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### Mixed trielides $A^{II}M^{III}_{2}$ ( $A^{II} = Ca, Sr, Ba;$ $M^{III} = Al, Ga, In$ ): A structural chemical and theoretical study

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The binary alkali earth trielides of the A<sup>II</sup>M<sup>III</sup><sub>2</sub> com-position exhibit a puzzling multitude of structure types [1] ranging from electron precise Zintl compounds like CaIn<sub>2</sub>[2], to the CeCu<sub>2</sub> type (with still four-bonded M<sup>-</sup>) and the AlB<sub>2</sub> structure (with graphite analogue M sheets) to the cubic Laves phase e.g. of CaAl<sub>2</sub>. The examination of the phase stabilities in mixed compounds AM1<sup>III</sup><sub>x</sub>M2<sup>III</sup><sub>2-x</sub> of two trielides allows to separate the stability ranges in a structure map, taking the electronegativity of M (EN) and the radius ratios  $(RR=r_M/r_A)$  into account: The CaIn<sub>2</sub> type is stable at comparatively large RR, for example over the whole range CaGa2- CaIn2 and even up to  $CaAl_{0.6}Ga_{1.4}$  and  $CaAl_{1.2}In_{0.8}$  and in  $SrIn_2$ , in this case also together with a small substitution x in  $SrM1_xIn_{2-x}$  by M1=Al (x=0.4) or M1=Ga (x=0.5). Only in a small RR around CaAl<sub>2</sub> the MgCu<sub>2</sub> type is stable, the Laves phase structure type being in accordance with the v.e.c. [3]. At high DEN and low RR values (e.g. Sr/Ba-Ga), the ideal AlB<sub>2</sub> structure type exhibits a distinct stability range. Starting from  $SrGa_2$  up to x=0.8 Ga can be substituted by Al. The  $CeCu_2$  type, which is domi-nating in AM<sub>2</sub> intermetallics with lower v.e.c., is ob-served in a region of lower RR and  $\Delta$ EN values: In BaIn<sub>2</sub>, a substitution of In by 50 % Al and 30 % Ga is possible without a general structure change, in SrAl<sub>2</sub> this holds for a content of up to 50 % In. For the binary trielides, FP-LAPW band structure calculations for the observed and several hypothe-tical structure types provide insight into the factors favoring the structural stability and also explain the structural changes qualitatively. Starting from the trielides, the influence of a reduced v.e.c. is analysed in a similar way using own and literature data of group 11 and 12 intermetallics (e.g. of the section CaCd<sub>2</sub> - CaGa<sub>2</sub> [4] and the ternary system  $CaAg_2 - CaZn_2 - CaAl_2 [5]$ ).

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# Solid state synthesis and crystal chemistry of new fillowite-type phosphates

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The fillowite group designates Fe-, Mn- and Na-bearing phosphate minerals which occur as primary phases in granitic pegmatites. The fillowite crystal structure is rhombohedral, space group *R*-3, with a = 15.28, c = 43.51 Å, and Z = 18. The simplified chemical formula is Na<sub>2</sub>Ca $M^{2+}$ <sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>, with  $M^{2+}$ = Mn, Mg or Fe<sup>2+</sup> [1]. In order to better understand the crystal chemistry of fillowite-type phosphates, the solid solutions Na<sub>2</sub>Ca( $Mn_{1-x}Mg_x$ )<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub> and Na( $Mn_{1-x}Mg_x$ )<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub> (x = 0 to 1), as well as the compounds Na $M^{2+}_4$ (PO<sub>4</sub>)<sub>3</sub> ( $M^{2+}$  = Ca, Zn, Cd and Ni), were synthesized by solid state reactions in air, between 650 and 900°C at 1 bar. The compositions  $Na_2CaMn_7(PO_4)_6$  and  $NaMn_4(PO_4)_3$  produce single-phase fillowite-type phosphates [2, 3], but the incorporation of Mg within the structure is limited, as shown by the crystallization of  $Mg_2P_2O_7$ . The composition  $NaCd_4(PO_4)_3$  produces a compound with a powder X-ray diffraction pattern similar to that of NaCd<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub> synthesized by Ben Amara *et al.* [4] (a =6.67(2), b = 15.1(3), c = 10.04 Å, space group *Pnma*). The  $Zn_3(PO_4)_2$  and NaZnPO<sub>4</sub>; NaNi<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub> gives Ni<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Na<sub>4</sub>Ni<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>. The crystal structure of single-phase fillowite-type  $NaMn_4(PO_4)_3$  was refined from the powder X-ray diffraction pattern (FeK $\alpha$ ,  $\lambda = 1.9373$  Å), by using the Rietveld method. The atomic coordinates of synthetic  $Na_4(Na,Mn)_4Mn_{22}(PO_4)_{18}$ .0.5 $H_2O[5]$  were used in the starting model, and the final unit-cell parameters are a = 15.294(7) and c = 43.441(1) Å. Due to the large number of parameters (45) atoms in the asymmetric unit), only 3 isotropic displacement parameters were refined, for Mn1-Mn11, Na12-Na31, and O1-O24, respectively. The Mn1 to Mn11 sites are exclusively occupied by Mn, and the Na12 and Na21 sites are occupied by Na. Na against Mn were refined on the Na13 and Na31 sites, and the final occupancy factors are 0.24(2) Na + 0.09(2) Mn and 0.47(5) Na + 0.53(5) Mn, respectively. A similar disordered distribution has already been observed by Keller et al. [5] on the Na13 and Na31 sites, but also on the Na12 site which is completely filled by Na in the compound investigated herein. The application of the Rietveld method to refine the crystal structure of fillowite-type compounds can be successful used to decipher the crystal chemistry of these phosphates, by investigating samples synthesized by solid state reactions which generally do not provide single crystals.

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