

Charge density in fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, from X-ray diffraction measurements on mineral and synthetic crystals

A. Huć¹, M. Stachowicz¹, D. E. Harlov², J. Parafiniuk¹, K. Woźniak³

¹Institute of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, Warsaw 02-089, Poland, Section 3.6, ²GeoForschungsZentrum, Telegrafenberg, 14473 Potsdam, Germany, ³Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, Warszawa 02-093, Poland

a.huc@student.uw.edu.pl

Apatite is a name currently used for a mineral supergroup which contains over 40 mineral species with a similar atomic framework structure. According to occupancy of the two metal-cation sites and the tetrahedral site in the crystal structure, the apatite supergroup is subdivided into five groups. One of these groups is the apatite group where the metal sites are occupied by the same dominant element: Ca, Pb, Mn or Sr, and the tetrahedral site is occupied by P, As, or V [1,2]. In common use, the name apatite comprises the calcium phosphate minerals in which the halogen site is occupied by the F^- , Cl^- or OH^- anions in the form of columns along the edges of the unit cell. If the column site is dominated by F, the apatite is referred to as fluorapatite which crystallizes in space group $P6_3/m$.

On the basis of a multipole refinement from high resolution x-ray diffraction data collected up to 0.4 Å, a quantitative experimental charge density distribution has been determined for natural (n) and synthetic analog (s) of fluorapatite. The Bader charges [3] for all atoms were determined from electron density integration within atomic basins (Fig. 1), $q^{\text{Ca}(1)}_{(n)}=+1.6e$; $q^{\text{Ca}(1)}_{(s)}=+1.5e$; $q^{\text{Ca}(2)}_{(n)}=+1.5e$; $q^{\text{Ca}(2)}_{(s)}=+1.6e$; $q^{\text{F}}_{(n)}=-0.4e$; $q^{\text{F}}_{(s)}=-0.4e$; $q^{\text{P}}_{(n)}=+3.4e$ $q^{\text{P}}_{(s)}=+3.5e$; $q^{\text{O}(1)}_{(n)}=-1.5e$; $q^{\text{O}(1)}_{(s)}=-1.5e$; $q^{\text{O}(2)}_{(n)}=-1.3e$; $q^{\text{O}(2)}_{(s)}=-1.4e$; $q^{\text{O}(3)}_{(n)}=-1.3e$; $q^{\text{O}(3)}_{(s)}=-1.4e$. The topological analysis of the electron density distribution showed, apart from the presence of strong Ca...F, Ca...O, P...O interactions, weak O...O interactions associated to charge-shift bonding [4,5].

The crystal structure model and the electron density distribution of fluorapatite serves as a reference for ongoing studies of the substituted F-Cl; F-OH and Cl-OH apatite series.

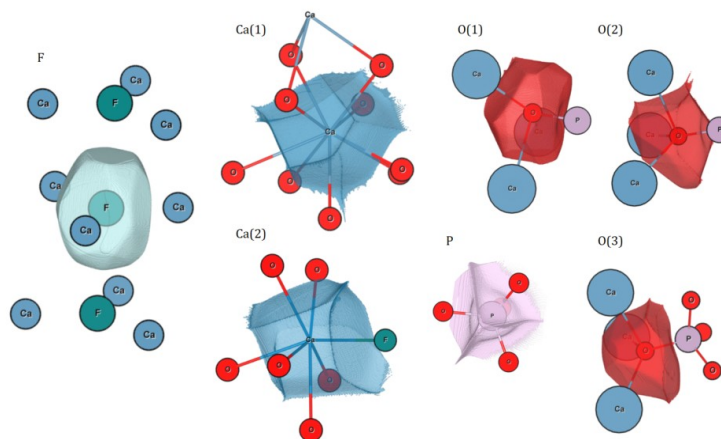


Figure 1. The atomic basin representation of all atoms from asymmetric unit of fluorapatite. Atomic basins are surrounded by atoms from their closest neighbourhood.

[1] Pasero M., Kampf A.R., Ferraris C., Pekov I.V., Rakovan J.F., White T.J. (2010). *European Journal of Mineralogy*, 22, 163-179.

[2] Hughes J.M., Rakovan J.F. (2015). *Elements*, 11, 165-170.

[3] Bader, R. F. W. (1994). *Atoms in Molecules: A Quantum Theory* Clarendon Press.

[4] Shaik, S., Danovich, D., Wu, W. & Hiberty, P. C. (2009). *Nat. Chem.* 1, 443–449.

[5] Stachowicz, M., Malinska, M., Parafiniuk, J. & Woźniak, K. (2017). *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 73, 643–653.

Keywords: fluorapatite; charge density; multipole model formalism; single-crystal

KW acknowledges a financial support within the Polish National Science Centre (NCN) OPUS17 grant - decision DEC-2019/33/B/ST10/02671.

Acta Cryst. (2021), A77, C1164