**$\text{Eu}_3(\text{AsS}_4)_2$ and $\text{A}_x\text{Eu}_{3-y}\text{As}_{5-z}\text{S}_{10}$ (A = Li, Na):
Compounds with Simple and Complex
Thioarsenate Building Blocks**

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Supplementary Information

Physicochemical characterization details
Crystallographic Data

1. **Powder X-ray diffraction** analyses were performed using a computer-controlled INEL CPS120 powder diffractometer with graphite monochromatized Cu K α radiation. Powder patterns were calculated with the PowderCell, v 2.3 software package.

2. **Electron Microscopy:** Quantitative microprobe analyses of the compounds were performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern energy dispersive spectroscopy (EDS) detector. Data were acquired with an accelerating voltage of 20 kV and a 40 s accumulation time.

3. **Magnetization measurement** as a function of applied magnetic field and temperature was done on a MPMS Quantum Design SQUID susceptometer in the temperature range of 2 to 300 K and magnetic field of 0 to ± 55000 Oe. The temperature dependent study was done with the magnetic field of 500 Oe. The sample consisted of about 21 mg of the compound. A diamagnetic correction was applied for three Eu²⁺ ions (66×10^{-6} emu/mol), two As³⁺ ions (12×10^{-6} emu/mol), and eight S²⁻ ions (240×10^{-6} emu/mol). Total diamagnetic correction of 318×10^{-6} emu/mol was applied during the calculation of the total magnetic susceptibility for the compound Eu₃(AsS₄)₂.

4. **Solid-State UV/Vis/Near-IR Spectroscopy:** Optical diffuse reflectance measurements were performed at room temperature using a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. The instrument is equipped with an integrating sphere and controlled by a personal computer. BaSO₄ was used as a 100% reflectance standard. The sample was prepared by grinding the crystals to a powder and spreading it on a compacted surface of the powdered standard material, preloaded into a sample holder. The reflectance versus wavelength data generated was used to estimate the band gap of the material by converting reflectance to absorption data.

5. **Raman spectrum** was recorded on a BIORAD FT-Raman II Spectrometer. It was equipped with a Nd:YAG infrared continuous wave laser ($\lambda = 1064$ nm) and a liquid nitrogen cooled germanium detector. Finely powdered sample in a capillary tube was used for the spectral study after calibrating the spectrometer with KBr.

Fig. 1S: Raman spectrum of Eu₃(AsS₄)₂.

6. The thermal behavior of the compound was investigated by differential thermal analysis using a Shimadzu DTA-50 thermal analyzer. Typically a sample (~20 mg) of ground crystalline material was sealed in a silica ampoule under vacuum. A similar ampoule of equal mass filled with Al_2O_3 was sealed and placed on the reference side of the detector. The sample was heated to the desired temperature at $10^\circ\text{C}/\text{min}$, and after 1-3 min it was cooled at a rate of $-10^\circ\text{C}/\text{min}$ to 50°C . Reproducibility of the results was checked by running multiple heating/ cooling cycles.

Fig. 2S. Differential thermal analysis of $\text{Eu}_3(\text{AsS}_4)_2$. The peaks at 610°C and 550°C are exothermic.

7. Inductively Coupled Plasma-Atomic Emission (Optical Emission)/Mass Spectroscopy [ICP-AES(OES)/MS] analyses: The presence of Li and Na in compounds **IIa** and **IIb** respectively was independently confirmed by ICP-AES using VISTA MPX CCD SIMULTANEOUS ICP-OES instrument. Crystals of each of those two compounds (~1mg) were dissolved separately in 0.5ml of a 3% acid solution of aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$) and diluted to 2ml. 10 standards (1-10ppm) of the ions of interest (Li^+ and Na^+) were prepared by diluting commercial ~1000 ppm ICP-standards of these ions (Na standard from Aldrich and Li standard from GFS chemicals). The calibration was linear with errors of 5-10%. The ICP-AES intensity was the result of three (30 seconds) exposures. For each sample, three readings of the ICP-AES intensity were recorded and averaged. The concentration of Li in **IIa** was found to be 1.8 ppm which corresponds to ~0.7 mol equivalent of Li in the compound **IIa**, whereas the concentration of Na in **IIb** was 1 ppm, which corresponds to ~0.1 mol equivalent of Na in **IIb**. A large discrepancy of Na content in **IIb**, between the single crystal refinement and the elemental analysis can be attributed to the error in our measurement caused by the natural abundance of Na.

8. Single-Crystal X-ray Crystallography for $\text{Eu}_3(\text{AsS}_4)_2$ (1): Single crystal data for $\text{Eu}_3(\text{AsS}_4)_2$ was collected on Bruker SMART CCD diffractometer with $\text{Mo K}\alpha$ radiation. A rectangular rod like crystal with dimensions of $1.2 \times 0.6 \times 0.7 \text{ mm}^3$ was mounted on a goniometer head and a full sphere of data was collected using the SMART software. An empirical absorption correction was applied using SADABS. The structure was solved by direct methods using the SHELXTL package. A rhombohedral unit cell with centrosymmetric space group $R\bar{3}c$ was chosen based on intensity statistics and systematic absences. The structure solution was straight-forward and after anisotropic refinement of all the atoms; the final $R1/wR2$ value was 2.38/5.80.

9. Single-Crystal X-ray Crystallography for $\text{Li}_{0.73}\text{Eu}_3\text{As}_{4.43}\text{S}_{10}$ (IIa): A rectangular rod like crystal with dimensions of $0.20 \times 0.08 \times 0.05 \text{ mm}^3$ was chosen for single crystal x-ray diffraction study. Data collection was done at 100K using a STOE imaging plate diffraction system (IPDS-2) with graphite-monochromatized Mo $K\alpha$ radiation. A numerical absorption correction was applied using X-area suite program. Intensity statistics and systematic absences confirm the centrosymmetric space group $P2_1/c$ with a monoclinic unit cell. Direct methods and full-matrix least squares refinement against F^2 for 169 variables were performed with SHELXTL package. All 3 Eu atoms, 5 As atoms and 10 S atoms were found in the early stage of the structure solution. Occupancy refinement for all 18 atoms in the asymmetric unit lead to a ~52% occupancy for As(5) and ~90% occupancy for As(4) atoms. At this point of refinement thermal parameters for As(4) were found to be quite high [$U(\text{eq}) \sim 30$] and a high residual electron density [$Q(1) = 11.0$] was there at $\sim 0.90 \text{ \AA}$ away from the As(4) site. Q(1) was found to be in an octahedral environment of 6 S atoms with Q(1)-S bond distances range from 2.730 – 3.08 Å. After assigning Q(1) as Li(1) and refining occupancy for As(4), As(5) and Li(1) using SUMP command, the final occupancy for these three atoms were 91%, 52% and 73% respectively, that lead to a charge balanced formula of $\text{Li}_{0.73}\text{Eu}_3\text{As}_{4.43}\text{S}_{10}$. The final anisotropic refinement for all atoms lead to $R1 = 3.66\%$, $wR2 = 9.38$ for $I > 2\sigma(I)$.

10. Single-Crystal X-ray Crystallography for $\text{Na}_{0.66}\text{Eu}_{2.86}\text{As}_{4.54}\text{S}_{10}$ (IIb): Data collection, absorption correction and initial structure solution were similar to that of IIa. All 3 Eu atoms, 5 As atoms and 10 S atoms were found in the early stage of the structure solution. Application of anisotropic refinement on those 18 atoms lead to $R1 = 8.42\%$ and $wR2 = 25.53\%$ with two high residuals; $Q(1) = 14.66$, $0.87 \text{ \AA}$ away from As(4) and $Q(2) = 7.96$, $0.59 \text{ \AA}$ away from As(5). Thermal parameters for As(4) and As(5) were very high; $U(\text{eq}) = 26$ for As(4) and $U(\text{eq}) = 56$ for As(5). A pseudo-merohedral twinning [Twin law: $R = (-1 \ 0 \ 0, 0 \ -1 \ 0, 1 \ 0 \ 1)$] was suspected as that was a common twinning observed with the rathite sulfosalt minerals. Both twin refinement ($\sim 7\%$ twin domain) and occupancy refinement for all atoms were done at this point of the refinement. Occupancy of Eu(1) atom was refined to 87.72%, whereas that for As(4) was 84.05% and 71.07% for As(5) with the residuals Q(1) and Q(2) remained almost intact. Similar to the refinement of IIa, Q(1) was assigned to Na(1) and occupancy was refined to 51.47%. The As(5) site was split into As(5A) and As(5B) to take care of the residual electron density, Q(2). Occupancy of the As(5A) was refined to 50.80% and that for As(5B) was 21.77%. An improved statistics was obtained with a mixed site of Eu(1) with Na(2). The occupancy of Eu(1) was refined to 85.66% and that for Na(2) was 14.34%. A final anisotropic refinement for all atoms lead to $R1 = 4.49\%$ and $wR2 = 9.81\%$ for $I > 2\sigma(I)$.

Acknowledgments: This work made use of the SEM facilities of the Center for Electron Optics at Michigan State University. We greatly acknowledged the SQUID facility of the Department of Physics and astronomy at Michigan State University. FT-Raman spectroscopic study was done at the Analytical Service Laboratory (ASL), Northwestern University.