Crystal structure of tetrapotassium diarsenidozincate, K₄ZnAs₂

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Abstract
K₄ZnAs₂, trigonal, R₃m (no. 166), a = 5.7529(6) Å, c = 26.866(4) Å, V = 770.2 Å³, Z = 3, Rgt(F) = 0.040, wR_ref(F²) = 0.092, T = 293 K.

Source of material
The first preparation of the title compound was carried out in the same routine as used for the K₄T₃As₂ series (T = Cd, Hg) [1,2] yielding a multi-phase product which was not suitable for further investigation. Pure K₄ZnAs₂ was obtained from an equimolar mixture of KZnAs and K₃As, which were synthesized as described by [3] and [4], respectively. The precursors were placed in an alumina crucible encapsulated in a steel ampule. Afterwards, the ampule was heated to 923 K over a period of 4 h and held at this temperature for 8 h followed by cooling down to room temperature within next 8 hours. Since the starting elements and products are air and moisture sensitive, all manipulations concerning the sample preparations were performed under inert conditions (glove box, N₂; H₂O ≤ 1 ppm, O₂ ≤ 1 ppm).

Experimental details
For single crystal investigation hexagonally-shaped plate-like crystals were encapsulated in glass capillaries. All investigated specimens showed the tendency of forming obverse/reverse twinned agglomerates with different fractions of the constituent domains. For the reported refinement, the ratio of the twin components was established to be equal 0.726(4):0.274 applying twin law 100,010,001. The lattice parameters were refined from 663 reflections in the selected 2θ/113 interval of 25-45° obtained during the single crystal data collection.

Discussion
The title compound adopts Na₄HgP₂ structure type [5] and is also isostructural with K₄CdAs₂ [1], K₄HgAs₂ [2], K₄HgP₂, K₃ZnP₂, K₄CdP₂ [5], K₃BeP₂ and K₃BeAs₂ [6-8]. The partial structure of potassium atoms in K₄ZnAs₂ corresponds to a close sphere packing with the sequence ABCBCABABCAB. As a result, layers of condensed K₈ cubes and K₁₄ polyhedra (polyhedron of type 14E, a combination of cube and hexagonal prism [9]) are built up which alternate along [001]. While the cubes remain empty, the 14E polyhedra are centered by the linear symmetrical anions [As–Zn–As]₄⁻.

The interatomic distances of 2.2931(6) Å within [As–Zn–As]₄⁻ units is significantly shorter than the sum of single bond radii of 2.46 Å (r(As) = 1.21 Å, r(Zn) = 1.25 Å [10]). Similarly, it is also shorter than the closest Zn—As contacts of 2.44 Å and 2.42 Å in KZnAs (Ni₂In type) [3] and ZnAs₂ (ZnP₂ type) [11] with trigonal planar and tetrahedral coordination of Zn (or As) atoms, respectively.

Table 1. Data collection and handling.

| Crystal: | metallic luster hexagonally-shaped prism, size 0.023 × 0.085 × 0.085 mm |
| Wavelength: | Mo Kα radiation (0.71073 Å) |
| μ: | 103.2 cm⁻¹ |
| Diffractometer, scan mode: | Rigaku AFC7, φ/ω |
| 2θ max: | 58° |
| N(hkl)measured, N(hkl)total: | 1925, 1925 |
| Criterion for Iobs, N(hkl)γ: | Iobs > 2σ(Iobs), 1680 |
| N(peak)/refined: | 13 |
| Programs: | SHELXL-97 [12], ATOMS [13] |
References