The heaviest lanthanoid-containing silver thiophosphate: Ag₃Lu[PS₄]₂

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Ag₃Lu[PS₄]₂ was synthesized without any crystalline by-products, as confirmed by powder X-ray diffractometry (PXRD), from lutetium sesquisulfide (Lu₂S₃), diphosphorus pentasulfide (P₂S₅) and silver hemisulfide (Ag₂S) in a stoichiometric ratio of 1:2:3. The title compound, incorporating the heaviest lanthanoid lutetium, crystallizes isotypically with other compounds Ag₃Ln[PS₄]₂ (Ln = Y, Dy, Ho, Er) adopting the Ag₃Y[PS₄]₂-type structure (a = 1687.4(3) pm, b = 919.0(2) pm, c = 931.2(2) pm and β = 123.17(3)° for Z = 4) in the monoclinic space group C2/c (no. 15). Following the lanthanoid contraction very well, the lattice parameters for Ag₃Lu[PS₄]₂: are a = 1696.02(9) pm, b = 920.39(5) pm, c = 932.47(5) pm and β = 123.278(3)° at room temperature (CSD number: 2219575).

Quite common for these types of thiophosphates(V), there are only slightly distorted tetrahedral [PS₄]³⁻ anions (d(P–S) = 202–207 pm) discretely present in the structure. Together with the bicapped trigonal prisms [LuS₆–]¹³⁻, they form individual strands, connected via common edges, propagating along the c-axis, as can be seen in Figure 1 (d(Lu–S) = 271–280 pm + 305 pm). These strands are separated in [100] direction by the (Ag₂)⁺ cations, which reside in tetrahedral sulfur surrounding in between. The (Ag₁)⁺ cations prevent connecting contact of the strands in the (001) plane. Possible Ag⁺-cation diffusion pathways within the structure (d(Ag–S) = 253–272 pm, C.N. = 4 for both) were calculated using bond valence energy landscape calculations based on the single-crystal X-ray diffraction data and hinted at moderate to good silver-ion conductivity (diffusion energy barrier in all three dimensions: $E \approx 0.08$ eV). The optical band gap was determined to be $E_g = 2.47$ eV using UV/Vis diffuse reflectance spectroscopy (DRS).

Ong et al.³ presented a screening for potentially super-conductive materials and performed theoretical calculations on lithium-ion conductivity for several thiophosphates. As a template, they also took silver thiophosphates into their screening including Ag₃Y[PS₄]₂. Their predictions concluded super-ionic Li⁺-cation conductivity for Li₃Y[PS₄]₂, on the basis of the Ag₃Y[PS₄]₂ structure, if silver was substituted with lithium in silico.³ Regarding the structured formula Ag₃RE[PS₄]₂, a similarity to the lithium analogue Li₃La[PS₄]₂⁴ seems obvious, although the two compounds crystallize very differently.

![Figure 1: Extended unit cell of the Ag₃Lu[PS₄]₂ structure with highlighted [PS₄]³⁻ tetrahedra and bicapped trigonal prisms [LuS₆–]¹³⁻ to emphasize the strands along the c-axis (left). The Ag⁺ cations reside in and between these chains, occupying tetrahedral voids (right).](image)


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