Electronic Supplementary Information

Tailored Synthesis of Nonlinear Optical Quaternary Chalcogenides: $Ba_4Ge_3S_9Cl_2$, $Ba_4Si_3Se_9Cl_2$ and $Ba_4Ge_3Se_9Cl_2$

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SURPOTING INFORMATION

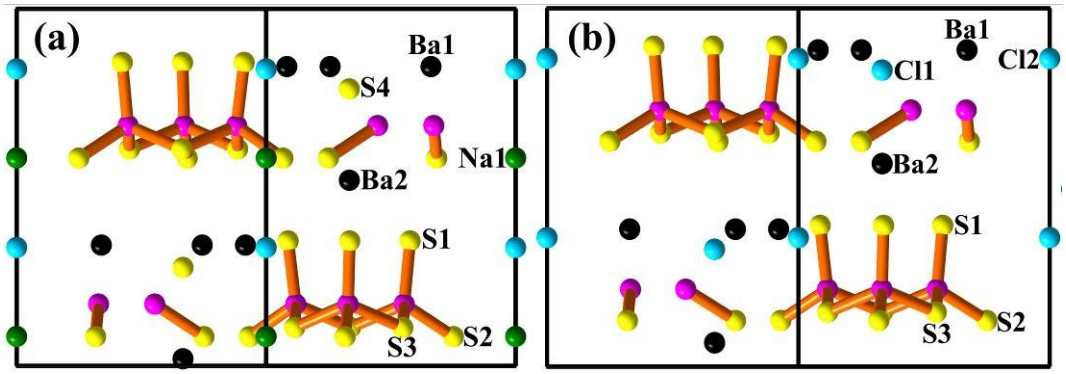

Figure S1a. Crystal structure of (a) $NaBa_4Ge_3S_{10}Cl$ and (b) $Ba_4Ge_3S_9Cl_2$viewed along the [110] direction.

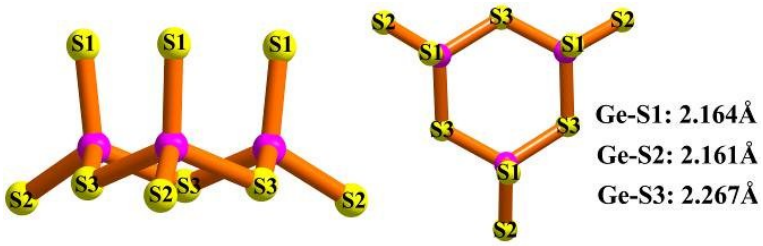

Figure S1b. The fundamental $[Ge_3S_9]$ ring viewed along the side and top direction with bond lengths.

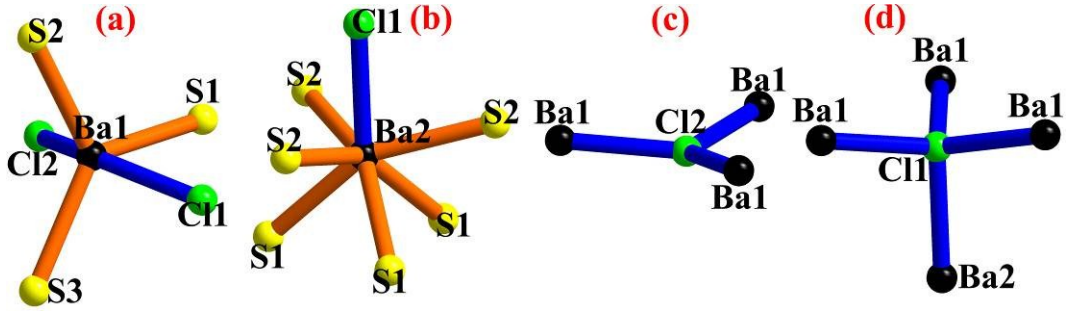

Figure S1c. Coordination environments of Ba and Cl atoms in $Ba_4Ge_3S_9Cl_2$. (a) Ba1 atoms. (b) Ba2 atoms. (c) Cl2 atoms. (d) Cl1 atoms.

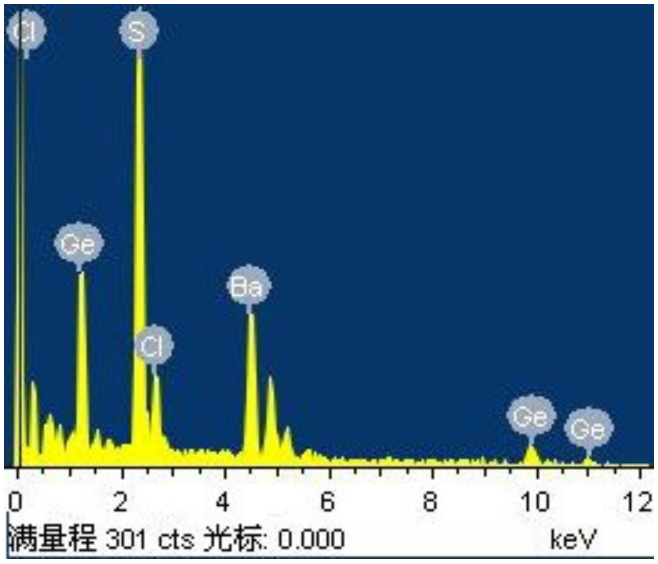

Figure S2a. The EDX spectrum of $Ba_4Ge_3S_9Cl_2$.

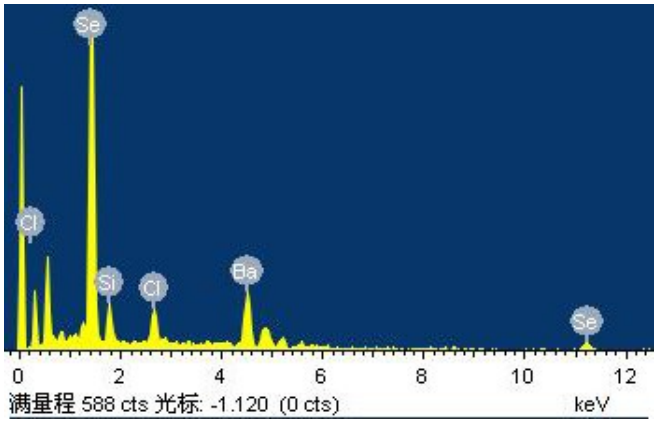

Figure S2b. The EDX spectrum of $Ba_4Si_3Se_9Cl_2$.

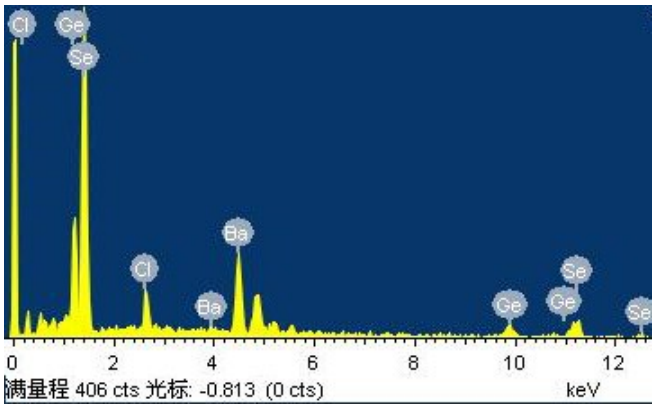

Figure S2c. The EDX spectrum of $Ba_4Ge_3Se_9Cl_2$.

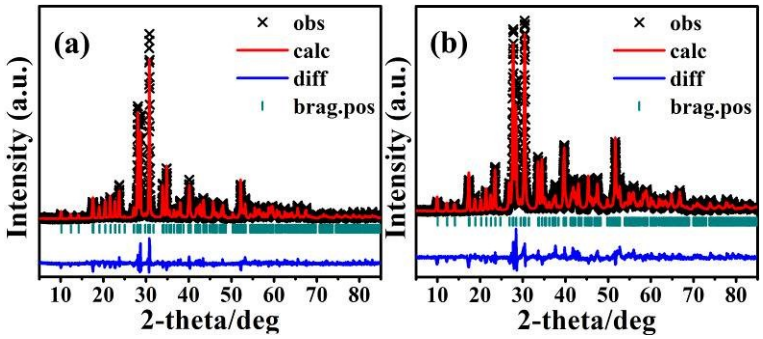

Figure S3. Experimental powder XRD (×), the calculated (red solid line) and difference (blue solid line) results of the fullprof refinements for (a) $Ba_4Si_3Se_9Cl_2$ and (b) $Ba_4Ge_3Se_9Cl_2$.

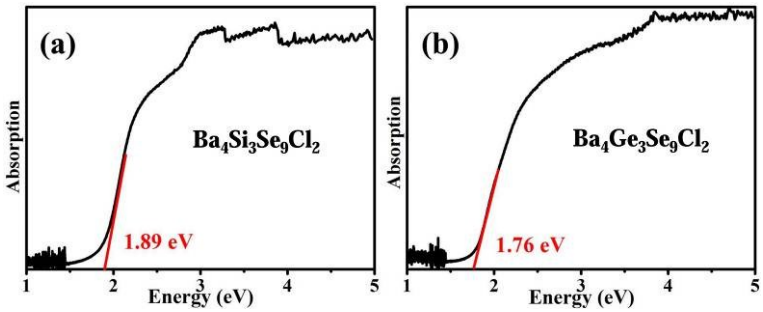

Figure S4. UV-vis diffuse-reflectance spectra of (a) $Ba_4Si_3Se_9Cl_2$ and (b) $Ba_4Ge_3Se_9Cl_2$.

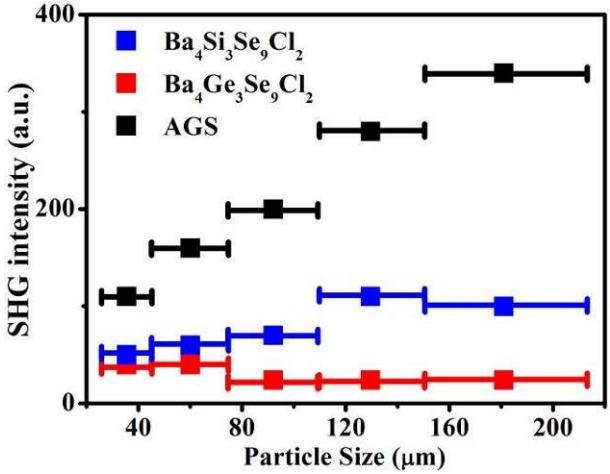

Figure S5. Phase-matching curves, i.e. particle size versus SHG response, for $Ba_4Si_3Se_9Cl_2$, $Ba_4Ge_3Se_9Cl_2$ and $AgGaS_2$ (as reference).

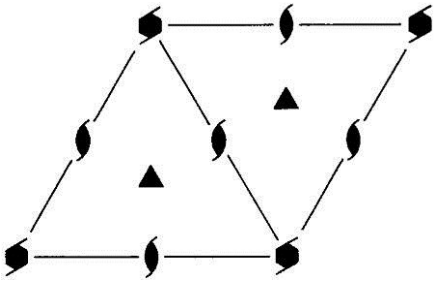

Figure S6. The diagram of symmetry elements of the hexagonal space group $P6_3$ (no. 173).