MS15-2-7 From AM_5 to A_2M_{17}: new crystallographically related intermetallics
#MS15-2-7

M. Otteny [1], K. Köhler [1], M. Wendorff [1], C. Röhr [1]
[1]Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität - Freiburg (Germany)

Abstract
In the systems Sr-Mg-Cd and Ba-Mg-Cd [1], three new ternary intermetallics A_2M_{17} [2] were obtained, which are crystallographically related to the $CaCu_5$-type structure. The corresponding relations will be demonstrated applying the Bärnighausen group-subgroup formalism [3]. Besides the common $CaCu_5$-type ($P6/mmm$, a≈511, c≈405 pm), which is not observed for either of the border phases of the ternary systems, the trigonal Th_2Zn_{17} ($R\bar{3}m$, a≈906, c≈1323 pm) and the hexagonal Th_2Ni_{17} ($P6_3/mmc$, a≈836, c≈816 pm) structure type as well as a new related structure ($P6_3/mmc$, a≈1033 c≈2021 pm) were synthesised.Their syntheses were performed by heating the elements under Ar atmosphere up to 750/800 °C (for A=Sr/Ba) followed by cooling with rates of 5-10 K/h.
The $CaCu_5$-type compounds (Fig. 1, a) are built up from |:AA:| stacked Mg/Cd kagomé nets (*M*, green), forming trigonal bipyramids M_5 (rose), connected via all vertices. Within the resulting large hexagonal channels running along [001] the Sr/Ba cations (pink, CN=18+2) are located. In the system Ba-Mg-Cd, the $CaCu_5$-type structure appears close to the composition $BaMg_{3.5}Cd_{1.5}$ only. Herein, both crystallographic *M* sites are statistically occupied by Mg and Cd.
In the structures forming the Th_2Zn_{17}-type (Fig. 1, b) each third of the *A* cations is replaced by M_2 dumbbells (blue-magenta). In the Ba system, this structure type was already known from older film data - which has been similarly verified by a recent single crystal structure refinement - for Ba_2Mg_{17} [4], in which up to 41.7% of the Mg atoms could be replaced by Cd. For *A*=Sr, it was only found in ternary phases with an approximate equimolar Mg:Cd ratio.
The Th_2Ni_{17} (Fig. 1, c) and the new structure type (Fig. 1, d) exhibit two different types of channels: For Th_2Ni_{17}, 1/3 of the channels are occupied by *A* cations exclusively, the remaining channels are alternatingly stuffed by *A* cations and M_2 dumbbels. For *A*=Sr, the latter structure type is yet known for Sr_2Mg_{17} [5], which hence has been reinvestigated herein. For *A*=Ba, a single Mg-rich Th_2Ni_{17} phase with the composition $Ba_2Mg_{14.4}Cd_{2.6}$ was obtained.In the newly characterized A_2M_{17} structure of this family 1/3 of the channels are alternatingly occupied by A/M_2, whereas in the remaining channels every 5th *A* cation is replaced by an M_2 dumbbell. This new structure type was obtained for *A*=Sr and with Cd proportions between 26 and 36%.
For the structures containing M_2 dumbbells, a preferred occupation of the concerning positions with Mg is observed. This can be explained by its decreased electronegativity, which is confirmed by the Bader charges obtained by lo+APW-DFT bandstructure calculations. The crystal-chemical parameters determining the stability of the three different A_2M_{17} structure types as well as the 'colouring' (Mg/Cd distribution at the *M* sites) will be discussed in this contribution.

References
[1] K. Köhler, C. Röhr, Z. Kristallogr. Suppl. 42, 162 (2022).[2] W. Steurer, J. Dschemuchadse, Intermetallics: Structures, Properties, and Statistics, 2016, Oxford University Press (vol 26, ed 2)[3] H. Bärnighausen, Match, Com. in Math. Chem. 9, 139 (1980).[4] E. Gladyshevskii, Sov. Phys. Crystallogr. 6, 207-208 (1961).[5] P. Kripyakevich, Kristallografiya, 7, 31-42 (1962).