

Solid solution in the fluorapatite-chlorapatite binary system: High-precision crystal structure refinements of synthetic F-Cl apatite

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ABSTRACT

Apatite sensu lato, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH},\text{Cl})_2$, is the tenth most abundant mineral on Earth, and is fundamentally important in geological processes, biological processes, medicine, dentistry, agriculture, environmental remediation, and material science. The steric interactions among anions in the $[0,0,z]$ anion column in apatite make it impossible to predict the column anion arrangements in solid solutions among the three end-members. In this work we report the measured atomic arrangements of synthetic apatite in the F-Cl apatite binary with nominal composition $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{Cl})_2$, synthesized in vacuum at high temperature to minimize both hydroxyl- and oxy-component of the apatite. Four crystals from the high-temperature synthesis batch were prepared to assess the homogeneity of the batch and the precision of the location of small portions of an atom in the apatite anion column by single-crystal X-ray diffraction techniques. Crystals were ground to spheres of 80 μm diameter, and full-spheres of $\text{MoK}\alpha$ diffraction data were collected to $\theta = 33^\circ$, with average redundancies >16 . Final $R1$ values ranged from 0.0145 to 0.0158; the lattice parameters ranged from $a = 9.5084(2)$ – $9.5104(3)$, $c = 6.8289(3)$ – $6.8311(2)$ Å. Based on this study, solid solution in $P6_3/m$ apatites along the F-Cl join is attained by creation of an off-mirror fluorine site at $(0,0,0.167)$, a position wherein the fluorine atom relaxes away from its normal position within the $\{00l\}$ mirror plane in $P6_3/m$ apatites; that relaxation is coupled with relaxation of a chlorine atom at the adjacent mirror plane away from the off-mirror fluorine, allowing acceptable F-Cl distances in the anion column. There are a total of four partially occupied anion positions in the anion column, including two for fluorine $[(0,0,1/4)$ and $(0,0,0.167)]$ and two for chlorine $[(0,0,0.086)$ and $(0,0,0)]$; the chlorine site at the origin was previously postulated but not observed in calcium apatite solid solutions.

Keywords: Apatite, solid solution, fluorapatite, chlorapatite