

High-resolution Raman spectroscopy of apatite along the F-OH, F-Cl, and Cl-OH binary joins

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Here, we conduct high-resolution Raman spectroscopy on synthetic calcium phosphate apatites along the F-OH, F-Cl, and Cl-OH joins to characterize perturbations in peak position, width, and topology that result from the crystallographic accommodations of the substitutions. Focus was directed to the $v_1(A_g+E_{2g})$ symmetric $(PO_4)^{3-}$ stretching mode at $\sim 964 \text{ cm}^{-1}$ given the intensity and sensitivity to mixing relative to the low-frequency apatite modes.

For F- and OH-apatites, a single peak fitting routine is adequate; however even at low concentrations ($X_{\text{Cl}} < 0.1$), the Cl-bearing apatite band contains shoulders, requiring a 4-peak routine using the Pearson VII Area model to deconvolve the spectra with acceptable fit statistics ($R^2 > 0.999$). Results show significant frequency shifts ($> 3 \text{ cm}^{-1}$) of the main peak with mixing along the F-Cl and OH-Cl joins, and only minor adjustments along the F-OH join. A significant increase in the full width half maximum (FWHM) of this primary band is also observed with mixing along the F-Cl and OH-Cl joins, increasing from $\sim 3 \text{ cm}^{-1}$ for the pure endmembers to $> 6 \text{ cm}^{-1}$ with $\sim 50:50$ F-Cl or OH-Cl mixing along either join. Peak widening is nominal along the F-OH join. These trends are the result of the significantly larger ionic radius of Cl relative to F (+32.31%), which results in O shifting and Ca repulsion [1], whereas the size of OH is much more similar (+2.31%) with a direct substitution for F occurring. These results allow for the precise determination of halogen ratios and correlation with solution calorimetric and volume data to understand non-ideality of mixing between end members.

[1] Schettler, Gottschalk, & Harlov (2011) *American Mineralogist* **96**, 138-152.