X-ray diffraction and Raman spectroscopy study of F, Cl, Br, I and OH substitutions in lead arsenate apatites (mimetites) Pb5(AsO4)3X

Julia Sordyl1, Bartosz Puzio1, Olaf Borkiewicz2, and Maciej Manecki1
1AGH-University of Science and Technology in Cracow, Poland (sordyljulia@gmail.com)
2X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States

Five Pb-As bearing apatites Pb5(AsO4)3X, where X stands for F, Cl, Br, I and OH, were synthesized by precipitation from an aqueous solution and analyzed with powder X-ray diffraction and Raman spectroscopy. High-resolution high-quality powder diffraction data were obtained at the 11-BM beamline of the Advanced Photon Source at Argonne National Laboratory, Argonne, IL, USA and the structure Rietveld refinements of mimetites with different halogenic substitutions were provided.

Mimetites precipitated from aqueous solutions crystallize in hexagonal crystal system (space group P63/m). The lattice parameters a and c, as well as the volume of the unit cell, increase with the increasing ionic radius of halogen substitution: a = 10.081Å, 10.247Å, 10.310Å, 10.351Å; c = 7.426Å, 7.442Å, 7.473Å, 7.528Å; V = 653.515Å³, 676.716Å³, 688.019Å³, 698.402Å³ for Pb5(AsO4)3F, Pb5(AsO4)3Cl, Pb5(AsO4)3Br, Pb5(AsO4)3I, respectively. The OH- ion has similar effect on the lattice parameter a = 10.187Å but much stronger effect on parameter c = 7.525Å and overall volume V = 676.274Å³ than halogens.

Systematic linear relations between the unit cell parameters and the Pb(2) – Pb(2) distance as well as the size of AsO4 tetrahedra are observed. The distance between the Pb(2) – Pb(2) increases (from 4.093Å for Pb5(AsO4)3F to 4.674Å for Pb5(AsO4)3I) indicating the systematic increase in the radius of hexagonal channels occupied by halogens and OH. In contrast, the size (volume) of AsO4 tetrahedra decreases (from 2.474Å³ for Pb5(AsO4)3F to 2.025Å³ for Pb5(AsO4)3I) with the substitution and with the increasing size of the unit cell.

These structural effects affect the Raman spectra of substituted mimetites resulting in systematic shift of the position of the bands. The most sensitive to isomorphic substitutions are symmetric stretching vibrations ν1 of the As-O bond in [AsO4] tetrahedra, position of which range from 813 cm⁻¹ for Pb5(AsO4)3F to 810 cm⁻¹ for Pb5(AsO4)3I. This, however, is not due to the increase in the mass of substituted anion. The position of the bands is directly affected by the increasing length of As-O bond: the increase in As-O bond length shifts the position of ν1 vibrations towards lower wavenumbers.

Financial support for the research was provided by the Polish National Science Centre (NCN) grant No. 2017/27/N/ST10/00776.