Synthesis and Crystal Structure of Barium Indide Ba_9In_4

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A new binary compound in the system Ba-In has been synthesized and structurally characterized. According to single-crystal X-ray diffraction data Ba_9In_4 crystallizes with tetragonal symmetry (*I*4/*m*, a = 13.948(2), c = 5.888(1) Å, V = 1145.5(3) Å^3, Z = 2, $R1$ = 0.037, $wR2$ = 0.071). The very moisture-sensitive compound could be obtained as single phase by reaction of metallic barium and indium at 350 °C.

Key words: Indium, Barium, Binary Indides, Crystal Structure

Introduction

Numerous compounds have been reported to exist in the binary *AE*-In (*AE* = alkaline earth metal) systems. The Ca-In and Sr-In systems were re-examined in the last ten years, however, only the In-rich part of the Ba-In system has been structurally described. Five compounds are known in the system Ca-In, *i. e.* Ca_3In, Ca_8In_3, Ca_2In, CaIn, and $CaIn_2$ [1 – 4], and thirteen compounds have been proposed in the Sr-In system, but only seven of them were confirmed: $Sr_{2.33}In_{0.92}$, Sr_5In_3, $Sr_{11}In_7$, SrIn, $SrIn_2$, Sr_3In_{11}, and $SrIn_4$ [2, 3, 5, 6]. Investigations of the system Ba-In were started in the 1970ies revealing six new compounds, $Ba_{13}In$, Ba_3In, Ba_2In, BaIn, $BaIn_2$, and $BaIn_4$ [7 – 10]. The last three of these are well described [3]. In contrast, still no details about the phases $Ba_{13}In$, Ba_3In, and Ba_2In are known. According to thermal analysis data the latter transforms from α-Ba_2In into a high-temperature modification, β-Ba_2In, at 505 °C [8].

Results and Discussion

A sample with the composition Ba_2In was prepared in order to investigate the structure of the previously identified compound α-Ba_2In. However, the X-ray investigation of selected single-crystals resulted in a composition Ba_9In_4, and the powder pattern of the complete sample showed Ba_9In_4 to be the main phase. The subsequent preparation of a sample with the appropriate stoichiometric ratio Ba:In = 9:4 led to a single phase product.

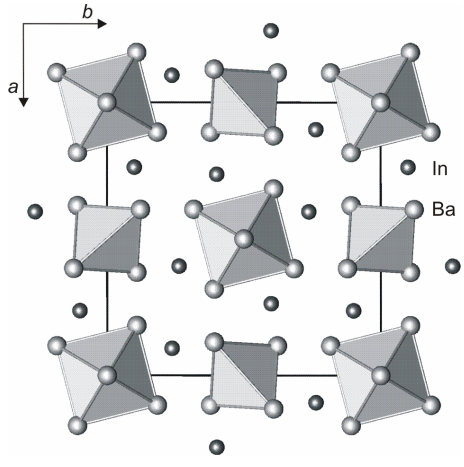

Fig. 1. Crystal structure of Ba_9In_4 projected along [001].

Details of the data collection and structure refinement are listed in Table 1, positional and anisotropic displacement parameters in Tables 2 and 3. Ba_9In_4 crystallizes in the $Nb_5Si_4Cu_4$ structure type [11], characterized by rows of corner-sharing Ba_6 (Nb_6) octahedra along [001] with In (Si) atoms above all their faces. The space between these rows is filled with chains of edge-sharing Ba_4 (Cu_4) tetrahedra (Fig. 1). According to its structure, the composition of Ba_9In_4 can thus be described as $(Ba_4Ba_{2/2}In_{8/2})(Ba_{4/2})_2 \cong Ba_9In_4$. Of course, what might be a meaningful description in the case of $Nb_5Si_4Cu_4$ due to the different bonding character Si–Nb *vs.* Si–Cu is rather artificial when it comes to $Ba_9In_4 \cong (Ba_4Ba_{2/2})(Ba_{4/2})_2In_4$, because the coordination of In in both octahedral and tetrahedral arrangements of the same element does not result in any clear priority in bonding. The In atom is surrounded by a highly distorted trigonal prism of Ba atoms with 5.89 Å height and Ba–Ba distances ranging from 4.04 to 4.34 Å in the trigonal face (Fig. 2). Two rectangular faces are capped by Ba atoms at Ba–In distances of 3.50 and 3.59 Å, whereas the third sees two, one at 3.72 Å and the other further away at 4.28 Å. The Ba–In distances in that coordination

Table 1. Crystal data and numbers pertinent to data collection and refinement of Ba_9In_4.

Empirical formula	Ba_9In_4
Formula weight	3390.7
Temperature, K	293(2)
Radiation; wavelength, Å	AgK_α; 0.56086
Crystal system	tetragonal
Space group	*I*4/*m*
a, Å	13.948(2)
c, Å	5.888(1)
Volume, Å^3	1145.5(3)
Z	2
Density (calcd.), g cm^{-3}	4.92
μ(AgK_α), mm^{-1}	10.1
F(000), e	1400
θ range deg	3.76 – 36.51
Index ranges *hkl*	−22, +22, ±9
Reflections collected / independent	11322 / 1519
Data averaging: R_{int} / R_σ	0.069 / 0.033
Data / ref. parameters	1519 / 22
Final indices *R*1 / *wR*2 [$I \geq 2\sigma(I)$][a]	0.037 / 0.071
Indices *R*1 / *wR*2 (all data)	0.049 / 0.075
Goodness-of-fit on F^2 [b]	1.14
Largest diff. peak and hole, e$^-$/Å^3	1.58 and −1.51

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Atomic coordinates and equivalent displacement parameters (Å^2) for Ba_9In_4.

Atom	Site	*x*	*y*	*z*	U_{eq}
Ba1	2*b*	0	0	1/2	0.0214(1)
Ba2	8*h*	0.10852(2)	0.18309(2)	0	0.02475(6)
Ba3	8*h*	0.39171(3)	0.12202(3)	0	0.03240(8)
In1	8*h*	0.26291(3)	0.40044(3)	0	0.02631(7)

polyhedron range from 3.50 to 4.28 Å, averaging to 3.81 Å to be compared with the sum of atomic radii, 3.91 Å. The closest Ba–Ba contacts are in the range 4.01 to 4.36 Å. In contrast to the three known structures of Ba-In compounds in the In-rich part of the phase diagram, no In–In bonds occur in Ba_9In_4, as expected.

Conclusions

Ba_9In_4 has been synthesized from barium and indium and characterized by single-crystal and powder X-ray diffraction. This compound obviously substitutes the earlier described phase "Ba_2In". In contrast to $BaIn_4$, $BaIn_2$ and BaIn it does not follow the Zintl-Klemm concept. The compositions and crystal structures of the other two previously reported Ba-rich phases Ba_3In and $Ba_{13}In$ have still to be clarified.

Table 3. Anisotropic displacement parameters (Å^2) for Ba_9In_4. $U_{12} = U_{13} = 0$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}
Ba1	0.0216(1)	U_{11}	0.0212(2)	0
Ba2	0.0249(1)	0.0220(1)	0.0274(1)	0.0001(1)
Ba3	0.0330(2)	0.0418(2)	0.0224(1)	−0.0122(1)
In1	0.0238(2)	0.0327(2)	0.0224(1)	−0.0017(1)

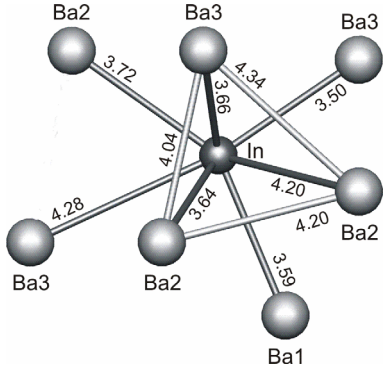

Fig. 2. Coordination polyhedron around In in Ba_9In_4.

Experimental Section

Reagents and synthesis

The compound $Ba_9In_4$was synthesized from the stoichiometric amounts of Ba metal (Merck, 99.9 %, distilled twice with intermediate heating at 1270 K under vacuum in a closed Ta container to remove hydrogen) and In metal (Merck 99.99 %) placed in a Ta ampoule under an Ar atmosphere. The ampoule was closed by arc-welding, and the reaction took place at 650 °C for 5 d, followed by cooling to 350 °C at 1 K h^{-1} and annealing at this temperature for 10 d. The resulting product was nearly single phase with only traces of impurities according to X-ray powder diffraction analysis. All handling of the educts as well as of the very moisture-sensitive product were performed under argon atmosphere in a glove box or using Schlenk techniques.

X-Ray investigation

Single crystals of Ba_9In_4 were sealed under argon atmosphere into glass capillaries, and their X-ray diffraction data were collected at r. t. using a Stoe IPDS-I diffractometer with monochromatized AgK_α radiation (oscillation around the ω axis). The starting atomic parameters derived *via* Direct Methods using the program SIR-97 [12] were subsequently refined by full-matrix least-squares on F^2 with the program SHELXL-97 [13] within the WINGX program package [14]. X-Ray powder diffraction patterns were collected on a powder diffractometer Stoe STADI P with monochromatized Mo$K_{\alpha1}$ radiation. ($10 \leq 2\,\theta \leq 28°$, step size 0.1°, 120 s per step).

Further details of the crystal structure investigation of Ba_9In_4 may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421410.

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