Fourier transform infrared spectroscopic study of hydroxylpyromorphite $\text{Pb}_{10}(\text{PO}_4)_6\text{OH}_2$ – hydroxylmimetite $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ solid solution series

Monika Kwaśniak-Kominek¹, Jakub Matusik¹, Tomasz Bajda¹, Maciej Manecki¹, John Rakovan², Tomasz Marchlewski², Barbara Szala¹

¹ AGH – University of Science and Technology, Faculty of Geology, Geophysics and Environment Protection, al. Mickiewicza 30, 30-059 Cracow, Poland, phone: +48126172756, e-mail: kwasniak@geol.agh.edu.pl

² Miami University, Department of Geology and Environmental Earth Science, 114 Shideler Hall Oxford, OH 45056

Abstract

A total of seven compounds of the hydroxylmimetite $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ – hydroxylpyromorphite $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HPY–HMI) solid solution series were synthesized at 80 °C from aqueous solutions and characterized using XRD, SEM-EDS and FTIR. The substitution effect of $[\text{PO}_4]^{3-}$ anions by $[\text{AsO}_4]^{3-}$ on systematic changes in lattice parameters and spectral properties has been explained based on correlation between chemical composition and the peak positions. The substitution results in systematic linear increase in unit cell parameters and unit cell volume. Isomorphic substitutions are apparent in IR as a change in the position and intensity of bands derived from phosphates, arsenates and hydroxyl ions. Main bands attributed to stretching and bending vibrations appear at 1109-948 cm^{-1} and 577-511 cm^{-1} for phosphates in HPY and bending vibrations at 853-747 cm^{-1} for arsenates in HMI. The most sensitive for substitution are ν_1 - PO_4 and ν_3 - PO_4 bands which shift toward lower wavenumbers from 931 cm^{-1} to 911 cm^{-1} for ν_1 - PO_4 and from 1109 cm^{-1} to 1086 cm^{-1} for ν_3 - PO_4 . Arsenate bands are less sensitive for substitution: ν_3 - AsO_4 shift from 853 cm^{-1} to 831 cm^{-1} . The strong correlations between the positions of the vibrational modes and the As/As+P ratios can be used to determine the composition of the phases from the hydroxylmimetite–hydroxylpyromorphite series.

Key words:

hydroxylpyromorphite, hydroxylmimetite, solid solution, FTIR, arsenates, phosphates

1. Introduction

Arsenic and lead are widespread environmental contaminants potentially toxic to humans and other living beings. Soils and wastes contaminated with coexisting Pb and As species are found

in both rural and urban settings. Uptake of arsenic from waste, soil or water by phosphate compounds, particularly hydroxylapatite, has been investigated previously [1-5]. The technology arises from the low solubility of lead apatites (including lead phosphates and lead arsenates) and from their rapid precipitation reactions.

Apatites are very tolerant to structural distortion and chemical substitution in cationic and anionic positions and consequently they are remarkably diverse in composition [6,7]. Given the potential for extensive solid solutions in the system of apatite group minerals the apatites precipitating in the environment are often not pure end members but rather solid solutions [8,9]. In contrast to calcium apatites, however, hydroxyl varieties of lead apatites are uncommon in nature. Hydroxyl analog of pyromorphite $\text{Pb}_{10}(\text{PO}_4)_6\text{OH}_2$ (hydroxylpyromorphite, HPY) and hydroxyl analog of mimetite $\text{Pb}_{10}(\text{AsO}_4)_6\text{OH}_2$ (hydroxylmimetite, HMI) have been synthesized and characterized before. HPY crystal structure is described by Barinova et al. [10]. This phase was also determined as a product of reaction between lead contaminated soils and apatites, used as a source of phosphates [11-13]. Moreover, solubility of HPY and carbonated HPY were recently compared [14]. Markl et al. [15] reports potential occurrence of natural OH-end-member corresponding to mimetite in the Schwarzwald mining district.

A complete solid solution between HPY and HMI was determined by Rao [16] and the infra-red spectra and solubilities of these synthetic phases (hydrothermal synthesis) are reported [16,17]. Unit cell parameters of end members characterized in these papers differ significantly from JCCD standards, and infra-red spectra received only qualitative description. Addressing the need for contemporary and precise characterization, we present the results of XRD and FTIR study of this environmentally important solid solution series. The phases have been synthesized from aqueous solutions and the effect of $[\text{PO}_4]^{3-}$ substitution by $[\text{AsO}_4]^{3-}$ on systematic changes in lattice parameters and spectral properties is explained based on correlation between chemical composition and the peak position or intensity.

2. Materials and methods

2.1 Synthesis

A total of seven samples from HPY–HMI solid solution series were synthesized. The syntheses were conducted so that the stoichiometry of the final products was $\text{Pb}_{10}[(\text{AsO}_4)_{6-x}(\text{PO}_4)_x](\text{OH})_2$, $x = 0, 1, 2, 3, 4, 5, 6$. Aqueous solutions of 0.05 M $\text{Pb}(\text{NO}_3)_2$ and 0.03 M KH_2AsO_4 and/or KH_2PO_4 (200 mL) were dosed with a 0.25 mL/min rate to a glass beaker initially containing 100 mL of distilled water at 80°C. The mixing of the solutions was controlled by Metrohm 846 Dosing Interface custom equipment (Miami University, USA), which maintained a

constant pH of 8 using 2 M KOH. After the reaction was completed, the precipitates were filtered using 0.22 μm Millipore filters and subsequently dried in an oven for 1 day at 80°C. Before the FTIR analysis, each sample was grinded in agate mortar, washed five times in redistilled water and centrifuged, then dried again at 80°C.

2.2 Solid characterization

Powder XRD patterns of the precipitates were recorded using a Philips PW 3020 X'Pert instrument (AGH Kraków, Poland) with curved crystal graphite monochromator and Cu radiation in a 3° to 73° 2 Θ range at constant step of 0.05° 2 Θ per second. The products of end members of the analyzed solid solution were identified using XRAYAN software by comparing sample patterns with the International Centre for Diffraction Data (ICDD) powder diffraction patterns database. Lattice parameters were calculated from powder XRD patterns using UNITCELL software for hexagonal crystal system (space group P6₃/m) based on position of 17 diffraction lines corrected against Si as an external standard.

For the determination of synthesis products' chemical composition and morphology of the precipitated solids, FEI QUANTA FEG 200 scanning electron microscope with energy-dispersive analyzer (SEM-EDS) was used (AGH Kraków, Poland). Chemical composition based on EDS (% wt. of oxides) was recalculated to molar content of elements (Pb, As, P, H). The results are presented as an average of ten analyses of each sample. The formulae of members were calculated based on general formula $\text{Pb}_{10}[(\text{AsO}_4)_{6-x}(\text{PO}_4)_x](\text{OH})_2$. All results were normalized to 10 atoms of Pb.

The IR spectra were collected using the DRIFTS technique (Praying Mantis accessory—Harrick) at Nicolet 6700 spectrometer (Thermo Scientific). The spectra of samples (3% wt. sample/KBr) were collected in a range of 4000–400 cm^{-1} with a 4 cm^{-1} resolution (64 scans). Deconvolution of IR spectra was carried out using Thermo Fisher Scientific software with specific parameters to fitting function. Processing was performed separately in three ranges: 500–650 cm^{-1} , 650–1200 cm^{-1} , and 3500–3600 cm^{-1} . The band fitting was done using Gaussian function with a constant baseline, small sensitivity factor, and primary peak width of 20 cm^{-1} .

3. Results and discussion

3.1 Solid characterization

All synthesized white precipitates were identified by XRD as crystalline phases belonging to HPY–HMI solid solution free of other phases within the detection limits of the method. End members were identified by comparing peak positions of samples with an ICDD powder diffraction

database: HPY (sample As0P6) with standard 87-2477 and HMI (sample As6P0) with standard 24-586 [18, 19]. For the solid solution series, the diffraction peaks shifted towards lower diffraction angles along with increasing As content (Fig. 1) indicating an increase in d-spacings. Lattice parameters were calculated assuming hexagonal crystal system (space group $P6_3/m$) which is the most typical for all phases in the apatite group, including lead apatites. Unit cell parameters and unit cell volume of end members are identical within analytical error to the standards (Table 1). Arsenate substitution for phosphate results in systematic linear increase in unit cell parameters and unit cell volume within the series (Fig. 2). This is an effect increasing size of the anion from 31 pm for $(PO_4)^{3-}$ to 47 pm for $(AsO_4)^{3-}$. The detailed structural study of this solid solution series is currently in progress and it will be published separately.

Figure 3 shows three representative SEM images of the synthesized end members and solid solution: samples As0P6, As3P3 and As6P0. Hexagonal rods and prisms, a morphology typical for lead apatites is observed. Bimodal size distribution indicates two generations of crystals resulting probably from aging. Impurities were not observed. The chemical composition of products analyzed with EDS was in agreement with the intended composition (Table 1). For all precipitates, the chemical composition depended on the initial concentrations of As and P in starting solutions and the mole ratio P/As. The atomic ratio Pb/(As+P) varies from 1.64 to 1.97 around the stoichiometric 1.67 ratio of the apatite structure. This also confirms the absence of secondary or amorphous products in the precipitates.

3.2 Infrared spectra

The IR spectra of apatite minerals such as pyromorphites and mimetites have been investigated by many authors [20-30]. The most intense absorption bands observed in the spectra of pyromorphite CPY and mimetite CMI and their solid solutions are derived from PO_4 and AsO_4 . Generally, the vibrational spectra of pyromorphite CPY exhibit modes: $932-913\text{ cm}^{-1}$ (ν_1), $436-393\text{ cm}^{-1}$ (ν_2), $1049-953\text{ cm}^{-1}$ (ν_3), and $595-541\text{ cm}^{-1}$ (ν_4) [20]. In turn, mimetite CMI spectrum exhibits ν_1 modes between 817 and 806 cm^{-1} , ν_3 mode between 815 and 752 cm^{-1} , and ν_4 mode between 424 and 369 cm^{-1} [20]. The OH stretching mode in apatites can be detected in the $3500-3600\text{ cm}^{-1}$ range [23,31]. Both the position of these bands and their intensity vary according to the chemical composition and isomorphic substitutions. The variations in peak position of each kind of vibrations may come from impurities, ionic substitutions in analyzed phases, or changes in vibration symmetry. Some of the bands are more sensitive to substitution than others.

The spectrum of synthetic HPY (sample As0P6) is presented in Figure 4. The complete spectra of end members in synthesized series are shown in Figure 5. Dominant spectral features are apparent at 1051 and 984 cm^{-1} assigned to phosphate mode ν_3 asymmetric stretching vibrations,

with 931 cm^{-1} shoulder assigned to P-O ν_1 symmetric stretching vibration. Three bands apparent at 578, 552, and 540 cm^{-1} are assigned to ν_4 -PO₄ deformational bending vibrations of O-P-O. The stretching OH band is at 3561 cm^{-1} .

The position of absorption bands in the FTIR spectrum of synthetic HPY is compared with that of hydroxylapatite Ca₁₀(PO₄)₆(OH)₂ (HAP) and pyromorphite Pb₁₀(PO₄)₆Cl₂ (CPY) (Table 2). Systematic shift of band positions toward lower wave numbers is observed in these isostructural phases in the order HAP–HPY–CPY. The shift results from the substitution of heavier atoms in the structure: Pb for Ca in the pair HAP–HPY and Cl for OH in the pair HPY–CPY [20,32].

The most sensitive for substitution is the ν_3 -PO₄ band. Comparison of HAP with HPY (Table 2) shows that the presence of much heavier Pb in Ca position shifts the absorption bands by over 40 cm^{-1} : from 1091 to 1051 and from 1034 to 984 cm^{-1} . Replacement of OH with Cl has a less significant effect (from 1051 in HPY to 1032 in CPY). This is because the ions have different positions in the structure and their mass difference is much smaller. The comparison between 984 cm^{-1} absorption band in HPY and 998 or 972 cm^{-1} band in CPY is inconclusive due to an unclear band assignment.

It should be noted that 931 cm^{-1} band assigned in HPY as ν_1 -PO₄ stretching symmetric vibration of P-O bonds may also be assigned as ν_3 -PO₄ vibrations. The occurrence of this band indicates lowering the symmetry of phosphate tetrahedron [24]. This band also shifts to lower wave numbers with an increasing mass of ions in the structure, from 962 cm^{-1} in HAP through 931 cm^{-1} in HPY to 926 cm^{-1} in CPY.

Three bands assigned for ν_4 -PO₄ deformational bending vibrations of O-P-O fragment are present in HPY spectrum at 578, 552, and 540 cm^{-1} . An HAP band of 540 cm^{-1} is listed in Table 2 in brackets because, despite the fact that it is apparent on published spectrum, it has not been assigned by Jastrzębski et al. [32]. A CPY band at 550 cm^{-1} apparent on published spectrum [20] is listed in Table 2 in brackets as well for the same reason. Deconvolution of ν_4 band into three components is characteristic for crystalline phases built mainly of [PO₄]³⁻ tetrahedron and indicates a reduction in symmetry of the phosphate tetrahedron from T_d to C_{2v} or C_s [25]. Similarly to ν_3 -PO₄, ν_4 -PO₄ bands are also systematically shifted to lower values. The shift is smaller showing that these bands are less sensitive to substitution. The position of band at 540 cm^{-1} is constant for all phases.

An absorption band at 474 cm^{-1} for HAP is also in brackets. This was assigned by Jastrzębski et al. [32] as ν_4 -PO₄. The assignment is inconclusive. A similar band in the spectrum of CPY at 436 cm^{-1} is assigned as ν_2 -PO₄ [20]. This may indicate that the ν_4 -PO₄ band also shifts to lower wave numbers when heavier ions are present in the structure. Due to the fact that our

measurement was done at 400–4000 cm^{-1} range, the position of ν_2 band for HPY has not been measured.

The band position recorded for the OH group shifts in a similar manner as the band derived from PO_4 : from higher wave numbers in HAP (3562 cm^{-1}) to lower in HPY (3561 cm^{-1}). Moreover, vibrational bands of OH group appear as well. Their position, however, shifts in the opposite direction: from 633 in HAP to 669 cm^{-1} in HPY. However, this band does not appear in all of the HAP spectra [32]. Its presence depends on the type of synthesis and possible other substitutions (e.g. at natural apatite). Furthermore, the discussed band overlaps with $\nu_4\text{-PO}_4$ band. Therefore, the shift of this band has not been considered in this paper due to its unpredictable behavior.

The FTIR spectrum of hydroxylmimetite HMI is shown in Figure 5b. Similarly to HPY, the asymmetric stretching band $\nu_3\text{-AsO}_4$ is predominant in the range of 891, 831, 785, and 747 cm^{-1} . The FTIR spectrum of synthetic HMI is compared with that of johnbaumite (JBA) $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$ and mimetite (CMI) $\text{Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2$ (Table 3). Bands derived from arsenates shift in the same direction as the bands derived from phosphates in pyromorphites described above. Their observed shift is toward lower wave numbers from JBA through the HMI to CMI. The assignment of the bands is less conclusive and apparent shifts are smaller than in phosphates. Bands ν_3 occur approximately 30 cm^{-1} lower in comparison with calcium hydroxylarsenate JBA (880, 847, 835 cm^{-1}) [34]. Mimetite CMI also has a triple $\nu_3\text{-AsO}_4$ band in the range of 814, 804, and 783 cm^{-1} , located at lower wave numbers than HMI.

Deformational bending vibrations $\nu_4\text{-AsO}_4$ have been compared only for JBA and CMI. They exhibit a shift from JBA (447 and 440 cm^{-1}) to CMI (410 and 372 cm^{-1}). This range was not registered in our study. Similarly to the phosphate ν_4 band in pyromorphites, this band also shifts to lower wave numbers when heavier ions are present in the structure.

The stretching vibration of hydroxyl group appears in HMI at 3552 cm^{-1} . This indicates a small shift toward lower wave numbers in comparison with JBA (3562 cm^{-1}), consistent with all previous observations.

The interpretation of IR spectra of intermediate phases in synthesized series is complicated and requires their deconvolution. Not all bands have demonstrated the physical meaning, as the distribution of bands is merely a mathematical fit to the measured curve. However, the complex band which requires separation appears only in the intermittent members not at the end of the series. Consequently, this may indicate changes (disturbances) in the symmetry of phosphate or arsenate tetrahedron.

The influence of substitution of $[\text{AsO}_4]^{3-}$ in HPY structure is characterized through a detailed study of deconvoluted IR spectra in synthesized solid solution (Figs. 4 and 6). The effects

are apparent in FTIR spectra in two ways. Firstly, the peaks position of arsenate, phosphate and OH bands exhibit systematic shifts with the composition of the phase. Secondly, band intensities vary proportionally to the content of P and As in the structure.

The increase of As content substituting for P in HPY results in a shift of PO_4 absorption bands toward lower wave numbers (Table 4). The effect of P substitution for As in HMI on the position of AsO_4 absorption bands is much less pronounced. The most sensitive vibrations for substitution are bands $\nu_1\text{-PO}_4$ and $\nu_3\text{-PO}_4$, stretching the symmetric and asymmetric vibration of P-O bonds [32,33]. Samples As5P1–As1P5 have four to six deconvolution peaks in the range 1109–948 cm^{-1} . By comparison, As0P6 has only three bands assigned to $\nu_3\text{-PO}_4$. The splitting of the bands means lowering the symmetry of phosphate tetrahedron. It can be observed that the aforementioned bands are shifted from 1109, 1051, and 984 cm^{-1} in pure phosphate variety As0P6 to 1086, 1029, 1004, 968, and 948 cm^{-1} in the sample As5P1. A shift of ν_3 bands toward lower wave numbers results from the stretching of $[\text{PO}_4]^{3-}$ by larger $[\text{AsO}_4]^{3-}$ tetrahedron [20,32]. Moreover, a decrease in the intensity of the bands with an increasing amount of As (decreasing content of P) in the structure is observed. The stretching asymmetric vibrations of arsenate tetrahedron shift with increasing P from 853, 825, and 790 cm^{-1} to 891, 831, 785, and 747 cm^{-1} . After deconvolution of bands coming from arsenates, four $\nu_3\text{-As}$ bands are apparent. The first and last are of low intensity, while the second and third are the main ν_3 bands. These main bands should be used to determine the shifts associated with inconsistencies in the structure (Fig. 4). Therefore, $\nu_{3a}\text{-AsO}_4$ in the sample As1P5 occurs at 825 cm^{-1} and moves toward higher wave numbers until 831 cm^{-1} in As6P0. The $\nu_{3b}\text{-AsO}_4$ band in the sample As1P5 (790 cm^{-1}) shifts in the opposite direction to 785 cm^{-1} . This may be due to the fact that the substitution of phosphorus by arsenic tetrahedron has less influence on the deformation than the substitution of As by PO_4^{3-} .

It should be noted that an additional band approximately 925 cm^{-1} assigned as $\nu_1\text{-PO}_4$ stretching symmetric vibration of P-O bonds occurs in the IR spectra of solid solution. Occurrence of this band indicates a lowering of the symmetry of phosphate tetrahedron [24]. In the analyzed solids, this band shifts from 931 cm^{-1} (As0P6) to 911 cm^{-1} (As5P1). The shift of this band towards the lower values of the wavenumber is quite significant (20 cm^{-1}). In contrast, deformational bending vibrations $\nu_4\text{-PO}_4$ are not sensitive to the substitution of arsenates in the HPY structure. Only small shift toward a lower wavenumber (ca. 7 cm^{-1}) as well as systematic decrease of intensity are apparent with an increase of As in the structure. In a similar solid solution of pyromorphite–mimetite series characterized by Flis et al. [27], degeneration of the pyromorphite structure is apparent also in splitting of $\nu_4\text{-PO}_4$ bands. In the hydroxyl variety however, significant splitting does not occur.

The peak position and the intensity of bands assigned for OH stretching vibration also vary within the analyzed solid solution. Stretching vibrations shift from 3561 cm^{-1} in As0P6 to 3552 cm^{-1} in As6P0 (Fig. 6). The bands required decomposition due to their complicated shape and width. In contrast to hydroxylapatite or johnbaumite, more than one band appears after deconvolution indicating the possible presence of OH^- ions in two distinct structural sites of the structure. The distance between oxygen atoms within tetrahedrons is significantly larger in lead apatites than in calcium apatites. Therefore, the tendency of location of OH^- in two structural positions is facilitated [21]. In the analyzed solid solutions, the width of the hydrogen bands is not only related to the lowering of the symmetry but also proves the two structural sites of OH ions in the structure: H is bonding with the nearest oxygen from the $[\text{PO}_4]^{3-}$ and the another one with OH^- from the apatite column [10].

3.3 Correlation of the intensity with chemical composition

Correlation of the integral intensities of absorption bands with phosphate and arsenate content is also possible. Obviously, the increase of As in the HPY–HMI solid solution causes an increase of arsenate modes intensity and decrease in the intensity of the phosphate bands and (Fig. 7 B-F). This correlation is linear for $\nu_1\text{-PO}_4/\nu_{3a}\text{-AsO}_4$ ($R^2 = 0.91$) presented in Fig. 7B, for $\nu_{3a}\text{-PO}_4/\nu_{3a}\text{-AsO}_4$ ($R^2 = 0.93$) and $\nu_{3b}\text{-PO}_4/\nu_{3a}\text{-AsO}_4$ ($R^2 = 0.90$) presented in Fig 7C and 7D, respectively. Also $\nu_4\text{-PO}_4$ modes have a good linear correlation ($R^2 = 0.93$) between intensity and chemical composition, presented in Fig. 7E and 7F. Identical background subtraction procedure was applied for all the spectra. The ratios rather than peak's height or peak area were used assuming this is more independent of the sample preparation and the conditions of the measurement. A high linear correlation between relative intensity of selected bands and molar content of As can be used for a semiquantitative determination the As/(As + P) molar ratio in analyzed solids.

4. Summary and conclusion

Continuous solid solution series between synthetic hydroxylpyromorphite $\text{Pb}_{10}(\text{PO}_4)_6\text{OH}_2$ and synthetic hydroxylmimetite $\text{Pb}_{10}(\text{AsO}_4)_6\text{OH}_2$ resulting from substitution of PO_4^{3-} and AsO_4^{3-} ions has been confirmed. The pure crystalline phases (within the detection limit of XRD and SEM) precipitate from aqueous solutions at 80 °C. Diffraction peaks exhibit systematic shift towards lower values of 2theta with increasing As content. Arsenate substitution for phosphate results in systematic linear increase in unit cell parameters and unit cell volume within the series. Infrared spectroscopy, however, proved to be a much more sensitive method for detecting and quantifying these substitutions. The isomorphic substitutions are apparent on the IR spectra as a change in the position and intensity of bands derived from PO_4 , AsO_4 and OH. The most sensitive for substitution

are $\nu_1\text{-PO}_4$ and $\nu_3\text{-PO}_4$ bands which shift toward lower wavenumbers. The inverse dependence for arsenate band is recorded. Good linear correlation between the position of $\nu_1\text{-PO}_4$ or certain band intensity ratios and As content is apparent. This allows for identification of solid solution members. The position and the intensity of bands assigned to OH stretching vibration also vary systematically within the analyzed solid solution. The effect of As substitution on all bands is stronger than that of P due to the mass effect.

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Table captions:

Table 1. Chemical composition and unit cell parameters of synthetic members of hydroxylpyromorphite – hydroxylmimetite solid solution series $\text{Pb}_{10}[(\text{AsO}_4)_{6-x}(\text{PO}_4)_x](\text{OH})_2$ determined with SEM-EDS.

Table 2. Summary of band position of calcium and lead phosphates: hydroxylapatite HAP, hydroxylpyromorphite HPY and pyromorphite CPY.

Table 3. Summary of band position of calcium and lead arsenates: johnbaumite JBA, hydroxylmimetite HMI and mimetite CMI.

Table 4. Peak assignment and position (cm^{-1}) based on deconvoluted FTIR spectra

Figure captions:

Fig. 1. X-Ray diffraction pattern of HPY – HMI solid solution series. The systematic shift towards lower diffraction angles from HPY (As_0P_6) to HMI (As_6P_0) is apparent (vertical line for reference).

Fig. 2. Linear increase of unit cell parameters and unit cell volume with As content in HPY – HMI solid solution series. The circles represent values for standard end members (JCCD card HPY: 87-2477 and HMI: 24-586).

Fig. 3. SEM images of analyzed solid solutions. (a) As_0P_6 (b) As_3P_3 (c) As_6P_0 . The morphology of the precipitates is typical for lead apatites: hexagonal columns and needles. Two populations of crystals are apparent which is at least partly a result of ageing of the precipitate. Back-scattered electron images, scale bar - $20\mu\text{m}$.

Fig. 4. Infra red spectra of deconvoluted phosphate and arsenate bands at range $1200\text{--}650\text{ cm}^{-1}$ and $650\text{--}500\text{ cm}^{-1}$. Phosphate stretching modes between 1100 and 925 cm^{-1} , arsenate stretching modes at $750\text{--}800\text{ cm}^{-1}$ and phosphate bending modes at $470\text{--}550\text{ cm}^{-1}$.

Fig 5. Infra red spectra of synthesized end members of solid solution. (A) synthetic hydroxylmimetite $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ (HMI), (B) synthetic hydroxylpyromorphite $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HPY).

Fig. 6. Deconvolution of OH stretching vibrations of analyzed solid solution series.

Fig. 7. Correlation diagrams of chemical composition of analyzed samples and peak position of selected phosphate bands (A) and between chemical composition and intensity ratios of arsenate ν_3 - AsO_4 and phosphate bands: ν_1 - PO_4 (B), ν_3 - PO_4 (C-D) and ν_4 - PO_4 (E-F).

TABLES

Table 1.

Sample ID	Molecular formula based on SEM-EDS elemental analysis	Pb/(As+P) molar ratio	Lattice parameters (Å)		Lattice volume (Å ³)
			a	c	
As6 P0	Pb ₁₀ (AsO ₄) _{5.08} (OH) ₂	1.97	10.14(8)	7.50(1)	669
As5 P1	Pb ₁₀ (PO ₄) _{1.04} (AsO ₄) _{4.41} (OH) ₂	1.84	10.13(4)	7.49(7)	666
As4 P2	Pb ₁₀ PO ₄) _{2.02} (AsO ₄) _{3.70} (OH) ₂	1.74	10.12(9)	7.49(0)	665
As3 P3	Pb ₁₀ (PO ₄) _{3.06} (AsO ₄) _{2.90} (OH) ₂	1.68	10.09(1)	7.47(2)	659
As2 P4	Pb ₁₀ (PO ₄) _{3.91} (AsO ₄) _{2.01} (OH) ₂	1.69	9.96(0)	7.46(0)	641
As1 P5	Pb ₁₀ (PO ₄) _{5.02} (AsO ₄) _{1.05} (OH) ₂	1.65	9.94(7)	7.44(4)	637
As0 P6	Pb ₁₀ (PO ₄) _{6.09} OH ₂	1.64	9.87(6)	7.42(4)	627

Table 2.

Suggested assignments	HAP $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$	HPY $\text{Pb}_{10}(\text{PO}_4)_6\text{OH}_2$	CPY $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$
	[32]	This study	[20]
	cm^{-1}		
OH	3572	3561	
	633	669	
$\nu_3\text{-P}$	1091	1051	1032
	1034	984	998
			972
$\nu_1\text{-P}$	962	931	926
$\nu_4\text{-P}$	602	578	575
	570	552	(550)
	(540)	540	540
$\nu_2\text{-P}$	(474)		436

Table 3.

Suggested assignments	JBA $\text{Ca}_{10}(\text{AsO}_4)_6\text{OH}_2$	HMI $\text{Pb}_{10}(\text{AsO}_4)_6\text{OH}_2$	CMI $\text{Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2$
	[34]	This study	[20]
	cm^{-1}		
OH	3562	3552	
$\nu_3\text{-As}$	-	891	-
	880	831	814
	-	-	804
	847	785	783
	835	747	-
$\nu_4\text{-As}$	447		410
	440		372
$\nu_2\text{-As}$			320

Table 4.

Suggested assignments	As0P6 HPY	As1P5	As2P4	As3P3	As4P2	As5P1	As6P0 HMI
	cm ⁻¹						
OH	3561	3558	3558	3553	3552	3552	3552
v ₃ -P	1109	1114	-	1117	1099	1086	
	-	1082	1058	1062	1043	1029	
	1051	1050	1027	1030	1016	1004	
	-	1020	-	997	-	-	
	984	985	984	970	982	968	
	-	955	954	945	950	948	
v ₁ -P	931	923	918	917	915	911	
v ₄ -P	577	576	574	573	573	571	
	552	553	553	552	557	556	
	538	539	540	540	540	540	
	518	514	514	507	506	511	
v ₃ -As		853	853	848	841	830	831
		825	822	823	824	-	-
		790	791	791	789	792	785
		-	765	761	758	763	747

FIGURES

Fig.1

Fig. 2.

Fig.3.

Fig.4.

Fig 5

Fig.6.

Fig.9.

The synthesized hydroxypyromorphite– hydroxymimetite solid solution series were characterized by FTIR. The effect of substitution of $[\text{PO}_4]^{3-}$ by $[\text{AsO}_4]^{3-}$ on changes in lattice parameters and spectral properties has been explained based on correlation between chemical composition and the peak positions. The As/As+P ratios can be used for composition determination.