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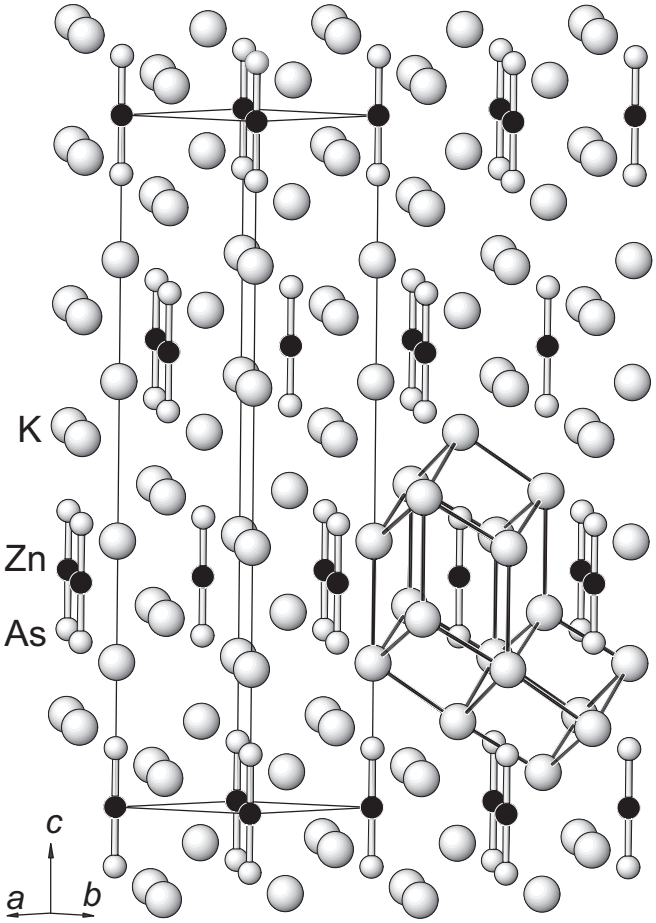
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Crystal structure of tetrapotassium diarsenidozincate, K_4ZnAs_2

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Abstract

K_4ZnAs_2, trigonal, $R\bar{3}m$ (no. 166), a = 5.7529(6) Å, c = 26.866(4) Å, V = 770.2 Å^3, Z = 3, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 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 K_4TAs_2 series (T = Cd, Hg) [1,2] yielding a multi-phase product which was not suitable for further investigation. Pure K_4ZnAs_2 was obtained in the form of black plate-like crystals from the solid state reaction of an equimolar mixture of KZnAs and K_3As, 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, N_2; $H_2O \leq 1$ ppm, $O_2 \leq 1$ 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 $\bar{1}00, 0\bar{1}0, 001$. The lattice parameters were refined from 663 reflections in the selected 2θ interval of 25-45° obtained during the single crystal data collection.

Discussion

The title compound adopts Na_4HgP_2 structure type [5] and is also isostructural with K_4CdAs_2 [1], K_4HgAs_2 [2], K_4HgP_2,K_4ZnP_2, K_4CdP_2 [5], K_4BeP_2, and K_4BeAs_2 [6-8]. The partial structure of potassium atoms in K_4ZnAs_2 corresponds to a close sphere packing with the sequence ABCBCABABCAB. As a result, layers of condensed K_8 cubes and K_{14} polyhedra (polyhedron of type ^{14}E, a combination of cube and hexagonal prism [9]) are built up which alternate along [001]. While the cubes remain empty, the ^{14}E 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 then the closest Zn—As contacts of 2.44 Å and 2.42 Å in KZnAs (Ni_2In type) [3] and $ZnAs_2$ (ZnP_2 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 K_α radiation (0.71073 Å)
μ:	103.2 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, φ/ω
$2\theta_{max}$:	58°
$N(hkl)_{measured}$, $N(hkl)_{total}$:	1925, 1925
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1680
$N(param)_{refined}$:	13
Programs:	SHELXL-97 [12], ATOMS [13]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	6*c*	0	0	0.20880(4)	0.0363(3)	U_{11}	0.0315(6)	$1/2U_{11}$	0	0
K(2)	6*c*	0	0	0.38479(5)	0.0312(3)	U_{11}	0.0674(9)	$1/2U_{11}$	0	0
Zn	3*a*	0	0	0	0.0267(2)	U_{11}	0.0249(4)	$1/2U_{11}$	0	0
As	6*c*	0	0	0.08535(2)	0.0297(2)	U_{11}	0.0265(3)	$1/2U_{11}$	0	0

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