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Crystal structure of tripotassium heptapentelides $K_3[As_xSb_{1-x}]_7$ with $x = 5/14$ and $x = 13/14$

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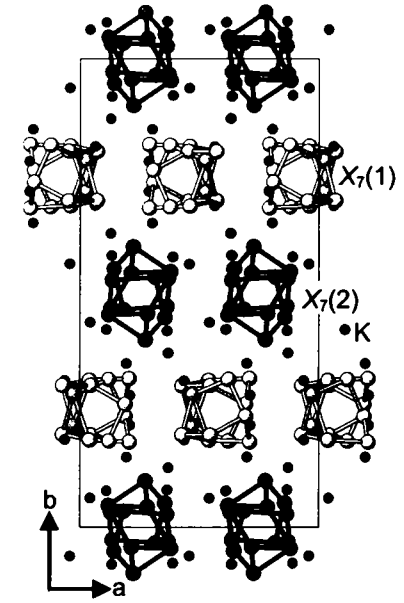

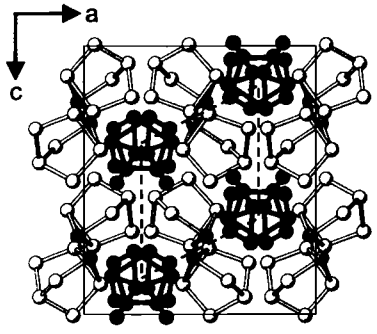

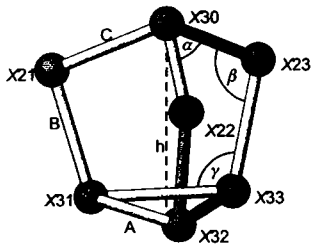

Abstract

$As_{2.5}K_3Sb_{4.5}$ (**1**), orthorhombic, *Pbca* (No. 61), $a = 13.330(2)$ Å, $b = 26.042(3)$ Å, $c = 15.983(3)$ Å, $V = 5548.3$ Å^3, $Z = 16$, $R_{gt}(F) = 0.119$, $wR_{ref}(F^2) = 0.356$, $T = 293$ K.

$As_{6.6}K_3Sb_{0.4}$ (**2**), orthorhombic, *Pbca* (No. 61), $a = 13.102(5)$ Å, $b = 25.737(9)$ Å, $c = 15.199(6)$ Å, $V = 5125.2$ Å^3, $Z = 16$, $R_{gt}(F) = 0.088$, $wR_{ref}(F^2) = 0.282$, $T = 293$ K.

Source of material

The grey mixed crystals (optical band gap 1.0 eV) are formed by reaction of the elements in welded Nb-tubes [1,2]. Step 1: xAs + (1–x)Sb; up to 873 K in 12 h, reaction time 36 h, cooling down to RT in 12 h. Step 2: K: (As,Sb) = 3:7; up to 953 K in 12 h, reaction time 48 h, cooling down to RT in 36 h. The compounds are very sensitive to hydrolysis and oxidation.

Experimental details

The relatively large residual factors reflect the poor crystal quality obtained so far and may be caused by the formation of mixed crystals and perhaps also by the known (from the binary compounds K_3X_7) first order phase transition from plastically crystalline HT to crystalline LT upon cooling. Also the applied absorption correction obviously does not fully account for the rather irregular shape of the crystals.

For the labelling of the nortricyclene compositions with respect to the As / Sb ratio the next simple numbers have been chosen, i.e. $K_3[As_xSb_{1-x}]_7$ with $x = 5/14$ (**1**) and $x = 13/14$ (**2**).

Discussion

The title compounds **1** and **2** form the *oP*160 structure type of LT-Rb_3As_7 [3], representing a hierarchical cluster replacement structure [4] of the hexagonal α-La type ($a \equiv c\text{-}\sqrt{3}/2$) (upper and middle figures). The two crystallographically independent Zintl anions $(X_7)^{3-}$ have different compositions (X = As, Sb), namely $(As_3Sb_4)^{3-}$ and $(As_2Sb_5)^{3-}$ in **1** but $(As_6Sb)^{3-}$ and $(As_7)^{3-}$ in **2**, respectively. The less electronegative Sb atoms prefer the 3-fold bonded (3b)$X^{\pm0}$ positions of the nortricyclene cages. The X—X bond lengths and the bond angles show the characteristic sequences A > C > B and $\alpha > \beta$ (lower figure) and the ratio Q = h/A = 1.27 – 1.31 of highly charged $(X_7)^{3-}$ anions [5,6]. The values of A, B, and C correspond nicely with the weigthed As—As and Sb—Sb single bond lengths. In compound **2**, the single Sb atom in the As cage causes a local distortion of the cage and therefore an alternative K position (K7) is found.

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1. The tripotassium heptapentelide $K_3As_{2.5}Sb_{4.5}$ ($K_3[As_x\ Sb_{1-x}]_7$ with x = 5/14)

Table 1. Data collection and handling.

Crystal:	grey block, size 0.2 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	178.11 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4879, 4879
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2339
$N(param)_{refined}$:	187
Programs:	SHELXL-97 [7], ATOMS [8], DIFABS [9]

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(301)[a]	8c		0.2052(2)	0.2597(1)	0.0714(2)	0.027(2)	0.035(2)	0.047(2)	0.003(1)	0.010(2)	0.003(2)
As(211)	8c	0.87(4)	0.2242(4)	0.3190(2)	0.1995(3)	0.054(4)	0.031(3)	0.052(4)	–0.002(2)	–0.020(3)	0.006(2)
Sb(211)	8c	0.13	0.2242	0.3190	0.1995	0.054	0.031	0.052	–0.002	–0.020	0.006
As(221)	8c		0.0524(4)	0.3009(2)	0.9961(3)	0.032(3)	0.043(3)	0.030(3)	0.004(2)	0.009(2)	0.005(2)
As(231)	8c		0.1231(4)	0.1792(2)	0.1403(4)	0.037(3)	0.017(2)	0.061(3)	0.003(2)	–0.004(3)	–0.003(2)
As(311)	8c	0.22(3)	0.0478(3)	0.3203(1)	0.2540(2)	0.046(2)	0.030(2)	0.035(2)	0.007(2)	0.001(2)	–0.001(1)
Sb(311)	8c	0.78	0.0478	0.3203	0.2540	0.046	0.030	0.035	0.007	0.001	–0.001
Sb(321)	8c		0.9249(3)	0.3048(1)	0.1116(2)	0.035(2)	0.036(2)	0.037(2)	0.003(2)	0.000(2)	0.003(2)
Sb(331)	8c		0.9758(2)	0.2195(1)	0.2169(2)	0.033(2)	0.030(2)	0.048(2)	–0.005(1)	–0.001(2)	0.011(2)
Sb(302)	8c		0.3164(3)	0.5439(1)	0.9515(2)	0.043(2)	0.031(2)	0.051(2)	0.005(2)	–0.010(2)	–0.012(2)
As(212)	8c	0.63(4)	0.1234(4)	0.5320(2)	0.9476(3)	0.044(3)	0.045(3)	0.058(3)	0.010(2)	0.010(3)	–0.004(2)
Sb(212)	8c	0.37	0.1234	0.5320	0.9476	0.044	0.045	0.058	0.010	0.010	–0.004
Sb(222)	8c		0.3753(3)	0.5345(2)	0.7963(3)	0.060(3)	0.065(3)	0.089(3)	–0.001(2)	0.004(3)	0.017(3)
As(232)	8c	0.73(4)	0.3629(4)	0.4525(2)	0.0145(3)	0.045(3)	0.042(3)	0.045(3)	0.001(2)	–0.001(2)	0.002(2)
Sb(232)	8c	0.27	0.3629	0.4525	0.0145	0.045	0.042	0.045	0.001	–0.001	0.002
Sb(312)	8c		0.1075(2)	0.4496(1)	0.8611(2)	0.029(2)	0.037(2)	0.050(2)	–0.009(2)	–0.003(2)	0.001(2)
As(322)	8c	0.12(2)	0.2872(3)	0.4512(1)	0.7603(2)	0.033(2)	0.035(2)	0.044(2)	0.000(2)	–0.002(2)	–0.014(2)
Sb(322)	8c	0.88	0.2872	0.4512	0.7603	0.033	0.035	0.044	0.000	–0.002	–0.014
As(332)	8c	0.36(2)	0.2801(3)	0.3964(1)	0.9093(3)	0.047(3)	0.027(2)	0.056(3)	0.002(2)	0.001(2)	0.001(2)
Sb(332)	8c	0.64	0.2801	0.3964	0.9093	0.047	0.027	0.056	0.002	0.001	0.001
K(1)	8c		0.1360(8)	0.5769(4)	0.7435(8)	0.032(6)	0.027(5)	0.066(8)	0.006(5)	0.002(6)	0.012(6)
K(2)	8c		0.0407(8)	0.4416(4)	0.6383(7)	0.033(6)	0.040(6)	0.050(7)	0.011(5)	–0.002(5)	–0.012(5)
K(3)	8c		0.1182(8)	0.4218(4)	0.0865(7)	0.028(5)	0.047(6)	0.036(6)	0.004(5)	0.003(5)	0.007(5)
K(4)	8c		0.2114(8)	0.2811(5)	0.8345(8)	0.033(6)	0.071(8)	0.049(7)	–0.004(6)	–0.009(6)	–0.014(6)
K(5)	8c		0.3667(9)	0.1333(5)	0.0981(9)	0.047(7)	0.044(7)	0.086(9)	–0.003(6)	0.024(7)	0.006(7)
K(6)	8c		0.965(1)	0.1785(5)	0.9696(8)	0.056(7)	0.050(7)	0.054(7)	–0.016(6)	0.004(6)	0.010(6)

a: labelling of the X (= As, Sb) atoms $X(ijk)$ with i = homoatomic connectivity, j = position in cluster (lower figure), k = number of X_7 cluster (upper figure).

2. The tripotassium heptapentelide $K_3As_{6.6}Sb_{0.4}$ ($K_3[As_xSb_{1-x}]_7$ with x = 13/14)

Table 3. Data collection and handling.

Crystal:	grey fragment, size 0.2 × 0.2 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	188.84 cm^{-1}
Diffractometer, scan mode:	Siemens P1, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4509, 4509
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1637
$N(param)_{refined}$:	195
Programs:	SHELXL-97 [7], ATOMS [8], DIFABS [9]

Table 4. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(301)[a]	8c		0.1922(3)	0.2628(2)	0.0647(3)	0.052(3)	0.056(3)	0.046(2)	0.003(2)	0.001(2)	-0.008(2)
As(211)	8c		0.2090(3)	0.3177(1)	0.1911(2)	0.049(2)	0.047(2)	0.046(2)	-0.007(2)	-0.001(2)	0.004(2)
As(221)	8c		0.0462(3)	0.3031(2)	0.9958(2)	0.060(3)	0.059(3)	0.032(2)	0.002(2)	-0.003(2)	0.004(2)
As(231)	8c		0.1221(3)	0.1843(1)	0.1243(3)	0.077(3)	0.044(2)	0.065(3)	0.000(2)	-0.018(3)	0.001(2)
As(311)	8c		0.0396(3)	0.3139(1)	0.2457(2)	0.061(3)	0.045(2)	0.035(2)	0.009(2)	-0.002(2)	-0.006(2)
As(321)	8c		0.9283(3)	0.3023(1)	0.1128(2)	0.043(2)	0.050(2)	0.039(2)	0.003(2)	-0.001(2)	0.002(2)
As(331)	8c	0.18(2)	0.9738(2)	0.2166(1)	0.2091(2)	0.048(2)	0.068(2)	0.043(2)	0.007(2)	-0.002(2)	0.002(2)
Sb(331)	8c	0.82	0.9738	0.2166	0.2091	0.048	0.068	0.043	0.007	-0.002	0.002
As(302)	8c		0.3160(3)	0.5343(2)	0.9597(3)	0.059(3)	0.069(3)	0.052(3)	-0.009(2)	0.003(2)	-0.023(2)
As(212)	8c		0.1352(3)	0.5278(1)	0.9482(3)	0.055(3)	0.050(2)	0.051(3)	0.015(2)	0.014(2)	0.006(2)
As(222)	8c		0.3703(3)	0.5320(1)	0.8086(3)	0.047(3)	0.055(2)	0.062(3)	0.004(2)	0.009(2)	0.018(2)
As(232)	8c		0.3563(3)	0.4482(2)	0.0109(3)	0.053(3)	0.093(3)	0.035(2)	0.005(2)	-0.003(2)	0.011(2)
As(312)	8c		0.1200(3)	0.4537(2)	0.8575(2)	0.048(2)	0.064(2)	0.038(2)	-0.016(2)	-0.009(2)	0.004(2)
As(322)	8c		0.2833(3)	0.4563(1)	0.7660(2)	0.057(2)	0.060(2)	0.036(2)	0.006(2)	-0.002(2)	-0.008(2)
As(332)	8c		0.2747(3)	0.4005(1)	0.9006(3)	0.066(3)	0.037(2)	0.055(3)	0.007(2)	0.010(2)	0.000(2)
K(1)	8c		0.1342(6)	0.5803(3)	0.7425(6)	0.057(5)	0.060(5)	0.057(6)	0.007(5)	0.014(5)	0.018(5)
K(2)	8c		0.0422(6)	0.4377(3)	0.6399(5)	0.053(5)	0.053(5)	0.052(6)	0.007(4)	-0.001(4)	-0.009(4)
K(3)	8c		0.1111(6)	0.4222(3)	0.0856(5)	0.034(5)	0.074(6)	0.041(5)	-0.007(4)	0.000(5)	0.022(4)
K(4)[b]	8c	0.89(2)	0.2114(7)	0.2820(3)	0.8288(6)	0.053(6)	0.069(7)	0.035(6)	-0.009(5)	-0.004(5)	-0.020(5)
K(5)[b]	8c	0.90	0.3701(9)	0.1276(4)	0.1099(7)	0.096(9)	0.076(8)	0.072(8)	-0.017(7)	0.044(7)	0.003(6)
K(6)[b]	8c	0.90	0.9370(7)	0.1868(4)	0.9602(6)	0.076(8)	0.068(7)	0.038(6)	-0.022(6)	-0.011(5)	-0.004(5)
K(7)[b]	8c	0.31	0.303(2)	0.6500(8)	0.911(1)	0.05(2)	0.03(1)	0.03(1)	-0.01(1)	-0.02(1)	0.01(1)

a: labelling of the X (= As, Sb) atoms $X(ijk)$ with i = homoatomic connectivity, j = position in cluster (lower figure), k = number of X_7 cluster (upper figure).
b: Occupancies refined with the condition $\Sigma Occ(K_i) = 3$, $i = 4 - 7$.

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