BaAuP and BaAuAs, Synthesis via Disproportionation of Gold upon Interaction with Pnictides as Bases

Jürgen Nuss^[a] and Martin Jansen^{*[a]}

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Abstract. Gold disproportinates in the presence of the Zintl phases Ba_3P_2 or Ba_3As_2 forming BaAuP and BaAuAs, respectively, and $BaAu_2$. The air and moisture sensitive ternary compounds crystallise in the ZrBeSi type of structure, an ordered variant of AlB₂: BaAuP (*P*6₃/*mmc*; *a* = 440.68(6) pm; *c* = 899.8(2) pm; *R*₁ =

Introduction

Ascribing to gold certain halogen-like behaviours has become a well established view in solid state chemistry [1]. Impressive factual evidence is provided by the isostructural couples of Ba_8As_5Au [2] and Ba_8P_5Cl [3], $[NMe_4]Au$ and $[NMe_4]Br$ [4], or $Rb_5[AuO_2]Au_2$ [5] and $K_5[AuO_2]I_2$ [6]. The auride anion acting as an acceptor in an N-H···Au⁻ hydrogen bond is displaying further halide-like behaviour [7]. Finally, gold and halogens both can disproportionate in the presence of bases [5, 8].

We tried to use gold as an oxidising reagent for Zintl phases, in analogy to e.g. iodine, which oxidises phosphorus in Ba_3P_2 forming BaI_2 and $Ba_3P_3I_2$, or $Ba_5P_5I_3$, respectively [9]. However, when gold reacted with Ba_3P_2 aiming at 'Ba_3P_3Au_2' or 'Ba_5P_5Au_3', it disproportionated, yielding a two-phase product consisting of $BaAu_2$ and BaAuP.

Results and Discussion

The Zintl phases Ba_3X_2 (X = P, As), containing isolated X^{3-} ions, react with gold, and a two-phase product consisting of BaAuX and BaAu₂ in an approximate molar ratio of 2:1 is formed quantitatively. Figure 1 shows the powder pattern of the product mixture. The power of reduction of X^{3-} is not sufficient to achieve the formation of Au^- ions together with X^{2-} or X^{1-} species. Such a redox process would have been necessary for obtaining a hypothetical compound 'Ba₃P₃Au₂'. Instead elemental gold dispro-

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 [a] Max-Planck-Institut f
ür Festkörperforschung Heisenbergstr. 1 70569 Stuttgart, Germany

0.0237; 183 independent reflections); BaAuAs ($P6_3/mmc$; a = 453.53(5) pm; c = 902.7(1) pm; $R_1 = 0.0255$; 168 independent reflections). Both compounds, which are accessible as pure phases by reacting BaP or BaAs with gold, can be classified as poor metallic conductors.

portionates under these conditions, with X^{3-} acting as a base, according to Equation (1) and (Equation (2).

$$Ba_3P_2 + 4 Au^{\pm 0} \rightarrow 2 BaAu^{+1}P + BaAu^{-1}_2$$
 (1)

$$Ba_3As_2 + 4 Au^{\pm 0} \rightarrow 2 BaAu^{+1}As + BaAu^{-1}_2$$
⁽²⁾



Figure 1. Powder diffraction pattern of the reaction product between Ba_3P_2 and gold (middle), with calculated intensity plots of $BaAu_2$ (top) and BaAuP (bottom). For clarity, the intensities (arbitrary units) are drawn in positive direction for BaAuP and the product, and in negative direction for $BaAu_2$.

The formation of BaAu₂ as a by-product can be avoided by using BaX as starting material. In this case pure samples of BaAuP and BaAuAs were obtained, which have been used for conductivity measurements. The specific electrical resistivity of BaAuP (BaAuAs) increases from 0.076 (0.041) Ω cm at 5 K to 0.137 (0.052) Ω cm at 300 K, thus displaying a typical behaviour of a poor metallic conductor (Figure 2). Because of the metallic conductivity, a description Ba⁺²Au⁺¹X⁻³ would not be valid in a strict sense; this should result in semiconducting behaviour. In Equation (1)

^{*} Prof. Dr. M. Jansen Fax: +49-711-689-1502

E-Mail: M.Jansen@fkf.mpg.de

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and (2) conventional oxidation states are given with the signs indicating the correct polarisation: gold has a positive charge $(Au^{+\delta})$ in BaAuX and a negative one $(Au^{-\delta})$ in BaAu₂.



Figure 2. Electric resistivity vs. temperature for BaAuP and BaAuAs.

Both, BaAuP and BaAuAs, crystallise in the space group $P6_3/mmc$ (no. 194, Pearson code hP6), as previously found by determination of the lattice constants from powder diffraction data [10]. The structure represents an ordered variant of the AlB₂ type of structure, similar to ZrBeSi. Complex anions $\frac{2}{\infty}$ [AuX]^{2–} are forming sheets corresponding to hexagonal boron nitride, with the barium cations inbetween (Figure 3), resulting in a 6+6 coordination for barium, and a mutual trigonal planar coordination for the pnictides and gold atoms (Table 1).



Figure 3. Perspective representation of the crystal structure of BaAuP, with the margins of the unit cell (grey).

Conclusions

BaAuP and BaAuAs have been synthesised by solid state reactions from Ba_3X_2 (BaX) and gold. The reaction

Table 1. Interatomic distances /pm for BaAuX, X = P, As (standard deviations).

Atomic contact		BaAuP	BaAuAs	multiplicity	
Au	-X	254.42(3)	261.84(3)	3	
	-Ba	339.61(4)	345.68(3)	6	
Ba	$-\mathbf{X}$	339.61(4)	345.68(3)	6	
	-Au	339.61(4)	345.68(3)	6	
Х	-Au	254.42(3)	261.84(3)	3	
	-Ba	339.61(4)	345.68(3)	6	

products have been characterised by powder diffraction, single crystal diffraction and resistivity measurements. It has been demonstrated that elemental gold disproportionates in the presence of pnictides Ba_3X_2 , whereby the pnictides are acting as bases.

Experimental Section

Synthesis

The BaAuX (X = P, As) compounds were prepared by the reaction of Ba_3X_2 and Au (1:4), with $BaAu_2$ as a by-product in stoichiometric amounts. An optimised synthesis, realised by the reaction of BaX with elemental gold, leads to pure samples of BaAuP and BaAuAs. The barium pnictides were prepared from the elements in corundum crucibles. The crucibles were sealed in quartz ampoules, and heated at 1020 K for 48 h.

Stoichiometric amounts of BaX and gold powder (fine gold powders can be obtained as described previously [11]) were mixed in a dry-box (MBraun, Garching, Germany) in an argon atmosphere (< 0.1 ppm O₂, H₂O) and sealed in tantalum ampoules. The reaction was carried out with the following temperature profile: 298 \rightarrow 1220 K (50 K · h⁻¹, subsequent annealing for 48 h); 1220 \rightarrow 298 K (50 K · h⁻¹).

The solidified black reguli are sensitive to humid air and must be handled in an inert atmosphere.

X-ray Analysis

All samples were examined by X-ray powder diffraction. Powder patterns were collected with a linear position-sensitive detector with a STADI P diffractometer in Debye–Scherrer geometry, with Ge-monochromated Cu- $K_{\alpha 1}$ radiation, $\lambda = 1.540598$ Å, $5 < 2\theta < 100^{\circ}$ (Stoe & Cie GmbH, Darmstadt, Germany). Samples were sealed in glass capillaries of 0.3 mm diameter.

For single-crystal X-ray diffraction experiments, black single crystals were selected in a dry-box and mounted in sealed glass capillaries. Data collection, at 296(2) K, was carried out with a STADI4 four circle diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) and a Smart 1000 K three circle diffractometer (Bruker AXS, Karlsruhe, Germany), respectively. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL program package [12]. Experimental details are given in Table 2, atomic coordinates and anisotropic displacement parameters are given in Table 3 and Table 4.

Electrical Resistivity

Temperature dependent resistivity has been obtained for pressed pellets using *van der Pauw* method [16]. The ground powders were

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 Table 2. Crystal data and structure refinement data of BaAuP and BaAuAs.

	BaAuP	BaAuAs	
Formula weight	365.28	409.23	
Space group (no.), Z	<i>P</i> 6 ₃ / <i>mmc</i> (194), 2	P63/mmc (194), 2	
Lattice constants /pm	a = 440.68(6)	453.53(5)	
*	c = 899.8(2)	902.7(1)	
	c/a = 2.042	1.990	
$V/Å^3$, $\rho_{\rm xray}/g\cdot {\rm cm}^{-3}$	151.33(4), 8.016	160.80(3), 8.452	
Diffractometer	STADI4 (Stoe & Cie),	Smart 1000 K	
	scintillations counter	(Bruker AXS),	
		CCD-detector	
Radiation	Mo- K_{α} ($\lambda = 71.073 \text{ pm}$),		
	graphite monochromated		
Absorption correction	X-Shape [13]	SADABS [14]	
2θ range /°	9.06 to 74.82	9.04 to 70.08	
Index range	$-7 \le h \le 7,$	$-7 \le h \le 7$,	
	$-7 \le k \le 7,$	$-7 \le k \le 7,$	
	$-15 \le l \le 15$	$-14 \le l \le 14$	
Reflection collected	2976	2637	
Data, R _{int}	183, 0.0196	168, 0.0535	
No. of parameters	8	8	
$R_1[F^2 > 2\sigma (F^2)]$	0.0237	0.0255	
$wR(F^2)$	0.0631	0.0585	
Extinction coefficient	0.023(2)	0.013(2)	
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} / {\rm e} \cdot {\rm \AA}^{-3}$	2.56, -3.31	1.41, -2.02	
Deposition no. [15]	CSD-420340	CSD-420341	

Table 3. Atomic coordinates and equivalent isotropic displacement parameters U_{eq} /pm² for BaAuP and BaAuAs.

Compound	Atom	Site	X	у	Ζ	$U_{\rm eq}$
BaAuP	Au	2d	1/3	2/3	3/4	150(2)
	Ва	2a	0	0	0	133(3)
	Р	2c	1/3	2/3	1/4	147(7)
BaAuAs	Au	2d	1/3	2/3	3/4	114(2)
	Ba	2a	0	0	0	102(2)
	As	2c	1/3	2/3	1/4	95(3)

pressed into 6 mm diameter by 1 mm thick pellets, and annealed for 24h at 723 K under argon atmosphere. The pellets were then connected to four probes of the resistivity measurement apparatus. Data were recorded in the temperature range 5-300 K at 5 K intervals.

Table 4. Anisotropic displacement parameters U_{ij} /pm² for BaAuP and BaAuAs ($U_{13} = U_{23} = 0$).

Compound	Atom	U_{11}	U_{22}	U ₃₃	U_{12}
BaAuP	Au	149(2)	U_{11}	151(3)	75(1)
	Ba	126(3)	U_{11}	146(4)	64(1)
	Р	115(9)	U_{11}	210(19)	58(5)
BaAuAs	Au	106(2)	U_{11}	132(3)	53(1)
	Ba	96(3)	U_{11}	114(4)	48(2)
	As	63(4)	U_{11}	161(6)	32(2)

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