$CaAg_xZn_{1-x}$: Zwischen CrB- und FeB-Strukturtyp – Eine Studie zu elektronischen Einflüssen auf die Stapelung von Zick-Zack-Ketten in polaren Erdalkalimetall-Monometalliden

$CaAg_xZn_{1-x}$: Between CrB and FeB Structure Type – A Study on Electronic Factors Influencing the Stacking of Zig-zag Chains in Polar Alkaline Earth Monometallides

Wiebke Harms, Viktoria Mihajlov, Marco Wendorff und Caroline Röhr

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstraße 21, D-79104 Freiburg, Germany

Reprint requests to Prof. Dr. C. Röhr. E-mail: caroline@ruby.chemie.uni-freiburg.de

Z. Naturforsch. **2009**, *64b,* 1127 – 1142; received August 9, 2009

Depending on both electronic (valence electron numbers) and geometric (atom size ratios) characteristics of the contributing elements, the 1 : 1 compounds $A^{II}M$ of the heavier alkaline earth elements A and electron-rich transition metals M form the well known CrB or FeB structure types. Both structure types exhibit M zig-zag chains, which are stacked in different orientations. In systematic studies of the pseudo-binary section $CaAg_xZn_{1-x}$ four new ternary phases with different stacking variants between the CrB (cubic stacking, c) and the FeB (hexagonal stacking, h_2) structure type have been prepared and characterized on the basis of single crystal X-ray data. Starting from CaAg (CrB type, orthorhombic, space group *Cmcm*, a = 405.22(7), b = 1144.7(2), c = 464.43(11) pm, Z = 4, $R1$ = 0.0197), up to 24 % of Ag ($CaAg_{0.76}Zn_{0.24}$: a = 408.6(2), b = 1144.3(5), c = 460.7(2) pm, $R1$ = 0.0208) can be substituted by zinc without a change in the structure type. Close to the 1 : 1 ratio of Ag and Zn, the HT-TbNi structure type with the stacking sequence $(hc_2)_2$, *i. e.* 33 % hexagonality ($CaAg_{0.52}Zn_{0.48}$: orthorhombic, space group *Pnma*, a = 2345.47(6), b = 454.370(10), c = 609.950(10) pm, Z = 12, $R1$ = 0.0298) is formed, followed by the SrAg type with 50 % hexagonality ($CaAg_{0.48}Zn_{0.52}$: orthorhombic, space group *Pnma*, a = 1571.0(2), b = 451.50(7), c = 609.80(9) pm, Z = 8, $R1$ = 0.0733). The amount of hexagonal stacking is further increased with increasing Zn content in $CaAg_{0.33}Zn_{0.67}$ ($Gd_{0.7}Y_{0.3}$ structure type, h_2c stacking, 67 % hexagonality, monoclinic, space group $P2_1/m$, a = 610.39(9), b = 448.53(5), c = 1195.7(2) pm, β = 96.829(14)°, Z = 3, $R1$ = 0.0221). Finally, a pure hexagonal stacking sequence, *i. e.* the FeB structure type (orthorhombic, space group *Pnma*, Z = 4) is observed from $CaAg_{0.14}Zn_{0.86}$ (a = 804.57(2), b = 443.050(10), c = 611.350(10) pm, $R1$ = 0.0131) to $CaAg_{0.06}Zn_{0.94}$ (a = 806.1(3), b = 441.0(2), c = 610.4(3) pm, $R1$ = 0.0255). Intriguingly, the series ends with the binary compound CaZn, which again crystallizes with the CrB structure type exhibiting cubic stacking of the zig-zag chains only (0 % hexagonality). In an accompanying computational study, the chemical bonding in the series Ca(Ge/Ga/Zn/Ag) of isotypic binary metallides with variable valence electron numbers has been analyzed using FP-LAPW band structure methods. The electronic structures of the two border stacking variants are compared using the crystal data of CaZn (CrB type) and $CaAg_{0.06}Zn_{0.94}$ (FeB type). Geometrical and electronic criteria are used to compare and discuss the stability ranges of the different stacking variants inbetween the CrB and the FeB structure type found in polar intermetallic 1 : 1 phases.

Key words: Intermetallic Compounds, Silver, Zinc, Crystal Structure, Band Structure Calculation