

The AsO₆ polyhedron in arsenates, statistics and the novel compound Ti¹⁺Ti³⁺As₄O₁₂

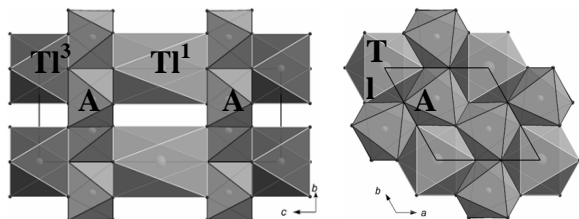
K. SCHWENDTNER¹, U. KOLITSCH² AND E. TILLMANN¹

¹Institut für Mineralogie und Kristallographie, Althanstraße 14, 1090 Wien, Austria
(karolina.schwendtner@univie.ac.at)

²Naturhistorisches Museum Wien, Burgring 7, 1010 Wien, Austria

Inorganic arsenates comprise a large number of compounds, demonstrated by 1145 entries in the ICSD (version 2006/2), however, only 23 compounds (R < 8 %) contain the rare AsO₆ octahedral unit.

Hydrothermal synthesis (Teflon-lined stainless steel autoclave, 7 d, 493 K) using the starting materials Ti₂CO₃ and arsenic acid led to the growth of hexagonal platelets of the novel compound Ti¹⁺Ti³⁺As₄O₁₂ (single-crystal X-ray diffraction, *P*-31*m*, Z = 1; *a* = 4.848(1), *c* = 11.091(2) Å, *V* = 225.75(8) Å³). The new compound is closely related to the following three structure types: M²⁺As₂O₆ (M²⁺ = Ca, Mn, Co, Ni, Cd, Hg, Pb), Hg₂As₂O₆ and LiAsO₃. All of these, as well as the novel compound, are built of layers of edge-sharing AsO₆ octahedra, which are connected by the usually octahedrally coordinated metal cations. In the case of Ti¹⁺Ti³⁺As₄O₁₂ Ti³⁺ is octahedrally coordinated whereas the coordination polyhedron of the larger Ti¹⁺ can be described as a trigonal antiprism.



Considering the scarce data available for AsO₆ polyhedra a statistical analysis of bond lengths in AsO₆ groups was conducted. A total of 40 AsO₆ polyhedra in 38 different compounds were analysed. The bond lengths in the AsO₆ octahedra range between 1.736 and 1.918 Å, with a mean value of 1.827(29) Å. The individual bond lengths are very strongly influenced by the next nearest neighbours. As-OH bond lengths are considerably shortened to a mean value of 1.767(14) Å, which gives the perfect bond valence contribution of 1.00 for this As-O bond. Exactly the opposite effect is found in protonated AsO₄ tetrahedra, where the As-OH bond lengths are elongated to a mean value of 1.719(27) Å. As-O bond lengths to other AsO₄ and AsO₆ polyhedra are very close to the mean value with 1.834(33) and 1.824(20) Å, respectively. The longest mean distances are to edges of other metal octahedra with 1.846(23) Å. No clear correlation between the bond-length distortion and mean bond lengths of individual polyhedra could be established. Financial support by a DOC-FORTE Fellowship of the Austrian Academy of Sciences (ÖAW) is gratefully acknowledged.

Detector strategies to measure Osmium isotope ratios in small samples by NTIMS

JOHANNES SCHWIETERS¹, DIETMAR TUTTAS¹,
CLAUDIA BOUMAN¹, JOHN C. LASSITER² AND
TODD B. HOUSH²

¹Thermo Fisher Scientific, Hannah-Kunath-Str. 11, 28199 Bremen, Germany;
(johannes.schwieters@thermofisher.com)

²Department of Geological Sciences, The University of Texas at Austin, USA

Negative Thermal Ionization Mass Spectrometry (NTIMS) is the method of choice for high precision Osmium isotope ratio measurements of small sample sizes. Because of its high selectivity and high ionization efficiency optimum sample utilization as well as low backgrounds are achieved.

One of the limiting factors when analyzing small samples with Faraday detectors, is the noise level of the current amplifiers. The noise level is reduced as the resistor value and the gain of the current amplifier is increased. Today's instruments use 10¹¹ Ohm amplifiers as a standard. Larger resistor values maybe used to reduce the noise level, however there is a practical limit due to the limited insulation resistance of the PCB as well as the insulation resistance of the Faraday cup and the feedthroughs itself.

Single collector ion counting or even multicollector ion counting detectors overcome the noise problem and promises higher precision touching the limit of counting statistics. Today's multicollector instruments are equipped with a single ion counting channel as a standard and very small samples can be measured in single collector by peak jumping procedures. The laminated magnet of the TRITON instrument from Thermo Fisher Scientific allows fast peak jumping sequences with short settling times between peak jumps. Nevertheless, this still is a sequential method, whereas the Multi-Ion-Counting (MIC) approach allows a simultaneous measurement of all isotopes of interest and thus maximises sample utilization and also eliminates the effect of signal fluctuations on the isotope ratio measurement.

In this experimental study, the performance of all three different detector strategies are compared on the basis of measured data of Osmium samples with different ion beam intensities ranging from >1 Mcps to a few Kcps. The different detector strategies are: (i) Faraday detectors combined with 10¹² Ohm amplifiers, (ii) fast peak jumping single collector ion counting using an SEM, and finally (iii) multi-ion-counting using multiple channeltron detectors. The best operation range and the pros and cons of each detector strategy for different signal intensities are discussed.