

Pseudosymmetry in Cs₃TaO₄

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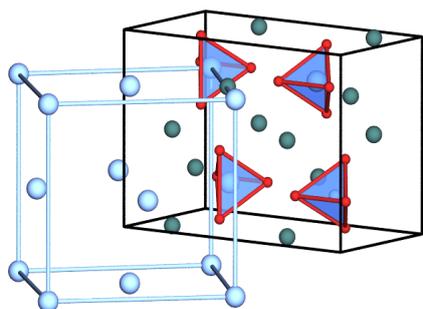


Fig 1: Unit cell of Cs₃TaO₄ and the distorted fcc arrangement of the [TaO₄] tetrahedra, indicated by the Ta atoms. Cs: green, Ta: blue, O: red

Several compounds crystallise in the K₃NO₄ [1] structure type, typically pnictogenates of heavy alkali metals like Cs₃AsO₄ [2]. An important characteristic of this structure type is the closest packing topology of the [PnO₄]³⁻ tetrahedra, in which the alkali metal ions fill the octahedral and tetrahedral voids. The orthorhombic unit cell can be transformed into the pseudo-cubic metric by the matrix ($\frac{1}{2} \ 0 \ 1 \ | \ 0 \ 1 \ 0 \ | \ \frac{1}{2} \ 0 \ -1$).

We have extended this compound family by the group 5 oxometalates Cs₃NbO₄ and Cs₃TaO₄. The compounds were the result of reacting Ta or Nb metal with Cs₂O at $T = 300 \text{ }^\circ\text{C}$ according to the reaction equation $\text{Ta} + 4 \text{Cs}_2\text{O} \rightarrow \text{Cs}_3\text{TaO}_4 + 5 \text{Cs}$. Cs₃TaO₄ crystallises with the K₃NO₄ type in space group *Pnma* with $a = 12.963(4) \text{ \AA}$, $b = 9.122(2) \text{ \AA}$ and $c = 6.774(1) \text{ \AA}$ (Fig. 1); Cs₃NbO₄ with $a = 12.928(2) \text{ \AA}$, $b = 9.177(3) \text{ \AA}$, $c = 6.739(4) \text{ \AA}$. Alongside the tabular light blue crystals, octahedral crystals (Fig. 2) were present in Cs₃TaO₄ samples.

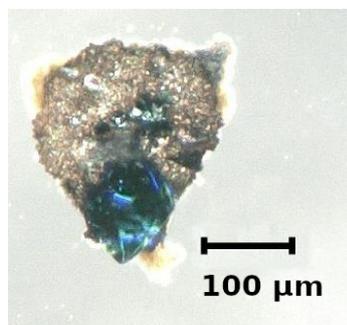


Fig 2: Octahedral crystal of caesium orthotantalate(V) in Cs metal

For the structure family of A₃MO₄ metalates a cubic structure with an fcc packing of disordered MO₄ tetrahedra has been established, derived from K₃NbO₄. [3] The octahedral Cs₃TaO₄ crystals give a cubic cell with $a = 9.296(2) \text{ \AA}$, as described in [3], however, a structure refinement leads to problems with allocating the oxygen atoms. When the transformation matrix to the orthorhombic unit cell is applied, refinement in *Pnma* with a suitable twin law leads to satisfying results. Thus, it could be shown that many of the reported cubic crystal structures may have to be assigned to the K₃NO₄ structure type. The reason for the wrong structure assignment is the contrast of atomic form factors. We give an overview over reported and new crystal structures and give some insight into the danger of erroneous structure assignment based on relevant structural and chemical parameters. Furthermore, we discuss whether there are examples for structural phase transition toward a cubic high-temperature phase.

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- [2] Emmerling F., Idilbi M., Röhr C., Neue Oxopnictate A₃M^VO₄: Darstellung und Kristallstruktur von A₃AsO₄ (A = K, Rb, Cs) und K₃BiO₄, Z. Naturforsch., 57b, 599-604 (2002)
- [3] Meyer G., Hoppe R., Zur Kenntnis der Strukturfamilie A₃MO₄ (A = K, Rb, Cs): Darstellung, Kristallographische und magnetisch Eigenschaften. Rev. Chim. Miner, 12, 454-465 (1975)

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