Crystal structure of barium arsenide auride, Ba_8As_5Au

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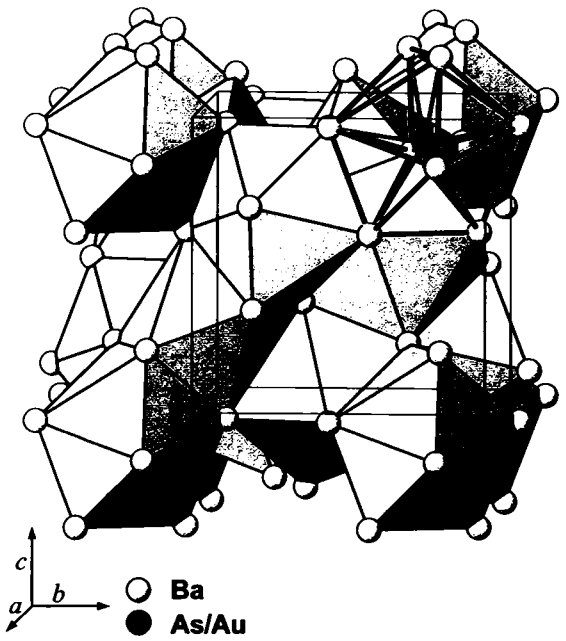

Abstract

As_5AuBa_8, cubic, $I\bar{4}3d$ (No. 220), $a = 9.9607(7)$ Å, $V = 988.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.053$, $T = 293$ K.

Source of material

Ba_8As_5Au was synthesized from BaAs, Ba and Au (ratio 5:3:1) in sealed tantalum ampoules at 1175 K. Single crystals were isolated from slowly cooled samples (cooling rate: 25 K/h).

Experimental details

The absolute configuration in respect to the polarity of the space group was proven by changing the sign of the hkl indices. The $wR(F^2)$ values for the possible orientations were 0.053 and 0.109, respectively. The first one represents the absolute configuration of the crystal studied.

Discussion

Ba_8As_5Au crystallizes in the anti-Th_3P_4 type of structure where arsenic and gold share the thorium position (12*a*). The site occupation factors were refined with the restraint SOF(12*a*) = SOF(As) + SOF(Au) = 1, converging to SOF(As) ≅ 5/6 and SOF(Au) ≅ 1/6, within standard deviations. Therefore SOF(As) = 5/6 and SOF(Au) = 1/6 were fixed, during the final refinements. This is compatible with the charge balance ($8 \times Ba^{2+}$; $5 \times As^{3-}$ and $1 \times Au^-$). Similar occupancies have been reported for several other compounds as Eu_4X_2Y (X = P, As, Sb, Bi; Y = S, Se, Te) [1] or Rb_4Cl_2O [2] with SOF(X):SOF(Y) = 2:1. The existence of isotypic barium phosphide chloride $Ba_{16}(P_{10.05}Cl_{1.86}\square_{0.09})$ [3] supports the assumption of an oxidation state of –1 for gold [4]. Barium is surrounded by six anions, and the coordination polyhedron can be described either by a distorted octahedron or a twisted trigonal antiprism of As/Au. The Ba atoms form a 3D framework of condensed Ba_8 dodecahedra, which are centered by As or Au (see figure) (d(As/Au—Ba) = 3.302(1) Å (4×) and 3.604(1) Å (4×)). The Ba_8 dodecahedra with $x_{Ba} = 0.06930(3)$ deviate from the regular one with $x = 0.0833 = 1/12$.

Table 1. Data collection and handling.

Crystal:	block with dark metallic lustre size 0.15 × 0.20 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	313.28 cm^{-1}
Diffractometer, scan mode:	SMART APEX Bruker AXS, ω
$2\theta_{max}$:	69.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6972, 363
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 349
$N(param)_{refined}$:	7
Programs:	SHELXTL-97 [5], ATOMS [6]

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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}
Ba(1)	16*c*		0.06930(3)	*x*	*x*	0.0187(2)	U_{11}	U_{11}	0.0011(1)	U_{12}	U_{12}
As(2)	12*a*	0.83	3/8	0	1/4	0.0214(4)	0.0149(3)	U_{22}	0	0	0
Au(2)	12*a*	0.17	3/8	0	1/4	U_{11}(As2)	U_{22}(As2)	U_{22}(As2)	0	0	0

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