Poster

Ca(Zn1−xCdx)≈3/5: Disorder models for known and new hexagonal intermetallics

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Starting from the long-known hexagonal zincides $CaZn_{3+x}$ [1] and $CaZn_{5+x}$ [2] a small Zn↔Cd substitution leads to ternary variants of these partly disordered border compounds. Similar to the border phase 'CaZn3', the ternary derivative Ca3M8[Ca]$_x$][Zn$_3$]$_{1-x}$ [x=1/3; hexagonal, space group $P63/mmc$, a=936.7(1), c=739.2(1) pm, $R1$=0.024] exhibits CaIn2-type structure elements besides sixfold μ_3-capped icosahedra (Fig. 1 b: yellow polyhedra).The latter follows from the dissection of the infinite columns of face-sharing icosahedra (cf. $BaLi_4$-type) by a 2:1 disorder M_3↔Ca (Fig 1 b).

For 'CaM_3', an increased Cd content of approx. 30% resulted in the formation of a new complex again hexagonal phase [space group $P6\bar{}2m$, a=1555.5(1), c=1531.3(1) pm, $R1$=0.087]. In this structure, which is topologically related to the CaCu5-type, [Zn@Zn_{12}] icosahedra (3 Cu of $CaCu_5$, Fig 1a: yellow) are connected via Zn-Zn exo-bond to form |:AA:| stacked kagome nets. The remaining 2 Cu positions are occupied by [Ca@M_{15}] FK15 ccp (dark gray). The large hexagonal channels (Ca site of $CaCu_5$) are stuffed by two [CaM_{16}] polyhedra sharing a common M_3 face. The disorder of this triangle and their surrounding causes the occurence of either cutouts of Zn kagome nets (part I: Ca_5M_{35}) or a Cd-rich building block (part II: Ca_8M_{29}) (Fig. 1 a). The final compound's composition ($Ca_{42.6}M_{100.8}$) is thus between $Ca_{41}M_{104}$ and $Ca_{44}M_{98}$.

In the case of the CaM5 section, a ternary variant of the $EuMg_{5+x}$-type structure [hexagonal, space group $P6_3/mmc$, a=926.7(1), c=942.0(1), $R1$=0.03] appears at a Cd proportion of 25 %. Herein, sixfold $\mu3$ extended double tetrahedra stars (M_{11}, DTS, red in Fig. 1 c) are connected with each other and with chains of empty M_8 cubes (blue). Here, the Cd↔Zn_2 disorder (cf. difference electron densities in Fig. 1 c) within the 00z channels finally lead to the overall composition Ca_6M_{30}[Cd][Zn_2] (=$Ca_3M_{5.5}$).

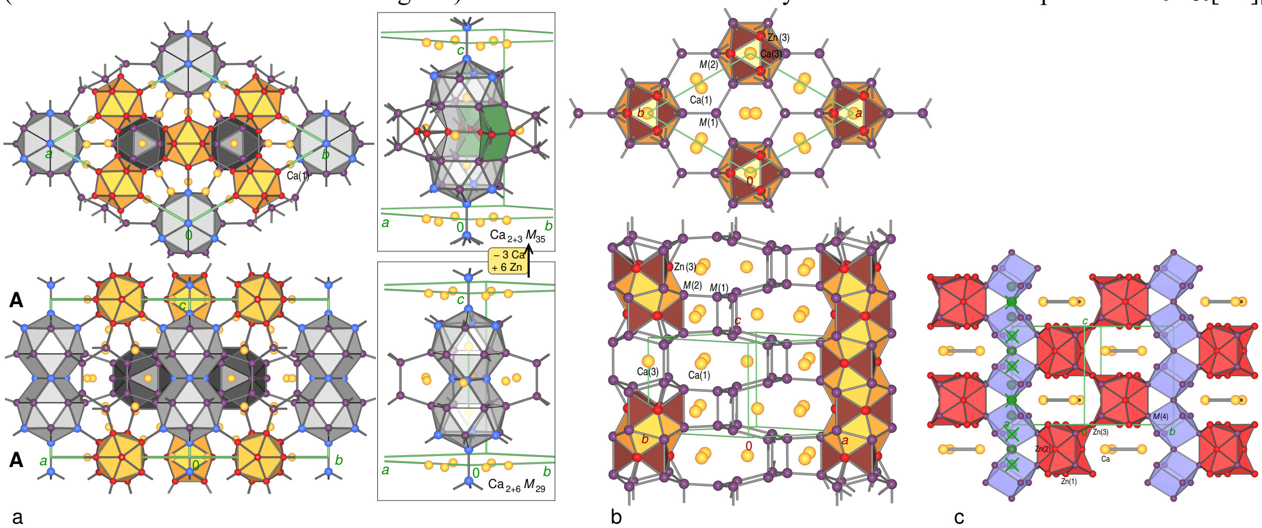

Fig. 1: Crystal structure of the hexagonal title compounds $Ca_{42.6}M_{100.8}$ (a), $Ca_{10}M_{31-\delta}$ (b) and Ca$M_{5.5}$ (c). [Ca/Zn/Cd/M atoms: yellow/red/blue/magenta balls; polyhedra:[M@M_{12}] icosahedra: yellow; [M_5M_6/2$M_{6/2}$] eDTS: red; selected Ca-ccps: gray polyhedra.]

In addition to these new compounds at the CaM3 and CaM5 section, we also report on the Zn/Cd phase widths of the border phases $CaZn_{11}$, $CaCd_6$ (1:1 approximant) and the iQC CaCd [4] as well a on the Ca-rich section Ca_3Cd_2−Ca_5Zn_3. Besides crystallographic aspects, theoretical calculations elucidate the chemical bonding of these polar zincide/cadmides.

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