

## Pseudosymmetry in Cs<sub>3</sub>TaO<sub>4</sub>

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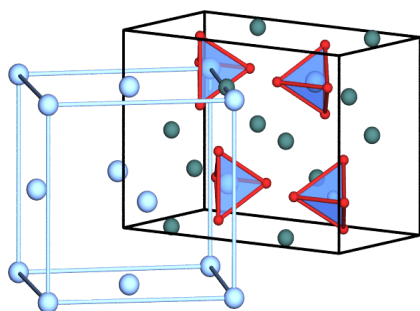


Fig 1: Unit cell of Cs<sub>3</sub>TaO<sub>4</sub> and the distorted fcc arrangement of the [TaO<sub>4</sub>] tetrahedra, indicated by the Ta atoms. Cs: green, Ta: blue, O: red

Several compounds crystallise in the K<sub>3</sub>NO<sub>4</sub> [1] structure type, typically pnictogenates of heavy alkali metals like Cs<sub>3</sub>AsO<sub>4</sub> [2]. An important characteristic of this structure type is the closest packing topology of the [PnO<sub>4</sub>]<sup>3-</sup> 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 ( $\frac{1}{2} 0 1 \mid 0 1 0 \mid \frac{1}{2} 0 -1$ ).

We have extended this compound family by the group 5 oxometalates Cs<sub>3</sub>NbO<sub>4</sub> and Cs<sub>3</sub>TaO<sub>4</sub>. The compounds were the result of reacting Ta or Nb metal with Cs<sub>2</sub>O at  $T = 300$  °C according to the reaction equation  $\text{Ta} + 4 \text{Cs}_2\text{O} \rightarrow \text{Cs}_3\text{TaO}_4 + 5 \text{Cs}$ . Cs<sub>3</sub>TaO<sub>4</sub> crystallises with the K<sub>3</sub>NO<sub>4</sub> type in space group *Pnma* with  $a = 12.963(4)$  Å,  $b = 9.122(2)$  Å and  $c = 6.774(1)$  Å (Fig. 1); Cs<sub>3</sub>NbO<sub>4</sub> with  $a = 12.928(2)$  Å,  $b = 9.177(3)$  Å,  $c = 6.739(4)$  Å. Alongside the tabular light blue crystals, octahedral crystals (Fig. 2) were present in Cs<sub>3</sub>TaO<sub>4</sub> samples.

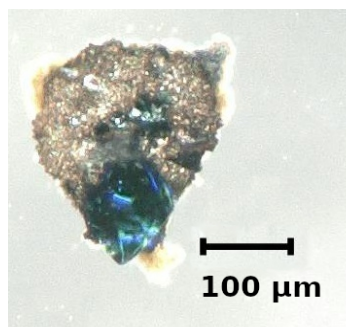


Fig 2: Octahedral crystal of caesium orthotantalate(V) in Cs metal

For the structure family of A<sub>3</sub>MO<sub>4</sub> metalates a cubic structure with an fcc packing of disordered MO<sub>4</sub> tetrahedra has been established, derived from K<sub>3</sub>NbO<sub>4</sub>. [3] The octahedral Cs<sub>3</sub>TaO<sub>4</sub> crystals give a cubic cell with  $a = 9.296(2)$  Å, 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 K<sub>3</sub>NO<sub>4</sub> 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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