



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

The vibration characterization of synthetic crystalline lead hydrogen arsenite chloride precipitates $\text{Pb}_2(\text{HAsO}_3)\text{Cl}_2$ -implications of solidification of As (III) and Pb (II)



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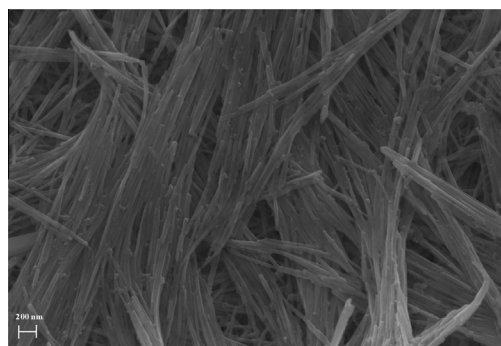
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HIGHLIGHTS

- New lead hydrogen arsenite chloride crystal are prepared by hydrothermal synthesis.
- Five IR spectra and four Raman spectra bands are used for the diagnostic features of AsO_3 unit in crystal structure.
- The crystal precipitates have implication for solidification of As (III) and Pb (II).

GRAPHICAL ABSTRACT

The SEM of synthetic crystalline lead hydrogen arsenite chloride precipitates.



ARTICLE INFO

Article history:

Received 13 July 2013

Received in revised form 29 August 2013

Accepted 7 September 2013

Available online 26 September 2013

Keywords:

Lead hydrogen arsenite chloride
Infrared spectroscopy
Raman spectroscopy

ABSTRACT

The lead hydrogen arsenite chloride precipitates ($\text{Pb}_2(\text{HAsO}_3)\text{Cl}_2$) are synthesized hydrothermally due to its structure trap for lead and arsenic. The synthetic precipitates have well-developed crystalline. The crystals of lead hydrogen arsenite chloride have a series of obvious IR bands at 790, 721, 645, 589 and 554 cm^{-1} . These bands are assigned to the A_g mode of As–O stretching vibration (790), the antisymmetric stretch of As–OH (721), A_g modes (554 and 589) and E_{1g} (645) of the symmetric deformation (ν_1 and ν_3) of AsO_3 unit. The Raman bands at 782, 723, 586, 559 cm^{-1} are attributed to As–O stretching vibration (ν_1) and the symmetric deformation (ν_1 and ν_3), of which the positions and assignments display in accordance with IR result. The most intense Raman band is found in 814 cm^{-1} and is attributed to the A_g mode of ν_1 symmetric stretching vibration of AsO_3 unit, which is not active in IR. The SEM image shows that the precipitates have needle morphology.

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Introduction

Arsenic and lead ions are often present in elevated concentrations in hydrothermal waste water of nonferrous metals [1]. The

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valences of arsenic in these solutions are mainly +3 and +5. Coprecipitation of arsenic using Fe (III) and Al (III) sulfate salt is more effective method for removing As (V) than As (III) [2]. Recently, some synthetic alunite and apatite analogues, such as beudantite $[\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6]$ [3], arsenic-instituted jarosite $[\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2]$ [4], mimetite $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$ [5], were suggested as stable mineral trap for storage arsenic and other toxic metals in water treatment and contaminated soil remediation. These methods originated from the underlying concept of “synthetic mineral

immobilization technology" (SMITE) which firstly was used to dispose radioactive wastes [6].

However, SMITE of As (III) was limited in hydrothermal environment due to less stable crystal phases than As (V). Lead hydrogen arsenite chloride ($\text{Pb}_2(\text{HAsO}_3)\text{Cl}_2$) is crystal which contains protonated arsenite and lead in structure. The only known natural minerals containing these analogous components from literature is trigonite ($\text{Pb}_3\text{Mn}(\text{AsO}_3)_2(\text{AsO}_2\text{OH})$) [7]. Effenberger and Pertlik reported lead hydrogen arsenite chloride belonged to monoclinic, $P2_1/m$ with the unit cell $a = 6.410 \text{ \AA}$, $b = 5.525 \text{ \AA}$, and $c = 9.293 \text{ \AA}$, $\beta = 90.69^\circ$, $V = 329.1 \text{ \AA}^3$ [8]. Recently, this kind of lead hydrogen arsenite crystal was found in ancient metallurgical slag from Punta Zeza area, Lavrion, Greece [9]. It was renewedly reported that its unit cell $a = 6.4235$, $b = 5.5399$, and $c = 9.321$, $\beta = 90.767$, $V = 331.67 \text{ \AA}^3$.

In light of slightly solubility of the families of lead hydrogen arsenite and arsenate chloride, they have potential significance of fixing arsenic (III) in hydrometallurgical processing. This aim of this paper is to synthesize the lead hydrogen arsenite chloride, and report its infrared and Raman spectra relevant to the structure.

Materials and methods

Precipitates synthesis

The crystals of lead hydrogen arsenite chloride precipitates $\text{Pb}_2(\text{HAsO}_3)\text{Cl}_2$ was prepared by addition 55.2060 g $\text{Pb}(\text{NO}_3)_2$ ($\text{Pb} = 5.6 \text{ mmol}$) and 12.9856 g NaAsO_2 ($\text{As} = 3.3 \text{ mmol}$) into mixture of 500 mL distilled water and 167 mL 1 mol/L HCl solution. The suspension solution was aged and mixed by agitator blade at 50 rpm under 60°C for 24 h, and then filtered by $0.25 \mu\text{m}$ membrane. The precipitates were washed by distilled water several times and freeze drying for 48 h. The final crystal is pure white and loose power.

X-ray diffraction

X-ray diffraction pattern of the lead hydrogen arsenite chloride crystal was collected using a PANalytical X'Pert PRO X-ray diffractometer (radius: 240.0 mm). Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 40 kV and 40 mA with Cu $K\alpha$ radiation of 1.540596 \AA . The scan step size and time per step is 0.033423° and 10.16 s, respectively. The continuous scan was run.

Infrared spectroscopy

The infrared spectra of pellet using the mixture of crystal and KBr were collected from a Nicolet Nexus 870 FTIR spectrometer. Spectra over the $4000\text{--}400 \text{ cm}^{-1}$ range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s .

Raman spectroscopy

The Raman spectroscopy of the power crystal was collected from Raman microscope installed with a 514 nm diode laser together with Leica DMLM optical microscope. The scan range is from 4000 to 300 cm^{-1} .

The spectroscopic band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package after performed baseline correction using the Spectra package GRAMS (Galactic Industries Corporation, NH, USA). The band fitting was done using a Lorentzian–Gaussian cross product function with

the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

X-ray diffraction and SEM

The synthetic precipitates have well-developed crystallinity (Fig. 1). X-ray diffraction pattern of precipitates displays in accordance with the patterns of PDF 79-2073 and PDF 22-667, showing that the precipitates mainly are crystalline $\text{Pb}_2(\text{HAsO}_3)\text{Cl}_2$ and also contains $\text{Pb}_5\text{O}_3(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ component. The SEM image of precipitates shows that the precipitates mainly appear in needle crystal with width of 50 nm (Fig. 2). This is well accordance with the single crystal shape of $\text{Pb}_2(\text{HAsO}_3)\text{Cl}_2$ in ancient metallurgical slag reported by Siidra et al. [9].

FT-IR spectroscopy

Fig. 3 shows the FT-IR spectrum in the region between 400 and 4000 cm^{-1} . Free AsO_3^{3-} is a planar molecular, it has C_{3v} symmetry and $2A_1$ (ν_1 and ν_2) + $2E$ (ν_3 and ν_4) modes, which has higher symmetry than pyramidal AsO_4^{3-} (T_d). Loehr and Plane [10] and Tossell [11] determined the fundamental modes of the free AsO_3^{3-} ion in solution, and they reported that the vibrations (ν_1 , ν_2 , ν_3 and ν_4) of AsO_3^{3-} occur in $752/690$, 340 , $680/672$ and 340 cm^{-1} . When AsO_3^{3-} unit enters into C_{6h} crystal, its vibration modes split into A_g , E_{2g} , B_u , E_{1u} , B_g , E_{1g} , A_u and E_{2u} modes. In our spectra, the vibrations of As–O mainly occur in the region of $500\text{--}900 \text{ cm}^{-1}$ (Fig. 1a). An obvious band is observed at 721 cm^{-1} and is assigned to the antisymmetric stretch of As–OH. A weak band at 790 cm^{-1} is assigned to A_g mode of As–O stretching vibration (ν_1). Three intense bands at 554 (A_g), 589 (A_g) and 645 (E_{1g}) cm^{-1} are ascribed to the symmetric deformations (ν_1 and ν_3). Siidra et al. reported that the obvious bands at 707 and 594 cm^{-1} are the characteristic band of lead hydrogen arsenite chloride [9]. According to this study, the two bands are further assigned to the antisymmetric stretch of As–OH and A_g mode of the symmetric deformation (ν_1).

The weak band is found at 516 cm^{-1} in the spectra (Fig. 3). This band also is observed in the spectra of NaAsO_2 , which occurs at 512 cm^{-1} . We deduced that the band comes from some Pb–AsO₂

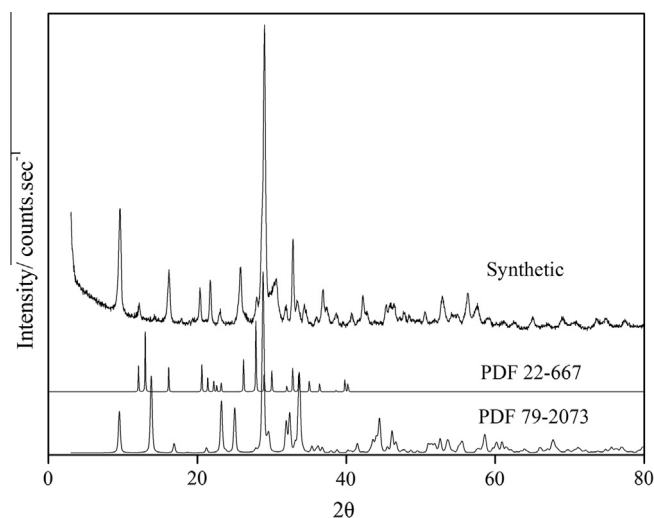


Fig. 1. XRD patterns of synthetic precipitates.

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