Crystal structure of tetrarubidium *tetrahedro*-tetraplumbide, Rb_4Pb_4 and of tetracaesium *tetrahedro*-tetraplumbide, Cs_4Pb_4

M. Baitinger[I], K. Peters[I], M. Somer[I], W. Carrillo-Cabrera[II], Yu. Grin[II], R. Kniep[III] and H. G. von Schnering*[,I],

[I] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany
[II] Max-Planck-Institut für Chemische Physik fester Stoffe, Pirnaer Landstr. 176, D-01257 Dresden, Germany
[III] Technische Universität Darmstadt, Eduard-Zintl-Institut, Hochschulstraße 10, D-64289 Darmstadt, Germany

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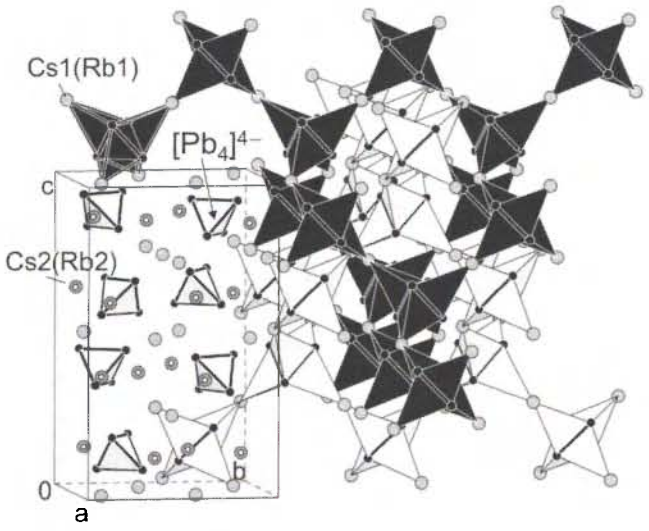

Abstract

Pb_4Rb_4, tetragonal, $I4_1/acd$ (No. 142), a = 11.892(1) Å, c = 19.429(2) Å, V = 2747.6 Å^3, Z = 8, $R_{gt}(F)$ = 0.035, $wR(F)$ = 0.035, T = 295 K.

Cs_4Pb_4, tetragonal, $I4_1/acd$ (No. 142), a = 12.244(1) Å, c = 20.001(2) Å, V = 2998.5 Å^3, Z = 8, $R_{gt}(F)$ = 0.084, $wR(F)$ = 0.074, T = 293 K.

Source of material

Stoichiometric mixtures of the elements were heated up to 1273 K for 1 day and annealed at 573 K for one week (Nb container, welded at 30kPa Ar). Single phases (by X-ray diffraction) with silvery grey crystals were formed. The compounds are very sensitive against oxidation and hydrolysis and have to be handled under inert conditions. Lattice parameters were determined from Guinier-Simon powder patterns [1] with Si standard ($\lambda(CuK_{\alpha 1})$ = 1.54051 Å ; a(Si) = 5.4305 Å).

Discussion

Both compounds form the *tI*64 structure of NaPb [2] as shown by Hewaidy et al. [3] from powder pattern, but detailed parameters were missing. The well-known structure type is characterized by two interpenetrating 3D frameworks of condensed M_4Pb_4 (M = Rb, Cs) *stellae quadrangulae* (distorted heterocubanes [4]), hierarchically related to the Cu_2O structure [5]. The tetrahedranide anions Pb_4^{4-} $\bar{d}$(Pb–Pb) = 3.098(4) Å (Rb_4Pb_4) $\bar{d}$(Pb–Pb) = 3.090(2) Å (Cs_4Pb_4)) are connected via twofold μ^3 -bridging M1 atoms to $^3(M1_{4/2}[Pb_4])$ substructures which are interconnected by 'interstitial' μ^2 -bridging M2 atoms. In total, 16 M atoms form cages around the tetrahedra with 3.824(3) d(Rb–Pb) 3.981(4) and 3.969(1) d(Cs–Pb) 4.133(2), respectively.

1. Tetrarubidium *tetrahedro*-tetraplumbide, Rb_4Pb_4

Table 1. Data collection and handling.

Crystal:	silvery grey, irregular, size 0.1 × 0.1 × 0.1 mm
Wavelength:	Ag K_α radiation (0.56088 Å)
μ:	352.1 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 400 exposures, $\Delta\varphi$ = 0.5°
$2\theta_{max}$:	61°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4391, 2155
Criterion for F_{obs}, $N(hkl)_{gt}$:	$F_{obs} > 4\,\sigma(F_{obs})$, 288
$N(param)_{refined}$:	21
Programs:	CSD [6], ATOMS [8]

* Correspondence author
(e-mail: baiti@vsibm1.mpi-stuttgart.mpg.de)

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb(1)	16*e*	0.8630(9)	0	1/4	0.038(5)	0.041(5)	0.041(4)	0	0	–0.010(5)
Rb(2)	16*f*	0.3798(6)	*x*+1/4	1/8	0.042(3)	U_{11}	0.042(4)	0.009(5)	–0.003(3)	$-U_{13}$
Pb	32*g*	0.0610(2)	0.1352(2)	0.93160(1)	0.032(1)	0.031(1)	0.032(1)	0.003(1)	–0.008(1)	0.009(1)

2. Tetracaesium *tetrahedro*-tetraplumbide, Cs_4Pb_4

Table 3. Data collection and handling.

Crystal:	dark plate, size 0.16 × 0.16 × 0.06 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	400.00 cm^{-1}
Diffractometer, scan mode:	Siemens-Nicolet, Wyckoff
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1550, 864
Criterion for F_{obs}, $N(hkl)_{gt}$:	$F_{obs} > 4\ \sigma(F_{obs})$, 631
$N(param)_{refined}$:	25
Programs:	SHELXTL-plus [7], ATOMS [8]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$, origin choice 2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	16*e*	0.8570(2)	0	1/4	0.032(1)	0.038(1)	0.045(1)	0	0	–0.010(1)
Cs(2)	16*f*	0.3817(2)	*x*+1/4	1/8	0.0384(9)	U_{11}	0.043(1)	0.001(1)	–0.0000(7)	$-U_{13}$
Pb(1)	32*g*	0.06114(8)	0.13984(8)	0.92974(5)	0.0306(6)	0.0298(6)	0.0344(6)	0.0020(4)	–0.0060(4)	0.0082(4)

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