

# High pressure behavior of fluorapatite: a *in situ* single-crystal X-ray diffraction and Raman spectroscopic investigation

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HP structural and vibrational behavior of a synthetic fluorapatite was investigated using a DAC connected with a single-crystal diffractometer and a raman microspectrometer. Lattice parameters determined until about 50 kbar showed an anisotropic behaviour: the mean  $\beta_a$  was  $3.8(2) \cdot 10^{-4} \text{ kbar}^{-1}$ , whereas  $\beta_c$  was  $2.8(1) \cdot 10^{-4} \text{ kbar}^{-1}$ ; the bulk modulus, calculated as the inverse of mean volume compressibility, was 980(20) kbar. Three structural refinements performed with data collected at 0.001, 27.6 and 42.6 kbar showed that Ca polyhedra are about three times more compressible than PO<sub>4</sub> tetrahedra: 910, 780 and 2500 kbar are respectively the bulk moduli of Ca1, Ca2 and P polyhedra. The largest reduction in the structure affected the F-channel: the channel size, reduced more than 2% between 0.001 and 42.6 kbar.

The vibrations of phosphate group changed linearly with *P*. The coefficients  $dv/dP$  (cm<sup>-1</sup>/kbar) of  $\nu_{3a}A_g$ ,  $\nu_{3b}A_g$ ,  $\nu_{3b}E_{2g}$ ,  $\nu_1A_g$ ,  $\nu_{4a}A_g$ ,  $\nu_{4b}A_g$ ,  $\nu_4E_{2g}$  were respectively: 0.58(3), 0.64(3), 0.66(3), 0.53(3), 0.25(2), 0.29(4), 0.18(3). Therefore the antisymmetric stretching mode ( $\nu_3$ ) and symmetric stretching mode ( $\nu_1$ ) were more sensitive to the change of P-O bond length than the bending mode ( $\nu_4$ ). The corresponding Grüneisen parameters were 0.49, 0.56, 0.59, 0.51, 0.38, 0.45, 0.28, smaller than the bulk Grüneisen parameter, due to the more rigid behavior of PO<sub>4</sub> tetrahedra with respect to the other polyhedra. HP structural data indicated that the decrease in factor group splitting of the  $\nu_3$  and  $\nu_4$  bands was generated by the shifts in the local environment surrounding tetrahedra rather than by geometric changes of the tetrahedra themselves.