



## **The vibrational study of halogenated mimetites.**

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The apatite-group minerals are tolerant to various chemical substitutions. Their diverse composition results in many geological, technological and environmental occurrences and applications. Here, we identified the systematic relation between structural and spectral properties of Pb-As – bearing apatites with different anionic substitutions. Although some of them may not have natural equivalents, they are highly informative in understanding the crystal chemistry of Pb-As – bearing apatites. Synthesis from aqueous solutions was used to precipitate five apatites  $Pb_5(AsO_4)_3X$ , where X stands for F, OH, Cl, Br or I. The pH was kept above 4.5 during synthesis to avoid precipitation of other phases. All five 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.

The substitution results in systematic linear increase in unit cell parameters and unit cell volume with the increasing size of the anion. All infrared spectra of halogenated mimetites show characteristic bands originating from the vibrations of As–O bonds in  $[AsO_4]$  tetrahedral: stretching  $\nu_3$  vibrations (832 – 810  $cm^{-1}$ ) and bending  $\nu_4$  vibrations at 385 – 415  $cm^{-1}$ . Isomorphic substitutions are apparent as systematic changes in the position and intensity of these bands. Strong correlations between the positions of the vibrational modes and the molar mass of halogenic substitution is apparent. The most sensitive for are  $\nu_3$  bands which shift toward lower wavenumbers with increasing molar mass of the halogen. Raman spectra also show the shifting of arsenate vibrations towards the lower wavenumbers ( $\nu_1=812 - 806$   $cm^{-1}$ ;  $\nu_3=780 - 775$   $cm^{-1}$ ). This correlation is strong and linear which corroborates the hypothesis that halogenic substitution implements regular changes in Raman and FTIR spectra. This work is funded by NCN research grant No. 2017/27/N/ST10/00776. MM is partially funded by AGH research grant No 11.11.140.158.