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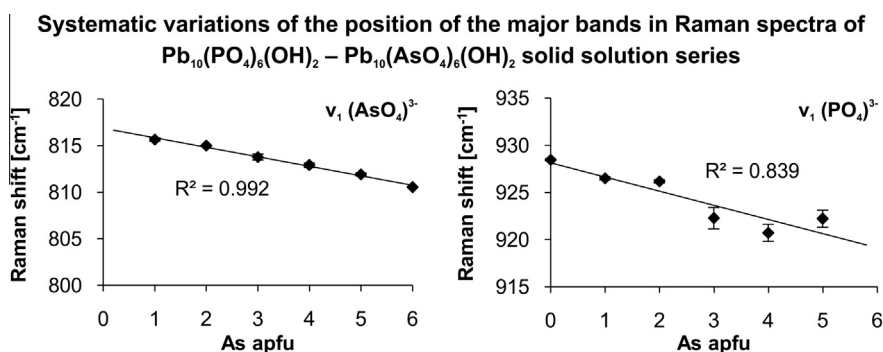
Arsenate substitution in lead hydroxyl apatites: A Raman spectroscopic study

Alicja Giera^a, Maciej Manecki^{b,*}, Tomasz Bajda^b, John Rakovan^c, Monika Kwaśniak-Kominek^b, Tomasz Marchlewski^c^a Institute of Geological Sciences, Polish Academy of Sciences INGPA, ul. Senacka 1, 31-002 Kraków, Poland^b Department of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland^c Department of Geology and Environmental Earth Science, Miami University, 114 Shideler Hall, Oxford, OH 45056, USA

HIGHLIGHTS

- Raman spectra of $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ – $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ solid solution series are compared for the first time.
- Linear shift of the position and intensity of major $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ bands is observed.
- Exponential correlation of the intensity ratio $I_{\text{As}}/I_{\text{P}}$ with As molar ratio is apparent due to different polarizability.
- Hydroxyl lead apatites adopt the $(\text{CO}_3)^{2-}$ ions, particularly at the arsenate end of the series.

GRAPHICAL ABSTRACT



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ABSTRACT

A total of seven compounds of the hydroxylpyromorphite $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ – hydroxylmimetite $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ (HPY–HMI) solid solution series were synthesized at 80 °C from aqueous solutions and characterized using Raman spectroscopy. The positions of the bands in all spectra of the series depend on the content of arsenates and phosphates shifting to lower wavenumbers with substitution of $(\text{AsO}_4)^{3-}$ for $(\text{PO}_4)^{3-}$. This shift results from the decreasing bond strength of X–O (where X = P, As) and higher atomic mass of As than P. The position and intensity of major $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ bands in Raman spectra exhibit linear correlation with As content, while the ratio of the intensities of these peaks shows exponential correlation. This results due to different polarizability of $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ molecules. A small carbonate band develops with increasing As content indicating that hydroxyl lead apatites adopt the $(\text{CO}_3)^{2-}$ ions, particularly at the arsenate end of the series.

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1. Introduction

Lead apatites are recently intensively studied due to their significance in the environmental cycle of Pb and As [1–11]. Existing data related to lead hydroxyl apatites with arsenate

substitution – forming hydroxyl analogs of pyromorphite–mimetite series – are rather superficial and outdated. Moreover, they focus mostly on lattice parameters and IR studies of end members [12–15]. Solid solutions have been examined so far in terms of pH dependence of their solubility, lattice constants as well as preliminary IR spectroscopic study [16–17]. Selected physicochemical studies of $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ may also be found in the sources concerning Ca–Pb substitution in hydroxyl apatites [18–19].

* Corresponding author.

E-mail address: gpmmanec@cyf-kr.edu.pl (M. Manecki).

Apatites can accommodate numerous substitutions, both cationic and anionic. Apatite is expressed by a general formula $\text{Me}_{10}(\text{TO}_4)_6(\text{X})_2$, where Me are divalent cations distributed on two distinct crystallographic sites (e.g., Ca^{2+} or Pb^{2+}), TO_4 is a trivalent oxyanion (e.g., PO_4^{3-} , AsO_4^{3-}), and X is a monovalent anion (dominated by OH^- , F^- , Cl^-), divalent anion (e.g. O^{2-} , CO_3^{2-}) or a vacancy [20–22]. Many mineral compounds crystallizing with the apatite structure are frequently discussed and reviewed in the literature on biomaterials, mineralogy, geology, environmental studies, and material science and technology, etc. [23]. However, the terms “hydroxylpyromorphite” and “hydroxylmimetite” have not yet been approved as the mineral names of $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ by the International Mineralogical Association. The occurrence of these phases in natural environment has been indicated to date only by fragmentary analyses of near end-members: OH-rich pyromorphite was found in Hares Valley (Pennsylvania, USA) by X-ray diffraction spectroscopy [24], while the presence of halogen-deficient mimetite in the Schwarzwald mining district (Germany) was suggested on the basis of electron microprobe analyses [25].

In vibrational spectroscopic study of Cl-varieties of lead apatites (pyromorphite–mimetite series), Bajda et al. [26] demonstrated systematic changes of peak positions and intensities in spectra of phases with different content of phosphates and arsenates. A strong correlation between the positions of the selected vibrational modes and the $\text{As}/(\text{As} + \text{P})$ ratio was revealed. The research on arsenate substitution in lead hydroxyl apatites using that analytical method was conducted due to two main reasons: successful application of Raman spectroscopy for nondestructive analysis of the pyromorphite–mimetite series and lack of Raman data on their hydroxyl analogs. The current work is based on the assumption that in the case of hydroxyl analogs of pyromorphite–mimetite series (HPY–HMI), similar correlations can be observed. Seven

synthetic crystalline powders with increasing As content were examined by Raman spectroscopy. Interpretation of raw Raman spectra followed by peak resolve operation in selected regions is presented indicating that systematic shifts in Raman spectra may be used for semiquantitative estimation of As content in lead apatites from this series. This extends the applications of Raman spectroscopy for environmental problems.

2. Experimental procedure

The procedure of the synthesis and characteristics of the research material (e.g. morphology, chemical composition, XRD patterns and crystal lattice parameters) are presented elsewhere [27]. Briefly, the samples were precipitated from aqueous solutions in computer-controlled chemistate (Metrohm 846 dosing interface) by mixing 0.05 M $\text{Pb}(\text{NO}_3)_2$ and a 0.03 M mixture of KH_2AsO_4 and KH_2PO_4 at pH 8 (KOH) and 80 °C. The assumed composition of the final products was $\text{Pb}_{10}[(\text{PO}_4)_{6-x}(\text{AsO}_4)_x](\text{OH})_2$, where $x = 0, 1, 2, 3, 4, 5, 6$. The syntheses yielded white, homogeneous, crystalline precipitates, identified with XRD and SEM-EDS as HPY–HMI solid solutions. The precipitates consist of hexagonal rods and prisms. Bimodal size distribution is observed: the average size of coarser crystals is 4 μm , while the size of the smaller ones is below 1 μm . This is probably a result of Ostwald ripening during aging [27]. In addition to the EDS data presented therein, the composition of the synthetic phases was determined by wet chemical analysis. An aliquot of 100 mg of solid was digested in 50 mL 0.02 EDTA and analyzed for Pb and As by atomic absorption spectroscopy (AAS) and for P using UV–Vis spectrophotometry (after reduction of As(V) to As(III) to avoid the interference).

The Raman spectra were recorded at room temperature using a DXR Raman microscope (Thermo Scientific). Approximately 0.5 g of dry crystalline powder sample was placed on a glass slide and

Table 1
Results of wet chemical analysis of the synthetic HPY–HMI series.

Intended sample composition		Sample composition by wet chemical analysis	
Chemical formula	Pb/(As + P) ratio	Chemical formula	Pb/(As + P) ratio
$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$	1.67	$\text{Pb}_{10}(\text{PO}_4)_{5.66}(\text{OH})_2^*$	1.77
$\text{Pb}_{10}[(\text{PO}_4)_5(\text{AsO}_4)](\text{OH})_2$		$\text{Pb}_{10}[(\text{PO}_4)_{5.04}(\text{AsO}_4)_{0.97}](\text{OH})_2$	1.66
$\text{Pb}_{10}[(\text{PO}_4)_4(\text{AsO}_4)_2](\text{OH})_2$		$\text{Pb}_{10}[(\text{PO}_4)_{3.89}(\text{AsO}_4)_{1.94}](\text{OH})_2$	1.72
$\text{Pb}_{10}[(\text{PO}_4)_3(\text{AsO}_4)_3](\text{OH})_2$		$\text{Pb}_{10}[(\text{PO}_4)_{2.83}(\text{AsO}_4)_{3.07}](\text{OH})_2$	1.69
$\text{Pb}_{10}[(\text{PO}_4)_2(\text{AsO}_4)_4](\text{OH})_2$		$\text{Pb}_{10}[(\text{PO}_4)_{1.95}(\text{AsO}_4)_{4.03}](\text{OH})_2$	1.67
$\text{Pb}_{10}[(\text{PO}_4)(\text{AsO}_4)_5](\text{OH})_2$		$\text{Pb}_{10}[(\text{PO}_4)_{0.99}(\text{AsO}_4)_{5.01}](\text{OH})_2$	1.67
$\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$		$\text{Pb}_{10}(\text{AsO}_4)_{5.58}(\text{OH})_2$	1.79

* OH ions assumed on ideal formula of phases.

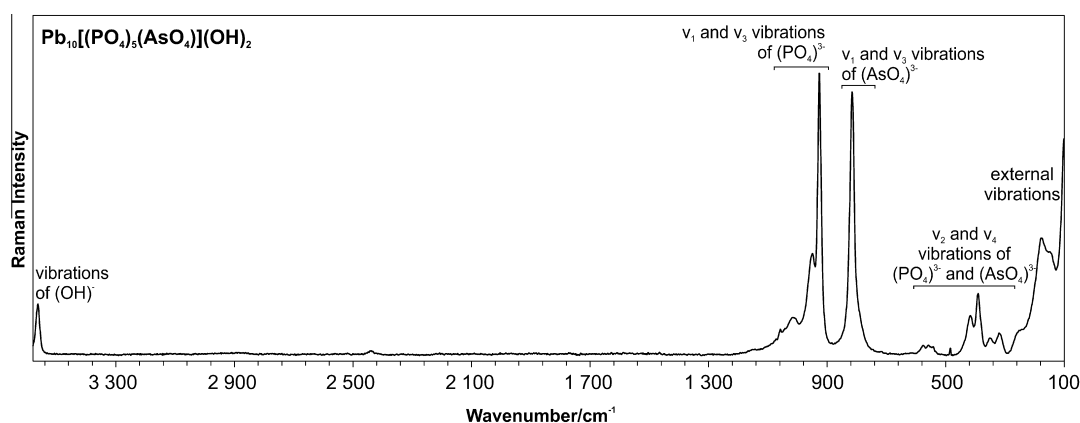


Fig. 1. Full range of Raman spectrum of synthetic $\text{Pb}_{10}[(\text{PO}_4)_5(\text{AsO}_4)](\text{OH})_2$.

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