

Cd₄Te₅O₁₄, consisting of [Te₅O₁₄]-chains, a novel structure element for oxidotellurates(IV)

F. Eder, M. Weil

TU Vienna, Getreidemarkt 9/164-SC, 1060 Vienna

felix.eder@tuwien.ac.at

Oxidotellurates show a vast structural diversity, especially with tellurium in the +IV oxidation state, which has been summarized and categorized recently by Christy *et al.* [1]. This can be attributed to the 5s² electron lone pair of Te^{IV}. Its large space consumption often leads to rather low symmetric and one-sided coordination polyhedra and to the formation of modular structures like clusters, chains, layers or open-framework clusters penetrated by channels [2].

Single crystals of Cd₄Te^{IV}₅O₁₄, a newly discovered compound in the Cd/Te^{IV}/O-system, were obtained under hydrothermal conditions from a mixture of Cd(NO₃)₂·4H₂O and K₂TeO₃ (molar ratio 4:5). The educts were mixed together in a teflon vessel, which was filled with water to about 2/3 of its volume and then heated inside a steel autoclave to 483 K for a week. The title compound appeared as a minor product besides CdTeO₃ [3]. Single crystals of Cd₄Te₅O₁₄ are colourless and bar shaped.

The asymmetric unit of the monoclinic unit cell (*C2/c*, *a* = 11.9074(3), *b* = 14.3289(3), *c* = 8.7169(2) Å, β = 113.629(1)°, *V* = 1362.58(6) Å³) contains three Te, three Cd and seven O sites. Except for one Te and two Cd sites that are located on the 4*e* position (site symmetry 2), all atoms are located on the general 8*f* Wyckoff position. The Cd sites are all coordinated by six oxygen atoms in a range of 2.235(2)-2.539(2) Å. By edge- and corner-sharing the [CdO₆]-polyhedra form an open three-dimensional framework. The Te^{IV} sites exhibit a coordination number of 4, which is better described as 3+1 for the Te1 and Te2 sites. The [TeO₄]-polyhedra have a bisphenoidal shape which is derived from a distorted [TeψO₄] trigonal bipyramid where the lone pair occupies an equatorial position.

The [TeO₄]-units are connected to each other by corner- and edge-sharing. This way they form helical [Te₅O₁₄]⁸⁻ chains oriented parallel [203]. The sequence of the atomic sites (-Te₃-Te₂-Te₁=Te₁-Te₂-) repeats after 5 atoms which makes it a *fünfer*-chain. For Te-O-single-chain structures only *zweier*, *dreier*, *vierer*, *sechser* and *achter*-chains (repeating units of 2, 3, 4, 6 and 8 Te-atoms) have been found [1]. Using the nomenclature used by Christy *et al.* [1] the chains are denoted as (...-◇-◇-◇=◇-◇-...). Considering the translational symmetry of the chain, a periodicity of 10 Te-atoms is found until the helix repeats itself (Fig. 1). Moving 10 Te-atoms up the chain corresponds to a translation of 2a+3c.

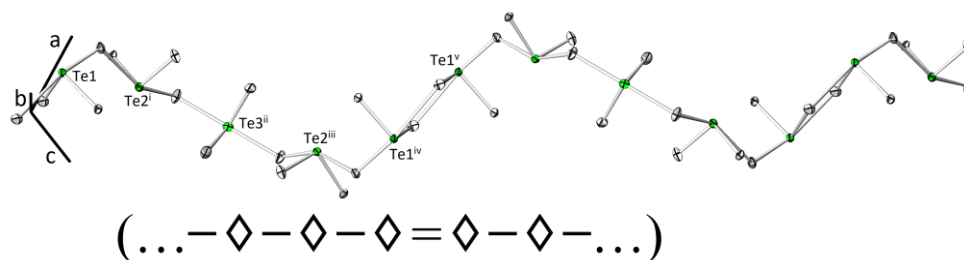


Figure 1. [Te₅O₁₄]-chains in Cd₄Te₅O₁₄; symmetry codes: i) 1/2-x, -1/2+y, 1/2-z; ii) 1/2-x, 1/2-y, 1-z; iii) 1/2+x, -1/2+y, 1+z; iv) 1-x, y, 1/2-z; v) 1+x, -y, 1/2+z

The only other known structures with the composition *M*₄Te₅O₁₄ are two polymorphs of Ca₄Te₅O₁₄ [4-5]. α-Ca₄Te₅O₁₄ [4] consists of [Te₈O₂₂]-*achter*-single chains (...-(◇-Δ)-◇-◇-(◇-Δ)-◇-◇-...) as well as isolated [TeO₃] groups. The high-pressure β-Ca₄Te₅O₁₄ [5] is formed by isolated [Te₃O₈]- and [TeO₃] groups.

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