

Carbonate substitution in hydroxylpyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{OH}$

M. Kwasniak, M. Manecki, M. Lempart, T. Bajda, and J. Matusik

AGH - University of Science and Technology, Faculty of Geology, Geochemistry and Environmental Protection,
(kwasniak@geol.agh.edu.pl)

Hydroxylpyromorphite is a phosphate mineral with a nominal formula $\text{Pb}_5(\text{PO}_4)_3\text{OH}$. Pyromorphite belong to the apatite supergroup, where carbonated form of hydroxylapatite are well-known and they are a inorganic constituent of bone and teeth. So far, carbonated substitution in pyromorphite has been ignored. Substitutions produce variations in unit cell parameters and particularly in the chemical properties like solubility or thermodynamic stability.

Material for this study was synthesised from aqueous solution at room temperature and $\text{pH}=9$. Carbonate ions were present in solution as dissolved NH_4HCO_3 . To avoid crystallization of cerussite, carbonate content was kept below cerussite saturation. Reference sample was synthesized without addition of carbonates in solution at $80\text{ }^\circ\text{C}$ to minimize natural carbonate content from dissolved air.

Solids were analyzed by X-ray powder diffraction (XRD), thermal analysis - TG/DTA, TG/EGA and FTIR. Both syntheses resulted in precipitation of hydroxylpyromorphite free of impurities, within the detection limit of XRD and FTIR.

A shift of certain diffraction peaks with respect to ICDD (JCPDS- International Centre for Diffraction Data) standard patterns was observed. Calculation of unit cell parameters for synthetic hydroxylpyromorphite formed in the presence of CO_3^{2-} ($a=9.8755\text{ \AA}$, $c=7.4329\text{ \AA}$) indicates increase of "c" parameters. The hydroxylpyromorphite synthesized in the absence of NH_4HCO_3 has following parameters: $a=9.9039\text{ \AA}$, $c=7.4357\text{ \AA}$. The melting point of both samples was around $970\text{-}990\text{ }^\circ\text{C}$.

An exothermic decarboxilation effect at $400\text{ }^\circ\text{C}$ associated with detected CO_2 escape was registered by DTA/TG/EGA. Aproximate content of carbonates in hydroxylpyromorphite structure is ca. 1 wt%, based on mass loss on TG curve. The presence of CO_3 was clearly confirmed by carbonate bands at 1455 and 1337 cm^{-1} in FTIR spectra.

These results confirm that, similarly to calcium hydroxylapatite, carbonate ion can incorporate into hydroxylpyromorphite structure. Even small presence of atmospheric CO_2 dissolved in aqueous solution results in precipitation of carbonate substituted hydroxylpyromorphite. It is environmentally important to further characterize structural position of CO_3^{2-} and the effects of substitution on stability and thermodynamic properties of hydroxylpyromorphite, which is an objective of ongoing research.

This project is partly funded from Polish NCN grant No 2011/01/M/ST10/06999.