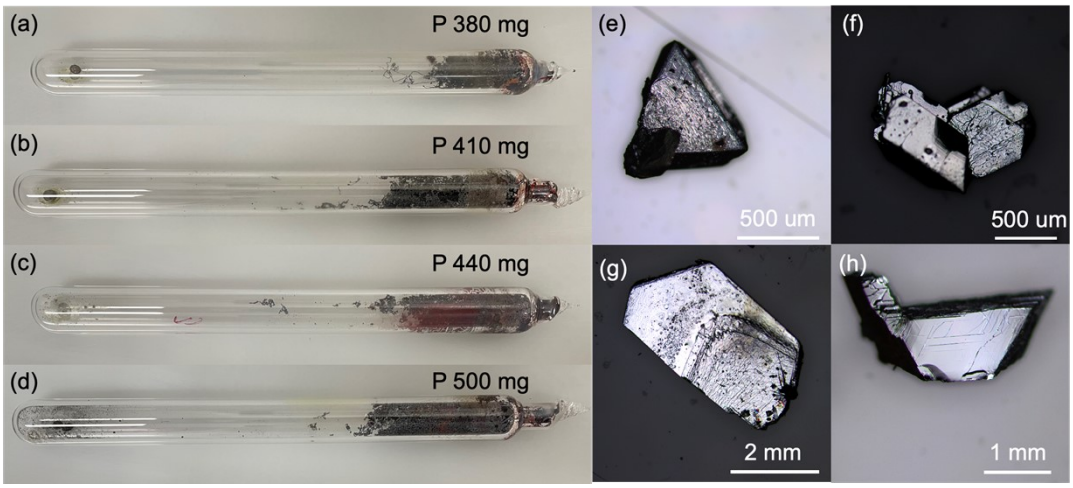

Figure S4. Optical images of the product mixtures (a, b, c, d) and antimony single crystal products (e, f, g, h) from 120 mg feedstock antimony and transport agents (Sn + SnI_4) with (a, e) 380 mg, (b,f) 410 mg, (c, g) 440 mg, and (h) 500 mg amorphous phosphorus.

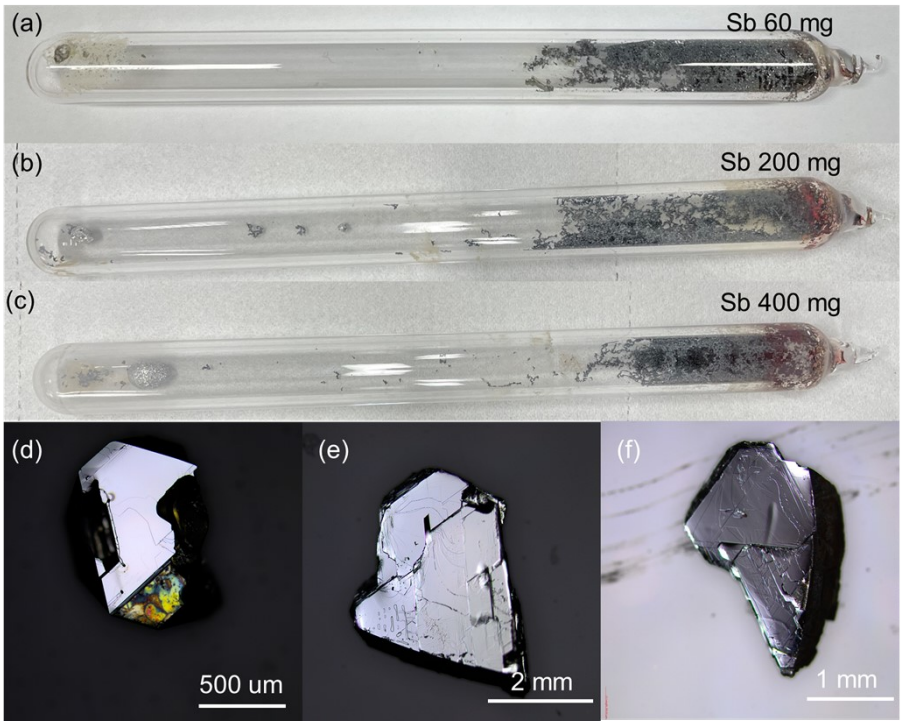

Figure S5. Optical images of the product mixtures (a, b, c) and antimony single crystal products (d, e, f) from 470 mg amorphous phosphorus and transport agents (10 mg Sn + 18 mg SnI_4) with (a, d) 60 mg, (b, e) 200mg, and (c, f) 400 mg feedstock antimony.

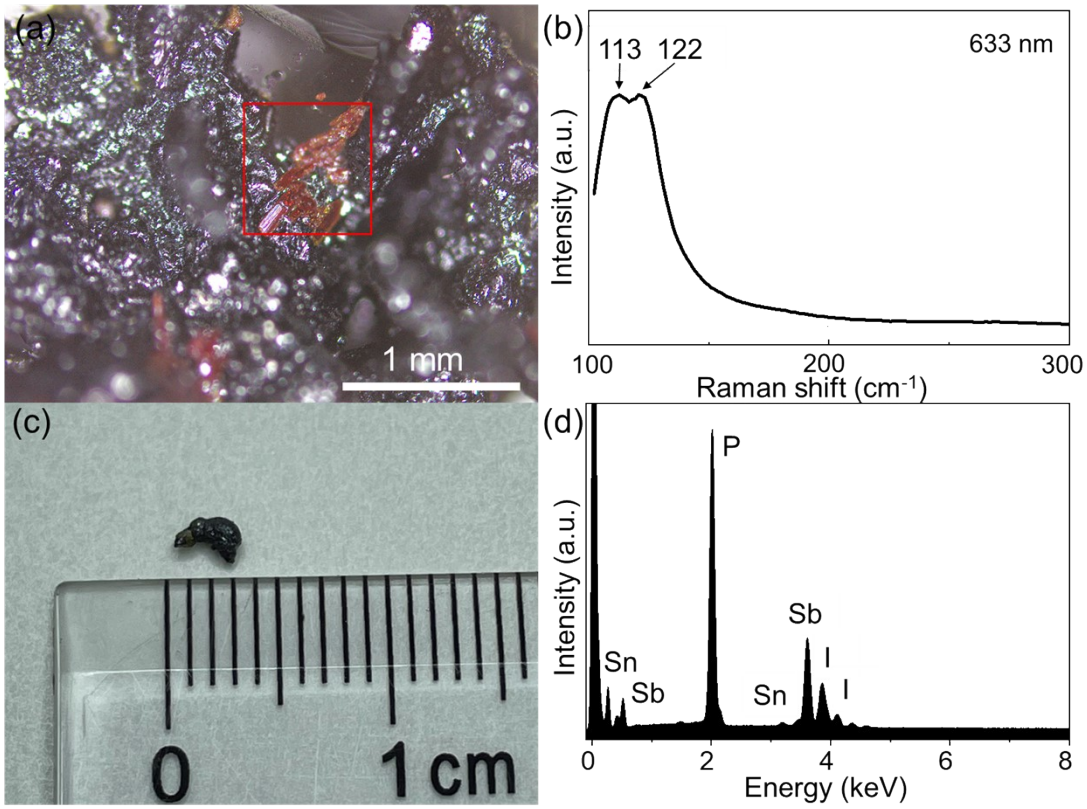

Figure S6. Optical image (a) and corresponding Raman spectrum (b) of the orange-red side products (red box) around insufficient grown violet phosphorus multicrystals; optical image (c) and corresponding EDS spectrum (d) of the as-obtained Sb-P–Sn–I side products around the wall of the tube.

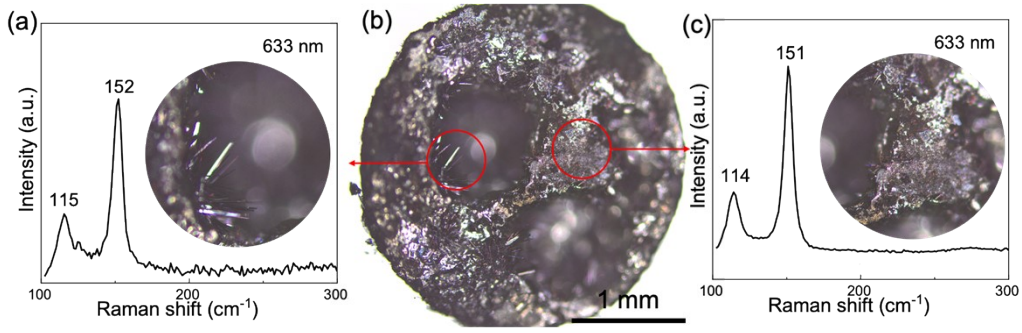

Figure S7. (a) Raman spectrum of shining flakes; (b) Optical images of the residue in the source zone after reaction; (c) Raman spectrum of the shining particles.

Table S1. Crystal data and structure refinement for a β-antimony single crystal.

empirical formula	Sb
formula weight	121.75
temperature /K	150.0

crystal system	trigonal
space group	Rm（No.166）
a /Å	4.2851(3)
b /Å	4.2851(3)
c /Å	11.3128(12)
β /°	90
γ /°	120
volume /Å^3	179.90(3)
Z	6
calculated density /g cm^{-3}	6.743
μ /mm^{-1}	22.079
F(000)	306.0
radiation	MoKα (λ = 0.71073)
2θ range for data collection /°	10.814 to 52.42
index ranges	$-4 \leq h \leq 5$, $-5 \leq k \leq 5$, $-13 \leq l \leq 13$
reflections collected	465
independent reflections	60 [R_{int} = 0.0591, R_{sigma} = 0.0529]
data/restraints/parameters	60/0/5
goodness-of-fit on F^2	1.338
final R indexes [I>=2σ (I)]	R_1= 0.0610, ωR_2 = 0.1482
final R indexes [all data]	R_1 = 0.0610, ωR_2 = 0.1482
largest diff. peak and hole /e Å^{-3}	2.76/-2.25

References

[1]. Dolomanov, O.V., et al., OLEX2: a complete structure solution, refinement and analysis program. Journal of applied crystallography, 2009. 42(2): p. 339-341.

[2]. Sheldrick, G.M., SHELXT–Integrated space-group and crystal-structure determination. Acta Crystallographica Section A: Foundations and Advances, 2015. 71(1): p. 3-8.