## Effect of thermal annealing treatment and defect analysis on

## AgGaGeS<sub>4</sub> single crystal

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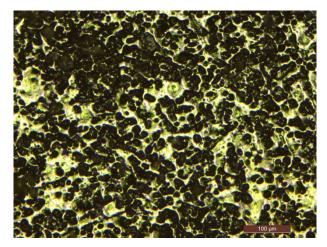
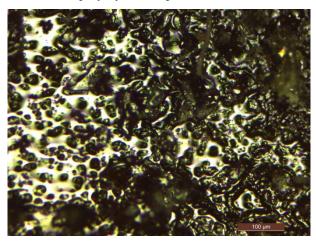


Figure S1. Metallographic microscope photographs of AgGaGeS<sub>4</sub> wafer surface after annealing



with polycrystalline powder at 600 °C

Figure S2. Metallographic microscope photographs of AgGaGeS<sub>4</sub> wafer surface after annealing

with polycrystalline powder at 650  $\,^{\circ}C$ 

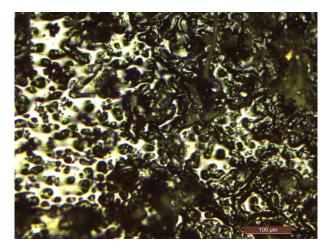
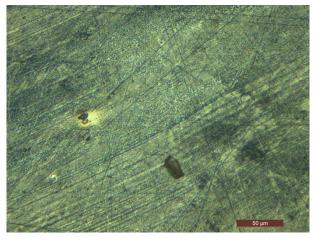


Figure S3. Metallographic microscope photographs of AgGaGeS<sub>4</sub> wafer surface after annealing



with polycrystalline powder at 700 °C

Figure S4. Metallographic microscope photographs of AgGaGeS<sub>4</sub> wafer surface after annealing in



vacuum at 500 ℃

Figure S5. Metallographic microscope photographs of  $AgGaGeS_4$  wafer surface after annealing in vacuum at 600 °C (additional experiment)

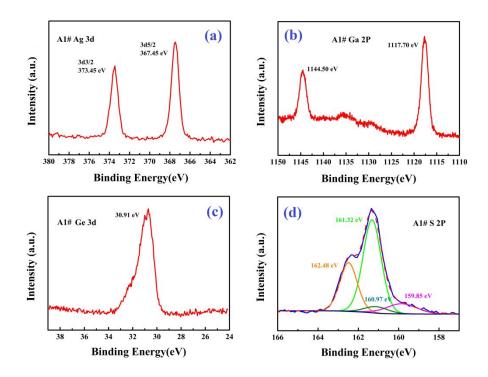


Figure S6. Detailed XPS recorded for polished surfaces of the A1# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

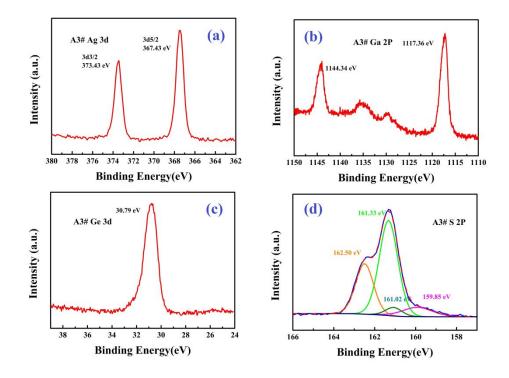


Figure S7. Detailed XPS recorded for polished surfaces of the A3# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

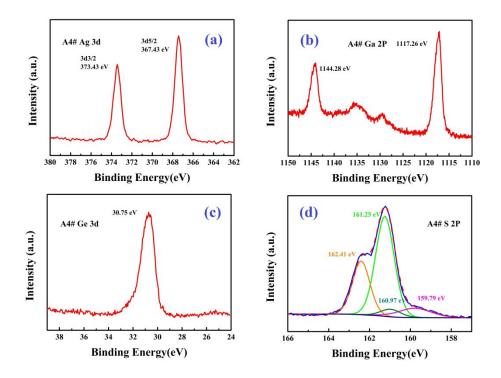


Figure S8. Detailed XPS recorded for polished surfaces of the A4# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

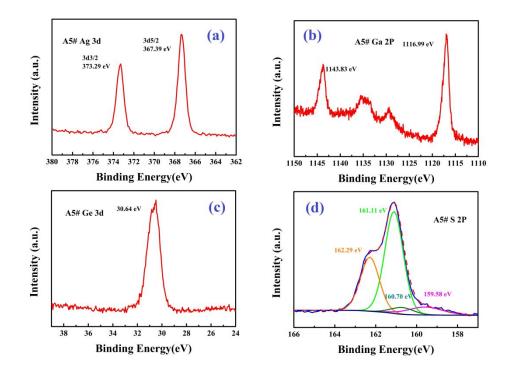


Figure S9. Detailed XPS recorded for polished surfaces of the A5# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

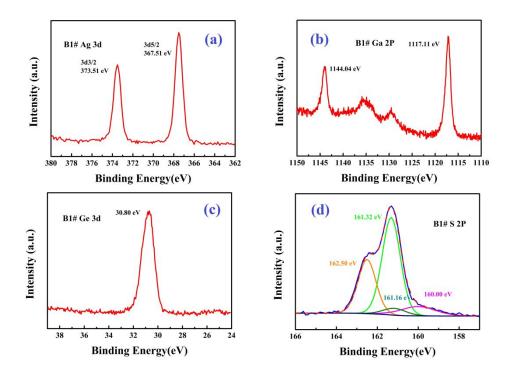


Figure S10. Detailed XPS recorded for polished surfaces of the B1# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

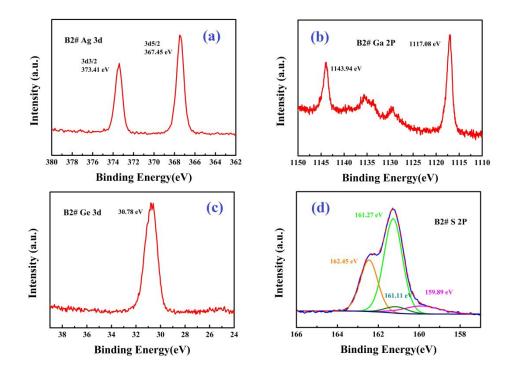


Figure S11. Detailed XPS recorded for polished surfaces of the B2# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

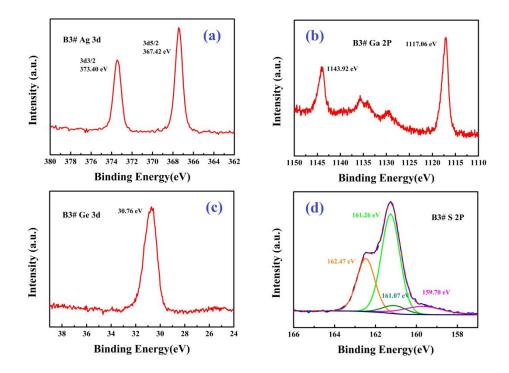


Figure S12. Detailed XPS recorded for polished surfaces of the B3# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

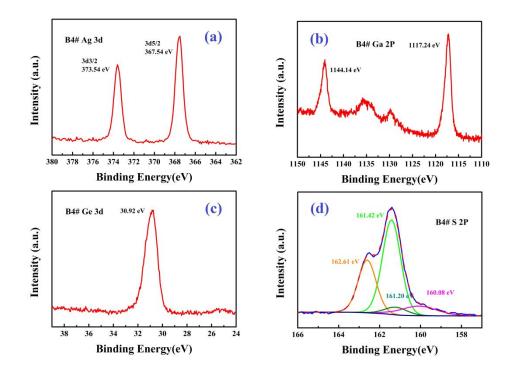


Figure S13. Detailed XPS recorded for polished surfaces of the B4# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p

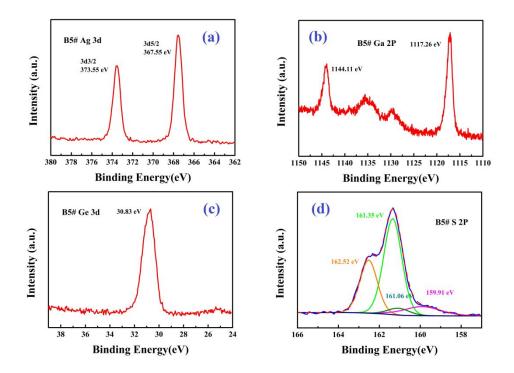


Figure S14. Detailed XPS recorded for polished surfaces of the B5# AgGaGeS<sub>4</sub> single crystals (a) Ag 3d; (b) Ga 2p; (c) Ge 3d; (d) S 2p