Gemischte Erdalkalimetall-Trielide $A^{\mathrm{II}}M1_x^{\mathrm{III}}M2_{2-x}^{\mathrm{III}}$ (A^{II} = Ca, Sr, Ba; M^{III} = Al, Ga, In). Strukturchemische und bindungstheoretische Untersuchungen

Mixed Alkaline Earth Trielides $A^{II}M1_x^{\mathrm{III}}M2_{2-x}^{\mathrm{III}}$ (A^{II} = Ca, Sr, Ba; M^{III}=Al, Ga, In). A Structural and Theoretical Study

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The binary alkaline earth trielides of the composition $A^{\mathrm{II}}M_2^{\mathrm{III}}$ exhibit a puzzling variety of structure types ranging from electron precise Zintl compounds like $CaIn_2$ and KHg_2 (both with networks of four-bonded M^- entities) and the AlB_2 structure type (with graphite analogue M sheets) to the cubic Laves phases *e. g.* of $CaAl_2$. The examination of the phase stabilities of mixed compounds $AM1_x^{\mathrm{III}}M2_{2-x}^{\mathrm{III}}$ of two trielides allows to separate the stability ranges in a structure map by taking the electronegativity differences of M^{III} and A^{II} (ΔEN) and the radius ratios (RR $= r_{\mathrm{M}}/r_{\mathrm{A}}$) into account: The $CaIn_2$-type is stable at comparatively large RR, for example over the whole range $CaGa_2$ – $CaIn_2$ and even up to $CaAl_{0.6}Ga_{1.4}$ and $CaAl_{1.2}In_{0.8}$, and in $SrIn_2$, together with a limited substitution of In by Al or Ga. The KHg_2-type is observed in a region of lower RR: In $BaIn_2$, a substitution of In by 50 % Al and 30 % Ga is possible without a general structure change, in $SrAl_2$ this holds for a content of up to 50 % In. At high ΔEN and low RR values (*e. g.* Sr/Ba-Ga), the ideal AlB_2 structure type exhibits a distinct stability range; only for small RR around $CaAl_2$ the $MgCu_2$-type is stable. FP-LAPW band structure calculations of the binary trielides allow to explain the structural changes qualitatively. In the case of the electron precise phases forming the $CaIn_2$, KHg_2 or AlB_2 structure type, details of the bonding situation (such as M-M distances) as well as differences to other isoelectronic compounds can be rationalized taking the incomplete charge transfer from the alkaline earth towards the triel elements into account. This causes a partial depopulation of some of the bonding and a population of predominantly antibonding states.

Key words: Trielides, Alkaline Earth, Band Structure Calculation, Structure Map