The first ternary sodium zincides/cadmides: Syntheses and crystal structures of $Na_8(Cd_{1-x}Zn_x)_{17}$ (x=0.124) and $Na_{47}(Cd_{1-x}Zn_x)_{102}$ (x=0.088)

I. Junker[1], K. Köhler[1], C. Röhr[1]

[1]*Institut für Anorganische und Analytische Chemie, University of Freiburg, Germany*

inga.junker@email.uni-freiburg.de

In the course of systematic studies on alkaline earth (A^{II}) zincides/cadmides, we expanded our recent work to include the corresponding sodium phases. In contrast to the wide variety of compounds found in the system Ca-Zn-Cd [1], the number of binary Na metallides is already very limited, ternary compounds were unknown. Besides '$NaCd_2$', both binary sections Na-Zn and Na-Cd contain only one intermetallic compound ($NaZn_{13}$, Na_2Cd_{11}). For these two Na-poor phases we determined a very small substitution of Zn Cd. Close to the complex cubic *Samson* phase '$NaCd_2$' [2], the isotypic ternary Zn-poor compound $Na_{47}Cd_{93}Zn_9$ (*Fd*3*m*, a=3034.2(8) pm, *R*1=0.0482) and a new orthorhombic phase, $Na_8Cd_{14.9}Zn_{2.1}$ (*Pnma*, *a*=972.34(3), *b*=1534.39(5), *c*=1572.74(5) pm, *Z*=4, *R*1=0.0569) are obtained. In the structure of the latter phase [Fig. 1 (a)], most sodium atoms exhibit [NaM_{12}] truncated tetrahedra (tt) as cation coordination polyhedra (ccps; blue/green/magenta polyhedra). In contrast to the *Laves* phases with mainly vertex-sharing [M_4] tetrahedra inbetween the tt, the space between the ccps consists of clusters of six face-sharing [M_4] tetrahedra forming icosahedra caps (light pink). The overall structure exhibits [M_4], [NaM_3] and [Na_2M_2] tetrahedra only, thus representing a further example of a tetrahedrally close packing (t.c.p., FK phase). For $Na_{47}Cd_{93}Zn_9$ the small amount of Zn serves to solve mainly all problems reported for the structure refinement of the pure cadmide '$NaCd_2$' [2-4] and related phases like e.g. β-Mg_2Al_3 (Na/Cd, Mg/Al mixed positions, partial site occupation etc.) and finally allows a reliable bandstructure calculation for these complex structures. The first of the two interpenetrating diamond-like networks [A, Fig. 1 (b)] shows a directly visible analogy to the classical *Laves* phases, whereas network B is commonly described using a cluster shell approach. Regardless of this different description, both substructures are again t.c.p. with tt as Na ccps (blue polyhedra) and therewith also show similar chemical bonding features [5].

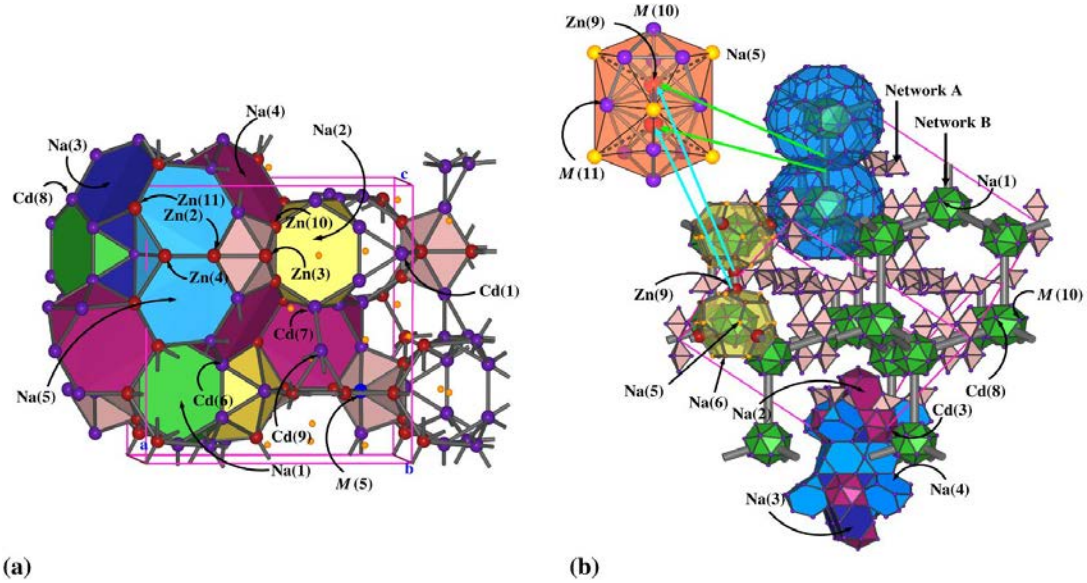

Figure 1: Crystal structure of (a) $Na_8Cd_{14.9}Zn_{2.1}$, (b) $Na_{47}Cd_{93}Zn_9$; $Zn(9)_2$ dumbbells, solving the disorder problem of larger Cd in the overlap region between the outer F_{40}^{76}[Cd(5,6,7,9,11,12)] balls (blue), additionally obliterating the disorder in the F_{16}^{28}[Na(5,6)/Zn(9)] shell (yellow).

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