Structure Refinement of $BaIrIn_2$

Jan F. Riecken and Rainer Pöttgen

Institut für Anorganische und Analytische Chemie,
Westfälische Wilhelms-Universität Münster,
Corrensstr. 36, D-48149 Münster, Germany

Reprint requests to R. Pöttgen.
E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **60b,** 118 – 120 (2005);
received September 22, 2004

$BaIrIn_2$ was synthesized from the elements in a sealed tantalum tube in an induction furnace. The indide was investigated by powder and single crystal X-ray data: *Cmcm*, $a = 443.3(1)$, $b = 1151.3(2)$, $c = 806.0(1)$ pm, $wR2 = 0.0471$, 352 F^2 values, and 16 variable parameters. The iridium and indium atoms build up two-dimensional $[IrIn_2]^{2-}$ polyanions (279 – 281 pm Ir–In and 310 — 314 pm In–In) which are separated and charge-balanced by the barium atoms. The two-dimensional character of the polyanion is responsible for the strong moisture sensitivity of $BaIrIn_2$. The coordination numbers for barium, iridium, and indium are 15, 9, and 12, respectively.

Key words: Indium, Crystal Structure, Solid State Synthesis

Introduction

The alkaline earth (*AE*) transition metal (*T*) indides $AETIn_2$ (*AE* = Ca, Sr, Ba; T = Ni, Cu, Rh, Pd, Ir, Pt, Au) [1 – 5] crystallize with the orthorhombic $MgCuAl_2$ structure [6]. From a geometrical point of view, they can be considered as transition metal filled variants of the binary Zintl phases $CaIn_2$, $SrIn_2$, and $BaIn_2$ [7 – 9]. While the three-dimensional character of the indium substructure of the binary Zintl phases almost remains in the $AETIn_2$ compounds with calcium and strontium as alkaline earth metal component, those with barium show an extreme elongation of one In–In bond leading to pronounced two-dimensional $[TIn_2]$ networks in $BaTIn_2$ (*T* = Rh, Pd, Ir, Pt) [5]. This has a drastic effect on the stability of the respective compounds. While the $CaTIn_2$ and $SrTIn_2$ indides are stable in moist air over months, the $BaTIn_2$ indides with the two-dimensional polyanions readily decompose with traces of moisture. So far, only the structures of $BaRhIn_2$ and $BaPtIn_2$ have been refined on the basis of single crystal data. The synthesis and structure refinement of isotypic $BaIrIn_2$ are reported herein.

Table 1. Crystal data and structure refinement for $BaIrIn_2$.

Empirical formula	$BaIrIn_2$
Formula weight	559.18 g/mol
Unit cell dimensions	$a = 443.3(1)$ pm
(Guinier data)	$b = 1151.3(2)$ pm
	$c = 806.0(1)$ pm
	$V = 0.4114$ nm^3
Pearson symbol	oC16
Structure type	$MgCuAl_2$
Space group	*Cmcm*
Formula units per cell	$Z = 4$
Calculated density	9.03 g/cm^3
Crystal size	$10 \times 20 \times 30$ μm^3
Transmission ratio (max/min)	2.57
Absorption coefficient	52.5 mm^{-1}
F (000)	924
Detector distance	60 mm
Exposure time	5 min
ω Range; increment	0 – 180°, 1.0°
Integration parameters A, B, EMS	11.6, 1.3, 0.037
θ Range for data collection	3° to 30°
Range in *hkl*	± 6, ± 16, ± 10
Total no. of reflections	2098
Independent reflections	352 ($R_{int} = 0.0915$)
Reflections with $I > 2\sigma(I)$	252 ($R_{sigma} = 0.1128$)
Data / parameters	352 / 16
Goodness-of-fit on F^2	0.770
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0396$; $wR2 = 0.0419$
R Indices (all data)	$R1 = 0.0785$; $wR2 = 0.0471$
Extinction coefficient	0.00064(9)
Largest diff. peak and hole	2.27 and -2.75 e/Å^3

Experimental Section

Synthesis

Starting materials for the preparation of $BaIrIn_2$ were a barium rod (Johnson Matthey, > 99%), iridium powder (Degussa-Hüls, 200 mesh, > 99.9%), and indium shot (ChemPur, > 99.99%). The barium rod was cut into smaller pieces under paraffin oil and subsequently washed with *n*-hexane. The paraffin oil and *n*-hexane were dried over sodium wire. The compact barium pieces were kept under argon in Schlenk tubes. The argon was purified over silica gel, molecular sieves, and titanium sponge (900 K).

Small barium pieces were subsequently mixed with a cold-pressed pellet of iridium and pieces of the indium shot in the ideal 1:1:2 atomic ratio and sealed in a tantalum tube under an argon pressure of about 600 mbar [10]. The tantalum tube was placed in a water-cooled quartz sample chamber [11] of a high-frequency furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300) and first heated within one hour

0932–0776 / 05 / 0100–0118 $ 06.00 © 2005 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

Table 2. Atomic coordinates and anisotropic displacement parameters (pm^2) for $BaIrIn_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$. $U_{12} = U_{13} = 0$.

Atom	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{eq}
Ba	4*c*	0	0.0542(1)	1/4	126(7)	85(9)	121(11)	0	111(4)
Ir	4*c*	0	0.7814(1)	1/4	83(5)	91(6)	72(7)	0	82(3)
In	8*f*	0	0.3362(1)	0.0550(2)	86(5)	111(7)	93(9)	−2(5)	97(3)

Table 3. Interatomic distances (pm) of $BaIrIn_2$ (standard deviations in parentheses), calculated with the powder lattice parameters.

Ba:	1	Ir	314.1(2)	In:	2	Ir	279.0(1)
	2	Ir	342.8(2)		1	Ir	280.6(2)
	4	In	354.2(1)		2	In	310.4(2)
	2	In	360.7(2)		1	In	314.4(3)
	4	In	369.9(2)		2	Ba	354.2(1)
	2	Ba	421.9(1)		1	Ba	360.7(2)
Ir:	4	In	279.0(1)		2	Ba	369.9(2)
	2	In	280.6(2)		1	In	387.5(3)
	1	Ba	314.1(2)				
	2	Ba	342.8(2)				

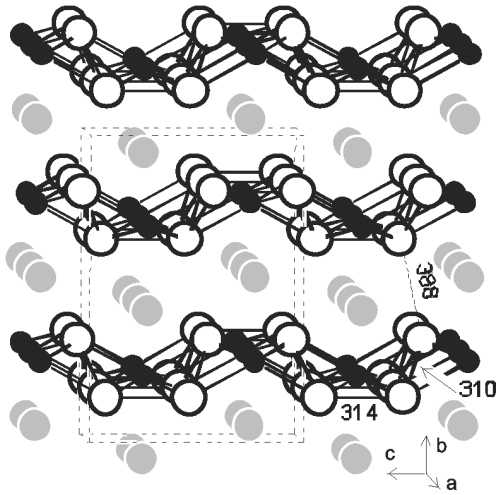

Fig. 1. Perspective view of the $BaIrIn_2$ structure approximately along the *a* axis. The barium, iridium, and indium atoms are drawn as grey, black, and open circles, respectively. Some relevant In–In distances are indicated. The two-dimensional $[IrIn_2]$ polyanion is emphasized.

to *ca.* 1300 K. The sample was annealed at that temperature for two min, then cooled to *ca.* 700 K within 40 min, kept at 700 K for 5 h, and finally quenched by switching off the generator.

The silvery grey sample could readily be separated from the tantalum tube by mechanical fragmentation. Since $BaIrIn_2$ is very sensitive to humidity, the sample was kept in a Schlenk tube.

X-ray film data and structure refinement

$BaIrIn_2$ was characterized through a Guinier powder pattern using Cu-$K_{\alpha 1}$ radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The Guinier camera was equipped with an image plate system (Fujifilm BAS–1800). The indexing of the powder data was facilitated by an intensity calculation [12] using the atomic parameters of the refined structure. The orthorhombic lattice parameters (Table 1) were obtained by least-squares fits of the Guinier data. The powder data compare well with the previous ones [5] of $a = 443.41(8)$, $b = 1150.7(2)$, and $c = 806.4(1)$ pm.

Irregularly shaped single crystals were isolated from the annealed sample by mechanical fragmentation under dried paraffin oil, sealed in small quartz capillaries and first examined on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS–1800) in order to establish suitability for intensity data collection. Single crystal intensity data were collected at room temperature on a Stoe IPDS–II diffractometer with graphite monochromatized MoK_α radiation. A numerical absorption correction was applied to the data. All relevant crystallographic data for the data collection and evaluation are listed in Table 1.

Analysis of the data set was consistent with space group *Cmcm*. The atomic positions of $BaRhIn_2$ [5] were then taken as starting values and the structure was refined using SHELXL-97 (full-matrix least-squares on F_o^2) [13] with anisotropic atomic displacement parameters for all sites. The occupancy parameters were refined in a separate series of least-squares cycles in order to check for the correct composition. They varied between 99(1)% for Ir and 101(1)% for In. Thus, all sites were fully occupied within one standard deviation. In the last cycles, the ideal occupancies were assumed again. A final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3. Further details on the structure refinement are available*.

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD–414434.

Discussion

The structure of $BaIrIn_2$ was refined from single crystal diffractometer data. In contrast to the respective calcium and strontium compounds, the $BaTIn_2$ structures exhibit pronounced two-dimensional $[TIn_2]$ polyanions as emphasized for $BaIrIn_2$ in Fig. 1. The Ir–In distances in the two-dimensional $[IrIn_2]$ polyanion of $BaIrIn_2$ (279 – 281 pm) and the three-dimensional $[IrIn_2]$ polyanion of $SrIrIn_2$ (277 – 279 pm) are almost similar and they compare well with the sum of the covalent radii of 276 pm [14]. In $SrIrIn_2$ the polyanionic layers are condensed *via* weak In–In contacts at an In–In distance of 352 pm [4]. These In–In distances are already larger than in elemental tetragonal body-centered indium [15], where each indium atom has four nearest indium neighbours at 325 pm and eight further neighbours at 338 pm. In $BaIrIn_2$ the $[IrIn_2]$ polyanionic layers are held together *via* the barium cations. The In–In distances of 388 pm between the layers cannot be considered as bonding. For further crystal chemical details on the $BaTIn_2$ indides we refer to a previous publication [5].

Acknowledgements

We thank Dr. R.-D. Hoffmann for the intensity data collection and the Degussa-Hüls AG for a generous gift of iridium powder. This work was financially supported by the Deutsche Forschungsgemeinschaft.

[1] V. I. Zaremba, O. Ya. Zakharko, Ya. M. Kalychak, O. I. Bodak, Dopov. Akad. Nauk. Ukr. RSR, Ser. B 44 (1987).
[2] L. V. Sysa, Ya. M. Kalychak, Crystallogr. Rep. **38**, 278 (1993).
[3] R.-D. Hoffmann, R. Pöttgen, G. A. Landrum, R. Dronskowski, B. Künnen, G. Kotzyba, Z. Anorg. Allg. Chem. **625**, 789 (1999).
[4] R.-D. Hoffmann, U. Ch. Rodewald, R. Pöttgen, Z. Naturforsch. **54b**, 38 (1999).
[5] R.-D. Hoffmann, R. Pöttgen, Chem. Eur. J. **7**, 382 (2001).
[6] H. Perlitz, A. Westgren, Ark. Kemi, Mineral. Geol. **16b**, 1 (1943).
[7] A. Iandelli, Z. Anorg. Allg. Chem. **330**, 221 (1964).
[8] G. Bruzzone, G. B. Bonino, Atti Accad. Nat. Lincei **48**, 235 (1970).
[9] G. Nuspl, K. Polborn, J. Evers, G. A. Landrum, R. Hoffmann, Inorg. Chem. **35**, 6922 (1996).
[10] R. Pöttgen, Th. Gulden, A. Simon, GIT-Laborfachzeitschrift **43**, 133 (1999).
[11] D. Kußmann, R.-D. Hoffmann, R. Pöttgen, Z. Anorg. Allg. Chem. **624**, 1727 (1998).
[12] K. Yvon, W. Jeitschko, E. Parthé, J. Appl. Crystallogr. **10**, 73 (1977).
[13] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[14] J. Emsley, The Elements, Oxford University Press, Oxford (1999).
[15] J. Donohue, The Structures of the Elements, Wiley, New York (1974).