

On the symmetry and crystal chemistry of britholite: New structural and microanalytical data

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ABSTRACT

We provide in this paper complete structural and micro-chemical characterization of two britholite samples with compositions $(\text{Mn}_{0.04}\text{Ca}_{4.75}\text{REE}_{4.37}\text{Th}_{0.72}\text{U}_{0.12})\Sigma_{10.00}(\text{Si}_{5.57}\text{P}_{0.25}\text{B}_{0.16})\Sigma_{5.98}\text{O}_{24}(\text{OH}_{0.23}\text{F}_{1.77})\Sigma_{2.00}$ (from Latium, Italy) and $(\text{Na}_{0.98}\text{Ca}_{2.01}\text{REE}_{6.97})\Sigma_{9.96}(\text{Si}_{5.07}\text{P}_{0.75})\Sigma_{5.82}\text{O}_{24}(\text{OH}_{0.53}\text{F}_{1.47})\Sigma_{2.00}$ (from Los Islands, Guinea). The crystal-chemical formulae were calculated by combining electron-microprobe analyses for intermediate-*Z* elements (Na, Ca, Mn, Si, P), ion-microprobe analyses for low-*Z* (H, Li, Be, B, F) and high-*Z* elements (Ba, Y, REE and actinides), and high-quality (R_{obs} 1.2–2.6) single-crystal structure refinements. Structure refinements indicate that the best approximation to the real symmetry is the $P6_3$ space group. In britholite, the lowering of symmetry with respect to the $P6_3/m$ space group of apatite means that the O3 and O3a atoms are no longer equivalent and allows the tetrahedron to rotate up to $\sim 4^\circ$ around the Si-O1 bond. Consequently, the O3a atom moves closer to the REE1a site, whereas the O3 atom moves farther from the REE1 site and closer to the REE2 site, which thus assumes a [7+1] coordination. The infrared spectrum of britholite from Latium shows a unique and very broad band in the OH-stretching region at 3437 cm^{-1} , which is consistent with the ordering of trivalent REE cations at the REE2 site. The calculated integral molar absorptivity ϵ_i is $23600\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$. A remarkable constancy in the unit-cell volume along the whole apatite-britholite compositional range is observed for values of the aggregate ionic radius at the REE sites shorter than 1.12 and longer than 1.15 Å, whereas large variations are observed for intermediate values; this behavior suggests constraints due to the rigidity of the tetrahedral group, that are further enhanced at high symmetry.