Crystal structure of tricaesium arsenide, Cs₃As

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Discussion

The compound was first mentioned by Gnutzmann [1] without assignment of a space group but excluding $P6_3/mmc$ [2]. Cs₃As crystallize in the Na₃As structure [3] (Cu₃P type) based on a hexagonal close packing of arsenic (As³⁻). All tetrahedral holes are filled with Cs⁺ off-centered towards a tetrahedral faces (Cs2) and towards a tetrahedral edge (Cs1). The cesium-atoms Cs3 and Cs4 (see figure) are strongly shifted along [001] away from the centres of the trigonal holes.

Table 1. Data collection and handling.

Crystal:	dark grey metallic needle, size 0.05 × 0.05 × 0.2 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	187.95 cm ⁻¹
Diffractometer, scan mode:	Stoe IPDS, φ
$2\theta_{\max}$:	56.32°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	897, 529
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 330
$N(\text{param})_{\text{refined}}$:	26
Programs:	SHELXL-97 [4], DIAMOND [5]

Abstract

AsCs₃, hexagonal, $P6_3cm$ (No. 185), $a = 10.783(2)$ Å, $c = 11.147(2)$ Å, $V = 1122.5$ Å³, $Z = 6$, $R_{\text{gt}}(F) = 0.031$, $wR_{\text{ref}}(F^2) = 0.059$, $T = 293$ K.

Source of material

The compound was synthesized from a stoichiometric mixture of the elements in a sealed steel-tube filled with inert gas (Ar). The sample was first heated up to a homogeneous melt at 670 K (1d). Well shaped, dark grey single crystals of the air sensitive compound were obtained after subsequent annealing at 540 K (four weeks).

Experimental details

Refinements assuming the space groups $P\bar{6}c2$ and $P6_3/mcm$ yielded higher $R_{\text{gt}}(F)$ values (0.107 and 0.188, respectively).

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(1)	6c	0	0.3284(3)	0.3443(4)	0.033(1)	0.0321(7)	0.0305(7)	0.0165(6)	0	-0.0009(6)
Cs(1)	6c	0.6331(2)	0	0.51043(9)	0.0544(6)	0.095(1)	0.0329(8)	0.0473(7)	-0.0017(9)	0
Cs(2)	6c	0.7043(2)	0	0.1789(1)	0.0654(8)	0.048(1)	0.0323(7)	0.0240(5)	0.0001(9)	0
Cs(3)	2a	0	0	0.4216(4)	0.0385(7)	U_{11}	0.069(1)	$U_{11}/2$	0	0
Cs(4)	4b	2/3	1/3	0.2958(3)	0.0332(5)	U_{11}	0.175(3)	$U_{11}/2$	0	0

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References

- Gnutzmann, G.; Dorn, F.W.; Klemm, W.: Über einige A₃B- und AB₂-Verbindungen der schweren Alkalimetalle mit Elementen der V. Gruppe. *Z. Anorg. Allg. Chem.* **309** (1961) 210-225.
- Brauer G.; Zintl, E.: Konstitution von Phosphiden, Arseniden, Antimoniden und Wismuthiden des Lithiums, Natriums und Kaliums. *Z. Phys. Chem.* **B37** (1937) 323-35.
- Hafner, P.; Range, K.-J.: Na₃As revisited: high-pressure synthesis of single crystals and structure refinement. *J. Alloys Comp.* **216** (1984) 7-10.
- Sheldrick, G. M.: SHELXL-97. A Program for Refining Crystal Structures. University of Göttingen, Germany 1997.
- Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System Crystal Impact GbR, Bonn, Germany 1997-2002.