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Arsenate substitution in synthetic hydroxylapatite – structural characterization of the $Ca_5(PO_4)_x(AsO_4)_{3-x}OH$ solid solution

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Occurences of dissolved As in surface and ground waters and observed adverse health effects have emphasized the need for better understanding of reactions that govern As mobility. Precipitation of Ca apatites is quite often used for immobilization of toxic forms P and As in the environment. Hydroxylapatite – $Ca_5(PO_4)_3OH$ (HAP) and johnbaumite – $Ca_5(AsO_4)_3OH$ (AsHAP) are isostructural apatite minerals naturally occurring in the oxidation zones.The main objective of this research is identification of systematic relation between structural and spectral properties and As content in the $Ca_5(PO_4)_3OH$, $Ca_5(PO_4)_2(AsO_4)OH$, $Ca_5(PO_4)_{1,5}(AsO_4)_{1,5}OH$, $Ca_5(PO_4)(AsO_4)_2OH$, $Ca_5(AsO_4)_3OH$. Recent studies of this isomorphic series provide inconsistent results (Lee et al. 2009, Zhu et al. 2009) indicating controversies and the need for further studies.

Awet method of synthesis from aqueous solutions was used to precipitate precisely defined phases from the series: HAP, AsHAP and three intermediate compositions. For the synthesis of pure HAP solution of $Na_2HPO_4$was mixed-drop wise using a syringe pump with a$Ca(NO_3)_2$ solution.The pH was set at 11 with 1M NH_4OH. Precipitated powders were washed five times in redistilled water and air dried. The other phases were precipitated in the presence of KH_2AsO_4 at various proportions. Johnbaumite was synthesized at 75°C. $Ca_5(PO_4)_3OH$, $Ca_5(PO_4)_2(AsO_4)OH$, $Ca_5(PO_4)_{1,5}(AsO_4)_{1,5}OH$, $Ca_5(PO_4)(AsO_4)_2OH$, $Ca_5(AsO_4)_3OH$ synthesized phases were characterized using scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), powder X-Ray diffraction (XRD), Infrared absorption spectroscopy (FTIR) and Raman spectroscopy.

SEM-EDS analysis confirms that the products of the synthesis are homogeneous. The crystals size varies between 0.1–1.0 µm and increases with the increase of Ascontent. Semi-quantitative elemental analysis by EDS indicates that Ca, O, P and Asare the only elements detected and that the molar proportions correspond to theoretical composition of HAP, $Ca_5(PO_4)_2(AsO_4)OH$, $Ca_5(PO_4)_{1,5}(AsO_4)_{1,5}OH$, $Ca_5(PO_4)(AsO_4)_2OH$ and finally AsHAP.

Systematic shift of peaks is apparent on the diffraction patterns. Hexagonal system and P63/m group of symmetry were used for unite cell parameters calculation. The results show systematic increase in the unit cell parameters with substitution of As for P in the series: parameter a from 9.41 to 9.43 and parameter *c* from 6.85 to 6.87. Crystal volumes also increase with increasing amount of As in synthesized phases. Calculated values are within the error similar to these reported by Zhu et al. (2009). In contrary to their results, a linear increase of unit cell parameters with As content is observed. This is in accordance with Lee et al. (2009).

The intensity and the position of PO_4 and AsO_4 absorption bands varies systematically in the FTIR spectra being shifted towards higher wavenumber with increasing As content. The bands originating from CaO and OH (3400 cm^{-1}) are practically not affected in all five spectra.

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The Raman spectra have shown systematic variation in stretching and bending vibrations in the series. Observed shifts in positions of Raman effects correlate linearly with As increase.This can be explained by the fact that atomic mass of As is higher than of P and that As-O bonds are longer than P-O bonds. Bands originating from P-O vibration modes shift in less regular manner. In the range of 610–550 cm^{-1} we observe shift of bands originating from CaO bond. The results correlate well with and expand upon the observations by Lee et al. (2009).

Taken together, in this research we have explored possibility of HAP-AsHAP isomorphic series synthesis and we found it structural properties. Obtained results suggest that further insights may be obtained frommore research on these minerals. It may find potential applications inremoval of toxic arsenic from the environment and this is a goal of future research.

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