Supplementary Information

Crystal Growth of α -AgSbS₂ and its Preliminary Characterization for Radiation Detector Applications

Venika Ekanayake, ^a Matthew F. Webster, ^b Manipaul Dhillon, ^c David A. Kunar, ^a Serge Nagorny, ^{d,e} Mert Turfanda, ^a Michael P. Lewis, ^a and Peng Li Wang *^{a,b}

^{a.} Department of Chemistry, Queen's University, Kingston, Ontario, Canada.

^{b.} Department of Physics, Engineering Physics & Astronomy, Queen's University, Kingston, Ontario, Canada.

^c Department of Chemistry, University of British Columbia, Vancouver, BC, Canada.

^{d.}Gran Sasso Science Institute, L'Aquila, I-67100, AQ, Italy.

^{e.}INFN – Laboratori Nazionali del Gran Sasso, Assergi, I-67100, AQ, Italy.

Corresponding author: wang.peng@queensu.ca

1. Introduction

Room temperature radiation detectors are highly applicable in biomedical imaging, high-energy physics, non-destructive testing, nuclear security, and national safety.^{1–3} Common semiconductor materials used in the direct radiation detection are CdZnTe, Si, high purity Germanium, and various halide perovskite materials.

AgSbS₂ is composed of elements with atomic numbers Z_{Ag} =47, Z_{Sb} =51, and Z_{S} =16. For industrial applications, the cost of raw materials starts to play a crucial role. Therefore, due to the high cost of silver metal, it is preferable to use the material with lower Ag content, thus we have focused our effort on the development of single crystal AgSbS₂ (% w/w Ag = 36.72%) rather than Ag₃SbS₃ (% w/w Ag = 59.77%) or Ag₅SbS₄ (% w/w Ag = 68.34%). Moreover, materials for gamma-ray detector applications should possess higher effective atomic mass (Z_{eff}), in our case, among all listed compounds, AgSbS₂ has the highest content of Sb.

2. Synthesis and crystal growth

Due to the importance of high material purity required by radiation detection applications, the purification of the starting materials is essential.

2.1 Cleaning of Silica ampoules

Silica ampoules and plugs used in the synthesis and crystal growth procedures underwent a preliminary treatment. They were subjected to etching with aqua regia, wherein a mixture of nitric acid (HNO₃) and hydrochloric acid (HCl) in a 1:3 ratio was employed to eliminate potential metallic impurities. The ampoules and plugs were thoroughly washed with deionized water and, thereafter, with semiconductor grade methanol. The processed ampoules and plugs were

subsequently dried at 130°C for 24 hours in an oven that was used for elimination of residual moisture.

2.2 Material purification

High purity silver shots (99.999%, thermo scientific), antimony shots (99.999%, Alfa Aesar), sulfur flakes (99.998%, Sigma Aldrich) were used as the starting materials. The starting materials were purified as follows. Sulfur was first placed into a sublimation apparatus under vacuum which was heated via sand bath to 100°C as shown in Fig. S1. Then dry ice was added to the inner chamber of the apparatus and the sand bath was heated further to 250°C for 2 hours to sublimate all the sulfur. During sulfur purification, heating at 100°C evaporates moisture, while at 250°C,



Fig. S 1 (a) Sublimation apparatus, (b) Purified sulfur, (c) sublimed sulfur at the bottom of the sublimation apparatus.

pure sulfur sublimes, leaving trace metal impurities.

For silver and antimony purification, as shown in Fig. S2, Silver and antimony shots were loaded into a cleaned silica tube, followed by heating under a dynamic vacuum to 150 °C, where the tube was maintained for 1 hour. Subsequently, the tube was exposed to a H_2 flow and further heated to 650 °C. After holding at the peak temperature for an hour, the sample was gradually cooled to room temperature at a rate of 3.0 °C per minute. The tube was maintained under H_2 until it was cooled below the melting point of antimony (631°C), after which it undergoes vacuum treatment while continuing to cool. At this stage, silver and antimony have fused to form a consolidated solid alloy ingot. The ingot was thoroughly washed with 5% HNO₃ in methanol to dissolve any residues of metal oxides on its surface, followed by a meticulous rinse with semiconductor-grade methanol and subsequent drying.

2.3 Crystal growth and postgrowth Processing

To synthesize AgSbS₂, the purified Ag-Sb ingot was placed above sulfur in a clean quartz tube. The vacuum sealed sample within a quartz tube assembly was positioned at the hot zone of a modified vertical Bridgman furnace and subjected to a prescribed heating protocol as shown in Fig. S3.

The precursors were heated to 400°C and dwelled for one day to allow the thorough reaction between gaseous sulfur and the Ag-Sb alloy. Afterwards, the temperature was further elevated to 850°C and held for a day to synthesize the AgSbS₂ ternary phase without any competing phase. This will ensure that at 850°C, all the precursors have exceeded melting points of Ag₂S and AgSbS₂ and are completely liquified.

The AgSbS₂ sample was subsequently cooled down to 570°C and retained at this temperature. Then it was gradually displaced from the hot zone (570°C) to the cold zone (300°C) at a rate of 0.5 mm per hour. Once the sample reached below 380°C, the growth process was terminated, and the developed crystal was gradually cooled down to room temperature. Lowering the temperature from 570°C to 380°C allowed us to control the thermal gradient during cooling and ensure the crystal fully formed in the monoclinic phase. Since the cubic phase transitions to the monoclinic modification at 380°C, through a first-order phase transition, this approach prevents cubic phase retention.⁴

Previous studies suggest that a slower growth rate and a steeper temperature gradient are essential for obtaining high-quality single crystals.^{5,6} In this study, we used a growth rate of 12 mm per day and a temperature gradient of 1.3 °C per mm, which are slower and steeper than those in previous methods. These conditions produced crystal ingots with dimensions of φ 10 mm × 20 mm (Fig. S5).

The polished crystal wafers exhibited a black colour with a metallic lustre (Fig. S2) and left a cherry red streak on the polishing paper. Crystals remained stable and no damage was observed on the crystal after post crystal growth processing or due to moisture.

AgSbS₂ ingots obtained from the vertical Bridgman crystal growth were sliced into 3 mm thick wafers perpendicular to the growth direction by using a Struers Accutom-10 precision saw machine. A cutting rate of 0.020 mm/s rate was preferred in precision cut parameters.

The wafer sections were affixed in epoxy resin and remained to be cured for a period of 48 hours. These epoxy-embedded wafers were then thinned to a thickness of less than 1 mm by using a Buehler EcoMet 30 Semi-Automatic Grinder lapping/polishing machine. SiC abrasive papers with grit specifications of 400, 800, and 1200 were used in succession. The fine polishing stage was conducted using an Al_2O_3 slurry with particle sizes of 1, 0.3, and 0.05 µm suspended in 99.9% HPLC grade 2-Propanol.



Fig. S 2 Overall schematic of the AgSbS2 crystal growth



Fig. S 3 Heating protocol of the modified vertical Bridgman furnace. Temperature rates of the temperature control are as follows: $r_1 = 0.5 \text{ C} / \text{minute}$, $r_2 = 0.2 \text{ C} / \text{minute}$. Translation rate of the sample: $r_i = 0.5 \text{ mm/hr}$.



Fig. S 4 Thermal gradient of the crystal growth at the solid-liquid interface.



Fig. S 5 Left: As grown ingot in the quartz ampoule. Right: Ingot taken out.

- 3. Characterization methods
- 3.1 Phase determination by powder X-ray Diffraction (pXRD)

Phase purity was determined by conducting X-ray powder diffraction analysis for AgSbS₂ powder samples taken from ingots using Bruker AXS D2 Phaser with Cu K α 1 radiation source (λ =1.54184 Å) over the 2 θ range of 8 to 80 degrees with a step size of 0.02 and compared to a theoretical pattern to look at any impurity peaks.

A sample displacement error correction of 0.794 mm was applied for the XRD measurements of the bulk α -AgSbS₂ single crystal sample to compensate for a calibration error. This correction prevented a peak shift of -0.422°.

3.2 Bandgap measurement

UV-Vis-NIR Diffuse reflectance spectra (DRS) of $AgSbS_2$ crystals were collected in the 240-850 nm wavelength range (1.46-5.17 eV) at room temperature using a Hitachi U-3900H UV-Vis Spectrophotometer equipped with Integrating Sphere to measure total diffuse reflectance measurement. Samples were prepared by drop-casting $AgSbS_2$ powder onto a glass substrate, forming a uniform layer over a 20 mm diameter area. The band gap of the α -AgSbS₂ single crystal



sample was measured by converting the Diffuse Reflectance Spectra (DRS) data to Tauc plot using the Kubelka-Munk (KM) function.⁷

3.3 Hardness measurement

Materials with varying mechanical properties necessitate distinct surface treatments for subsequent processing and device fabrication.⁸ For instance, softer materials subjected to wafer processing and mechanical polishing are susceptible to the introduction of surface defects, which results in a diminished detector performance.⁹ Knoop hardness measurements offer valuable insights into the material's hardness, aiding in the selection of the most appropriate approach for postgrowth processing.

AgSbS₂ wafer with a fine polished surface (1 μ finish) was used for hardness measurement. During this procedure, attentively ensured that both faces of the wafer remained parallel. This alignment was essential to ensure that when the wafer was placed on the anvil, the indentation was perpendicular to the polished surface as shown in Fig S7. Subsequently, the microindentation measurements were conducted using the Leitz Wetzlar miniload hardness tester equipped with a Knoop tip. Seven indentations were made at random positions on the finely polished AgSbS₂ wafer surface, each applying a load of 50 g for a 15-second load duration. Knoop hardness values were determined by referencing the Knoop hardness table with the corresponding load and indentation length, and the median value from the seven indentations was determined as shown in Table 1.

| Load/g | Indent length/ μ | Knoop hardness/ HK |
|--------|------------------|--------------------|
| 50 | 80.5 | 110 |
| 50 | 79.5 | 113 |
| 50 | 77 | 120 |
| 50 | 76.8 | 121 |
| 50 | 76.5 | 122 |
| 50 | 75.8 | 124 |
| 50 | 73.8 | 131 |

Table 1 Knoop hardness measurement data



Fig. S 7 (a) Microindentation measurements were conducted using the Leitz Wetzlar miniload hardness tester, (b) Indentation made on the crystal surface.

3.4 Detector fabrication, I-V and photoresponse measurements.

AgSbS₂ ingots grown using the Bridgman method were sliced into wafers, then lapped and polished. The polished wafers were mounted on a glass slide, and electrical connections were made using thin copper wires attached to copper contacts.

A colloidal silver paint was used to connect copper wires to the surfaces of the AgSbS₂ wafer samples. To compare the detector performance, devices featuring In/Au contacts with each layer thickness of 50 nm were produced through the e-beam physical vapor deposition technique.

Current-voltage (I-V) characteristics and Photoresponse of Ag/AgSbS₂/Ag device configuration was evaluated through a bias range from 100 V- 700 V. The detector was positioned within an electrically shielded dark box for current-voltage (I-V) measurements. Voltage bias was connected to the bottom electrical contact and current was measured from the top contact, using a Keithley 6517b electrometer. In I-V measurements, an external bias was applied

systematically swept from -V to +V test range, with each data point derived from the average of every 10 individual measurements. The photo-current responses for different constant voltage biases of Ag/AgSbS₂/Ag devices were collected under the illumination of a white LED with an optical power of 24 mW. The LED was toggled on and off at a 10 second interval. Current-voltage



characteristics (Fig S8) and photoresponses (Fig S9) were precisely measured via a LabVIEW program.

Fig. S 8 Current-voltage characteristics of Ag/AgSbS₂/Ag device. ρ = 3.7 x 1010 Ω ·cm.



Fig. S 9 Photoresponse of Ag/AgSbS₂/Ag devices.

3.5 Radiation detection measurement

The charge pulses were acquired using a Kromek eV-550 preamplifier, Ortec 575A Amplifier, and an Ortec 928 MCB digitizer. The top contact was negatively biased and measurement through the preamplifier, while the bottom contact was grounded. Each pulse-height spectrum was collected over 300 s. The background spectrum, i.e. with device not exposed to alpha source, was collected over 300 s at -150V bias.

4. References

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