Poster Presentations

[MS24-P12] A systematic crystal chemical study of calcium rich mixed tetrelides.

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In this work, the systematic investigation of ternary Calcium-rich tetrelides Ca_xM_y (M=Ge, Sn, Pb) is presented. Therefore, the corresponding isotypic binary phases of the compositions x:y=2:1, 5:3 and 1:1 have been taken as starting points. 2:1: The phases $Ca_2Sn_zGe_{1-z}$ crystallize in the well known Co_2Si structure type (Pnma) [1]. The noble gas isosteric Sn and Ge ions, accordingly, are substituted against each other in a statistical manner without forming any kind of superstructure and the lattice parameters and unit cell volumes satisfy Vegard's law. 5:3: Nearly all calcium tetrelides A_5M_3 [2] crystallize in the Cr_5B_3 structure type (I4/mcm) hence also obeying the Zintl concept ($5 \cdot Ca^{2+} + {}^{1b}[M_2]^{6-} + [M]^{4-}$). The only exception is Ca_5Pb_3 crystallizing in an own structure type (P63mc). Therefore, it is not remarkable, that the phases containing Ge or Sn also show a continuous phase width $Ca_5[SnzGe_{3-z}]$ (e. g. z=2.02, I4/mcm, a=795.1(1), c=1506.4(1) pm, R1=0.024), whereas in Ca_5Pb_3 not any lead atom could be substituted by germanium. According to the preferred occupation of the M2 dumbbells by germanium, the coloring of the anions is terminated by size effects only. 1:1: The monotetrelides [2,3] of germanium and tin and the whole series CaSnzGe1−z both form the CrB structure type (e. g. z=0.37, Cmcm, a=465.6(1), b=1108.0(3), c=411.5(1) pm, R1= 0.032) exhibiting zigzag chains (2bM2−). CaPb crystallizes in the AuCu structure type. Hence, it is not surprising, that Ge in CaGe could only be substituted by small amounts of Pb (8%). 3:2−5:3: In the small x:y composition range between 5:3 and 3:2 the compounds $Ca_{26}Sn_{17-z}Gez$ (e.g. z=1.7, P4bm, a = 1242.3(1), c = 1664.3(1) pm, R1 = 0.029), $Ca_{31}Sn_{20}$ [5,6] and $Ca_{36}Sn_{23}$ [2] can be located. They show linear Mn chain pieces of differing lengths n, wherefore they no longer follow Zintl's electron counting rule. Beyond that, their structures exhibit M2 dumbbells and isolated M anions. All three structures can be described via the general formula $A_{5m}+{}_6M_{3m}+5$ [4] and can be built up from varying numbers of blocks A_3M_2 and A_5M_3 which structurally correspond to the Y_3Rh_2 and the W_5Si_3 type (leading to chain lengths ofMn with n=4 ($Ca_{26}Sn_{17}-zGez$), n=5 ($Ca_{31}Sn_{20}$) and n=6 ($Ca_{36}Sn_{23}$), respectively) Interestingly, these two structure types are not observed as binary compounds in the systems Ca-Ge-Sn and Ca-Ge-Pb.

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