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Crystal chemistry of synthetic Ti-Mg-bearing hibonites: A single-crystal X-ray study

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Abstract

Hibonite single crystals were synthesized using two different techniques: hot-pressing of polycrystalline hibonite by means of piston-cylinder apparatus and solid state reaction using citrate-based sol-gel precursors. Chemical analyses, UV/Vis spectroscopy, and single-crystal X-ray characterization were performed on four sets of Ti-Mg-bearing hibonites to investigate the substitution mechanism of Ti^{3+}, Ti^{4+}, and Mg^{2+}, relevant for hibonites found in calcium-aluminum-rich inclusions in meteorites. The unit-cell volume of hibonite depends linearly on the concentration of Ti and Mg: $V = 8.21(3)\cdot(Ti_{tot} + Mg)_{apfu} + 586.06(1)$. Structural refinements, carried out in the space group $P6_3/mmc$, demonstrate that Ti occupies two sites: M2, a trigonal bipyramid, and M4, a distorted octahedron occurring in face-sharing pairs. The Ti occupancy factor was refined at both sites. Due to the repulsion of neighboring Ti cations the bond distance M4-O3 increases with increasing Ti content and the cations are displaced from the central position of the polyhedron. The displacement factors $(U_{33})_{M2}$ and the site occupancy factor for Ti in the M2 site positively correlate for the samples, which have more than 0.3–0.4 Ti_{apfu}, while $(U_{33})_{M2}$ remains that of pure hibonite for small Ti occupancies at the M2 site. This plateau of displacement factor reflects the local strain fields around the substituted Ti atoms and its magnitude indicates that these strain fields begin to overlap at a Ti-Ti separation of about 1–2 unit cells. For a sample synthesized at low oxygen fugacity we detected Ti^{3+} by means of UV/Vis absorption spectroscopy. The presence of Ti^{3+} has a clear effect on the M4-M4 distance, which deviates from the linear trend described by samples containing mainly Ti^{4+}. The average bond length M3-O depends linearly on the Mg content of these synthetic hibonites clearly indicating that Mg occupies this site.

Keywords: Hibonite, X-ray diffraction, single crystal, calcium hexaluminates, titanium