Poster

From Laves to Zintl: $A^{II}(Mg_{1-x}In_x)_2$ compounds (A^{II} = Ca, Sr, Ba)

M. Otteny[1], C. Röhr[1]

[1]*Institute for Inorganic and Analytical Chemistry, University of Freiburg*
markus.otteny@ac.uni-freiburg.de

The binary compounds $A^{II}M_2$ (M=Mg/In) belong to different structure families such as Laves phases, which are dominated by packing effects (FK phase), and Zintl phases, like e.g. the $CaIn_2$- or KHg_2-type structure which obey the well-known electron counting rules. As the crystal structure formation strongly depends on geometric (radii) [1] as well as electronic (e.g. *ve*/*M*) parameters the series of ternary compounds $A^{II}(Mg_{1-x}In_x)_2$ is a case in point to investigate and demonstrate these influences (Fig.1a).

The basic and most famous Laves phases consist of hexagonal (*h*, $MgZn_2$), cubic (*c*, $MgCu_2$) and double hexagonal (*hc*, $MgNi_2$) stacked kagomé layers. For ternary phases and changing *vec* some more complex stacking variants are known [2] as it's the case in the investigated systems. Figure 1b shows the [110] projection of the $(hhc)_3$ stacked Sr compound [x=0.39, $R3m$, a=630.03(3), c=4591.96(2) pm]. In addition, superstructures are known [3], in our case for A^{II}=Ca [x≈0.43, $P6_3/mcm$, a=1063.82(6), c=972.35(6) pm] an ordered $MgZn_2$ variant is observed, which is stabilized by additional Coulomb effects.

Whereas for A^{II}=Ca, Sr the In sites in the $CaIn_2$-type structure is only slightly substituted by Mg, for A^{II}=Sr and Ba, the KHg_2 structure could be observed for x=0.7-1 (A^{II}=Ba) and intermediate x-values (A^{II}=Sr). For Sr with even higher Mg contents the EuAuSn-type structure [Fig.1c, x=0.60, $Imm2$, a=504.34(2), b=4040.62(14), c=878.30(3) pm], a KHg_2 superstructure appears [4]. For A^{II}=Ca (x≈0.75) disordered variants of the AlB_2 -type can be observed in which the hexagonal layers are slightly puckered.

Syntheses were performed by heating the elements under Ar atmosphere up to 1000 °C followed by cooling with rates of 10-15 K/h. The structures of the obtained crystals were determined by single crystal X-ray diffraction. lo+APW-DFT bandstructure calculations of chosen model compounds were performed to discuss the results.

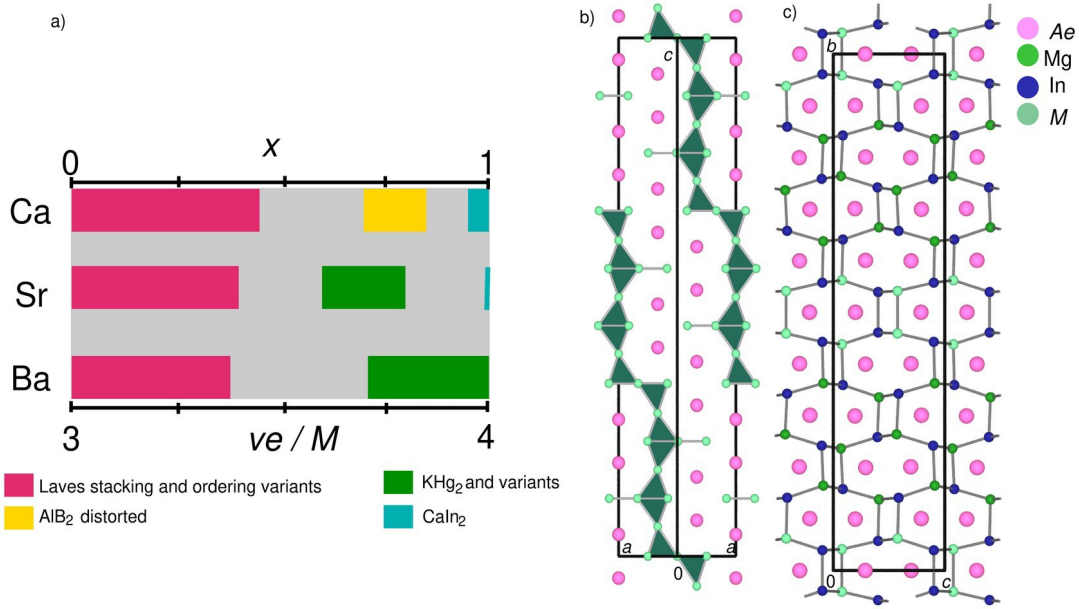

Figure 1. Diagram with an overview of the phase formation for $A^{II}(Mg_{1-x}In_x)_2$ (a), [110] projection of a nine layered Laves variant (b) and [100] projection of a compound forming the EuAuSn-type structure.

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