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

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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. © 2014 American Chemical Society.

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