$Ca_3TiO_4Cl_2$: A NEW COMPOUND WITH FIVE-COORDINATED TITANIUM

Krüger, H.[1], Jaeger, F.D.[1], Konrad, B.[1], Schellhorn, M.[1], Hümmer, M.[1], Pauluhn, A.[2] & Olieric, V.[2]

[1]Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria
[2]Swiss Light Source, Paul Scherrer Institute, 5232 Villigen, Switzerland
Hannes.Krueger@uibk.ac.at

Single crystals of a new calcium oxochloro titanate were discovered as by-products in synthesis experiments using Ca_2Cl_2 as a flux. Analyses revealed, that small amounts of titanium were substituted by iron. Consequently, we performed more synthesis experiments in an iron-free environment and finally obtained $Ca_3TiO_4Cl_2$ as a powder (by solid state reaction), and as single crystals (flux synthesis in sealed Pt-capsules). The crystal structure was determined using X-ray, and refined using synchrotron radiation diffraction experiments (performed at X06DA, Swiss Light Source, Villigen). The compound crystallises in space group *Pnma*, (a = 10.6009(2), b = 3.9246(1), c = 16.3193(3) Å, Z = 4). The crystal structure was refined using 1153 unique reflections. A final fit of R_{obs} = 0.023 was obtained utilising 61 parameters.

The titanium atoms exhibit five-fold coordination polyhedra, which can be described as trigonal bipyramids: Distances are 1.89, 1.79, 1.88 to O1, O2, O3, and 2.01 Å to O4 (2×). The polyhedra are corner-linked (via O4) and form chains parallel to *b*. The structure exhibits a layered character, as sheets with chains and Ca-Cl layers alternate along *c*.
Within the iron-containing synthesis, we also found a monoclinic form of the compound, which was intergrown with the orthorhombic structure. However, the monoclinic cell could be indexed from the composite diffraction pattern, and the structure was solved. Lattice parameters are a = 16.79, b = 3.93, c = 10.56 Å, β = 102.5°, Z = 4, the space group is *C2/m*. The reciprocal lattices of the composite are related by the following transformation:
$\boldsymbol{a}_{mon}^* = \boldsymbol{c}_{or}^*$, $\boldsymbol{b}_{mon}^* = -\boldsymbol{b}_{or}^*$, $\boldsymbol{c}_{mon}^* = \boldsymbol{a}_{or}^* + \boldsymbol{c}_{or}^*/3$
The structures are closely related, and differences are caused by configuration and stacking sequence of the layers.