

MS15-2-2 Cs₃La[AsS₄]₂: a caesium-containing lanthanum thioarsenate(V)
#MS15-2-2

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Abstract

The structural diversity of alkali-metal thiophosphates with transition or even rare-earth metal participation has been studied intensively in the past years. However, only few investigations on thioarsenates(V) were conducted although they might as well exhibit a large variety of different stoichiometries and structures.

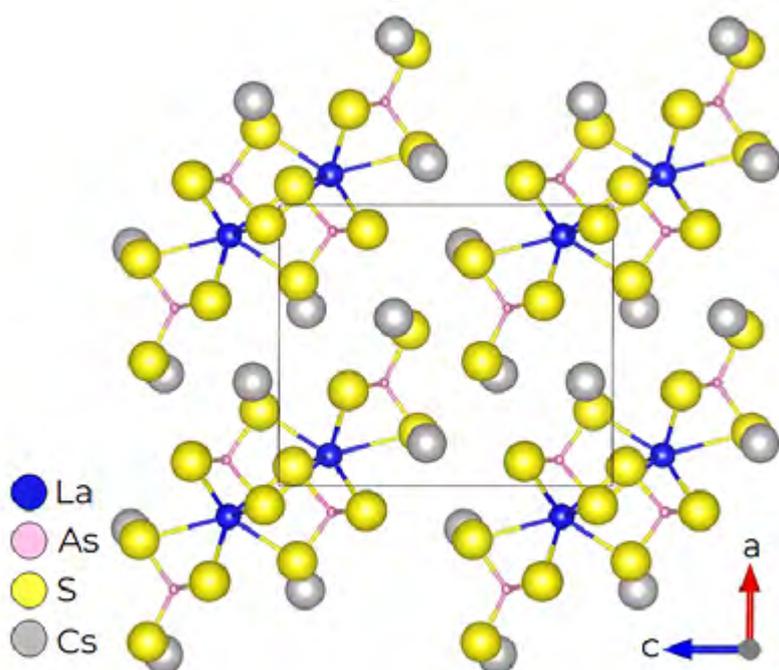
The target compound was synthesized from metallic lanthanum (La), caesium polysulfide (Cs₂S_x, x ≈ 3), arsenic sesquisulfide (As₂S₃) and elemental sulfur in a stoichiometric ratio of 1:1:1:6. Caesium polysulfide was prepared from the elements (two equivalents of caesium with three equivalents of sulfur) via ammonothermal synthesis in an autoclave for two days until the complete conversion of the elemental caesium. The starting materials were filled into a fused glassy silica ampoule in an argon-filled glove box and sealed under dynamic vacuum. The ampoule was placed inside a muffle furnace and heated to 600 °C with 30 °C/h, held for 4 days and then cooled back to room temperature with 3 °C/h. Afterwards, the bulk product was inspected for suitable single crystals since the powder X-ray diffraction pattern revealed more than one phase.

Here we present a caesium-containing lanthanum thioarsenate(V) with the composition Cs₃La[AsS₄]₂ (CSD number: 2156995). This stoichiometric formula seems familiar as K₃RE[AsS₄]₂ compounds with RE = Nd, Sm, Gd and Dy have previously been published by Bensch et al. [1,2]. The novel caesium compound Cs₃La[AsS₄]₂ does not share the same structure type (K₃Gd[AsS₄]₂: a = 1034.84(7) pm, b = 1880.39(14) pm, c = 882.38(6) pm, β = 117.063(7)°, Z = 4; monoclinic, C2/c) [2], however. Cs₃La[AsS₄]₂ crystallizes monoclinically as well, but with the non-centrosymmetric space group P21 and the lattice parameters a = 1014.71(6) pm, b = 702.68(4) pm, c = 1192.35(7) pm, β = 90.232(3)° for Z = 2. There is only one unique La³⁺-cation position within the asymmetric unit surrounded by eight S²⁻ anions (d(La³⁺–S²⁻) = 295.5 – 299.9 + 325.4 + 327.3 pm) building a bicapped trigonal prism. Connected via corners, these [LaS₆₊₂]¹³⁻ prisms form one-dimensional infinite chains propagating along the b-axis, which are separated from each other by three crystallographically independent Cs⁺ cations in 9- to 11-fold sulfur coordination. Moreover, all sulfur atoms participate in the arsenic(V) coordination forming isolated [AsS₄]³⁻ tetrahedra (d(As⁵⁺–S²⁻) = 212.2 – 218.9 pm, (S–As–S) = 97.3 – 123.2°).

References

[1] Y. Wu, C. Näther, W. Bensch, *Inorg. Chem.* **2006**, 45, 8835–8837. [2] Y. Wu, W. Bensch, *Solid State Sci.* **2009**, 11, 1542–1548.

Extended unit cell of Cs₃La[AsS₄]₂, along [010].



(001) projection to emphasize chains along [010]

