Geology, Geophysics & Environment 2014, vol. 40 (1): 141–142

Halogen substitution in synthetic lead apatite compounds Raman spectroscopy study

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Mimetite $Pb_{10}(AsO_4)_6Cl_2$, vanadinite $Pb_{10}(VO_4)_6Cl_2$ and pyromorphite $Pb_{10}(PO_4)_6Cl_2$ are minerals isostructural with apatite occurring in the oxidation zones of Pb deposits. They exhibit hexagonal structure and rod-shape morphology. To date, most published research on crystal chemistry of lead apatites concentrated on cationic substitutions in crystalline structure (Ca, Pb, Sr etc.). Little is known, however, on anionic solid solutions, particularly on systematic changes in the structure and properties due to halogen substitutions in lead apatites. Precipitation of lead apatites is often used for immobilization of toxic forms of Pb and As in the environment. More recently, immobilization of radioactive isotope ^{129}I in the form of lead apatites was proposed. This isotope is released as a result of accidents at nuclear power plants (Zhang et al. 2007, Stennet et al. 2011, Redfern et al. 2012). Halogen varieties of lead apatites are also used in chemical engineering as environmentally friendly catalysts (Masaoka & Kyono 2006).

The objective of this project was synthesis of halogen-substituted lead apatites in pyromorphite series $Pb_{10}(PO_4)_6(F, Cl, Br, I)_2$, mimetite series $Pb_{10}(AsO_4)_6(F, Cl, Br, I)_2$, and vanadinite series $Pb_{10}(VO_4)_6(F, Cl, Br, I)_2$, followed by characteristics of X-ray diffraction patterns and Raman spectra. This will contribute to our knowledge on mechanisms and effects of anionic substitutions in this group of mineral phases.

Based on the literature and pilot experiments we developed an efficient method of synthesis of Pb apatite solid solutions which allows for full control on stoichiometry, and results in crystalline, homogeneous precipitate. Lead apatites were synthesized at room temperatures from aqueous solutions of Pb_{aq}, phosphates/arsenates/vanadates, and F_{aq}, Cl_{aq}, Br_{aq}, or I_{aq} solutions mixed in stoichiometric proportions. Solutions are mixed dropwise in large (2 dm^3) reactor with distilled water. Suspension is left for 48 hours for aging, filtered and air-dried. X-ray powder diffraction is used for identification of solid phases. Qualitative analysis allows also for identification of systematic shifts in diffraction patterns resulting from halogen substitutions. Calculation of lattice parameters is used to quantify the systematic effects of substitutions on unit cell dimensions. For the first time Raman spectroscopy was applied to most of crystalline phases in question. Analysis of systematic spectral shifts with anionic substitutions was performed which allowed for explanation of molecular structural reasons for spectral shifts as well as for development of identification procedures with the use of Raman spectroscopy.

All phases preserve their hexagonal crystalline structure. Both diffraction patterns and Raman spectra corresponding to each synthesized phases exhibit systematic shifts in the series. The most pronounced features on Raman spectrum are shifts of double bands resulting from phosphate stretching mode from 968/932 through 945/918 to 941/910 cm^{-1} for F, Cl and Br substituted pyromorphites, respectively. Similar trends are observed for mimetite and vanadinite series. These shifts progress towards lower angles 2θ in XRD patterns and lower Raman shifts on the spectra which is consistent with the increasing ionic radius and atomic mass of the elements resulting in larger unit cell and more rigid chemical bonds. These results confirm that solid-solutions between these phases are possible and result in systematic changes in the structure and spectroscopic properties.

This work was supported by AGH-UST statutory grant no. 11.11.140.319.

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