Gemischte Erdalkalimetall-Trielide $A^{II}M_{1}^{III}M_{2}^{III}_{2-x}$
($A^{II} = \text{Ca}, \text{Sr}, \text{Ba}; M^{III} = \text{Al}, \text{Ga}, \text{In}$). Strukturchemische und bindungstheoretische Untersuchungen

Mixed Alkaline Earth Trielides $A^{II}M_{1}^{III}M_{2}^{III}_{2-x}$ ($A^{II} = \text{Ca}, \text{Sr}, \text{Ba}; M^{III} = \text{Al}, \text{Ga}, \text{In}$).
A Structural and Theoretical Study

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The binary alkaline earth trielides of the composition $A^{II}M_{1}^{III}M_{2}^{III}_{2-x}$ 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 $A^{II}M_{1}^{III}M_{2}^{III}_{2-x}$ of two trielides allows to separate the stability ranges in a structure map by taking the electronegativity differences of $M^{III}$ and $A^{II}$ ($\Delta EN$) and the radius ratios ($RR = r_M/r_A$) 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$_1$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 $\Delta EN$ 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