Journal of Physical Chemistry A 2014 vol.118 N8, pages 1519-1526

Combination of EPR measurements and DFT calculations to study nitrate impurities in the carbonated nanohydroxyapatite

Biktagirov T., Gafurov M., Mamin G., Klimashina E., Putlayev V., Orlinskii S.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

We demonstrate the application of the combined experimental-computational approach for studying the anionic impurities in hydroxyapatite (HAp). Influence of the carbonation level (x) on the concentration of the NO3 2- radicals in the HAp nanocrystals of Ca10-xNa x(PO4)6-x(CO3)x(OH) 2 with x in the range 0 < x < 2 and average sizes of 30 nm is investigated by different analytical methods including electron paramagnetic resonance (EPR). Stable NO3 2- radicals are formed under X-ray irradiation of nano-HAp samples from NO3 - ions incorporated in trace amounts during the wet synthesis process. Density functional theory (DFT) based calculations show energetic preference for the PO4 group substitution by NO3 - ions. Comparison of the calculated and experimental spectroscopic parameters (g and hyperfine tensors) reveals that EPR detects the NO3 2- radicals located in the positions of the PO4 group only. It is shown that with the increase in x, the carbonate ions substitute the NO3 2-/NO3 - ions. DFT calculations confirm that carbonate incorporation in HAp structure is energetically more favorable than the formation of the nitrate defect.

http://dx.doi.org/10.1021/jp410900m