

MS38-P5 Triel-rich mixed potassium
indides/gallides: Ternary variants of binary
trielides and the new 3:11 compound



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Alkali gallides and indides exhibit a fascinating complex structural chemistry inbetween electron-precise Zintl phases (e.g. NaIn), Wade cluster compounds (e.g. KGa_3), boron-analogs (e.g. $\text{K}_{17}\text{In}_{41}$) and simple intermetallics (like e.g. KIn_4). In a systematic experimental study, mixed In/Ga trielides have been synthesized from the elements to i. explore the 'coloring' of the polyanions with the two triels differing both in size and electronegativity and to ii. explore additional new polyanion topologies.

In the most In-rich indide KIn_4 [2,3] indium can be substituted by up to 1.12 atoms of Ga, which takes the more negatively charged tips of pyramids in the BaAl_4 -type structure [1]. Starting from KGa_3 [4] which is a Zintl phase in containing exo-bond *closo* dodecahedra Ga_8^{2-} and one 4-bonded Ga^- per tripled formula unit, an only small amount of Ga can be substituted against In. This also holds for the related gallide K_3Ga_{13} . The new cluster compound of overall composition $\text{K}_3(\text{Ga}/\text{In})_{11}$ with an In proportion of $\approx 20\%$ and a very small In/Ga phase width crystallizes in a singular orthorhombic structure type (*Cmmm*, $a=1577.39$, $b=3354.71$, $c=654.97$ pm), which has been determined by means of single crystal X-ray data ($R1=4.8\%$). It contains 6 K and 13 triele positions, of which one [In(1)] is a pure In site, four (denoted *M*) are mixed Ga-rich positions (82-92% Ga) and the remaining sites are occupied by Ga only. The In/Ga atoms form two crystallographically different icosahedra [M^1_{12}] [built up from $M(1)/\text{Ga}(2)/M(6)/\text{Ga}(8)$] and [M^2_{12}] [$M(4)/M(9)/\text{Ga}(11)$] (dark gray polyhedra) in a 2:1 ratio and the new [Ga_{13}] cluster [formed by $\text{Ga}(5/7/10/13)$, light gray]. The latter consists of two pentagonal pyramids sharing one corner. The clusters are connected among each other and the 4-bonded $M(3)$ and $\text{Ga}(12)$ atoms. According to $\text{K}_{15}\text{M}_{55}=15 \text{K}^+ + 2[M^1_{12}]^{2-} + [M^2_{12}]^{2-} + [M_{13}]^{3-} + [M]_6$ the compound obeys the Zintl concept extended by the Jemmis electron counting rules, if the new double cluster is counted as 'intermediately' connected [5]. The experimental studies are accompanied by DFT band structure calculations.

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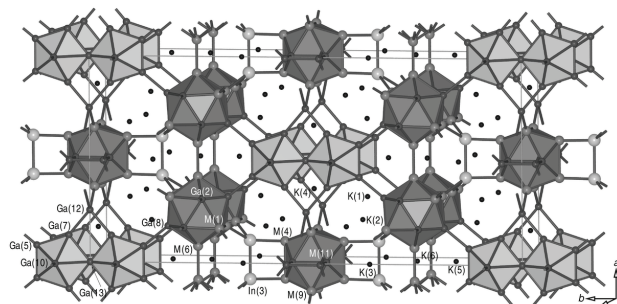


Figure 1. Crystal structure of the new mixed potassium Ga/In trielide $\text{K}_{15}\text{Ga}_{45(2)}\text{In}_{10(2)}$

Keywords: Indides, Gallides, Intermetallics, Bandstructure calculation