

A Raman spectroscopic study of hydroxyl analogues of pyromorphite-mimetite solid solutions

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Pyromorphite $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ and mimetite $\text{Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2$, minerals belonging to apatite group, receive increased attention recently. Induced precipitation of pyromorphite and mimetite in soil pore solutions or waste solutions belongs to the best remediation and reclamation methods (Ma et al. 1995, Maniecki et al. 2009). These phases are the most stable forms of Pb^{2+} and As^{5+} in the environment. Deficiency of Cl^- in the environment can cause formation of their hydroxyl forms: $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ or their solid solutions. Apatite structure allows for extensive and varied ionic substitutions in all positions. The isomorphic substitutions affect unit-cell parameters and chemical properties of these minerals (Botto et al. 1997).

Solid solutions of hydroxyl analogues of pyromorphite and mimetite have not been sufficiently characterized to this day. A detailed description of phases from this series is, however, necessary for optimization of the remediation methods. A Raman spectroscopic study of mimetite-pyromorphite series demonstrated a strong correlation between the positions of the vibrational modes and the $\text{As}/(\text{As}+\text{P})$ ratio (Bajda et al. 2011). Such a correlation may be used to determine the composition of the examined samples of minerals from the series. The current research is based on the assumption that in the case of solid solutions of their

hydroxyl analogues similar correlations occur. Therefore, the aim of this study is structural (X-ray diffraction) and spectroscopic (Raman) investigation of the effect of PO_4 - AsO_4 isomorphic substitution on the structure and vibrational spectra.

Seven phases were synthesized in computer-controlled chemistate at $\text{pH} = 11$ and 80°C by dropwise mixing of solutions containing Pb^{2+} , PO_4^{3-} and AsO_4^{3-} in stoichiometric proportions. The composition of the final products was $\text{Pb}_{10}[(\text{PO}_4)_{6-x}(\text{AsO}_4)_x](\text{OH})_2$, where $x = 0, 1, 2, 3, 4, 5, 6$. High-resolution powder X-ray diffraction data was obtained using the diffractometer at beamline 11-BM at the Advanced Photon Source (Argonne National Laboratory, Chicago). A detailed Raman spectroscopy was performed with the use of confocal Raman microscope and OMNIC software (AGH Kraków). The morphology and elemental composition of the samples were characterized by means of Fei Quanta variable pressure SEM/EDS (AGH UST Kraków). Moreover, the chemical composition of synthetic phases was determined by wet chemical analysis.

Unit cell parameters increase with substitution of AsO_4 for PO_4 . Parameter a increases from 9.879 \AA to 10.189 \AA , while parameter c – from 7.427 \AA to 7.516 \AA . This is consistent with other solid solution series of lead apatites (Flis et al. 2009). The area under selected Raman effects is

also strongly correlated with P and As content. Additionally, systematic shift of the position of Raman effects is observed. The band attributed to the $(\text{AsO}_4)^{3-} \nu_1$ symmetric stretching mode shifts from 808 cm^{-1} in $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ to 814 cm^{-1} in $\text{Pb}_{10}[(\text{PO}_4)_5(\text{AsO}_4)](\text{OH})_2$. The range of the peak positions for the $(\text{PO}_4)^{3-} \nu_1$ symmetric stretching mode is even wider: from 918 cm^{-1} in $\text{Pb}_{10}[(\text{PO}_4)(\text{AsO}_4)_5](\text{OH})_2$ to 926 cm^{-1} in $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$. The observed correlations may be used for semi-quantitative estimation of As and P content using non-destructive Raman spectroscopy.

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