MS25-P5 New binary and Cd-substituted barium mercurides: $BaHg_3$, $Ba_3(Hg/Cd)_{11}$ and $Ba_7(Hg/Cd)_{32}$

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Recently, we reported on the new binary Hg-rich Ba mercurides $BaHg_6$ [1] and $Ba_{20}Hg_{103}$ (together with a small Zn/Cd substitution) [2]. For the Ba-richer compounds in the range $BaHg_3$ to $BaHg_{\sim 5}$ (and again their Cd-substituted derivatives) experimental (synthesis from stoichiometric amount of the elements at T_{max} of 800 to 900 ºC) and crystallographic (single crystal) investigation also require a further revision of the Ba-Hg phase diagram [3] and the composition and structure of the 7:31 phases. Additionally, the new phase $BaHg_3$ was obtained. It crystallizes with a new structure type in the rare space group *P*4/*ncc* (a = 1193.04(3), c = 958.02(5) pm, Z = 12, $R1$ = 0.0461, fig. a). The three crystallographically different Hg atoms form holey distorted flat square pyramids, a structure motif which is similarly found in the 3:11 compounds (see below and fig. (b) and (c)) and in K_5Hg_{19} [4]. The Ba polyhedra exhibit coordination numbers of 12 and 14. The electronic bandstructure, which has been calculated within the framework of FP-LAPW theory, exhibits a pronounced pseudo band gap.

The phase width of the Cd-containing La_3Al_{11}-type structure (orthorhombic *Immm*, fig. (c)) reaches from the already described fully ordered phase Ba_3CdHg_{10} (9.1 % Cd, [5]) up to a Cd content of 47 % ($Ba_3Cd_{5.2}Hg_{5.8}$). At the same 3:11 composition, but with a further reduced Cd proportion of only 3 %, the orthorhombic Ba_3ZnHg_{10}-type [2] (fig. (b)) was obtained, which also occurs with a very small Ga-content in $Ba_3Ga_{0.2}Hg_{10.8}$ [5].

The composition and structure of the hexagonal '7:31' compounds (powder data for the mercuride [3], single crystal data film data for the cadmide [6]) were investigated for the whole Hg-Cd series. Herein, the formation of different types of orthorhombic and monoclinic superstructures (with complex twinning) was observed, which all exhibit M_4 squares instead of disordered M_3 triangles as common faces between the Ba(4) polyhedra (gold in fig. (d)) around the pseudo-hexagonal c axis, leading to a 7:32 instead of the originally reported 7:31 composition.

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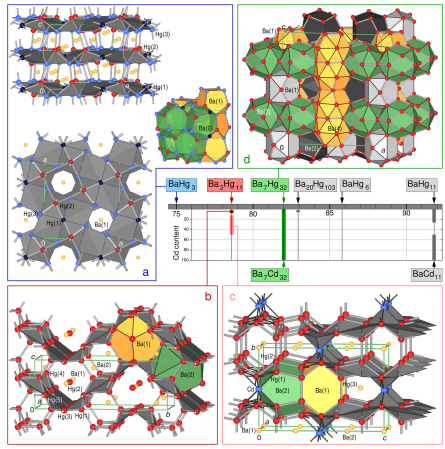

Figure 1. Phase widths and crystal structures of Ba mercurides and its ternary Cd derivatives: (a) $BaHg_3$ (new structure type); (b, c): Cd-containing 3:11 phases of the Ba_3ZnHg_{10}- and the La_3Al_{11}-type, (d): polyhedra representation of the structure of the corrected pseudohexagonal 7:32 compounds.

Keywords: Mercurides, Synthesis, Bandstructure calculation