On the existence of a new $MgWO_4$ polymorph

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Single-crystals of a quenchable high-temperature polymorph of magnesium tungstate ($MgWO_4$-II) have been grown using the flux method. Polycrystalline material of the same compound could be obtained from solid-state reactions performed at 1200 °C. Basic crystallographic data of the previously unknown modification are as follows: triclinic symmetry, space group $P\overline{1}$, $a = 6.5525(6)$ Å, $b = 7.5883(7)$ Å, $c = 7.6976(6)$ Å, $\alpha = 119.064(9)°$, $\beta = 95.545(7)°$, $\gamma = 107.645(8)°$, $V = 304.84(5)$ Å^3 and $Z = 4$. The crystal structure was solved from single-crystal diffraction data using direct methods and subsequently refined including fractional atomic coordinates and anisotropic displacement factors for all atoms to a residual value of $R1 = 2.16$ % for 1517 independent observed reflections ($I > 2\sigma(I)$) and 110 parameters.

Both the divalent and hexavalent cations exhibit an octahedral oxygen coordination environment. The coordination spheres of the two symmetrically independent tungsten cations involve one very long W–O distance each and, therefore, one could also denote them as (5+1) coordinated. By sharing common edges and corners, the octahedra form a three-dimensional network, which can be built up from infinite rod-like elements running along [010] having a 2 × 2 octahedra wide cross section. Actually, a single rod can be imagined to be cut from the ReO_3-structure type and contains a total of four corner-sharing single-chains of octahedra. Within each single chain, strictly alternating cation sequences corresponding to …Mg–W–Mg–W… can be observed. The [WO_6]-groups show a pronounced distortion due to second-order Jahn-Teller effects.

$MgWO_4$-II is topologically equivalent to the monoclinic so-called VO_2(HT) structure-type. A detailed analysis of the relationships with other ABO_4-compounds is presented based on concepts of group theory. Solid-state characterization has been supplemented by micro-Raman spectroscopy. Finally, the thermal expansion tensor of $MgWO_4$-II between ambient temperature and about 700 °C has been determined. The calculations indicate that the thermal expansion in $MgWO_4$-II is highly anisotropic and quasi two-dimensional with a very low value α_2 along the direction of the above-mentioned octahedral chains of the network.

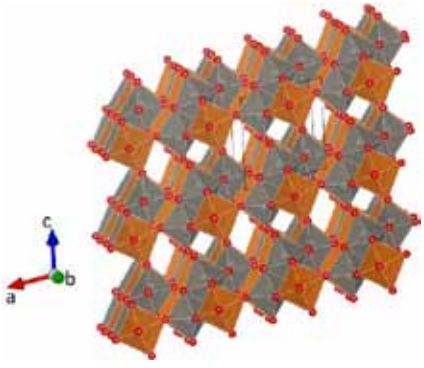

Figure 1. Side view of the crystal structure of $MgWO_4$-II. The MgO_6- and WO_6-octahahedra are colored orange and grey, respectively. Small red spheres represent oxygen atoms. The outline of a single unit-cell is shown as well.

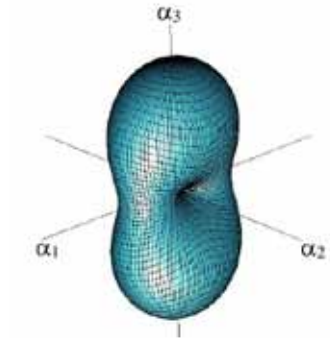

Figure 2. Three-dimensional representation surface of the thermal expansion tensor α_{ij} of $MgWO_4$-II at 500 °C.