MS19-O4 Fluorite-related framework in the $Pd_{11}As_2L_2$ family of crystal structures

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Recently, the crystal structures of palladium minerals with common formula $Pd_{11}As_2L_2$ (*L*=Sb, Te, Bi) were studied [1]. Isomertieite, $Pd_{11}As_2Sb_2$ (I), and törnroosite, $Pd_{11}As_2(Te,Bi)_2$ (II), are cubic, sp.gr. *Fd*-3*m*, *Z*=8, unit-cell parameters for (I): a 12.297(5) Å, V 1859.3(2) $Å^3$; for (II): a=12.350(2) Å, V=1883.6(4). Minerals are structurally isotype.

Isomertieite and törnroosite are intermetallid compounds, but their crystal structures can be described in terms Pauling polyhedrons. Palladium atom is considered as a center of a polyhedron, and As, Sb (or Te) atoms are considered as ligands. There are three types of Pd polyhedrons in the structure: $PdAs_4$ tetrahedra, $PdSb_3As$ or $PdTe_3As$ tetrahedra, and $PdSb_3As_3$ or $PdTe_3As_3$ octahedra. Pd polyhedrons share common edges forming three-dinemtional framework.

Fluorite-related framework can be seen in the isomertieite crystal structure type. The framework of F-centered tetrahedra (FCa_4) is one of classic description of fluorite crystal structure. Kang and Eyring [2] used anion-centered tetrahedra for description of the rare earths oxides. Fluorite-related frameworks are made by four types "*fluorite module*" in the Kang-Eyring systematic. Krivovichev [3] extended Kang-Eyring system for to the wide range of fluorite-related structures with vacancies in both anion and cation sites.

Fluorite modules of $\mathbf{D_1}$ and $\mathbf{U^3}$ types can be described in the structure of isomertieite and törnroosite. They are built up from seven tetrahedrons: six PdL_3As tetrahedra and one $PdAs_4$ tetrahedra. *The supermodule* in the $Pd_{11}As_2L_2$ structure is made by 8 *fluorite modules*. The *supermodule* has *p* x *q* x *r* dimensions equal 2x2x2 (accordance to Krivovichev system). Alternation of modules $\mathbf{D_j}$ and $\mathbf{U^i}$ types in the unit-cell is: layer 1 $\mathbf{D_1\ U^3\ U^3\ D_1}$ / layer 2 $\mathbf{U^3\ D_1\ D_1\ U^3}$. Four Pd-octahedra are joined together via common edges in a clusters. Pd-octahedra clusters located in a cavities of the tetrahedral framework.

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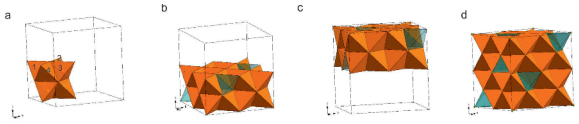

Figure 1. Fluorite modules (a) and their alternation (b, c); and tetrahedral framework (d) in the isomertieite structure type.

Keywords: crystal structure, palladium arsenide, palladium tellurid, fluorite-related framework