Supplemental Information File

Synthesis-Enabled Exploration of Chiral and Polar Multivalent Quaternary Sulfides

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S1. Experimental Details

S1.1. Synthesis

The powders of \((RE)_6(TM)_x(Tt)_Q\) \((RE = Sc, Y and La; TM = all transition metals except for Y, Te, and Os; Tt = Si, Ge and Sn; Q = S and Te)\) were synthesized using pre-arc-melted precursors and sulfur without flux, while crystals were grown using a salt flux synthesis from a pre-arc-melted precursor and sulfur.

**Materials used:** Tin powder (99.8%, Strem, USA), Sulfur powder (99.5%, Alfa Aesar, USA), Tellurium powder (99.5%, Matheson, Coleman & Bell, USA), Lanthanum Sulfide (99.9%, Strem, USA), Silicon powder (99.99%, Strem, USA), Titanium powder (99.9%, Strem, USA). Scandium, yttrium, and lanthanum pieces as well as all transition metals, silicon and germanium were acquired from the Materials Preparation Center at Ames Laboratory, which is supported by the US DOE Basic Energy Sciences: Scandium chunk (99.99%), Yttrium chunk (99.9999%), Lanthanum chunk (99.9999%), Titanium pellets (99.999%), Vanadium dish (99.95%), Chromium flakes (99.99%), Manganese pieces (99.99+%), Iron lumps (99.95%), Cobalt buttons (99.9%), Nickel pellets (99.99%), Copper pellets (99.995%), Niobium chunks (99.9%), Molybdenum rod (99.95%), Ruthenium powder (99.99%), Rhodium powder (99.99%), Palladium pieces (99.99%), Silver shot (99.99%), Hafnium plate (99.95%), Tantalum sheet (99.995%), Tungsten wire (99.95%), Rhenium pieces (99.9%), Iridium pieces (99.99%), Platinum shot (99.99%), Gold shot (99.99%), Silicon lumps (99.9999996%), and Germanium lumps (99.999%).

**S1.1.1. Metal Silicide Precursors**

\(RE-TM-Tt\) precursors were prepared using pieces of appropriate metals and tetrel. Samples with a total mass of 0.6 - 1 g were weighed out in a ratio of \(RE : TM : Tt = 6 : 1 : 2.05\) \((RE = Sc, Y and...\)
La; $T_i = $ Si, Ge and Sn; for all $TM$. Additionally, $(TM)_{x}Si_y$ ($TM = $ Sc, Ti, V, Cr, Mn, Zr, Nb, Mo, Ru, Pd, La, Hf, Ta, and Re) precursors were prepared. **Table S1** lists the phase composition for most precursors used. Slight excess of tetrel was used to account for its evaporation during arc melting. The samples were then placed in an arc-melter on a copper hearth along with oxygen getter materials (zirconium metal). The arc-melter chamber was later sealed and evacuated for 20 minutes followed by purging with argon; this process was repeated 3 times to ensure no oxygen was present in the chamber. During arc-melting, the getters were melted first to ensure the absorbance of any trace oxygen, and then the samples were heated for $T \sim 1$ minute at a current of $I \sim 80$ Amperes (A) until molten, allowed to solidify, flipped and re-arced 2 more times to ensure homogeneity under a current of $I \sim 100$ A. The precursor ingots were then crushed into a powder using a steel Plattner-style diamond crusher.

**Stability:** The precursors were kept in desiccators outside of a glovebox. Most La-$TM$-Si precursors are stable with about a year shelf life. Samples more than a year old have been found to contain small amounts of lanthanum hydroxide. The notable exceptions are compositions with $TM = $ Fe and Mn as well as Ge analogous, where most of the La is converted into the hydroxide at approximately 3 months mark.

**S.1.1.2. Single Crystals**

Single crystals of most compositions were grown using pre-arc-melted precursor, sulfur powder, and potassium iodide (KI) salt flux. The ratio of (precursor + sulfur) to KI flux was kept at 1 to 30 ratio by mass (for 0.1g of reactants 3g of KI was used). The reactants and KI salt were added to a silica ampule, which was sealed under vacuum. The samples were heated to 950 – 1050°C (depending on the transition metal used) over 12 hours, allowed to dwell over 72 - 120 hours and then cooled down to room temperature over 8 hours. The KI flux was washed with deionized water,
the sample was then vacuum filtered and allowed to dry. In most cases the crystals resemble rods with a hexagonal cross section, either narrow and long (1-3 mm) or short and bulky (1-2 mm). The crystals are typically dark colored, almost black, with a slight hint of color. The crystals with Cu, Ag, and Au have a transparent yellow-gold appearance. Some compositions, which produced clean bulk powder failed in crystal growth with KI: La₆(TM)ₓSi₂S₁₄ (TM = Ru, Pd, and Ir).

S.1.1.3. Bulk Powders

Bulk powders of the materials were synthesized using pre-arc melted precursor and sulfur powder. Samples were prepared by loading the metal silicide precursor and sulfur in a fused silica ampoule in a 1:14 precursor to sulfur ratio. The ampoules were then flame sealed under vacuum. The samples were heated over 12 hours to 950 – 1050°C (depending on the transition metal used), dwelled for 72 - 120 hours and then allowing them to cool to room temperature over 8 hours.

S.1.1.4. Control Test Reactions from Elements and Binary Precursors

Binary sulfides of Ti, Rh, and Si were prepared by combining powders of corresponding metal with S in 1:2.1 ratio. The ampoules were then flame sealed under vacuum. The samples were heated over 12 hours to 700 °C and dwelled for 72 hours and then allowing them to cool to room temperature over 8 hours. The products of the reactions were (TiS₂ + Ti₈S₃(impurity)) and (Rh₂S₃ + RhS₂(min)). The synthesis of SiS₂ was unsuccessful.

The synthesis of quaternary phases was performed from elements using the following ratio of reactants: 6La : 0.67(TM) : 2Si : 14S (TM = Ti and Rh). Furthermore, the synthetic attempt was performed using binary sulfides in the following ratio: 3La₂S₃ : 0.67TiS₂ : 2Si : 4S and 3La₂S₃ : 0.33Rh₂S₃ : 2Si : 4S. Elemental Si and S were used in lieu of SiS₂. The ampoules were then flame
sealed under vacuum. The samples were heated over 12 hours to 1050 °C and dwelled for 72 hours and then allowing them to cool to room temperature over 8 hours (Figure S3F).

**S1.2. X-ray Diffraction**

Powder X-ray diffraction (PXRD) was performed using a Rigaku Miniflex 600 with Cu-\(K_\alpha\) radiation and a Ni-\(K_\beta\) filter. Sample holders were composed of zero-background silicon plates.

Single crystal X-ray diffraction (SCXRD) was performed using a Bruker D8 Venture diffractometer using Mo-\(K_\alpha\) radiation. All crystal datasets were collected at 100 K under a \(N_2\) stream. All datasets had \(\omega\)-scans recorded at a 0.3 - 0.6 ° step width and were integrated with the Bruker SAINT software package.

Structure determination and refinement of the crystal structures were carried out using the SHELX suite of programs.\(^1\) The site occupancy of transition metal was refined in all cases. For mono- and divalent metals occupancy of the two-fold site was found to be close to 100% and 50%, correspondingly, within few e.s.d. For trivalent metals, such as Sc, Ti, V, Cr, and Rh the refined occupancy was close to 33% (except for V). In addition, S3 atoms coordinating \(TM\) were found to have extremely elongated atomic displacement parameters (ADPs). This sulfur atom was further refined isotropically revealing a significant difference electron density peak indicating a split S site. Further refinement was performed with the constrains of 100% total occupancy and equivalent ADPs for split S3/S33 site which reduces the \(R\)-values and difference electron density peaks substantially. Occupancy of the split sites were found to be close to 67%/33% demonstrating good correlation with transition metal occupancy. In some cases, S33 site occupancy was restrained to be identical to the transition metal site occupancy. For \(TM = Sc\), additional splitting of La site with 67/33% occupancy was necessary to properly describe electron density in the vicinity of La atomic
site. La site ADPs for other 3+ and 4+ metals were elongated in ab plane, but Sc case was the extreme. Final refinement was performed anisotropically for all atoms including transition metal and split S3/S33 site. Similar refinement logic was used for 4+ metal (Pt, Zr, Hf) which occupancy was close to 25%. Further details are provided in Table S1 and corresponding CIFs.

**S1.3. Synchrotron Experiments at Advanced Photon Source at Argonne National Laboratory (APS ANL)**

*In-situ* variable temperature PXRD experiments were carried out at the 17-BM beamline at APS ANL, $\lambda = 0.24155$ Å. To study the mechanism of formation of La$_6$Rh$_{0.7}$Si$_2$S$_{14}$, a small amount of precursor (with a nominal composition of La$_6$Rh$_{0.7}$Si$_2$) was ground in an agate mortar with S in 1 : 14 ratio, loaded in a 0.5mm (ID) capillary, and sealed under vacuum using a flame. For synthesis experiments, the following profile was used: heating at 10 °C/min to 1000°C, hold 10 minutes, then cooling at 100 °C/min to room temperature.

**S1.4.1. $^{29}$Si and $^{45}$Sc Solid State NMR**

All solid-state nuclear magnetic resonance (NMR) spectroscopy experiments were carried out using a Bruker AVANCE III 400 MHz spectrometer using a 3.2 mm low-temperature magic angle spinning (MAS) probe operated at a temperature of approximately 100 K. $^{29}$Si MAS NMR spectra were acquired with the use of a rotor-synchronized Hahn echo pulse sequence with a radiofrequency (rf) power of 50 kHz, a relaxation delay of 130 s, and an MAS frequency of 8 kHz. $^{45}$Sc NMR experiments utilized a Bloch decay sequence, with a 10 μs central transition-selective excitation pulse, a 300 s relaxation delay, and an MAS rate of 14 kHz.

$^{45}$Sc NMR data were processed using the two-dimensional one-pulse (TOP) approach, as implemented in dmfit. This enables for the separation of centerband signals belonging to the
central transition (CT) and satellite transitions (ST). The observed chemical shift of a given resonance from a specific transition of a quadrupolar nucleus is given by

$$\delta_{\text{obs}} = \delta_{\text{iso}} - \frac{3P_Q^2 I(I + 1) - 9m(m - 1) - 3}{40v_0^2 I^2(2I - 1)^2} 10^6 \text{ppm/Hz}$$

where $I = 7/2$ for $^{45}\text{Sc}$ and $m = 1/2$ for the central transition (CT) and $3/2$ (or -1/2) for the inner satellite transitions (ST). As such we have the following peak positions for the CT and inner ST:

$$\delta_{\text{obs},\text{CT}} = \delta_{\text{iso}} - \frac{P_Q^2 10^6 \text{ppm/Hz}}{v_0^2 \cdot 392}$$

$$\delta_{\text{obs},\text{ST}} = \delta_{\text{iso}} - \frac{P_Q^2 10^6 \text{ppm/Hz}}{v_0^2 \cdot 980},$$

and their difference is given by

$$\delta_{\text{obs},\text{ST}} - \delta_{\text{obs},\text{CT}} = \frac{3P_Q^2 10^6 \text{ppm/Hz}}{v_0^2 \cdot 1960}.$$

Having extracted the inner ST and CT centerbands through TOP, the quadrupolar product ($P_Q$) is readily determined, along with the isotropic chemical shift $\delta_{\text{iso}}$. $P_Q$ is related to the quadrupolar coupling constant ($C_Q$) as $P_Q = C_Q \sqrt{1 + \frac{\eta^2}{3}}$ and ranges from $C_Q$ to $1.15C_Q$; $\eta$ is the quadrupolar asymmetry parameter.

**S1.4.2. Density Functional Theory**

Density-functional theory (DFT) calculations were carried out using the CASTEP software package. Simulations of NMR parameters were performed using the gauge-including projector-augmented wave (GIPAW) approach, as implemented in CASTEP. The default on-the-fly-
generated ultrasoft pseudopotentials were used for all atoms, and the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{7} generalized gradient approximation exchange-correlation functional was used for all calculations. Prior to performing magnetic shielding and electric field gradient calculation, the fractional coordinates of the atoms were optimized using a plane-wave kinetic energy cut-off of between 360 eV and 570 eV, depending on the identity of the transition metal, and a $2 \times 2 \times 2 \Gamma$-centered $k$-point mesh. The atomic positions were optimized using a total energy convergence tolerance of $5 \times 10^{-6}$ eV/atom, a maximum ionic force tolerance of 0.01 eV/Å, and a maximum atomic displacement tolerance of $5 \times 10^{-4}$ Å. Subsequent NMR parameter calculations used a similar plane-wave energy cut-off, but a much denser $k$-point grid, with a $k$-point spacing of 0.03 Å\textsuperscript{-1}.

$^{29}$Si magnetic shielding constants ($\sigma_{\text{iso}}$) were converted to chemical shifts ($\delta_{\text{iso}}$) through the usual relation: $\delta_{\text{iso}} = \sigma_{\text{ref}} - \sigma_{\text{iso}}$, where $\sigma_{\text{ref}}$ is the shielding of a reference compound with a known chemical shift. In this study the shielding of SiS$_2$ ($\sigma_{\text{ref}} = 315.87$ ppm, $\delta_{\text{iso}} = -21.1$ ppm\textsuperscript{8}) was used as a secondary reference (relative to tetramethylsilane), based on the structure reported by Evers et al.\textsuperscript{9}$^{45}$Sc shielding was not studied computationally due to the difficulty in finding a suitable reference material.

$^{45}$Sc EFGs were calculated by generating several $2 \times 2 \times 2$ supercells with varying occupancy of the Sc $TM$ site. The $C_Q$ and $\eta$ for each individual Sc site were calculated for each structure. The average values are reported in Table S6.

**S.1.5. Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS)**

Elemental analysis of samples was conducted using a FEI Quanta 250 field emission-SEM with EDS detector (Oxford X-Max 80, ThermoFischer Scientific, Inc., USA) and analyzed using the
Aztec software. Powder samples were mounted in epoxy, polished to a level surface, and coated with a conductive layer of carbon. Large crystals were mounted on double-sided carbon tape. An accelerating voltage of 15kV was used to study all samples.

S1.6. Solid-State Diffuse Reflectance Spectroscopy

The UV/Vis diffuse reflectance spectra were measured from 200-1080 nm with a BLACK-Comet C-SR-100 spectrometer. Powder samples were finely ground and flattened on a microscope slide. Band gaps were estimated through extrapolation of the linear slope in the corresponding Tauc plots by plotting \((A\hbar\nu)^{1/r}\) vs \(\hbar\nu\) where \(r = \frac{1}{2}\) for direct and \(r = 2\) for indirect band gaps.

S1.7. SQUID Magnetometry

Magnetic properties were obtained using SQUID magnetometer, model MPMS XL-7, manufactured by Quantum Design. The powder samples were placed into quartz sample holders and sealed with Teflon tape. Magnetization was measured as a function of temperature in applied magnetic field of \(H = 1\) kOe and 20 kOe from 2 to 300 K (on heating) and, isothermally, as a function of applied magnetic field at 2 and 300 K between -70 and 70 kOe (full hysteresis loop). AC susceptibility was measured between 2 and 50 K wit \(H_{dc} = 5\) Oe, \(H_{dc} = 0\), and \(f = 100\) Hz.

S1.8. EPR Analysis

Electron paramagnetic resonance (EPR) spectra were collected using an X-band ELEXYS E580 EPR Spectrometer (Bruker BioSpin) equipped with an SHQE resonator operating at 9.4 GHz, and a Bruker variable temperature accessory for heating/cooling. Powder samples were loaded into a 4 mm suprasil synthetic quartz tube (SP Wilmad-LabGlass) to minimize background signal from naturally occurring metals. Spectra were acquired with a sweep width of 4000 G, center field of 3350 G, receiver gain of 40 dB, 4096 points, sweep time of 83.9 s, time constant of 0.04 ms, and
5 G modulation amplitude. The 298 K spectrum was acquired with 1.986 mW microwave power and 1 scan, while the 110 K spectrum was acquired with 4.975 mW microwave power and 4 scans.

**S1.9 Second Harmonic Generation (SHG) and Laser Damage Threshold (LDT)**

Through the Kurtz and Perry method, powder SHG responses were investigated by a Q-switch laser (2.09 μm, 3 Hz, 50 ns) with different particle sizes, including 38–55, 55–88, 88–105, 105–150, 150–200, and 200–250 μm. The AgGaS₂ crystal was ground and sieved into the same size range as the reference. The LDTs were evaluated on powder sample (150–200 μm) with a pulsed YAG laser. Similar size of AgGaS₂ was chosen as the reference. To adjust different laser beams, an optical concave lens is added into the laser path. The damage spot is measured by the scale of optical microscope.
Table S1A. SCXRD data collection and refinement parameters for La₆(TM)ₓSi₂S₁₄ (TM = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni; x = 2 – 0.5)

| CSD-number | La₆Sc₀.₆₅(1)Si₂S₁₄ | La₆Ti₀.₆₂(1)Si₂S₁₄ | La₆V₀.₇₇(1)Si₂S₁₄ | La₆Cr₀.₆₆(1)Si₂S₁₄ | La₆Mn₀.₉₈(1)Si₂S₁₄ | La₆Fe₁.₀₅(1)Si₂S₁₄ | La₆Co₁.₀₁(1)Si₂S₁₄ | La₆Ni₀.₉₉(1)Si₂S₁₄ |
|------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Space group | P6₃              |                  |                  |                  |                  |                  |                  |                  |
| λ (Å)      |                  |                  |                  |                  |                  |                  |                  |                  |
| T (K)      |                  |                  |                  |                  |                  |                  |                  |                  |
| a (Å)      | 10.338(5)        | 10.2970(5)       | 10.2960(4)       | 10.2888(12)      | 10.3337(4)       | 10.2991(3)       | 10.3141(11)      | 10.2725(6)       |
| c (Å)      | 5.7459(4)        | 5.7720(3)        | 5.7356(3)        | 5.7503(9)        | 5.7285(3)        | 5.7389(3)        | 5.7313(10)       | 5.7287(4)        |
| V (Å³)     | 531.85(6)        | 529.95(5)        | 526.56(5)        | 527.17(15)       | 529.76(5)        | 527.18(4)        | 528.02(15)       | 523.53(7)        |
| Z          |                  |                  |                  |                  |                  |                  |                  |                  |
| ρ (g•cm⁻³) | 4.269            | 4.287            | 4.345            | 4.324            | 4.364            | 4.401            | 4.395            | 4.432            |
| Absorption correction | multi-scan |                  |                  |                  |                  |                  |                  |                  |
| μ (mm⁻¹)   | 13.437           | 13.515           | 13.704           | 13.690           | 13.860           | 14.062           | 14.105           | 14.333           |
| θ (°)      | 2.27 – 40.13     | 2.29 – 32.99     | 2.28 – 40.24     | 2.29 – 33.05     | 2.28 – 40.36     | 2.28 – 40.23     | 2.18 – 33.07     | 2.29 – 32.95     |
| Data / param. | 1805/46         | 1339/43          | 1789/40          | 1340/42          | 1795/38          | 1787/38          | 1337/38          | 1340/38          |
| R₁         | 0.019            | 0.015            | 0.020            | 0.021            | 0.026            | 0.019            | 0.011            | 0.037            |
| wR₂        | 0.031            | 0.028            | 0.036            | 0.034            | 0.044            | 0.036            | 0.025            | 0.047            |
| Goodness-of-fit | 1.05             | 1.05             | 1.05             | 1.05             | 1.03             | 1.12             | 1.13             | 1.05             |
| Flack Param. | 0.01(1)          | 0.03(2)          | -0.006(11)       | -0.01(1)         | 0.02(3)          | 0.01(2)          | 0.010(8)         | 0.01(3)          |
| Diff. peak/hole (e•Å⁻³) | 1.09/-1.21       | 0.93/-1.29       | 2.02/-1.83       | 1.76/-2.07       | 1.25/-1.78       | 0.83/-1.52       | 0.71/-0.60       | 1.67/-1.51       |
Table S1B. SCXRD data collection and refinement parameters for La₆(TM)ₓ(Tt)₂S₁₄ (TM = Zr, Rh, Pd, Hf, Pt, Cu, Ag, and Au; Tt = Si, Ge, and Sn; x = 2 – 0.5)

| CSD-number | La₆Zr₁.₅₂(1)₆S₁₄ | La₆Rh₁.₆₉(1)₆S₁₄ | La₆Hf₁.₄₈(2)₆S₁₄ | La₆Pt₁.₅₃(1)₆S₁₄ | La₆Cu₁.₉₇(1)₆S₁₄ | La₆Au₁.₉₂(3)₆S₁₄ | La₆Au₁.₉₈(2)₆Ge₆S₁₄ | La₆Au₁.₉₄(2)₆Sn₆S₁₄ |
|------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| λ (Å)      | Mo-Kα: 0.71073   |                  |                  |                  |                  |                  |                  |                  |
| T (K)      | 100(2)           |                  |                  |                  |                  |                  |                  |                  |
| a (Å)      | 10.3189(6)       | 10.2507(5)       | 10.3188(6)       | 10.2530(3)       | 10.3231(14)      | 10.3804(15)      | 10.3905(16)      | 10.4001(19)      |
| c (Å)      | 5.7543(4)        | 5.7490(3)        | 5.7612(5)        | 5.7717(3)        | 5.7991(8)        | 5.8250(14)       | 5.8848(10)       | 6.0178(14)       |
| V (Å³)     | 530.63(7)        | 523.15(16)       | 531.25(8)        | 525.46(4)        | 535.19(16)       | 543.6(2)         | 550.22(19)       | 563.7(2)         |
| Z          | 1                |                  |                  |                  |                  |                  |                  |                  |
| ρ (g•cm⁻³) | 4.337            | 4.474            | 4.451            | 4.557            | 4.541            | 5.238            | 5.479            | 5.597            |
| μ (mm⁻¹)   | 13.522           | 13.996           | 15.644           | 16.921           | 15.074           | 25.789           | 28.446           | 27.056           |
| θ (°)      | 2.28 – 32.78     | 2.29 – 33.11     | 2.28 – 32.49     | 2.29 – 33.05     | 2.28 – 33.18     | 2.27 – 33.18     | 2.27 – 33.24     | 2.27 – 33.25     |
| Data / param. | 1189/42        | 1340/43          | 1289/41          | 1220/42          | 1362/39          | 1372/39          | 1364/39          | 1436/39          |
| R₁         | 0.024            | 0.018            | 0.026            | 0.039            | 0.012            | 0.013            | 0.013            | 0.016            |
| wR₂        | 0.036            | 0.029            | 0.043            | 0.086            | 0.023            | 0.025            | 0.024            | 0.025            |
| Goodness- of-fit | 1.05             | 1.07             | 1.07             | 1.11             | 1.11             | 0.97             | 1.09             | 1.02             |
| Flack Param. | 0.03(3)        | 0.02(3)          | 0.04(4)          | 0.04(5)          | 0.026(15)        | 0.012(6)         | 0.019(6)         | 0.020(6)         |
| Diff. peak/hole (e•Å⁻³) | 0.97/1.10 | 1.51/-1.96 | 1.05/-1.49 | 2.56/-2.04 | 0.62/-0.49 | 1.81/-0.74 | 0.95/-0.76 | 2.12/-0.96 |
Table S2. Phase composition of precursors used for the synthesis of quaternary phases.

| RE | TM | Nominal Composition | Crystalline Phases Identified by PXRD in Brittle Fraction of Precursor |
|----|----|---------------------|---------------------------------------------------------------------|
| Sc | -  | 5Sc : 3Si           | Sc5Si3 + Sc                                                         |
|    | Ti | 6Sc : Ti : 2Si      | Sc5Si3 + Sc + ScMn                                                |
| Mn |   | 6Sc : Mn : 2Si      | Sc5Si3 + Fe + FeSi2 + ScFe                                        |
| Fe |   | 6Sc : Fe : 2Si      | Sc5Si3 + FeSi2 + ScFe                                             |
| Co |   | 6Sc : Co : 2Si      | Sc5Si3 + ScCo + ScCo                                             |
| Ni |   | 6Sc : Ni : 2Si      | Sc5Si3 + ScNiSi3                                                 |
| Cu |   | 6Sc : 2Cu : 2Si     | Sc5Si3 + ScCu                                                 |
| Rh |   | 6Sc : Rh : 2Si      | Sc5Si3 + Sc55.8Rh13.8                                           |
| Ag |   | 6Sc : 2Ag : 2Si     | ScAg + ScSi3                                                   |
| Ir |   | 6Sc : Ir : 2Si      | Sc5Si3 + ScIrSi3 + Ir3Si5                                        |
| Au |   | 6Sc : 2Au : 2Si     | ScAu + Sc5Si3                                                   |
| Y  |   | 5La : 3Si           | La5Si3 + La3Si4                                                   |
|    | Sc | 6La : Sc : 2Si      | La5Si3 + ScSi3 + LaScSi                                          |
|    |   | 6La : Sc : 2Ge      | La5Ge3 + LaScGe + Ge                                            |
| Ti |   | 6La : Ti : 2Si      | La5Si3 + La + Ti                                               |
| Mn |   | 6La : Mn : 2Si      | La5Si3 + YSi3 + Y + Si + YSi2                                    |
| Fe |   | 6La : Fe : 2Si      | Y5Si3 + Y + Fe + Y                                                |
| Co |   | 6La : Co : 2Si      | Y5Si3 + Y3Co                                                     |
| Ni |   | 6La : Ni : 2Si      | Y5Si3 + Y3Ni + Si + Y                                           |
| Cu |   | 6La : 2Cu : 2Si     | Y5Si3 + YCu + YSi2                                               |
| Cr |   | 5La : 3Si           | La5Si3 + La3Si4                                                   |
|    | Sc | 6La : Sc : 2Si      | La5Si3 + ScSi3 + LaScSi                                          |
|    |   | 6La : Sc : 2Ge      | La5Ge3 + LaScGe + Ge                                            |
| La |   | 6La : Mn : 2Si      | La5Si3 + La + Mn                                               |
| Mn |   | 6La : Mn : 2Si      | La5Si3 + La + Mn                                               |
|    |   | 6La : Mn : 2Si      | La5Si3 + La + Mn + LaFe10.6Si2                                    |
|    |   | 6La : Mn : 2Ge      | La5Si3 + La + Mn + LaFe10.6Si2                                    |
|    |   | 6La : Mn : 2Sn      | La5Si3 + La + Mn + LaFe10.6Si2                                    |
| Fe |   | 6La : Fe : 2Si      | La5Si3 + La + Mn                                               |
|    |   | 6La : Fe : 2Ge      | La5Si3 + La + Mn                                               |
|    |   | 6La : Fe : 2Sn      | La5Si3 + La + Mn                                               |
| Co |   | 6La : Co : 2Si      | La5Co3 + La3Co + La3Co + La3Co                                        |
| Ni |   | 6La : Ni : 2Si      | La5Ni0.26Si2 + La3Ni                                           |
|    |   | 6La : Ni : 2Ge      | Ge + La3Ni + La5Ge                                           |
|    |   | 6La : Ni : 2Sn      | Ge + La3Ni + La5Ge                                           |
| Cu |   | 6La : 2Cu : 2Si     | La5Si3 + LaCu4                                                  |
|    |   | 6La : 2Cu : 2Ge     | Ge + La5Ge + La(CuGe)                                      |
| Element | Composition | Reaction |
|---------|-------------|----------|
| Zr      | 6La : 2Cu : 2Sn | La₅Sn₃ + LaCu + Cu₆Sn₅ |
|         | 6La : Zr : 2Si | La₅Si₃ + Zr₅Si₃ |
|         | Zr : Si       | ZrSi + Zr₅Si₃ |
| Nb      | 6La : Nb : 2Si | La₅Si₃ + Nb₅Si₃ |
|         | Nb : Si       | Nb₅Si₃ + NbSi₂ |
| Mo      | 6La : Mo : 2Si | La₅Si₃ + Si |
|         | Mo : 2Si      | Mo₅Si₂ + Mo + Si |
| Ru      | 6La : Ru : 2Si | Ru + La₅Si₃ + Si |
|         | Ru : Si       | Ru₅Si + Ru₅Si₃ + Ru₅Si₃ |
|         | 6La : Ru : 2Ge | Ru + LaGe + La₃Ge |
| Ru      | 6La : Ru : 2Sn | La₅Sn₃ + Sn + La + LaRuSn₃ + La₃Ru₄Sn₁₃ |
| Rh      | 6La : Rh : 2Si | La₅Si₃ + La₇Rh₃ |
|         | 6La : Rh : 2Ge | La₅Ge + La₇Rh + Ge |
|         | 6La : Rh : 2Sn | La₅Sn₃ + Sn + La₇Rh₃ + La₁₆Rh₆Sn₃ |
| Pd      | 6La : Pd : 2Si | Si + La + La₅Si₂ + La₇Pd₃ |
|         | 2Pd : Si      | Pd₅Si |
|         | 6La : Pd : 2Ge | La₅Ge₃ + La₇Pd₃ |
|         | 6La : Pd : 2Sn | La₅Sn₃ + La₇Pd₃ + La₅Sn₄ |
| Ag      | 6La : 2Ag : 2Si | LaAg + La₅Si₂ + Si + La |
|         | 6La : 2Ag : 2Ge | La₄Ge₃ + LaAg + LaGe + Ge |
|         | 6La : 2Ag : 2Sn | La₅Sn₃ + LaAg |
| Hf      | 6La : Hf : 2Si | La₅Si₃ + Hf₃Si₃ |
|         | Hf : Si       | Hf₅Si + Hf₃Si₄ + Hf₃Si₂ |
| Ta      | 6La : Ta : 2Si | La₅Si₃ + Ta₃Si₃ |
|         | Ta : Si       | Ta₅Si₃ + Ta₅Si₂ + Ta₂Si |
| W       | 6La : W : 2Si | La₅Si₃ |
|         | W : 2Si       | WS₁₃ + W₅Si₃ + Si |
| Re      | 6La : Re : 2Si | La₅Si₃ + La + Re |
|         | 4Re : 7Si     | Re₅Si₂ + ReSi + Si + Re |
|         | 6La : Re : 2Ge | La₅Ge + La₅Ge₃ + ReGe₂ |
|         | 6La : Re : 2Sn | La₅Sn₃ |
| Ir      | 6La : Ir : 2Si | La₅Si₃ + La + Si + Ir₂Si |
|         | 6La : Ir : 2Ge | La₅Ge₃ + La + Ge + La₅Ir₂ + La₃Ir₇ + La₅Ir₂ |
|         | 6La : Ir : 2Sn | IrSn₂ + La₅Sn₃ + La₅Sn + Sn |
| Pt      | 6La : Pt : 2Si | La₅Si₃ + La₇Pt₃ |
|         | 6La : Pt : 2Ge | La₅Ge₃ + La + Ge + Pt₃Ge |
|         | 6La : Pt : 2Sn | La₅Sn₃ + La₇Pt₃ + La₁₁Sn₁₀ |
| Au      | 6La : 2Au : 2Si | La₅Si₂ + La₅Si₂ + Au₅La₁₄ + Si |
|         | 6La : 2Au : 2Ge | Ge + La₅Ge₄ + LaAuGe + AuLa₂ |
|         | 6La : 2Au : 2Sn | La₅Sn + Sn + La₅Sn₃ + AuSn₂ |
| TM   | Tt     | Precursor          | Max. Temp. (°C) | Dwell Time (hrs) | Phases in Product                                      |
|------|--------|--------------------|-----------------|------------------|-------------------------------------------------------|
| Sc   | Si     | La₆Sc₀.₇Si₂        | 1000            | 72               | La₆Sc₀.₆₇Si₂S₁₄ + S₈ + LaScS₃                          |
|      | Ge     | La₆ScGe₂ + KI     | 1000            | 72               | La₆Sc₀.₆₇Ge₂S₁₄ + S₈ + LaS₂₃ + LaScS₃                |
| Ti   | Si     | La₆Ti₀.₇Si₂        | 1050            | 72               | La₆Ti₀.₆₇Si₂S₁₄                                        |
| V    | Si     | La₅Si₃ + V₅Si₃    | 1000            | 72               | La₅V₀.₇₇Si₂S₁₄ + LaS₂ + S₈                           |
| Cr   | Si     | La₆Cr₀.₇Si₂        | 1050            | 72               | La₆Cr₀.₆₇Si₂S₁₄ + S₈                                 |
| Zr   | Si     | La₅Si₃ + ZrSi     | 1000            | 72               | La₅Zr₀.₅Si₂S₁₄ + La₂Si₅ + ZrS₂ + La₂ZrS₅              |
| Nb   | Si     | La₅Si₃ + NbSi     | 1000            | 72               | La₂Si₅ + La₅Nb₇S₂₂ + S₈                               |
| Mo   | Si     | La₅Si₃ + MoSi₂    | 1000            | 72               | La₂Si₅ + S₈ + MoS₂                                    |
| Hf   | Si     | La₅Si₃ + 0.5HfSi  | 1000            | 72               | La₆Hf₀.₅Si₂S₁₄ + La₂Si₅                               |
| Ta   | Si     | La₅Si₃ + TaSi     | 1000            | 72               | La₂Si₅ + TaSi2                                        |
| W    | Si     | La₅Si₃ + WSi₂     | 1000            | 72               | La₂Si₅ + WSi₂                                        |
| Mn   | Si     | La₅Si₃ + MnSi     | 1000            | 72               | La₆MnSi₂S₁₄ + La₂Si₅(min)                            |
| Ge   | La₅MnGe₂ | 1050            | 72               | La₄MnGe₂S₁₄ + La₂S₁ + MnS                            |
| Sn   | La₆MnSn₂  | 1050            | 72               | La₆MnSn₂S₁₄                                           |
| Fe   | Si     | La₆FeSi₂          | 1050            | 72               | La₆FeSi₂S₁₄ + La₂S                                    |
| Ge   | La₆FeGe₂ | 1000            | 72               | La₆FeGe₂S₁₄ + GeS₂ + S₈                              |
| Sn   | La₆FeSn₂  | 1000            | 72               | La₆FeSn₂S₁₄ + La₂S₃                                    |
| Co   | Si     | La₆CoSi₂          | 1050            | 0                | La₆CoSi₂S₁₄ + LaS₂                                    |
| Ge   | La₆CoGe₂ | 1000            | 72               | La₆CoGe₂S₁₄ + S₈                                     |
| Sn   | La₆CoSn₂  | 1000            | 72               | La₆CoSn₂S₁₄ + La₄CoS₇ + SnS                           |
| Ni   | Si     | La₆NiSi₂          | 1050            | 72               | La₆NiSi₂S₁₄ + La₄NiS₇                                  |
| Ge   | La₆NiGe₂ | 1000            | 72               | La₆NiGe₂S₁₄                                            |
| Sn   | La₆NiSn₂  | 1000            | 72               | La₆NiSn₂S₁₄ + La₂S₃                                    |
| Ru   | Si     | La₆RuSi₂          | 1050            | 72               | La₆RuSi₂S₁₄ + S₈                                     |
| Ge   | La₆RuGe₂ | 1050            | 72               | La₆RuGe₂S₁₄ + La₂S₃ + S₈                              |
| Sn   | La₆RuSn₂  | 1100            | 72               | La₆Sn₄ + La₂Sn₅ + RuS₂                                  |
| Rh   | Si     | La₆Rh₀.₇Si₂       | 1000            | 72               | La₆Rh₀.₆₇Si₂S₁₄ + S₈                                  |
| Ge   | La₆RhGe₂ | 1000            | 72               | La₆RhGe₂S₁₄ + LaS + GeS₂                              |
| Sn   | La₆RhSn₂  | 1050            | 72               | La₆RhSn₂S₁₄ + La₄Rh₈Sn₃                                 |
| Pd   | Si     | La₆PdSi₂          | 1050            | 72               | La₆PdSi₂S₁₄ + La₄PdS₇ + Pd₃S₂                         |
| Ge   | La₆PdGe₂ | 1050            | 72               | La₆PdGe₂S₁₄ + LaPd₃S₄ + La₂S₃                         |
| Sn   | La₆PdSn₂  | 900             | 72               | La₄Pd₄S₄ + La₂Sn₅ + La₂S + Sn                          |
| Re   | Si     | La₆ReSi₂          | 1000            | 72               | La₂Si₅ + ReS₂ + S₈                                    |
| Ge   | La₆ReGe₂ | 1000            | 72               | La₂GeS₅ + La₄Ge₃S₁₂ + La₂S₃ + Ge                      |
| Sn   | La₆ReSn₂  | 1050            | 72               | La₂S₃ + ReS₂ + Sn + S₈                                |
| Ir   | Si     | La₆Ir₀.₇Si₂       | 1000            | 72               | La₆Ir₀.₆₇Si₂S₁₄ + La₂S + S₈                           |
| Ge   | La₆IrGe₂ | 1000            | 72               | La₆Ir₃Ge₂S₁₄ + La₂S₃ + Ge                             |
| Sn   | La₆IrSn₂  | 900             | 72               | La₂Sn₅ + La₂S₃ + IrS + SnS                             |
| Pt   | Si     | La₆PtSi₂          | 1000            | 72               | La₆Pt₀.₅Si₂S₁₄ + PtS + La₂S₃                         |

**Table S3A.** Synthesis conditions for phase formation of La₆(TM)₆(Tt)₆S₁₄ (TM = Group 3 – 11, Tt = Si, Ge and Sn; x = 2 – 0.5). Quaternary phases are highlighted in bold for cases where they are the major products.
|   |   |   |   |   |
|---|---|---|---|---|
| Ge | La₆PtGe₂ | 1000 | 72 | La₆Pt₆Ge₂S₁₄ + PtGeS + La₂S₃ |
| Sn | La₆PtSn₂ | 1050 | 72 | PtSnS + La₂S₃ + La₂SnS₅ + LaSn₃ |
|   |   |   |   |   |
| Cu | Si | La₆Cu₂Si₂ | 1000 | 72 | La₆Cu₂Si₂S₁₄ |
|   | Ge | La₆Cu₂Ge₂ | 1000 | 72 | La₆Cu₂Ge₂S₁₄ + S₈ |
|   | Sn | La₆Cu₂Sn₂ | 1000 | 72 | La₆Cu₂Sn₂S₁₄ + CuSnS₃.₆ |
|   |   |   |   |   |
| Ag | Si | La₆Ag₂Si₂ | 1000 | 72 | La₆Ag₂Si₂S₁₄ |
|   | Ge | La₆Ag₂Ge₂ | 1000 | 72 | La₆Ag₂Ge₂S₁₄ + S₈ |
|   | Sn | La₆Ag₂Sn₂ | 1000 | 72 | La₆Ag₂Sn₂S₁₄ + SnS |
|   |   |   |   |   |
| Au | Si | La₆Au₂Si₂ | 1000 | 72 | La₆Au₂Si₂S₁₄ + LaS₂ |
|   | Ge | La₆Au₂Ge₂ | 1000 | 72 | La₆Au₂Ge₂S₁₄ |
|   | Sn | La₆Au₂Sn₂ | 1000 | 72 | La₆Au₂Sn₂S₁₄ + SnS |
Table S3B. Selected results for the attempts to form Sc₆(TM)₆Si₂S₁₄ (unsuccessful) and Y₆(TM)₆Si₂S₁₄ (successful) for TM = Ti, Cr – Ni, Rh, Ir, Cu, Ag, and Au. Quaternary phases are highlighted in bold for cases where they are the major products.

| RE | TM  | Precursor     | Max. Temp. (°C) | Dwell Time (hrs) | Phases in Product                      |
|----|-----|---------------|-----------------|------------------|----------------------------------------|
| Sc | Ti  | Sc₆TiSi₂      | 900             | 72               | Sc₂S₃                                  |
|    |     |               | 1050            | 72               | ScS + Sc₂S₃ + TiS₁₅ + S₈               |
|    | Mn  | Sc₆MnSi₂      | 750             | 72               | Sc₂S₃ + MnS + MnSc₂S₄                  |
|    |     |               | 1000            | 72               | MnS + MnSc₂S₄ + Mn₂SiS₄ + SiS₂ + Sc₂S₃ |
|    | Fe  | Sc₆FeSi₂      | 750             | 72               | Sc₂S₃ + FeC₂S₄ + Sc₅Si₃                |
|    |     |               | 1000            | 72               | FeScS₄ + Sc₂S₃                         |
|    | Co  | Sc₆CoSi₂      | 750             | 72               | Sc₂S₃ + CoS₂                          |
|    |     |               | 1000            | 72               | Sc₂S₃ + CoS₂ + SiS₂                    |
|    | Ni  | Sc₆NiSi₂      | 750             | 72               | Sc₂S₃ + S₈ + NiSc + NiS₂               |
|    |     |               | 1000            | 72               | Sc₂S₃ + Rh₂S₃ + RhS₂                   |
|    | Rh  | Sc₆RhSi₂      | 900             | 72               | Sc₂S₃ + Rh₂S₃ + ScS + S₈               |
|    |     |               | 1050            | 96               | Sc₂S₃ + Sc₂S₃ + Rh₂S₃ + RhS₂           |
|    | Ir  | Sc₆IrSi₂      | 900             | 72               | Sc₂S₃ + IrS₂ + SiS₂                    |
|    |     |               | 1050            | 96               | Sc₂S₃ + IrS₂ + Sc₂S₃ + SiS₂            |
|    | Cu  | Sc₆Cu₂Si₂     | 900             | 72               | ScS + Sc₂S₃ + Si + Sc + Cu₅Si₃S₈      |
|    |     |               | 1050            | 96               | ScS + CuSc₂S₂ + Sc + S₈ + Sc₂S₃ + SiO₂ |
|    | Ag  | Sc₆Ag₂Si₂     | 900             | 72               | ScS + Sc₂S₃ + Si                       |
|    |     |               | 1050            | 96               | Sc₂S₃ + SiO₂ + SiS₂                    |
|    | Au  | Sc₆Au₂Si₂     | 900             | 72               | Au + ScS + Sc₂S₃ + S₈                  |
|    |     |               | 1050            | 96               | Au + ScS + Sc₂S₃                       |
| Y  | Cr  | Y₆CrSi₂       | 1050            | 72               | Y₆Cr₀.₆₇Si₂S₁₄ + Y₂S₃                  |
|    | Mn  | Y₆MnSi₂       | 1050            | 72               | Y₆MnSi₂S₁₄ + Y₃S₃                      |
|    | Fe  | Y₆FeSi₂       | 1050            | 72               | Y₆FeSi₂S₁₄ + Y₂S₃                      |
|    | Co  | Y₆CoSi₂       | 1050            | 72               | Y₆CoSi₂S₁₄ + Y₂S₃                      |
|    | Ni  | Y₆NiSi₂       | 1050            | 72               | Y₆NiSi₂S₁₄ + Y₂S₃                      |
|    | Cu  | Y₆Cu₂Si₂      | 1050            | 72               | Y₆Cu₂Si₂S₁₄                           |
**Table S3C.** Synthesis conditions for the attempts to form tellurides La₆(TM)ₓSi₂Te₁₄.

| TM  | Precursor   | Max. Temp. (°C) | Dwell Time (hrs) | Phases in Product                                                                 |
|-----|-------------|-----------------|------------------|-----------------------------------------------------------------------------------|
| Co  | La₆CoSi₂    | 750             | 72               | LaTe₂ + La₂Te₅ + LaTe₃ + CoTe₂                                                    |
|     |             | 900             | 72               | (La₂Te₃)₀.₉ + LaTe₂ + Si + Co                                                     |
|     |             | 1050            | 72               | LaTe₂ + LaTe₃ + CoSi₂                                                            |
| Ni  | La₆NiSi₂    | 750             | 72               | LaTe₂ + NiTe₂ + Te                                                               |
|     |             | 900             | 72               | LaTe₂ + NiTe₂ + Si                                                                |
|     |             | 1050            | 72               | LaTe₂ + LaTe₃ + LaNi₁Si₆ + La₆Ni₂Si₃ + LaTe                                    |
| Cu  | La₆Cu₂Si₂   | 750             | 72               | LaTe₂ + Si₂Te₃ + Cu₂Si₃Te₃ + Cu + LaTe₃ + Cu₃Si                                  |
|     |             | 900             | 72               | LaTe₂ + Cu₃Te₃ + Cu₃Si                                                           |
|     |             | 1050            | 72               | LaTe₂ + Cu₇Te₄                                                                   |

**Table S4.** EDS composition summary for La₆(TM)ₓ(Tt)₂S₁₄ (TM = Group 3 – 11, Tt = Si, Ge and Sn). All compositions are normalized to 6 La atoms. Errors are given in parenthesis.

| RE  | TM  | Tt | Average EDS Composition                                      | TM content from SCXRD |
|-----|-----|----|-------------------------------------------------------------|-----------------------|
| La  | Sc  | Si | La₆Sc₀.₆₅(1)Si₀.₉₅(6)S₁₃.₅₈(10)                              | 0.67                  |
| La  | Ti  | Si | La₆Ti₀.₆₄(5)Si₁₂.₀₁(7)S₁₃.₁₈(7)                              | 0.67                  |
| La  | V   | Si | La₆V₀.₆₉(4)Si₁₁.₉₆(2)S₁₃.₁₃(10)                            | 0.77                  |
| La  | Cr  | Si | La₆Cr₀.₆₄(3)Si₁₁.₉₄(2)S₁₃.₁₆(10)                            | 0.67                  |
| La  | Mn  | Sn | La₆Mn₀.₉₁(5)Sn₂₁.₁₃(1)S₁₃.₀₉(1₃)                           | 1.0                   |
| La  | Co  | Si | La₆Co₀.₉₂(2)Si₂₀.₅₂(2)S₁₃.₇₁(1₇)                           | 1.0                   |
| La  | Ni  | Si | La₆Ni₀.₉₃(3)Si₁₁.₉₃(6)S₁₃.₁₇(2₄)                           | 1.0                   |
| La  | Zr  | Si | La₆Zr₀.₄₈(2)Si₁₁.₉₇(5)S₁₁.₉₅(4)                            | 0.5                   |
| La  | Ru  | Si | La₆Ru₀.₈₆(6)Si₁₂.₀₁(7)S₁₃.₁₅(1₁)                           | N/A                   |
| La  | Rh  | Si | La₆Rh₀.₆₇(2)Si₁₁.₉₅(3)S₁₁.₀₄(1₂)                            | 0.67                  |
| La  | Rh  | Ge | La₆Rh₀.₆₇(2)Ge₁₇.₇₈(2)S₁₃.₁₅(9)                             | 0.67                  |
| La  | Rh  | Sn | La₆Rh₀.₅₄(2)Sn₂₁.₁₇(7)S₁₁.₈₃(1₃)                           | N/A                   |
| La  | Pd  | Si | La₆Pd₀.₉₉(4)Si₁₁.₉₈(4)S₁₁.₁₂(1₂)                           | 1.0                   |
| La  | Hf  | Si | La₆Hf₀.₄₇(3)Si₂₀.₀₈(2)S₁₁.₀₄(1₆)                           | 0.5                   |
| La  | Ir  | Si | La₆Ir₀.₆₉(2)Si₁₁.₉₄(3)S₁₁.₁₈(8)                             | 0.67                  |
| La  | Ir  | Ge | La₆Ir₀.₇₆(₈)Ge₁₈.₈₀(₅)S₁₃.₃₀(₂₃)                           | N/A                   |
| La  | Pt  | Si | La₆Pt₀.₅₈₁Si₁₀.₉₆(₂)S₁₁.₄₃(₄)                              | 0.5                   |
| La  | Cu  | Si | La₆Cu₁₈.₁₅(₅)Si₁₀.₀₄(₄)S₁₁.₇₀(₁₆)                          | 2.₀                   |
| La  | Cu  | Ge | La₆Cu₁₈.₆₃(₅)Ge₂₂.₃₉(₃₂)S₁₄.₁₇(₇₁)                         | 2.₀                   |
| La  | Au  | Si | La₆Au₁₉.₈₂(₂)Si₂₂.₄₄(₅)S₁₄.₁₆(₅)                           | 2.₀                   |
| La  | Au  | Ge | La₆Au₁₈.₈₈(₂)Ge₁₇.₇₄(₂)S₁₁.₇₈(₆)                           | 2.₀                   |
| La  | Au  | Sn | La₆Au₁₇.₇₆(₆)Sn₂₀.₄₄(₄)S₁₁.₃₄(₁₃)                          | 2.₀                   |
Table S5. Experimental and DFT-calculated $^{29}$Si chemical shifts.

| Sample          | Experimental | Calculated |
|-----------------|--------------|------------|
|                 | $\delta_{\text{iso}}(^{29}\text{Si}) / \text{ppm}$ | $\delta_{\text{iso}}(^{29}\text{Si}) / \text{ppm}$ | $\sigma_{\text{iso}}(^{29}\text{Si}) / \text{ppm}$ |
| $\text{La}_6\text{Cu}_2\text{Si}_2\text{S}_7$ | 3.0          | 2.6        | 313.3       |
| $\text{La}_6\text{Ag}_2\text{Si}_2\text{S}_7$ | 4.9          | 9.8        | 306.1       |
| $\text{La}_6\text{Au}_2\text{Si}_2\text{S}_7$ | 7.7          | 12.5       | 303.5       |
| $\text{La}_6\text{RhSi}_2\text{S}_14$         | 0.4          |            |             |
| $\text{La}_6\text{Sc}_{0.66}\text{Si}_2\text{S}_14$ | 0.6          |            |             |

*The magnetic shielding constants for these materials could not be calculated due to the positional disorder in the crystal structure.*

Table S6. Experimental and DFT-calculated $^{45}$Sc NMR parameters.

| Sample          | Experimental | Calculated |
|-----------------|--------------|------------|
|                 | $\delta_{\text{iso}}(^{45}\text{Sc}) / \text{ppm}$ | $C_Q / \text{MHz}$ | $P_Q / \text{MHz}$ | $|C_Q| / \text{MHz}$ | $\eta$ | $|P_Q| / \text{MHz}$ |
| $\text{La}_6\text{Sc}_{0.67}\text{Si}_2\text{S}_14$ | 472.2        |            | 3.0 | 2.0(2) | 0.17(5) | 2.0(2) |
| $\text{La}_6\text{Sc}_{0.67}\text{Ge}_2\text{S}_14$ | 474.5        |            | 2.8 |       |         |         |
| $\text{LaScS}_3$ | 377.2        | 8.4        | 0.28 | 8.5 | 6.52 | 0.28 | 6.60 |

Table S7. Second harmonic generation (SHG) signal for select compounds.

| Particle size (µm) | 38.5-54 | 54-88 | 88-105 | 105-150 | 150-200 |
|-------------------|---------|-------|--------|---------|---------|
| Phase             | SHG Intensity (mV) |
| $\text{AgGaS}_2$  | 15.0    | 26.0  | 35.0   | 80.0    | 113.0   |
| $\text{La}_6\text{CoSi}_2\text{S}_14$ | 0.8  | 0.8   | 0.8    | 0.8     | 0.8     |
| $\text{La}_6\text{Rh}_{0.67}\text{Si}_2\text{S}_14$ | 14.0 | 12.8  | 13.6   | -       | 13.0    |
| $\text{La}_6\text{Ir}_{0.67}\text{Si}_2\text{S}_14$ | 13.5 | 13.6  | 13.2   | 12.2    | 12.6    |
| $\text{La}_6\text{Cu}_2\text{Si}_2\text{S}_14$ | 1.5  | 1.3   | 0.8    | 0.75    | 0.8     |
| $\text{La}_6\text{Cu}_2\text{Ge}_2\text{S}_14$ | 20   | 24    | 37     | -       | -       |
| $\text{La}_6\text{Ag}_2\text{Si}_2\text{S}_14$ | 0.4  | 0.4   | 0.3    | -       | -       |
| $\text{La}_6\text{Au}_2\text{Si}_2\text{S}_14$ | 7.7  | 6.8   | -      | 1.5     | 2.4     |
Table S8A. A summary of structural data for La₆(TM)₆Si₂S₁₄. O₉ = octahedron

| Metal | Ox. State/Spin state | R_{ion}a (Å) | R_{calc}b | V_{Oh-full}(Å³) | V_{Oh-empty}(Å³) | V_{full}/V_{empty} | d_{M-S} for filled O₉ | a/c | V (Å³) |
|-------|---------------------|--------------|-----------|-----------------|-----------------|-------------------|----------------------|-----|--------|
| Sc    | 3                   | 0.75         | 0.77      | 23.53           | 28.94           | 0.81              | 2.605 | 2.608 | 0.999 | 1.798 | 531.9 |
| Ti    | 3                   | 0.67         | 0.73      | 22.49           | 29.91           | 0.75              | 2.562 | 2.569 | 0.997 | 1.784 | 529.9 |
| V     | 2                   | 0.79         | 0.71      | 22.12           | 27.27           | 0.81              | 2.551 | 2.552 | 1.000 | 1.795 | 526.6 |
|       | 3                   | 0.64         |           |                 |                 |                   |        |       |       |       |       |
| Cr    | 3                   | 0.62         | 0.70      | 21.87           | 28.95           | 0.76              | 2.537 | 2.546 | 0.996 | 1.789 | 527.2 |
| Mn    | 2/hs                | 0.83         | 0.81      | 24.77           | -               | -                 | 2.640 | 2.660 | 0.992 | 1.804 | 529.9 |
|       | 2/ls                | 0.67         |           |                 |                 |                   |        |       |       |       |       |
| Fe    | 2/hs                | 0.61         | 0.78      | 23.87           | -               | -                 | 2.610 | 2.620 | 0.996 | 1.795 | 527.2 |
|       | 2/ls                | 0.78         |           |                 |                 |                   |        |       |       |       |       |
| Co    | 2/hs                | 0.65         | 0.78      | 23.91           | -               | -                 | 2.610 | 2.630 | 0.992 | 1.793 | 523.5 |
|       | 2/ls                | 0.75         |           |                 |                 |                   |        |       |       |       |       |
| Ni    | 2                   | 0.69         | 0.75      | 23.14           | -               | -                 | 2.590 | 2.590 | 1.000 | 1.793 | 523.5 |
| Zr    | 4                   | 0.72         | 0.81      | 24.62           | 28.53           | 0.86              | 2.636 | 2.659 | 0.991 | 1.793 | 530.6 |
| Rh    | 3                   | 0.67         | 0.70      | 21.83           | 28.93           | 0.76              | 2.538 | 2.541 | 0.999 | 1.783 | 523.2 |
| Hf    | 4                   | 0.71         | 0.72      | 22.3            | 27.30           | 0.82              | 2.538 | 2.579 | 0.984 | 1.791 | 531.2 |
| Pt    | 4                   | 0.63         | 0.76      | 23.35           | 30.60           | 0.76              | 2.594 | 2.604 | 0.996 | 1.776 | 525.5 |

a Ionic radii taken from Shannon,10 min and max observed values are highlighted in bold.

b Radii are calculated by subtracting ionic radius of S²⁻ (Shannon¹⁰) from the average value of TM-S bond.
Table S8B. Ionic radii for select transition metals in octahedral environment. Values highlighted in green lie between 0.63 and 0.83 Å, a proposed range to form target quaternary sulfides La6(TM)xSi2S14.

| Metal | Ox. State | R_{ion}, Å<sup>a</sup> |
|-------|-----------|------------------------|
| Pd    | 2 square planar 0.64 | |
|       | 2 O<sub>h</sub> 0.86 | |
| Ru    | 3          0.68  | |
|       | 4          0.62  | |
| Ir    | 3          0.68  | |
| Nb    | 3          0.72  | |
|       | 4          0.68  | |
|       | 5          0.64  | |
| Mo    | 3          0.69  | |
|       | 4          0.65  | |
|       | 5          0.61  | |
|       | 6          0.59  | |
| Ta    | 3          0.72  | |
|       | 4          0.68  | |
|       | 5          0.64  | |
| W     | 4          0.66  | |
|       | 5          0.62  | |
|       | 6          0.60  | |
| Re    | 4          0.63  | |
|       | 5          0.58  | |
|       | 6          0.55  | |
|       | 7          0.53  | |
| Os    | 4          0.63  | |
|       | 5          0.58  | |
|       | 6          0.55  | |
|       | 7          0.53  | |

<sup>a</sup> Ionic radii taken from Shannon<sup>10</sup>.
**Figure S1.** Correlation of hexagonal unit cell parameters ($a$ and $c$), unit cell volume and ionic radii$^{10}$ for metals for La$_6$($TM$)$_x$Si$_2$S$_{14}$ ($x = 2 – 0.5$).

**Figure S2.** *Ex-situ* PXRD patterns showing phase formation in the La$_6$CoSi$_2$S$_{14}$ system. Each pattern represents a different reaction with corresponding maximum reaction temperature. The pre-arc-melted “La$_6$CoSi$_2$” and S reactants form La$_6$CoSi$_2$S$_{14}$ (*P6$_3$*) at ~750 ºC.
Figure S3A. PXRD patterns for La₆(TM)ₓ(Tt)₂S₁₄ (x = 2 – 0.5) samples: (top) TM = Sc - Cr, Tt = Si and Ge; (bottom) TM = Zr – W, Tt = Si. Patterns in black and grey are for reference. Pattern for La₂SiS₅ is taken from ICSD 240952. Experimental conditions are given in Table S3A.
Figure S3B. PXRD patterns for La₆(TM)ₓ(Tt)₂S₁₄ (x = 2 – 0.5) samples: (top) TM = Re, Tt = Si; (bottom) TM = Mn and Fe, Tt = Si, Ge and Sn. Patterns in black and grey are for reference. Pattern for La₂SiS₅ is taken from ICSD 240952. Experimental conditions are given in Table S3A.
Figure S3C. PXRD patterns for La$_6(TM)_x(Tt)_2S_{14}$ ($x = 2 - 0.5$) samples: (top) $TM = \text{Co and Ni}$, $Tt = \text{Si, Ge, and Sn}$; (bottom) $TM = \text{Ru and Rh}$, $Tt = \text{Si, Ge and Sn}$. Patterns in black and grey are for reference. Experimental conditions are given in Table S3A.
Figure S3D. PXRD patterns for La₆(TM)ₓ(Tt)₂S₁₄ (x = 2 – 0.5) samples: (top) TM = Pd and Ir, Tt = Si, Ge and Sn; (bottom) TM = Pt and Cu, Tt = Si, Ge and Sn. Patterns in black and grey are for reference. Experimental conditions are given in Table S3A.
Figure S3E. PXRD patterns for $(RE)_6(TM)_x(Tt)_2S_{14}$ $(x = 2 - 0.5)$ samples: (top) $RE = La$, $TM = Ag$ and Au, $Tt = Si$, Ge, and Sn; (bottom) $RE = Y$, $TM = Cr$ - Cu. Patterns in black and grey are for reference. Pattern for $Y_6Cr_xSi_2S_{14}$ is taken from ICSD 626629. Experimental conditions are given in Table S3A.
Figure S3F. PXRD patterns for La₆(TM)₀.₆₇Si₂S₁₄ prepared from elements and binary sulfides and compared to the PXRD pattern for synthesis using a metal silicide precursor. (Top) TM = Ti; (bottom) TM = Rh. Patterns in black are calculated from single crystal data. Reaction conditions such as sample scale, ampoule size, ramping and annealing time, and temperature are identical for all shown samples.
**Figure S4.** Optical images and band gap values (eV) for La₆(TM)ₓ(Tt)₂S₁₄ (TM = group 7 - 11; Tt = Si, Ge, and Sn; x = 2 – 0.5) samples. Only cases where single-phase bulk samples could be acquired were measured. For each metal, the first column is data for Si, second for Ge, and third for Sn. NSP = not a single-phase sample; No phase = quaternary phase formation was not observed. Extensive temperature optimization was not performed for Sn-containing samples which require lower synthetic temperatures than Si- and Ge-containing analogues.
Figure S5. Tauc plots for select compositions for La₆(TM)₂S₁₄ (TM = Fe, Co, Ru, Rh, Ir, Pt, Cu, Ag and Au; x = 2 – 0.5) plotted as direct band gap materials.
Figure S6. SEM BSE images of select crystals of La₆(TM)₃S₁₄ (TM = Ni, Cu, Pd and Au; x = 2 – 0.5). The magnifications are 50x, 150x, 150x and 80x, for Ni, Cu, Pd and Au, respectively.
Figure S7. Optical microscope images of select crystals for La₆(TM)ₓ(Tt)₂S₁₄ (TM = Sc, Ti, Ni, Co, Pd and Au; Tt = Si and Ge; x = 2 – 0.5). Each cell on the graph paper is 1×1 mm.
Figure S8. EPR data for La₆(TM)₀.₆₇Si₂S₁₄ (TM = Ti and Cr), showing Ti³⁺ and Cr³⁺ with g values of 2.01246 and 1.99336, respectively. La₆V₀.₇₇Si₂S₁₄ sample did not produce a good-intensity signal down to 6 K.
Figure S9. Top: Magnetic data ($\chi$, $\chi^{-1}$ and $\chi^*T$) for La$_6$V$_{0.77}$Si$_{2}$S$_{14}$; Bottom: isothermal moment versus field at 2 K for La$_6$V$_{0.77}$Si$_{2}$S$_{14}$ and La$_6$Ir$_{0.67}$Si$_{2}$S$_{14}$ (bottom).
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