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Composite-like crystal structure of mariinskite

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A chromium analogue of chrysoberyl mariinskiskite $Be(Cr,Al)_2O_4$ was recently approved as a new mineral (IMA No. 2011-057). It was discovered at the Mariinskoe deposit (Middle Ural, Russia) in association with chromite, fluoroflogopite, Cr-bearing muscovite as well as eskolaite, fluoroapatite, zircon and tourmaline group minerals. In spite of simple chemical composition and proposal structural type of mariinskite, it is characterized by a bad quality of samples with parting and microtwinning intergrowth [1]. That is why previous single crystal X-ray studies had no success.

Crystal structure of mariinskite was determined on 2 samples (exp. 1, exp. 2). These crystals were extracted from the same transparent polished sample. Diffraction experiments were carried out using Xcalibur CCD diffractometer. Orthorombic unit-cell parameters are: a = 4.4871(5) Å, b = 5.6285(9) Å, c = 9.7316(15) Å, V = 245.78(1) A^3,a = 4.4778(9) Å, b = 5.6202(18) Å, c = 9.746(3) Å, V = 245.27(3) A^3 for crystal 1 (exp. 1) and crystal 2 (exp. 2), respectively. Space group $P2_12_12_1$, Z=4. The structures were solved by direct methods and were refined to final $R_{exp.1}$=8.9 and $R_{exp.2}$=5.9, with 350F >4σF and 304F >3σF.

Crystal chemical formulas are: exp.1 = $(Al_{0.49}Cr_{0.280.33})$ $(Cr_{0.67}Al_{0.150.18})(Cr_{0.310.69})$ $(Cr_{0.170.83})$ $(Be_{0.650.35})$ $(Be_{0.250.75})O_4$; exp.2 = $(Al_{0.55}Cr_{0.230.22})$ $(Cr_{0.63}Al_{0.190.18})(Cr_{0.30.7})$ $(Cr_{0.160.84})$ $(Be_{0.70.3})$ $(Be_{0.20.8})O_4$. Idealized formulas Ñr$_{1.43}$Al$_{0.64}$Be$_{0.9}$O$_4$ (exp. 1) and Ñr$_{1.32}$Al$_{0.74}$Be$_{0.9}$O$_4$ (exp. 2) are in consent with chemical composition (wt. %): (mean for 3 analyses of crystal 1 Al_2O_3 17.73, Cr_2O_3 63.50, TiO_2 0.26, V_2O_3 0.29, MnO 0.13, Fe_2O_3 0.22, tot. 82.13; mean for 92 analyses of holotype sample BeO 16.3, Al_2O_3 23.89, Cr_2O_3 58.67, TiO_2 0.61, V_2O_3 0.26, Fe_2O_3 0.026, tot. 99.98).

There are two components in the crystal structure of mariinskite. These components are characterized by olivine structural type. Dominant component is formed by olivine-like ribbons going along b. Each ribbon contains a chain of edge-shared $M1$-octahedra with composition $(Al_{0.49}Cr_{0.28})$ and $M2$-octahedra $(Cr_{0.67}Al_{0.15})$ which are linked with the chain alternately on either side. These ribbons are displaced on 1/2T along a and axes in chess-like order. $M1$,2-octahedra and Be1-tetrahedra (occupancy 65%) form heteropolyhedral framework which is linked by common horizontal edges with triple $2M1\cdot M2$-octahedra.

Olivine-like model assumes anion arrangement under the hexagonal double layer close package law. Cations fill 1/2 octahedral and 1/8 tetrahedral cavities. There is statistic occupancy by Cr and Al atoms not only basic $M1$,2-octahedral positions, but also octahedral cavities with the centers in $M3$ and $M4$ positions in the structure of mariinskite. Additional positions are linked with basic ones by reflection in mirror plane which is going through the close packing layer. Anion matrix in this composite-like structure is common for two components and it provides a horizontal border linkage of polyhedral along [100]. Filling of additional M3- and $M4$-octahedral positions by Cr atoms (occupancy 30% and 17% respectively) forms an olivine-like ribbons. As a result, a strong cluster is formed. In this cluster Be1-tetrahedron is linked not only with three main $M1$ and $M2$-octahedra, but also divides three vertical edges with triad of $2M3\cdot M4$-octahedra. Besides, Be1-tetrahedron is serially mirror-symmetrical linked with additional Be2-tetrahedron (occupancy 25%) through common horizontal border and apical vertex. Be2-tetrahedron is linked with $2M3\cdot M4$-octahedra by horizontal edges and with $2M1\cdot M2$-octahedra by vertical edges.

This type of structure is possible when $M3(M4)$ and Be1, as well as $M1(M2)$ and Be2, Be1 and Be2 are occupied alternatively, because distances M-Be and Be-Be in all cases are rather small ($\sim$1.7 and $\sim$1.4 Å, respectively). Distances between centers of border-shared $M1$-$M3$- and 2-4-octahedra are in standard range. Possibility of occupancy vacant octahedral positions by Cr and Al atoms relates structure of mariinskite with structures of its associate minerals: eskolaite Cr_2O_3 and chromite $FeCr_2O_4$. Oxygen atoms in the structure of eskolaite (corundum structural type) are formed hexagonal close packing where Cr atoms fill 2/3 octahedral cavities. The pairs of border-shared

Cr-octahedra are connected together perpendicular to close packing layer. Such situation presents in mariinskite. In the structure of chromite (spinel structural type) anions form triple layer cubic close package. Cr atoms fill 1/2 octahedral cavities and Fe atoms fill 1/8 tetrahedral cavities. Spinel octahedral layer is formed perpendicular to a diagonal of cubic cell. This layer is also trace in the structure of mariinskite.

[1] Pautov, L.A., Popov, M.P., Erokhin, Yu.V., Khiller, V.V., Karpenko, V. Yu. (2012) Zapiski RMO (Proc. Rus. Mineral. Soc.). 141 (in press).