MS23-2-3 $A_{49}Ga_2Tl_{108}$ (A = K, Rb), examples of mixed trielides of the $K_{49}Tl_{108}$ structure type
#MS23-2-3

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Abstract

In the course of our studies on the structures of ternary trielides with mixed triel positions (Ga/In) [1] and (Ga/Tl) [2], we succeeded to synthesize the new compounds $K_{49}Ga_2Tl_{108}$ and $Rb_{49}Ga_2Tl_{108}$. Beside A_8GaTl_{10} (A = K, Rb, Cs) [2] with isolated clusters $[Ga@Tl_{10}]^{8-}$, these compounds represent a further example of a structure containing Ga-centred polyhedra, which in this case however are not isolated but part of a three-dimensional network. For the synthesis of both compounds the elemental metals were used in a ratio of $K_{47}Ga_5Tl_{105}$ and $Rb_{49}Ga_{10}Tl_{100}$ respectively. $K_{49}Ga_2Tl_{108}$ could be obtained in pure phase, whereas $Rb_{49}Ga_2Tl_{108}$ was yielded as a byproduct beside the main phase $Rb_{15}Tl_{27}$ [3]. Both compounds are isotypic with the known thallides $K_{49}Tl_{108}$ [4] and $Rb_{49}Tl_{109.7}$ [5] and crystallize in the cubic space group Pm-3 ($K_{49}Ga_2Tl_{108}$, a = 1722.8 pm, $R1$ = 0.045; $Rb_{49}Ga_2Tl_{108}$, a = 1752.7 pm, $R1$ = 0.055). The Ga atoms occupy the Wyckoff positions 1a and 1b, which are empty in $K_{49}Tl_{108}$ and statistically occupied by Tl in $Rb_{49}Tl_{109.7}$. The trielide polyanion thus consits of Ga-centred icosahedra (Fig. 1. c.) which are all-exo bonded to monocapped Tl-centred hexagonal antiprisms of Tl (Fig. 1. b.). Each of those antiprisms is connected via exo-bonds to four icosahedra and nine neighbouring antiprisms, whereby the exo-bond between the capping atoms is connecting the antiprisms to dumbbells (Fig. 1. a.). The two cluster types are arranged in a hierarchic variant of the Cr_3Si-type with the icosahedra occupying the Si positions and the antiprisms taking the Cr positions. The latter are thus forming non-intersecting chains running parallel to the cell axes. The monocapping of the antiprisms causes a symmetry reduction from the space group Pm-3n to Pm-3, which is described by a Bärnighausen group-subgroup tree. The incorporation of Ga into the icosahedra leads to an increase of the volumes ofthese polyhedra from $71.1 \cdot 10^6$ pm^3 to 74.2 resp. $75.4 \cdot 10^6$ pm^3. The Ga-Tl distances amount to 309 pm and are thus enlarged with respect to the Ga-Tl bond lenghts in A_8GaTl_{10} (290 pm). However, the distances nicely correspond to the value of 313 pm expected on the basis of the metallic radii of Ga and Tl. This indicates considerable metallic bonding contributions. The bonding situation in both the binary and the ternary compounds was analyzed on the basis of band structure calculations.

References

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a. Unit Cell b. Hexagonal Antiprism c. Icosahedron