Electronic Supplementary Information (ESI)

Investigation of the sublimation mechanism of GeSe and GeS

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This file contains Experimental Section and Fig. S1-S5.

Experimental Section

Chemicals. Germanium monoselenide powder (GeSe, 99%) and germanium monosulfide powder (GeS, 99%) were purchased from Jiangxi Ketai Advanced Materials Co. Ltd.

Materials characterization. The crystal structure of GeSe and GeS powders were characterized by powder XRD (Regaku, D/Max-2500 diffractometer equipped with a Cu Kα1 radiation, λ = 1.54056 A) at elevated temperatures. TGA (PerkinElmer Instruments, Diamond TG/DTA6300) was performed in a flowing N_2 atmosphere at 10 °C/min to study the weight loss of GeSe and GeS powders at elevated temperatures. MS spectra were acquired on a GCT-MS instrument (Waters, Manchester, UK).

Calculation method. We employed the Vienna ab initio simulation package (VASP)[1,2] to perform first-principles calculations to study crystal geometries and electronic structure in conjunction with GGA+PBE.[3] The approximation proposed by Grimme is used to model the non-locality of electron correlation of the Van der Waals forces. An energy cutoff of 500 eV was used for the plane-wave basis and Brillouin-Zone (BZ) integrals[4] was sampled with the k-point of 5×5×1. A maximum force criterion of 0.02 eV/Å and the perpendicular force of 0.01 eV/Å were set.

Ab initio molecular dynamics (AIMD) simulations were carried out to study the bond variations at high temperature, using the local density approximation (LDA)[5] with the projector augmented wave (PAW) method.[6] The AIMD calculations were also employed with the periodic boundary conditions in all directions with maintained the parameters. A 5×5×3 supercell (300 atoms) was constructed to achieve a better variation trend of bond lengths at high temperatures. On this system, we performed a total of 1μs simulation with a separate of 1 fs. The total energy was evaluated to an accuracy of 10^{-5} eV per atom with the same energy cutoff (500 eV). Only Γ-point was considered in the Brillouin zone. The atoms were relaxed until all components of all forces smaller than 0.02 eV/Å.

To obtain a representative crystal at 673K, we enlarged the lattice parameters according to the values obtained in the AIMD calculation (Fig. 1c and d). The crystal

structure was further optimized through DFT calculations. This relaxed structure was then used to describe the crystal at high temperatures.

References

1. G. Kresse, J. Hafner. *Phys, Rev. B*, 1994, **49**, 14251-14269.

2. G. Kresse, J. Furthermuller. *Phys. Rev. B*, 1996, **54**, 11169-11186

3. J.P. Perdew, K. Burke, M. Ernzerhof. *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

4. H.J. Monkhorst, J.D. Pack. *Phys. Rev. B*, 1976, **13**, 5188-5192.

5. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, 1980, **45**, 566

6. P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.

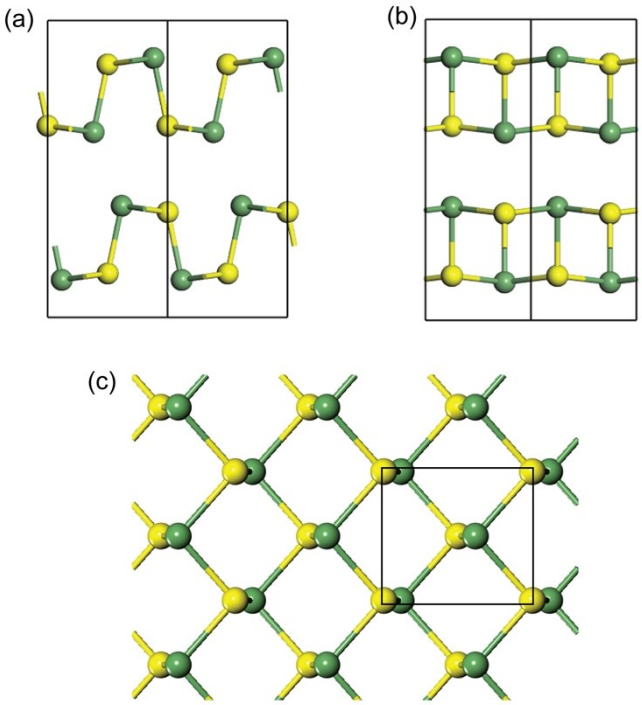

Fig. S1 Crystal structure of GeSe from (a) side view along armchair direction, (b) side view along zigzag direction, and (c) top view.

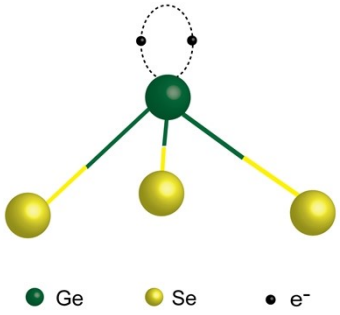

Fig. S2 Schematic representation of the local atomic environment of Ge in GeSe.

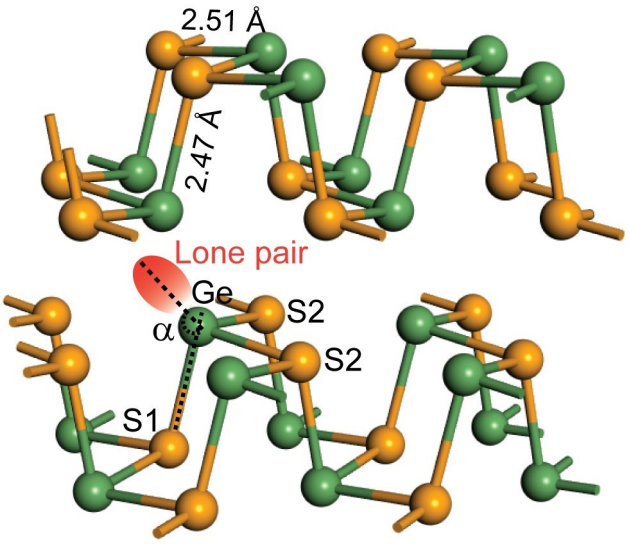

Fig. S3 Ge-S bond lengths in GeS crystal structure, and schematic of the lone pair on Ge atom.

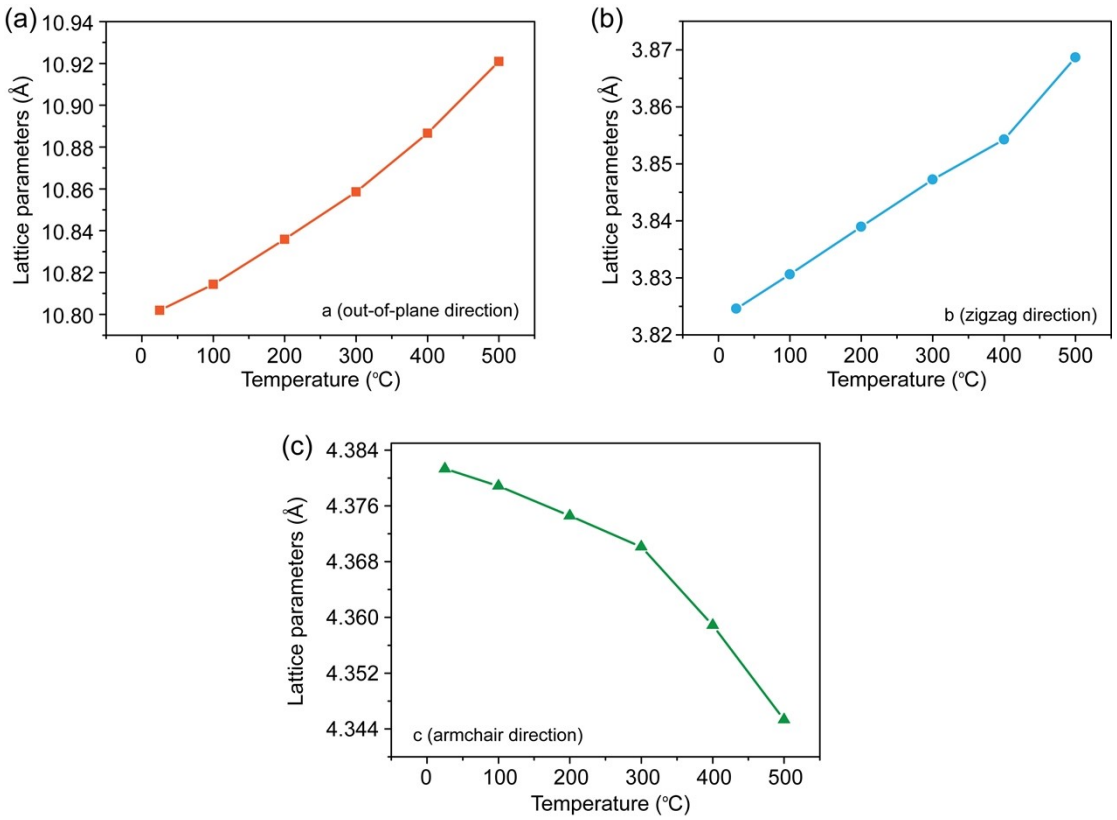

Fig. S4 Temperature-dependent lattice parameters of GeSe along (a) out-of-plane direction, (b) zigzag direction, and (c) armchair direction.

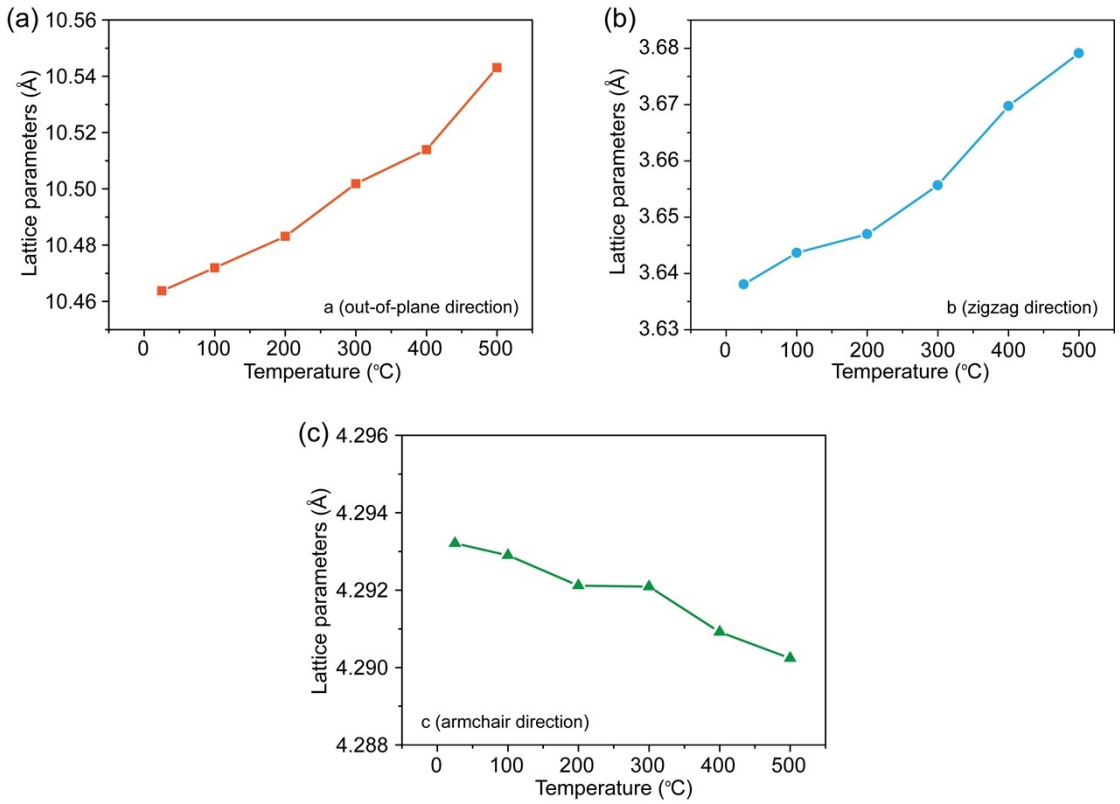

Fig. S5 Temperature-dependent lattice parameters of GeS along (a) out-of-plane direction, (b) zigzag direction, and (c) armchair direction.