Zink-reiche Erdalkalimetall-Verbindungen AZn_5 und AZn_{11}: Kristallstrukturen und chemische Bindung

Zinc-rich Alkaline Earth Compounds AZn_5 and AZn_{11}: Crystal Structures and Chemical Bonding

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The zinc-rich compounds in the binary systems with the heavier alkaline earth elements $CaZn_{11}$ and AZn_5 (A = Ca, Sr, Ba) have been synthesized from melts of the elements. Their crystal structures, which were in principle known from very early powder or single crystal film experiments, have been refined on the basis of modern single crystal X-ray data. $CaZn_5$ (hexagonal, space group $P6/mmm$, a = 538.99(2), c = 424.56(1) pm, Z = 1, $R1$ = 0.0144) crystallizes with the $CaCu_5$ structure type and exhibits a small but distinct phase width $Ca_{1-x}Zn_{5+2x}$ up to a composition of $Ca_{0.87}Zn_{5.26}$ (a = 533.38(1), c = 430.04(1) pm, $R1$ = 0.0170) achieved through a gradual substitution of Ca by Zn_2 dumbbells. The high-temperature form of $SrZn_5$, which was prepared by quenching of melted samples, also adopts the ideal $CaCu_5$ structure type (a = 554.1(2), c = 428.2(2) pm, $R1$ = 0.0314). The room temperature modification of $SrZn_5$ (orthorhombic, space group $Pnma$, a = 1313.3(3), b = 529.91(10), c = 669.72(13) pm, Z = 4, $R1$ = 0.0349) forms a singular structure, whereas the Ba compound of corresponding composition (orthorhombic, space group $Cmcm$, a = 1078.3(7), b = 839.8(5), c = 532.0(3) pm, Z = 4, $R1$ = 0.0281) crystallizes with a third, also rather uncommon structure. For the compound $CaZn_{11}$ ($BaCd_{11}$ structure type; tetragonal, space group $I4_1/amd$, a = 1068.11(10), c = 682.81(7) pm, Z = 4, $R1$ = 0.0299) the originally proposed structure type was confirmed and also refined using single crystal data. The chemical bonding in all title compounds is analyzed using FP-LAPW band structure methods. Together with geometrical criteria and observed valence electron numbers of isotypic compounds, the results are used to compare and discuss the stability of the different structures of the intermetallic phases in the systems AZn_5 and AM_{11} (M = Zn, Cd, Hg).

Key words: Zinc, Intermetallics, Band Structure Calculation