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Natural cubic perovskite, $Ca(Ti,Si,Cr)O_{3-\delta}$, a versatile potential host for rock-forming and less-common elements up to Earth's mantle pressure

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Abstract

Perovskite, $CaTiO_3$, originally described as a cubic mineral, is known to have a distorted (orthorhombic) crystal structure. We herein report on the discovery of natural cubic perovskite. This was identified in gehlenite-bearing rocks occurring in a pyrometamorphic complex of the Hatrurim Formation (the Mottled Zone), in the vicinity of the Dead Sea, Negev Desert, Israel. The mineral is associated with native α-(Fe,Ni) metal, schreibersite (Fe_3P), and Si-rich fluorapatite. The crystals of this perovskite reach 50 μm in size and contain many micrometer-sized inclusions of melilitic glass. The mineral contains significant amounts of Si substituting for Ti (up to 9.6 wt% SiO_2), corresponding to 21 mol% of the davemaoite component (cubic perovskite-type $CaSiO_3$), in addition to up to 6.6 wt% Cr_2O_3. Incorporation of trivalent elements results in the occurrence of oxygen vacancies in the crystal structure; this is the first example of natural oxygen-vacant ABO_3 perovskite with the chemical formula $Ca(Ti,Si,Cr)O_{3-\delta}$ (δ ~0.1). Stabilization of cubic symmetry (space group $Pm\bar{3}m$) is achieved via the mechanism not reported so far for $CaTiO_3$, namely displacement of an O atom from its ideal structural position (site splitting). The mineral is stable at atmospheric pressure to 1250 ± 50 °C; above this temperature, its crystals fuse with the embedded melilitic glass, yielding a mixture of titanite and anorthite upon melt solidification. The mineral is stable upon compression to at least 50 GPa. The *a* lattice parameter exhibits continuous contraction from 3.808(1) Å at atmospheric pressure to 3.551(6) Å at 50 GPa. The second-order truncation of the Birch-Murnaghan equation of state gives the initial volume V_0 equal to 55.5(2) Å^3 and room temperature isothermal bulk modulus K_0 of 153(11) GPa. The discovery of oxygen-deficient single perovskite suggests previously unaccounted ways for incorporation of almost any element into the perovskite framework up to pressures corresponding to those of the Earth's mantle.

Keywords: Cubic perovskite, site splitting, disordered oxygen vacancies, davemaoite, mantle, high pressure, pyrometamorphism, Dead Sea Transform