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Crystal structure of novel high-pressure perovskite $K_{2/3}Th_{1/3}TiO_3$, a possible host for Th in the upper mantle

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ABSTRACT

The high-pressure perovskite $K_{2/3}Th_{1/3}TiO_3$ was synthesized at $P = 6$ GPa and $T = 1200$ °C. This compound does not form at ambient pressures, as both solid-state reaction and synthesis from the melt yield a mixture of thorianite (ThO_2) and jeppeite ($K_2Ti_6O_{13}$). $K_{2/3}Th_{1/3}TiO_3$ is a partially ordered derivative of the ideal perovskite structure, which crystallizes with tetragonal symmetry, in space group $P4/mmm$, $a = 3.9007(2)$, $c = 7.8099(7)$ Å, $V = 118.83(2)$ Å^3, $Z = 2$. The structure of this compound was refined by the Rietveld method from the X-ray diffraction powder data. The degree of disorder calculated from the refined cation occupancies of the 1a and 1b sites is 58%. The K^{1+} cations preferentially enter the 1a site, whereas most Th^{4+} is accommodated in the comparatively smaller 1b site (polyhedral volumes are 53 and 46 Å^3, respectively). In response to this two-dimensional (planar) ordering, the Ti^{4+} cations are displaced by about 0.1 Å toward the planes populated by the lower-charged cations. $K_{2/3}Th_{1/3}TiO_3$ and related structures may be a viable repository for Th in Ti-rich alkali metasomatites in the lithospheric upper mantle.