Arsenate substitution in lead hydroxyl apatites: a Raman spectroscopic study

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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.

Graphical abstract

Keywords

pyromorphite, mimetite, solid solution, lead apatite, carbonate in apatites, Raman band shift

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with arsenate substitution — forming hydroxyl analogs of pyromorphite–mimetite series — are rather superficial and outdated.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].

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 As/(As + 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 and 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 analyzed with a green laser ($\lambda = 532$ nm, laser power of 5 mW, slit aperture of 25 μm , resolution of 1.9 cm^{-1} in the range between 100.6 and 3579.6 cm^{-1}). A total of 10 exposures of 3 seconds were taken for each spectrum. To minimize any possible anisotropy effect on the intensity resulting from random crystallographic orientation of analyzed grains [28] and to avoid sample thickness effect, the analysis of each specimen was repeated 4 times on various grains. Interpretation of spectra was performed with the aid of OMNIC for Dispersive Raman software. Each collected spectrum was processed separately and the averaged results are presented.

3. Results and discussion

The results of wet chemical analysis presented in Table 1 are in accordance with the intended composition of products of synthesis as well as with the EDS data [27]. Observed small deviations from stoichiometry result from limitations of applied analytical methods and calculations [8] (OH content is assumed based on ideal formula, potential presence of carbonate ion is not considered). A good agreement between the solution composition and the resulting precipitate is commonly observed for synthetic solid solutions of apatites precipitated from aqueous solutions [e.g. 29-31 and the literature cited therein]. The mechanisms causing nonstoichiometry of cationic substitution observed by Jambor & Dutrizac [32] do not apply here. The adoption of modified synthesis procedure presented by Flis et al. [29] results in precipitation of expected phases.

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
$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$		$\text{Pb}_{10}(\text{PO}_4)_{5.66}(\text{OH})_2^*$	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
$\text{Pb}_{10}[(\text{PO}_4)_3(\text{AsO}_4)_3](\text{OH})_2$	1.67	$\text{Pb}_{10}[(\text{PO}_4)_{2.83}(\text{AsO}_4)_{3.07}](\text{OH})_2$	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

The internal vibrations of the free undistorted tetrahedral ions (XO_4) are generally divided into four types. For the isolated $(\text{PO}_4)^{3-}$ ion, the position of nondegenerate symmetric stretching vibration ν_1 of the P–O bond is observed at 938 cm^{-1} , while the triply degenerate antisymmetric stretching vibration ν_3 is observed at 1017 cm^{-1} . The positions of the O–P–O angle deformation vibrations ν_2 (doubly degenerate) and ν_4 (triply degenerate) are at 420 and 567 cm^{-1} , respectively. For the free $(\text{AsO}_4)^{3-}$ ion, the position of ν_1 mode coincides with the position of ν_3 vibration at 810 cm^{-1} . The bending vibration ν_2 of O–As–O angle is observed at 342 cm^{-1} , while the ν_4 vibration is observed at 398 cm^{-1} [33].

The symmetry of a molecule in crystal structure is usually lower than in the isolated state owing to intermolecular interactions. This may cause splitting of the degenerate vibrations [34]. Such splitting is observed in Raman spectra of HPY–HMI solid solution series. A representative of composite spectrum of $\text{Pb}_{10}[(\text{PO}_4)_5(\text{AsO}_4)](\text{OH})_2$ with relevant band assignment is presented in Figure 1. The internal vibrations of $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ molecules are observed in the range between 290 and 3579.6 cm^{-1} . Coupling between the ν_1 and ν_3 vibrations as well as between ν_2 and ν_4 vibrations, noted previously on Cl-pyromorphite and Cl-mimetite spectra [26, 35–39], is also evident for their hydroxyl analogs. A weak band corresponding to the vibrations of $(\text{OH})^-$ ions is apparent near the upper limit of the spectra. The external (lattice) vibrations occur at low frequencies (below 290 cm^{-1}). They include the librational modes of $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ ions as well as translational modes of Pb^{2+} , $(\text{PO}_4)^{3-}$, and $(\text{AsO}_4)^{3-}$ [37].

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

The average positions of Raman effects for all synthetic phases in the range between 290 and 1100 cm^{-1} with the assignment of the vibrational modes are presented in Figure 2. The effect of crystal field and presence of the Pb^{2+} and $(\text{OH})^-$ ions on symmetry of $(\text{AsO}_4)^{3-}$ or $(\text{PO}_4)^{3-}$ ions are apparent. The most intensive band in HPY spectrum (928 cm^{-1}) corresponds to the nondegenerate symmetric P–O stretching vibration ν_1 , whereas the highest one in HMI spectrum (811 cm^{-1}) may be attributed to both ν_1 and ν_3 modes of As–O bond. The triply degenerate As–O stretching vibration ν_3 is further split into two bands at 754 and 775 cm^{-1} . The ν_3 mode in the HPY Raman spectrum is apparent at 961, 1014, and 1026 cm^{-1} . The bending vibrations ν_2 of the O–P–O angle are observed at 392, 415, and 425 cm^{-1} in HPY spectrum, while the ν_4 vibrations are observed at 542, 558, and 580 cm^{-1} . The bands in HMI spectrum corresponding to the ν_2 vibrations are apparent at 314 and 340 cm^{-1} , whereas those attributed to the ν_4 mode are apparent at 372, 406, and 424 cm^{-1} . Due to the overlapping of the ν_4 vibrations of $(\text{AsO}_4)^{3-}$ and the ν_2 mode of $(\text{PO}_4)^{3-}$, the bands at 408–418 cm^{-1} in the spectra of intermediate members of the series were not assigned to either of them. The peak at 484–485 cm^{-1} is probably an artifact of impurities adsorbed on the surface: repeated washing of the selected samples with redistilled water using laboratory equipment resulted in reduction of that band. On the other hand, the peak at around 1055–1058 cm^{-1} was not reduced by washing. It most likely corresponds to the vibrations of $(\text{CO}_3)^{2-}$ molecules [40]. Despite the fact that synthesis was performed at 80°C, small amount of CO_2 dissolved from the air was incorporated into the structure of analyzed phases.

Fig. 2 Average position of the vibrational modes in Raman spectra of HPY-HMI solid solution series in the range between 290 and 1100 cm^{-1}

The variations of average positions of the major $(\text{AsO}_4)^{3-}$ and $(\text{PO}_4)^{3-}$ bands, corresponding to the ν_1 vibrations of As–O and P–O, respectively, are presented in Figure 3. 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 As–O bond is longer and weaker than P–O because of larger ionic radius: $\text{As}^{5+} = 0.46 \text{ \AA}$, while $\text{P}^{5+} = 0.17 \text{ \AA}$ [29]. The position of the major $(\text{PO}_4)^{3-}$ band in the spectra of phases containing more than three As atoms per formula unit is determined with the higher uncertainty due to the relatively low intensity of that band in comparison to the intensity of major $(\text{AsO}_4)^{3-}$ band. The changes in intensities of these two bands correlate almost linearly with the chemical composition (Fig. 4). Quantitative determination of peak intensity is, however, sensitive to sample preparation and instrumental settings. Therefore, the ratio of the intensities were determined as potentially less dependent on artifacts. The average ratio of the major band intensities $I_{\text{As}}/I_{\text{P}}$ shows strong exponential correlation with increasing As content (Fig. 4). In general, intensity of bands is determined by the change in polarizability during the vibration [41]. The lower polarizability of $(\text{PO}_4)^{3-}$ ion than that of $(\text{AsO}_4)^{3-}$ results in a nonlinear relation between the intensities of bands corresponding to the vibrations of these molecules.

Fig. 3 Systematic variations of average positions of the major ν_1 mode of arsenate (a) and phosphate (b) ions as a function of chemical composition of HPY–HMI solid solution series. Error bars represent 2SD (95% confidence interval)

Fig. 4 Systematic variations of average intensity of the major arsenate ν_1 band (a), phosphate ν_1 band (b), and their I_{As}/I_P ratio (c) as a function of chemical composition of HPY–HMI solid solution series. Error bars represent 2SD (95% confidence interval)

The position of the peak attributed to the $(OH)^-$ mode shifts to the lower wavenumbers from 3565 cm^{-1} in HPY spectrum to 3556 cm^{-1} in HMI spectrum (Fig. 5 and 6). In the apatite structure, the hydroxyl ion is located in the channels along the c-axis. It is

surrounded by other $(\text{OH})^-$ ions and by Pb^{2+} , $(\text{PO}_4)^{3-}$ and/or $(\text{AsO}_4)^{3-}$. As Hadrich et al. [42] noticed, the $\text{OH}\cdots\text{OH}$ distance is too long for a hydrogen bond. This indicates that the shift of this band with anionic substitution results from interaction of $\text{OH}\cdots\text{O}(\text{PO}_3)$ and $\text{OH}\cdots\text{O}(\text{AsO}_3)$. The substitution of arsenates for phosphates results probably in slight systematic displacement of a hydroxyl anion in the channel. This issue will be addressed in a separate study using high resolution X-ray diffraction data.

Fig. 5 Average position of the $(\text{OH})^-$ vibrational mode in Raman spectra of HPY–HMI solid solution series

Fig. 6 Variations of average position of the $(\text{OH})^-$ vibrational mode in Raman spectra of HPY–HMI solid solution series

A very strong coupling between the ν_1 and ν_3 vibrations as well as between ν_2 and ν_4 vibrations causes hiding of some bands. Moreover, the mean values of certain peak positions are established with relatively high standard deviations (up to 6 cm^{-1} with a 95% confidence interval) indicating that these bands are composed of two or more split vibrational modes. Therefore, the peak resolve operation for all of the spectra was performed using the Peak Resolve function of the OMNIC software.

The average positions of resolved bands in the range between 700 and 1100 cm^{-1} are presented as composite patterns in Figure 7. The antisymmetric stretching vibrations ν_3 of the P–O bond are split into four peaks at 950, 962, 1011, and 1029 cm^{-1} in the spectrum of HPY end member, while in the solid solutions a fifth band corresponding to that mode appears at 1029–1042 cm^{-1} . Splitting of the peaks constitute evidence of cancellation of the degeneration whereas the additional band in the intermediate phases indicates even more extended reduction in the symmetry of the phosphate anion due to partial isomorphic substitution by $(\text{AsO}_4)^{3-}$. For the As–O bond, four peaks are observed in the range between 760 and 818 cm^{-1} in different samples. Further subdivision into ν_1 and ν_3 modes is not well-defined, because even for the isolated $(\text{AsO}_4)^{3-}$ ion, the position of ν_1 mode coincides with the position of the ν_3 mode. In the analyzed phases, the ν_3 mode splits into three bands and one of them overlaps with the peak of ν_1 vibrations in the range between 802 and 818 cm^{-1} in various specimens. In the spectrum of HMI end member, the peaks of the ν_3 mode are discerned at 760 and 775 cm^{-1} . The third band of ν_3 mode overlapping with the peak of the ν_1 mode occurs at 810–811 cm^{-1} . The positions of the resolved peaks may be influenced by the initial settings of OMNIC Peak Resolve operation. This type of

processing becomes more subjective as the intensity of analyzed band decreases, which particularly affects the ν_3 vibrational modes of $(\text{PO}_4)^{3-}$.

Fig. 7 Results of peak resolve operation of Raman spectra of HPY-HMI series in the range between 700 and 1100 cm^{-1}

The variations of the positions of resolved peak with the 95% confidence interval error bars as a function of chemical composition are shown in Figure 8. Linear correlation for most of them is apparent. In the case of certain peaks (e.g., the ν_1 mode of P–O bond), the variation of Raman shift along the series is small, being at the level of spectral resolution and precision of the method.

Fig. 8 Systematic variations of the positions of resolved Raman bands in spectra of HPY–HMI series in the range between 700 and 1100 cm^{-1} , corresponding to vibrational modes of phosphate (a) and arsenate (b) ions. Error bars represent 2SD (95% confidence interval)

Peak resolve operation of Raman spectra in the range between 290 and 700 cm^{-1} was performed only for the end members (Fig. 9) The bands which correspond to ν_2 and ν_4 O–X–O angle deformation vibrations (where X = P or As) coincide with each other and it is not possible to resolve them correctly for solid solutions. The ν_2 mode of $(\text{PO}_4)^{3-}$ in HPY spectrum splits into four peaks at 542, 558, 573, and 582 cm^{-1} , while the ν_4 vibration splits into five bands at 383, 392, 402, 414 and 426 cm^{-1} . In HMI spectrum, the subdivision of the O–As–O angle deformation vibrations ν_2 and ν_4 is inconclusive due to their very strong coincidence. As regards the existing data of Cl-mimetite [26, 38], additional peaks in

spectra of OH-mimetite occur at 330 and 445 cm^{-1} . The other bands are observed at 314, 345, 373, 389, 406, and 429 cm^{-1} .

Fig. 9 Results of peak resolve operation of Raman spectra of HPY (upper) and HMI (lower) end members in the range between 290 and 700 cm^{-1}

For the Cl-pyromorphite–Cl-mimetite solid solutions, Bajda et al. [26] reported that the peak positions of the antisymmetric stretching (v_3) and bending (v_4) vibrations correlate linearly with the As/(As + P) molar ratio. It was also concluded that such correlation might be used to estimate the As and P content in phases from this series. For hydroxyl analogs of these phases, the peak positions in raw Raman spectra as well as in the resolved ones also vary as a function of chemical composition. The correlation between the positions of major peaks attributed to the v_1 modes of $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ in raw spectra could be used to estimate the As and P content. Similar slight variations of the v_1 vibrations of $(\text{PO}_4)^{3-}$ and $(\text{VO}_4)^{3-}$ correlated with chemical composition of solid solutions between lead fluorapatite and lead fluorvanadate apatite are reported by He et al. [8]. This confirms that observed changes in band position reflects the chemical composition and cannot be explained by experimental setup or instrument settings. Resolved spectra, however, may be influenced, to some extent, by subjective interpretation. Additionally, the estimation of chemical composition based on the positions of major peaks in raw spectra should be performed with caution due to small variation in Raman shift.

Band assignment to the internal vibrations of the $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ molecules in HPY and HMI unresolved Raman spectra collated with band assignment for relevant

apatites [26, 43-44] is presented in Table 2. The vibrational modes of HPY spectrum are shifted to higher wavenumbers than the vibrations of hydroxyl apatite. This is related to the higher atomic mass of lead atom in $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ than calcium in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. A similar effect is observed in the pair HMI $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ and johnbaumite $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$. Full vibrational data are not yet available for johnbaumite. The influence of the substitution of Cl by OH on vibrational modes of $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ is unclear. Furthermore, stronger coupling of ν_1 and ν_3 vibrations is observed on raw Raman spectra for HPY and HMI than for Cl-pyromorphite and Cl-mimetite [26]. Enhancement of the coupling of these vibrations can be associated with broadening of the peaks due to the presence of carbonates in the crystal structure [40]. Moreover, the peak corresponding to the vibrations of carbonate molecules is the least apparent in the spectrum of HPY end member and clearly develops with increasing As content. This may lead to a conclusion that hydroxyl analogs of pyromorphite–mimetite series adopt the $(\text{CO}_3)^{2-}$ ions to a greater extent than chlorine-containing varieties, particularly at the arsenate end of the series. Incorporation of carbonates into the structure of pyromorphite–mimetite solid solution series is the object of the ongoing work [45].

Table 2 Band assignment to the internal vibrations of the $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ molecules in HPY and HMI unresolved Raman spectra in comparison to relevant minerals from apatite supergroup

Phase	X–O vibrations [cm^{-1}]		O–X–O vibrations [cm^{-1}]		References
	ν_1	ν_2	ν_3	ν_4	
hydroxylapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	964	433, 448	1029, 1034, 1041, 1048, 1057, 1064, 1077	580, 591, 607, 614	[43]
OH-pyromorphite $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$	928	392, 415, 425	961, 1014, 1026	542, 558, 580	[this study]
pyromorphite $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$	920	393, 409	945, 984, 1016, 1045	548, 553, 577	[26]
johnbaumite $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$	830, 860, 960*				[44]
OH-mimetite $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$	811	314, 340	754, 775, 811	372, 406, 424	[this study]
mimetite $\text{Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2$	813	315, 339	736, 767, 789	372, 409, 421	[26]

* only partial data are available for johnbaumite, no band assignment

4. Conclusions

Arsenate substitution in lead hydroxyl apatites is unlimited. Raman spectroscopy applied to this continuous solid solution series of hydroxylpyromorphite $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ –hydroxylmimetite $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ indicates the systematic changes apparent in the spectra. This method offers a fast and nondestructive analysis of microcrystalline precipitates, natural or synthetic. If used with caution, the correlation of the position or intensities of selected bands may be applied for semiquantitative estimation of chemical composition of lead apatites from this series. This extends the applications of Raman spectroscopy for environmental and engineering problems.

The presence of CO_3^{2-} bands on Raman spectra of all synthetic phases from the series indicates for the first time the incorporation of carbonate ion in lead hydroxyl arsenates. This is despite the fact that the synthesis was performed from aqueous solutions at 80°C which minimizes the concentration of carbonate ion dissolved from the air. Even though all the phases from the solid solution series were synthesized at the very same conditions, the relative intensity of the carbonate Raman band increases with As content. This means that HMI structure exhibits higher affinity for $(\text{CO}_3)^{2-}$ or easily accommodates carbonates than HPY structure. There is no doubt that lead apatites precipitating at ambient conditions from natural solutions will form in the presence of much higher concentrations of $(\text{CO}_3)^{2-}$. Therefore, the effect of carbonates on the structure and thermodynamic stability of these phases (HMI in particular) needs to be investigated.

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