

The distribution of chromium in chromian pumpellyite from Sarani, Urals, Russia: a TOF neutron and X-ray Rietveld study

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The crystal structure of a chromian pumpellyite from Sarani in the Russian Urals was refined using complementary time-of-flight neutron and X-ray Rietveld methods, to investigate the crystal chemical behavior of chromium in pumpellyite. Average chemical composition of the chromian pumpellyite is CaO 22.06±0.39, MgO 3.95±0.37, Cr₂O₃ 14.39±1.19, Al₂O₃ 16.71±0.79, total Fe₂O₃ 0.15±0.08, and SiO₂ 35.73±0.63 wt.% (n = 38). Site occupancy of Mg at the octahedral X site refined with the neutron diffraction data was 0.48(3), the same as that obtained by chemical analysis. The occupancies of Cr and Al refined with the X-ray diffraction data were 0.32(1)Cr and 0.20Al at the X site, and 0.31Cr and 0.69Al at the Y site. Bond-valence considerations support the validity of the refined occupancies and the assumption that Cr is trivalent. Accordingly, the formula is established as Ca_{8.00}(Mg_{1.92}Cr_{1.28}Al_{0.80})_{sum}4.00(Al_{5.52}Cr_{2.48})_{sum}8.00Si_{12.00}O_{42.12}(OH)_{13.88}. Although Cr³⁺ ions occur at both the X and Y sites, the distribution coefficient ((Cr/Al)^X/(Cr/Al)^Y = 3.56) indicates stronger preference of Cr for the X site than the Y site. The unit-cell parameters were refined as *a* = 8.8193(5), *b* = 5.9396(3), *c* = 19.161(1) Å, beta = 97.603(2) deg and *V* = 994.86(9) Å³ (neutron data); *a* = 8.8132(2), *b* = 5.9342(1), *c* = 19.1466(3) Å, beta = 97.603(2) deg and *V* = 992.54(3) Å³ (X-ray data). Substitution of chromium for aluminum at the Y site increases mean Y-O distance by expansion of the octahedra of the Y site, which causes increase in the *a*, *b*, and *c*-dimensions. However, mean X-O distance is not correlated with mean ionic radius at the X site. Distortion parameters of the Y site tend to decrease with increasing mean Y-O distance and volume of the Y site. This indicates that expansion of octahedra by ionic substitutions of larger cations for Al at the Y site causes gradual change of the octahedra to a highly symmetrical and regular form.