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SHORT COMMUNICATION

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

Jürgen Nuss,^[a] and Martin Jansen^{*[a]}**Keywords:** Gold; Ternary pnictides; Alkaline earth metals; Conducting materials; Crystal structures

Abstract. Gold disproportionates 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 crystallize in the ZrBeSi type of structure, an ordered variant of AlB_2 : BaAuP ($P6_3/mmc$; $a = 440.68(6)$ pm; $c = 899.8(2)$ pm; $R_1 = 0.0237$; 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 Au, can be classified as poor metallic conductors.

* Prof. Dr. M. Jansen
Fax: +49-711-689-1502
E-mail: M.Jansen@fkf.mpg.de
[a] Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1
D-70569 Stuttgart, Germany

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 $\text{Ba}_8\text{As}_5\text{Au}$ [2] and $\text{Ba}_8\text{P}_5\text{Cl}$ [3], $[\text{NMe}_4]\text{Au}$ and $[\text{NMe}_4]\text{Br}$ [4], or $\text{Rb}_5[\text{AuO}_2]\text{Au}_2$ [5] and $\text{K}_5[\text{AuO}_2]\text{I}_2$ [6]. The auride anion acting as an acceptor in a $\text{N-H}\cdots\text{Au}^-$ hydrogen bond is displaying further halide-like behaviour [7]. Finally, gold and halogens, both can disproportionate in the presence of bases [5, 8].

We have tried to use gold as an oxidizing reagent for Zintl phases, in analogy to e.g. iodine which oxidizes phosphorous in Ba_3P_2 forming BaI_2 and $\text{Ba}_3\text{P}_3\text{I}_2$, or $\text{Ba}_5\text{P}_5\text{I}_3$, respectively [9]. However, when reacting gold with Ba_3P_2 , aiming at ' $\text{Ba}_3\text{P}_3\text{Au}_2$ ' or ' $\text{Ba}_5\text{P}_5\text{Au}_3$ ', instead gold disproportionated, yielding a two-phase product consisting of BaAu_2 and BaAuP.

Results and Discussion

The Zintl phases Ba_3X_2 ($\text{X} = \text{P}, \text{As}$), containing isolated X^{3-} ions, react with gold, and a two-phase product consisting of BaAuX and BaAu_2 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^- anions together with X^{2-} or X^{1-} species. Such a redox process would have been necessary for obtaining a hypothetical compound ' $\text{Ba}_3\text{P}_3\text{Au}_2$ '. Instead elemental gold disproportionates under these conditions, with X^{3-} acting as a base, according to equations (1) and (2).

Figure 1. Powder diffraction pattern of the reaction product between Ba_3P_2 and Au (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 BaAu_2 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) Ωcm at 5 K to 0.137 (0.052) Ωcm at 300K, thus displaying a typical behaviour of a poor metallic conductor (Fig. 2). Because of the metallic conductivity a description $\text{Ba}^{+2}\text{Au}^{+1}\text{X}^{-3}$ would not be valid in a strict sense; this should result in semiconducting behaviour. In equations (1) and (2) conventional oxidation states are given with the signs indicating the correct polarisation: gold has a positive charge ($\text{Au}^{+\delta}$) in BaAuX and a negative one ($\text{Au}^{-\delta}$) in BaAu_2 .

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

Both, BaAuP and BaAuAs, crystallize in the space group $P6_3/mmc$ (no. 194, Pearson code $hP6$) as was found by determination of the lattice constants from powder diffraction data, previously [10]. The structure represents an ordered variant of the AlB_2 type of structure, similar to $ZrBeSi$. Complex anions ${}^\infty[AuX]^{2-}$ are forming sheets corresponding to hexagonal boron nitride, with the barium cations in-between (Fig. 3), resulting in a 6+6 coordination for Ba, 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).

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	— X	339.61(4)	345.68(3)	6
	— Au	339.61(4)	345.68(3)	6
X	— Au	254.42(3)	261.84(3)	3
	— Ba	339.61(4)	345.68(3)	6

Conclusions

BaAuP and BaAuAs have been synthesized by solid state reactions from Ba_3X_2 (BaX) and gold. The reaction products have been characterized 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 BaAu₂ as a by-product in stoichiometric amounts. An optimized 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 Au powders can be obtained as described previously [11]) were mixed in a dry-box (MBraun, Garching, Germany) in an argon atmosphere (< 0.1 ppm O_2 , H_2O) 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 on a STADI P diffractometer in Debye-Scherrer geometry, with Gemonochromated $MoK\alpha_1$ 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 on a STADI4 four circle diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) and a Smart 1000K 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 4.

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

	BaAuP	BaAuAs
Formula weight	365.28	409.23
Space group (no.), <i>Z</i>	<i>P</i> 6 ₃ / <i>mmc</i> (194), 2	<i>P</i> 6 ₃ / <i>mmc</i> (194), 2
Lattice constants /pm	<i>a</i> = 440.68(6) <i>c</i> = 899.8(2) <i>c/a</i> = 2.042	453.53(5) 902.7(1) 1.990
<i>V</i> /Å ³ , ρ_{Xray} /g cm ⁻³	151.33(4), 8.016	160.80(3), 8.452
Diffraction	STADI4 (Stoe & Cie), scintillations counter	Smart 1000K (Bruker AXS), CCD-detector
Radiation	MoK α (λ = 71.073 pm), graphite monochromatated	
Absorption correction	X-Shape [13]	SADABS [14]
2 θ range /°	9.06 to 74.82	9.04 to 70.08
Index range	$-7 \leq h \leq 7$, $-7 \leq k \leq 7$, $-15 \leq l \leq 15$	$-7 \leq h \leq 7$, $-7 \leq k \leq 7$, $-14 \leq l \leq 14$
Rflection collected	2976	2637
Data, <i>R</i> _{int}	183, 0.0196	168, 0.0535
No. of parameters	8	8
<i>R</i> _i [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0237	0.0255
<i>wR</i> (<i>F</i> ²)	0.0631	0.0585
Extinction coefficient	0.023(2)	0.013(2)
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ /e Å ⁻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	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
BaAuP	Au	2 <i>d</i>	1/3	2/3	3/4	150(2)
	Ba	2 <i>a</i>	0	0	0	133(3)
	P	2 <i>c</i>	1/3	2/3	1/4	147(7)
BaAuAs	Au	2 <i>d</i>	1/3	2/3	3/4	114(2)
	Ba	2 <i>a</i>	0	0	0	102(2)
	As	2 <i>c</i>	1/3	2/3	1/4	95(3)

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

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

Electrical Resistivity

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

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Powder diffraction pattern of the reaction product between Ba_3P_2 and Au (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 .
120x69mm (600 x 600 DPI)

Electric resistivity vs. temperature for BaAuP and BaAuAs.
120x89mm (600 x 600 DPI)

Perspective representation of the crystal structure of BaAuP, with the margins of the unit cell (grey).
85x86mm (600 x 600 DPI)