Crystal structure of the low-temperature modification of trirubidium heptaarsenide, LT-Rb₃As₇

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Abstract

As₇Rb₃, orthorhombic, *Pbca* (No. 61), *a* = 13.194(3) Å, *b* = 25.878(5) Å, *c* = 15.881(3) Å, *V* = 5422.3 Å³, *Z* = 16, *R*_{gt}(*F*) = 0.082, *wR*_{obs}(*F*²) = 0.140, *wR*_{all}(*F*²) = 0.320, *T* = 293 K.

Source of material

Light crimson-red Rb₃As₇ (optical band gap 2.1 eV) is formed by reaction of stoichiometric mixtures of the elements in welded Nb-tubes (12 h up to 873 K, 36 h at 873 K, down to 293 K within 36 h) [1,2]. The transformation to HT-Rb₃As₇ takes place at 608 K. The compound is very sensitive to hydrolysis and oxidation, and evaporates congruent dissociatively above 900 K in dynamic vacuum.

Experimental details

The relatively large residual factor reflects the poor crystal quality caused by the low transition temperature from HT to LT phase (at about 608 K). Also, the absorption correction obviously does not account for the remaining differences in the *U*_{ij} values.

Discussion

LT-Rb₃As₇ forms a new *oP*160 structure type. The arrangement of the two crystallographically independent Zintl anions (As₇)^{3−} (upper and middle figures) represents a hierarchical cluster-replacement structure [3] of the hexagonal *α*-La type. For a direct comparison, the *cab* setting must be chosen (in the *abc* setting: *a*_{orth} ≡ *c*_{orth}√3/2 ≡ *a*_{hex}, *b*_{orth} ≡ *c*_{hex}). The quasi-hexagonal unit cell is emphasized by broken lines in the middle figure.

The mean As—As bond lengths and the bond angles (*A* = 2.510 Å, *B* = 2.343 Å, *C* = 2.387 Å, *α* = 101.4°, *β* = 99.6°, *γ* = 104.7°, *h* = 3.317 Å; lower figure) are characteristic for strongly ionic nortri-cyclenes with *A* > *C* > *B*, *α* > *β* and *Q* = *h*/*A* = 1.32 Å [4,5]. The Rb⁺ cations connect 4–6 (As₇)^{3−} anions (*d*(Rb—As) = 3.43 Å–4.20 Å) and show the preformation of Rb₃As₇ molecules [5,6] and especially (Rb₂As₇–Rb–Rb₂As₇)[−] subunits. The first order phase transition to the plastically crystalline cubic HT-Rb₃As₇ [6] (hierarchical cluster-replacement Li₃Bi structure) requires considerable rearrangements.

Table 1. Data collection and handling.

Crystal:	light crimson-red polyhedron, size 0.2 × 0.3 × 0.3 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
<i>μ</i> :	276.90 cm ^{−1}
Diffractometer, scan mode:	Siemens P1, <i>ω</i>
2 θ _{max} :	50°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	4777, 4777
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 <i>σ</i> (<i>I</i> _{obs}), 1308
<i>N</i> (<i>param</i>) _{refined} :	182
Programs:	SHELXS-97 [7], SHELXL-97 [8] ATOMS [9], DIFABS [10]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
As(301) ^a	8c	0.2056(5)	0.2593(3)	0.0655(7)	0.040(4)	0.042(4)	0.045(6)	0.006(3)	-0.004(5)	0.003(5)
As(211)	8c	0.2288(6)	0.3139(3)	0.1836(7)	0.052(5)	0.036(4)	0.056(7)	-0.012(3)	0.001(5)	0.019(5)
As(221)	8c	0.1308(6)	0.1853(3)	0.1293(7)	0.060(5)	0.025(4)	0.050(7)	0.003(3)	-0.022(5)	-0.015(4)
As(231)	8c	0.0575(6)	0.2981(3)	0.0023(6)	0.046(4)	0.041(4)	0.030(5)	0.005(3)	0.000(5)	0.007(4)
As(311)	8c	0.0651(6)	0.3132(3)	0.2405(6)	0.063(5)	0.041(4)	0.040(6)	0.014(4)	-0.017(5)	0.001(5)
As(321)	8c	-0.0009(6)	0.2242(3)	0.2072(6)	0.046(4)	0.041(4)	0.052(7)	-0.010(3)	-0.020(5)	0.014(5)
As(331)	8c	-0.0499(5)	0.3000(2)	0.1173(6)	0.039(4)	0.032(4)	0.038(6)	0.002(3)	-0.003(5)	0.003(4)
As(302)	8c	0.3163(5)	0.5414(3)	-0.0485(6)	0.049(4)	0.027(4)	0.040(6)	0.005(3)	-0.010(5)	-0.013(4)
As(212)	8c	0.1373(5)	0.5301(3)	-0.0531(6)	0.035(4)	0.050(4)	0.037(6)	0.012(3)	0.012(5)	-0.003(5)
As(222)	8c	0.3661(5)	0.5357(3)	-0.1922(7)	0.036(4)	0.054(5)	0.012(5)	0.004(4)	-0.004(5)	0.012(5)
As(232)	8c	0.3644(5)	0.4576(3)	0.0083(6)	0.046(4)	0.040(4)	0.036(6)	0.000(3)	-0.007(5)	0.013(5)
As(312)	8c	0.1272(6)	0.4550(3)	-0.1360(6)	0.047(5)	0.051(5)	0.034(6)	-0.011(4)	0.010(5)	0.001(5)
As(322)	8c	0.2858(6)	0.4572(3)	-0.2253(6)	0.049(4)	0.044(4)	0.039(6)	0.005(3)	-0.002(5)	-0.011(5)
As(332)	8c	0.2825(6)	0.4057(3)	-0.0926(6)	0.060(5)	0.025(4)	0.042(6)	0.002(3)	-0.002(5)	-0.004(4)
Rb(1)	8c	0.1260(5)	0.5832(2)	-0.2545(7)	0.052(4)	0.032(3)	0.052(6)	-0.005(3)	0.002(5)	0.002(5)
Rb(2)	8c	0.0514(6)	0.4410(3)	-0.3554(5)	0.052(4)	0.046(4)	0.019(5)	0.003(3)	0.008(4)	-0.003(4)
Rb(3)	8c	0.1153(5)	0.4249(3)	0.0885(6)	0.051(5)	0.048(4)	0.035(5)	0.010(3)	-0.020(5)	0.007(4)
Rb(4)	8c	0.2303(5)	0.2823(3)	-0.1627(6)	0.053(5)	0.039(4)	0.051(6)	-0.005(3)	0.003(5)	-0.012(4)
Rb(5)	8c	0.3764(6)	0.1297(3)	0.1065(8)	0.070(6)	0.061(5)	0.085(9)	-0.008(4)	0.041(7)	0.005(6)
Rb(6)	8c	-0.0351(6)	0.1750(3)	-0.0445(7)	0.082(6)	0.049(4)	0.058(7)	-0.027(4)	-0.004(6)	0.003(5)

a: labelling of the As atoms As(*ijk*) with *i* = homoatomic connectivity, *j* = position in cluster (lower figure), *k* = number of As₇ cluster (upper figure).

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