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REVISION 1

Single Crystal Raman Spectroscopy of Natural Paulmooreite $Pb_2As_2O_5$ and in Comparison with the Synthesised Analogue

SILMARILLY BAHFENNE[1], LLEW RINTOUL[1], JÖRGEN LANGHOF,[2] RAY L. FROST [1] •

[1]Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[2] Curator of minerals, Department of Mineralogy, Swedish Museum of Natural History, Box 50007, SE-104 05 Stockholm

ABSTRACT

The single crystal Raman spectra of natural mineral paulmooreite $Pb_2As_2O_5$ from the Långban locality, Filipstad district, Värmland province, Sweden are presented for the first time. It is a monoclinic mineral containing an isolated $[As_2O_5]^{4-}$. Depolarised and single crystal spectra of the natural and synthetic sample compare favorably and are characterized by strong bands around 186 and 140 cm^{-1} and three medium bands at 800 – 700 cm^{-1}. Band assignments were made based on band symmetry and spectral comparison between experimental band positions and those resulting from Hartree-Fock

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

calculation of an isolated $[As_2O_5]^{4-}$ ion. Spectral comparison was also made with lead arsenites such as synthetic $PbAs_2O_4$ and $Pb_2(AsO_2)_3Cl$ and natural finnemanite in order to determine the contribution of the terminal and bridging O in paulmooreite. Bands at 760 – 733 cm^{-1} were assigned to terminal As-O vibrations, whereas stretches of the bridging O occur at 562 and 503 cm^{-1}. The single crystal spectra showed good mode separation, allowing bands to be assigned a symmetry species of A_g or B_g.

KEYWORDS: paulmooreite, finnemanite, single crystal Raman spectroscopy; $PbAs_2O_4$; $Pb_2(AsO_2)_3Cl$

INTRODUCTION

Paulmooreite is a lead arsenite mineral containing dimeric $[As_2O_5]^{4-}$ units, which was first announced as a new mineral by Dunn et al. (1979). The natural paulmooreite sample was kindly supplied by the Swedish Museum of Natural History (specimen number NRM532109). In preparing a synthetic analogue of paulmooreite, hydrothermal and wet synthetic methods were explored including the method given by Pertlik (1988) who reported the presence of $Pb_2As_2O_5$ among the products of the hydrothermal synthesis of $Pb_2(AsO_2)_3Cl$. The details of the different synthetic routes will be discussed in the Experimental section.

No other pyroarsenite compounds had been studied to date with Raman spectroscopy apart from the theoretical study by Tossell (1997). Vajdakite, $[(MoO_2)_2(H_2O)_2As_2O_5].H_2O$, also possesses $[As_2O_5]^{4-}$ units (Ondrus *et al*., 2002) and had been studied previously with Raman spectroscopy (Cejka *et al*., 2010). However the presence of two inequivalent $MoO_5(H_2O)$ units makes it difficult to identify and assign the vibrations of the unit since there may be

some coincidence of the bands. A study on some pyroantimonite compounds had been published (Hirschle and Röhr, 2000). In $Cs_4Sb_2O_5$ the SbO_3 pyramids of the $[Sb_2O_5]^{4-}$ unit have the 180° orientation. Its Raman spectrum is similar to that of paulmooreite in the 800 – 600 cm^{-1} region; a strong band at 700, a medium band at 650, and a weak band at 615 cm^{-1} (Fig. 4 of Hirschle and Röhr, 2000). The first two bands were assigned to terminal Sb-O and the last to bridging Sb-O vibrations. This assignment agrees broadly with assignments made in the present study.

To aid the determination of the contribution of the diarsenite unit to the vibrational spectra, the Raman spectrum of an isolated $[As_2O_5]^{4-}$ ion was calculated using Hartree-Fock methods. Furthermore to determine the contribution of the bridging and terminal As-O atoms the spectra of $Pb_2As_2O_5$ was compared with related synthetic compounds $PbAs_2O_4$ and $Pb_2(AsO_2)_3Cl$ and natural finnemanite $Pb_5(AsO_3)_3Cl$. The vibrational spectra of paulmooreite and the above compounds have not been previously published. This study presents the single crystal data for natural and synthetic paulmooreite and makes band assignments according to symmetry and type.

Experimental

Minerals

Single crystals of paulmooreite and finnemanite were supplied by the Swedish Museum of Natural History of specimen numbers NRM532109 and NRM883736 respectively. The specimen originated from the Långban locality, Filipstad district, Värmland province, Sweden. The mineral is colourless to pale yellow. (see http://www.mindat.org/min-3135.html).

Synthesis of the mineral paulmooreite

Pertlik (1988) reported the hydrothermal synthesis of $Pb_2(AsO_2)_3Cl$. Three types of reactions were performed. The first entailed mixing $PbCl_2$ and PbO in a 1:10 weight ratio and As_2O_3 in 1M acetic acid with varying conditions (P1 - 150°C for 4 days, P2 - 50°C for 4 days, P3 - 150°C for 10 days, and P4 - 60°C for 7 days). In the second set of reactions PbO and As_2O_3 were hydrothermally reacted in a mole ratio of 2:1. In all cases 1M acetic acid was used as solvent unless indicated. The conditions were: H1- 150°C for 10 days using 1M acetic acid, H2- 210°C for 4 days using 1M acetic acid, H3- 60°C for 7 days using 1M acetic acid purged with N_2, H4 - 150°C for 2 days using 1M acetic acid purged with N_2, and H5 - 150°C for 2 days using water purged with N_2. The third set were wet synthesis methods in which. NaOH and As_2O_3 were mixed in a ratio of 4:1 to give one mole of $Na_4As_2O_5$, which was then mixed with two moles of $Pb(NO_3)_2$. The precipitate and mother liquor were aged for 7 days at W1 - room temperature, W2 - 40°C, and W3 - 60°C.

Raman Microscopy

A natural crystal of paulmooreite was placed on the corner of a cube and aligned parallel to the sides of the cube. It was assumed that the crystal laid on its perfect (001) cleavage plane. In the plane of the crystal, the long axis corresponded to the *b* axis, and the *a* axis was at right angles to the long axis. Crystals of paulmooreite are tabular on [100] or [001], leading to easier collection of spectra on these faces and avoiding birefringence. The synthetic crystal was not oriented due to its small size.

The instrument used was a Renishaw 1000 Raman microscope system, which also includes a monochromator, a Rayleigh filter system and a CCD detector coupled to an Olympus BHSM microscope equipped with 10x, and 50x objectives. The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing plane polarised light at 633 nm and collected at a resolution of better than 4 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 120 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal-to-noise ratio in the spectra. The instrument was calibrated prior to use using the 520.5 cm^{-1} line of a silicon wafer. In the normal course of spectral accumulation 20 scans were accumulated at 20 s time intervals.

Spectral manipulation such as baseline correction/adjustment was performed using the GRAMS software package (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package (version 1) that enabled the type of fitting function to be selected and allows

specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Lorentzian-Gaussian 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.

Hartree-Fock Calculations

Calculations were performed using the Gaussian 03 program (Frisch *et al*., 2004) and the GaussView 4.0 (Gaussian, Inc.,Wallingford, CT) front end, running on an SGI Origin 3000 supercomputer. The wavenumber of the fundamental modes were calculated using Hartree-Fock (HF) with B3-LYP method and a 6-31G(d) basis set for O atoms and Lanl2dz for As. A scaling factor of 0.972 was applied. Raman intensities were calculated from the Gaussian activities based on 633 nm excitation.

DESCRIPTION OF CRYSTAL STRUCTURE

Paulmooreite structure was refined by Moore *et al*. (1980) who placed it in the monoclinic space group $P2_1/a$ (C_{2h}^5), a = 13.584, b = 5.650, c = 8.551 Å, and Z = 4. It belongs to a small group of diarsenite minerals consisting of vajdakite $[(MoO_2)_2(H_2O)_2As_2O_5].H_2O$ (Ondrus *et al*. 2002) and gebhardite $Pb_8(As_2O_5)_2OCl_6$ (Klaska and Gebert, 1982); the dimeric unit in each mineral differing by the orientation of one trigonal pyramid to the other. In paulmooreite, the triangular bases of the dimer are oriented nearly normal to each other (Moore *et al*. 1980).

Paulmooreite is monoclinic with space group $P2_1/a$ (C_{2h}^5) and four formula units (Moore et al., 1980). The crystal cell dimensions are a = 13.584, b = 5.650, c = 8.551 Å. Two non-equivalent As^{3+} atoms are connected through a common O atom and two other O atoms each, forming a dimeric $[As^{3+}_2O_5]^{4-}$ unit. Each AsO_3 pyramid in the $[As_2O_5]^{4-}$ unit may be oriented in number of different ways with respect to the other; parallel orientation (Fig.1a), 90°

orientation, and 180° orientation. In paulmooreite the dimers have approximately 90° orientation (Fig.1b), where one AsO_3 pyramid is rotated 90° from the ideal parallel orientation. There are also two inequivalent Pb^{2+} atoms in distorted tetragonal pyramidal geometry. The symmetry of the AsO_3 pyramids is reduced to C_1 from the ideal trigonal pyramid (C_{3v}) symmetry. The bridging $O_{(3)}$ atom has longer bond lengths to $As_{(1)}$ and $As_{(2)}$ than the terminal O atoms. $As_{(1)}$-$O_{(3)}$ and $As_{(2)}$-$O_{(3)}$ bond lengths are 1.826 and 1.842 Å, respectively. The bond lengths of the terminal O atoms belonging to $As_{(1)}$ are 1.747 and 1.750 Å, and those belonging to $As_{(2)}$ are 1.733 and 1.772 Å.

Insert Figures 1a and 1b here

RESULTS

X-ray Diffraction

The first set of reactions had resulted in the formation of $PbAs_2O_4$ and $Pb_2(AsO_2)_3Cl$ instead of $Pb_2As_2O_5$ as reported by Pertlik [5]. Fig. 2 shows the XRD pattern of the product of P3. The reactions H1 and H2 gave hydroxymimetite $Pb_5(AsO_4)_3OH$ (Fig. 3). In an attempt to minimise oxidation of As3+, subsequent reactions used N2-purged solvents. Only $PbAs_2O_4$ resulted from the reaction H3, whereas H4 and H5 gave $Pb_2As_2O_5$ and $PbAs_2O_4$ at ratios of 70:30 and 50:50 respectively. Wet synthesis reactions W1 and W2 gave $Pb_2As_2O_5$ as the major constituent. The product of W3 also shows $Pb_2As_2O_5$; however $PbAs_2O_6$ is also detected among other products that could not be identified.

Insert Figure 2 and 3 here

Scanning Electron Microscopy

The SEM micrographs of $Pb_2As_2O_5$ synthesised by reactions W1 and W2 are shown in Fig. 4 a, b. The product of W1 appears to have three different morphologies. There are aggregates of small fibrous particles, between which are interspersed thin plates of about 10 – 20 microns arranged in a pine-needle formation A significant amount of the crystals takes the form of flat plates of about 20 – 100 microns. The product of W2 appears uniform in morphology and very similar to the fibrous particles in W1 except that in this case they form spheres.

Insert Figures 4a and 4b here

Factor Group Analysis (FGA)

The unit cell of paulmooreite is the primitive unit cell and it contains four formula units. Thus a primitive unit cell contains 36 atoms. The number of allowable modes is 105 consisting of $27A_g$, $27B_g$, $26A_u$, and $25B_u$. The form of the polarisability tensor for C_{2h} crystals dictates that A_g modes are observed in the aa, bb, cc, and ac orientations and B_g modes in the ab and bc orientations. The isolated $[As_2O_5]^{4-}$ ion with the pyramidal bases in a parallel orientation has C_{2v} symmetry and 15 normal modes of vibration consisting of $5A_1 + 3A_2 + 3B_1 + 4B_2$. On a C_1 site, such as the case with paulmooreite, each of the above modes turns into an A mode, and each A mode splits into A_g, B_g, A_u and B_u in a C_{2h} crystal.

Raman Spectroscopy

Paulmooreite is biaxially positive with a birefringence of about 0.110. The optical direction which coincides with the *b* axis is Y, meaning that light travelling along the *b* axis will not encounter circular sections and will therefore experience birefringence. Crystals of paulmooreite are tabular on [100] or [001], leading to easier collection of spectra on these faces and avoiding birefringence.

Fig. 5 shows spectra collected on the *a* and *c* faces of natural paulmooreite and a spectrum of the product of reaction W2. All three spectra compare favourably, with minor differences. The strongest band in all three spectra occurs at 186 cm^{-1}, followed in intensity by a band near 140 cm^{-1}, and a group of bands in the 800 – 600 cm^{-1} region. The synthetic spectrum shows bands at 637 and 598 cm^{-1} which were not observed in the natural spectra. A strong band near 140 cm^{-1} seems to be broader and may consist of two bands in the synthetic spectrum, and sharper in the natural spectra. Whether or not the above bands are 'real' will be explored in later sections based on the single crystal data.

The single crystal data of natural paulmooreite are presented in Figs. 6, 9 and 10. Two non-polarised spectra collected on the *a* and *c* faces are shown, along with the parallel and perpendicular spectra of each face. Single crystal spectra of synthetic paulmooreite are shown in Figs. 7 and 8. A non-polarised, parallel, and perpendicular spectrum was collected on the tabular face of the crystal.

A group of bands in the 800 – 700 cm^{-1} region (Fig. 6) appears to consist of two A_g and B_g bands, whereas the group of bands in the 700 – 600 cm^{-1} region (Fig. 7) consists of three bands instead of the four observed in the non-polarised spectrum of synthetic paulmooreite

(Figs. 7 and 9). The assignment of the bands around 640 and 598 cm^{-1} in the synthetic spectrum is uncertain since neither the parallel nor perpendicular spectra show these bands. However the natural non-polarised spectrum collected on the *a*-face and the ABCA spectrum show the 640 cm^{-1} band clearly defined and thus assigned to B_g symmetry. The weak band at 598 cm^{-1} is only observed in the Raman spectra of products of reactions H4, W2 and W3 and hence may be due to edge effect, resulting from the small crystal domain size. The same applies to the very weak band just above 350 cm^{-1}. A band at 560 cm^{-1} is detected only in the spectra collected on the *a*-face. Although it is weak, it is clearly defined in the depolarised *a*-face and ABCA spectra and was determined to be of B_g symmetry. The presence of two components in the band near 140 cm^{-1} as suggested by the broadness of this band in the depolarised synthetic spectrum is confirmed by the presence of the weak B_g band just above 140 and the strong A_g band just below 140 cm^{-1}. The complete band symmetry assignments are presented in Table 2.

Insert Figures 5 to 10 here

Discussion

Out of the 54 allowable Raman modes of paulmooreite 27 modes were observed consisting of $11A_g$ and $16B_g$ modes. Two types of As-O stretches can be expected corresponding to terminal and bridging As-O atoms. The symmetry of each AsO_3 group in the $[As_2O_5]^{4-}$ ion is reduced from the ideal trigonal pyramid (C_{3v}) symmetry to C_1. In an isolated $[As_2O_5]^{4-}$ ion with parallel orientation (thus having C_{2v} symmetry), stretches of the bridging O gives A_1 (symmetric) and B_2 (antisymmetric) modes while its symmetric deformation gives A_1 mode. Stretches of the terminal O atoms should give A_1, A_2, B_1, and B_2 modes. If the ion occupies a C_1 site such as the case with paulmooreite each vibration will turn into a vibration of *A*

symmetry, each of which will split into an A_g and B_g component in a C_{2h} crystal. The low symmetry in paulmooreite limits the value of factor group analysis in band assignment, therefore to aid in the task of assigning bridging and terminal O vibrations the spectra of paulmooreite are compared with the HF calculated Raman spectrum and the spectra of a number of lead arsenite compounds containing polymeric and discrete AsO_3 groups.

Insert Table 1 here

Spectra of natural paulmooreite collected on the *a* and *c* faces of the crystal are shown in Fig. 14 along with $PbAs_2O_4$ resulting from reaction H5, $Pb_2(AsO_2)_3Cl$ from reaction P3, natural finnemanite ($Pb_5(AsO_3)_3Cl$), and the HF calculated Raman spectrum of an isolated $[As_2O_5]^{4-}$ with parallel orientation (C_{2v} symmetry).

$PbAs_2O_4$ and $Pb_2(AsO_2)_3Cl$ consist of polymerised AsO_3 groups arranged into As_4O_8 rings (Dinterer *et al*., 1988) and open-branched single chains (Pertlik, 1988), respectively. Finnemanite, on the other hand, possesses isolated AsO_3 pyramids (Pertlik and Effenberger, 1979).

Insert Figure 11 here

All of the compounds show two or three bands in the 850 – 700 cm^{-1} region. A band at 734 cm^{-1} (υ_1) is the most intense in the finnemanite spectrum, with the other bands down to 200 cm^{-1} having medium or weak intensity. $PbAs_2O_4$ and $Pb_2(AsO_2)_3Cl$ show bands of higher intensity than paulmooreite in the 660 – 480 cm^{-1} region. The next group of bands which the dimeric/polymeric arsenites have in common is located in the 450 – 250 cm^{-1} region.

Bands in the 850 – 700 cm^{-1} region in the spectrum of paulmooreite are assigned to terminal As-O stretches since these bands are found in the spectra of all of the above lead arsenite compounds, including finnemanite which does not contain bridging O atoms. Single crystal data show two B_g bands at 760 and 755 cm^{-1}, and two A_g bands at 750 and 733 cm^{-1}. HF calculated data on an isolated $[As_2O_5]^{4-}$ ion presented in a study by Tossell (1997) assigned terminal O stretches to bands at 751, 740, 739 and 734 cm^{-1} which agrees closely to the experimental data and HF calculated data of this study which showed bands at 736, 720, 710, and 703 cm^{-1}. Factor group analysis (FGA) on an isolated $[As_2O_5]^{4-}$ ion predicts that each of these bands (which should possess A_1, A_2, B_1 and B_2 symmetry) is split into A_g and B_g components but the observed number of bands is rather less than that predicted, possibly due to accidental degeneracies arising from the highly similar terminal bond lengths of the two inequivalent As atoms.

Bands in the 660 – 480 cm^{-1} region are more intense in the spectra of $PbAs_2O_4$ and $Pb_2(AsO_2)_3Cl$, which contain two As-O_b bonds to one As-O_t, than in the spectrum of paulmooreite which contains one As-O_b and two As-O_t bonds. The above observation suggests that this region corresponds to various stretching vibrations of the bridging O atoms. The spectrum of paulmooreite shows two bands at 562 (B_g) and 503 cm^{-1} (B_g). The HF data of Tossell (1997) showed bridging As-O-As stretches at 554 and 496 cm^{-1}, in excellent agreement with the experimental data. The HF data in this study calculated Raman bands corresponding to the symmetric and antisymmetric bridging O stretches at 538 and 521 cm^{-1}, which also supports the above assignments. FGA on an isolated $[As_2O_5]^{4-}$ ion predicts stretches of the bridging O giving bands of A_1 and B_2 symmetry; thus it is reasonable to assign each of the calculated bands to either A_1 or B_2. Even though there should be an A_g and

281 B_g component to each of the above modes, the A_g components in this region may be too weak
282 to be observed. Though it may be an orientation effect, the A_g band might be stronger if we
283 had measured the spectrum in an alternate orientation that wasn't available owing to
284 birefringence on the b axis.
285
286 The observation that the terminal As-O stretch occurs at a higher wavenumber fits in well
287 with the shorter terminal As-O bond lengths (ranging from 1.733 to 1.772 Å) compared to the
288 bridging As-O bond length (1.826 and 1.842 Å). Between vibrations of terminal and
289 bridging O, there are three bands at 658, 635, and 613 cm^{-1} in the spectra of paulmooreite that
290 have not been accounted for. They were not observed in the calculated data for the isolated
291 $[As_2O_5]^{4-}$ ion, indicating the unlikelihood that these bands correspond to As-O vibrations.
292 Bands of similar appearance and intensity, however, are observed in the spectrum of
293 $PbAs_2O_4$, which makes it possible that these bands correspond to Pb-O vibrations.
294
295 The next group of bands which dimeric/polymeric lead arsenites have in common occurs at
296 460 – 240 cm^{-1}. Bands around 380 cm^{-1} have been associated with deformations of the As-O-
297 As unit (Tossell, 1997; Tossell and Zimmermann, 2008; Gout *et al*., 1997; Pokrovski *et al*.,
298 1996), and the HF data in this study calculated Raman bands corresponding to deformations
299 of the terminal O atoms to occur at 386 – 382 cm^{-1}, and deformations of the bridging O atoms
300 (although some coupling occurs with the terminal O) at 324 – 318 cm^{-1}. The spectra of
301 paulmooreite exhibit $2A_g + 3B_g$ bands at 383 – 268 cm^{-1} and $2A_g + 2B_g$ bands at 460 – 409
302 cm^{-1}; the former region assigned to deformations of the terminal O and the latter to
303 deformations of the bridging O. Except for the presence of an extra B_g band in the former
304 region, the above observation follows the expectation that each calculated band should split
305 into two components (A_g and B_g) caused by the lower symmetry. Similar to the previous

region, bands in this region have a higher intensity in the spectrum of $PbAs_2O_4$ compared to the other lead arsenites.

It is difficult to determine whether the experimental Raman spectrum reflects that predicted by factor group analysis. The low site symmetry caused by the 90° orientation of the AsO_3 units in the $[As_2O_5]^{4-}$ ion converts all vibrational modes to *A* modes and thus the experimental Raman spectrum only reflects the crystal symmetry. Furthermore it is also difficult to accurately model and calculate the Raman spectrum of the arsenite ion since its conformation in paulmooreite is not at an energy minimum in the free ion.

The Raman spectra of synthetic and natural paulmooreite are characterised by three medium bands at 800 – 700 cm^{-1}, weak-medium bands near 650, 430, 410, 365, and 310 cm^{-1}, and strong bands near 190 and 140 cm^{-1}. The single crystal data of both natural and synthetic also compare favourably. It is difficult to make band assignments based on symmetry alone due to the low site symmetry. Spectral comparison with lead arsenites such as synthetic $PbAs_2O_4$ and $Pb_2(AsO_2)_3Cl$ and natural finnemanite suggests bands at 760, 755, 750, and 733 cm^{-1} in the spectra of paulmooreite correspond to terminal As-O vibrations, whereas stretches of the bridging O occur at 562 and 503 cm^{-1}. The assignment above is confirmed by the shorter terminal As-O bond compared to bridging bonds and by the Raman spectrum of an isolated $[As_2O_5]^{4-}$ ion calculated by HF methods. Factor group analysis predicted $27A_g + 27B_g$ modes in the Raman spectrum and in this study $11A_g + 16B_g$ modes were observed.

REFERENCES

Cejka, J., Bahfenne, S., Frost, R. L. and Sejkora, J. (2010) Raman spectroscopic study of the arsenite mineral vajdakite $[(Mo^{6+}O_2)_2(H_2O)_2As^{3+}{}_2O_5].H_2O$. Journal of Raman Spectroscopy, 41, 74 – 77.

Dinterer, F., Effenberger, H., Kugler, A., Pertlik, F., Spindler, P. and Wildner, M. (1988) Structure of lead (II) arsenate (III). Acta Crystallographica, C44, 2043 – 2045.

Dunn, P. J., Peacor, D. R. and Darko Sturman, B. (1979) Paulmooreite, a new lead arsenite mineral from Langban, Sweden. American Mineralogist, 64, 352 – 354.

Frisch, M. J. *et al*. (2004) *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT

Gout, R., Pokrovski, G., Schott, J. and Zwick, A. (1997) Raman spectroscopic study of arsenic speciation in aqueous solutions up to 275° C. Journal of Raman Spectroscopy, 28, 725 – 730.

Hirschle, C. and Röhr, C. (2000) Alkalimetall-oxoantimonate: synthesen, kristallstrukturen und schwingungsspektren von $ASbO_2$ (A = K, Rb), $A_4Sb_2O_5$ (A = K, Rb, Cs) und Cs_3SbO_4. Zeitschrift für Anorganische und Allgemeine Chemie, 626, 1305 – 1312.

Klaska, R. and Gebert, W. (1982) Polytypie und struktur von gebhardit – $Pb_8OCl_6(As_2O_5)_2$. Zeitschrift für Kristallographie, 159, 75 – 76.

Moore, P. B., Araki, T. and Brunton, G. D. (1980) Type crystal structure of paulmooreite, $Pb_2[As_2O_5]$: dimeric arsenite groups. American Mineralogist, 65, 340 – 345.

Ondrus, P., Skala, R., Cisarova, I., Veselovsky, F., Fryda, J. and Cejka, J. (2002) Description and crystal structure of vajdakite, $[(Mo^{6+}O_2)_2(H_2O)_2As^{3+}{}_2O_5].H_2O$ – A new mineral from Jachymov, Czech Republic. American Mineralogist, 87, 983 – 990.

Pertlik, F. (1988) The single chain arsenites $Pb(AsO_2)Cl$ and $Pb_2(AsO_2)_3Cl$. Preparation and structure investigation. Zeitschrift für Kristallographie, 184, 191 – 201.

Pertlik, F. and Effenberger, H. (1979) Die Kristallstruktur des Finnemanits, $Pb_5Cl(AsO_3)_3$, mit einem Vergleich zum Strukturtyp des Chloroapatits, $Ca_5Cl(PO_4)_3$. Tschermaks Mineralogische und.Petrographische Mitteilungen, 26, 95 – 107.

Pokrovski, G., Gout, R., Schott, J., Zotov, A. and Harrichoury, J. (1996) Thermodynamic properties and stoichiometry of As(III) hydroxide complexes at hydrothermal conditions. Geochimica et Cosmochimica Acta, 60, 737 – 749.

Tossell, J. A. (1997) Theoretical studies on arsenic oxide and hydroxide species in minerals and in aqueous solution. Geochimica et Cosmochimica Acta, 61, 1613 – 1623.

Tossell, J. A. and Zimmermann, M. D. (2008) Calculation of the structures, stabilities, and vibrational spectra of arsenites, thioarsenites and thioarsenates in aqueous solution. Geochimica et Cosmochimica Acta, 72, 5232 – 5242.

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381

Band Position (cm^{-1})		Assignment
Natural	Synthetic	
760	761	Bg
755	755	Bg
750	751	Ag
733	733	Ag
658	658	Bg
635	637	Bg
613	613	Bg
	599	?
562		Bg
503	501	Bg
460		Bg
433	434	Ag
412	411	Ag
409	409	Bg
383	384	Bg
367	364	Ag
	355	?
344	344	Bg
312	312	Bg
310	310	Ag
272	274	Ag
268	270	Bg
219	214	Bg
210	209	Ag
186	186	Ag
142	144	Bg
138	139	Ag
120	120	Bg
108	107	Ag

Table 1 Band symmetry assignments of paulmooreite

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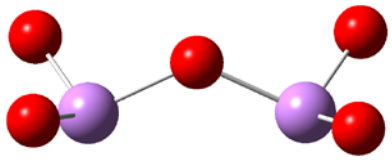
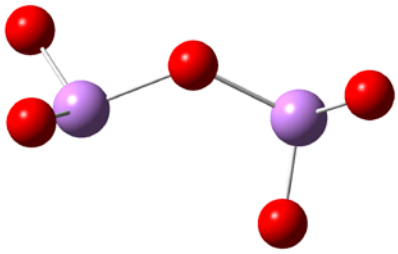


387

388 **Fig 1a $[As_2O_5]^{4-}$ dimer in parallel orientation (As:purple)**



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391 **Fig 1b – $[As_2O_5]^{4-}$ dimer in paulmooreite (90° orientation)**

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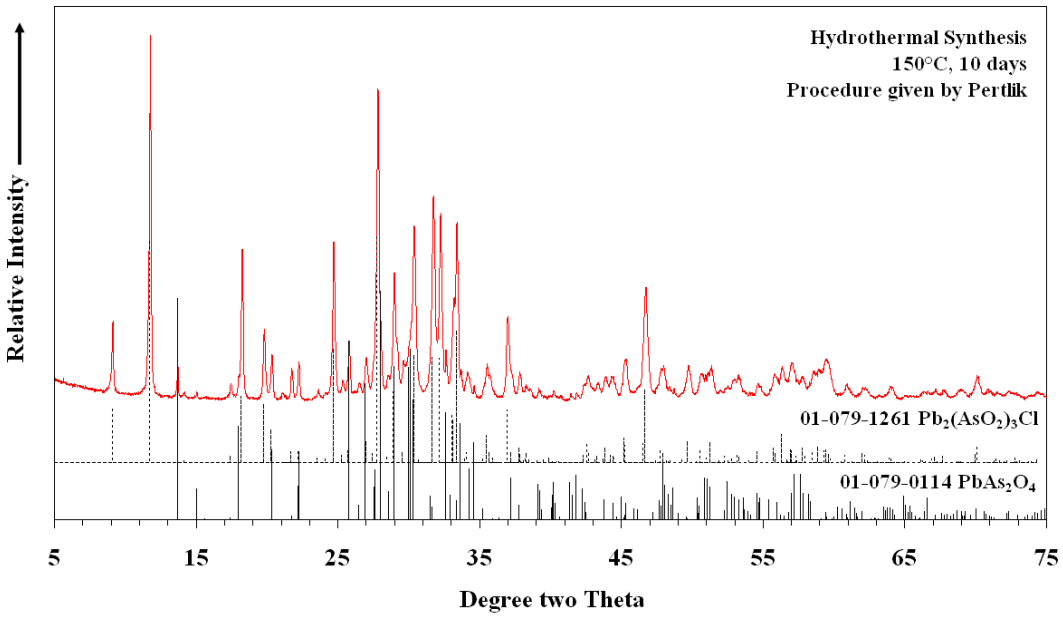
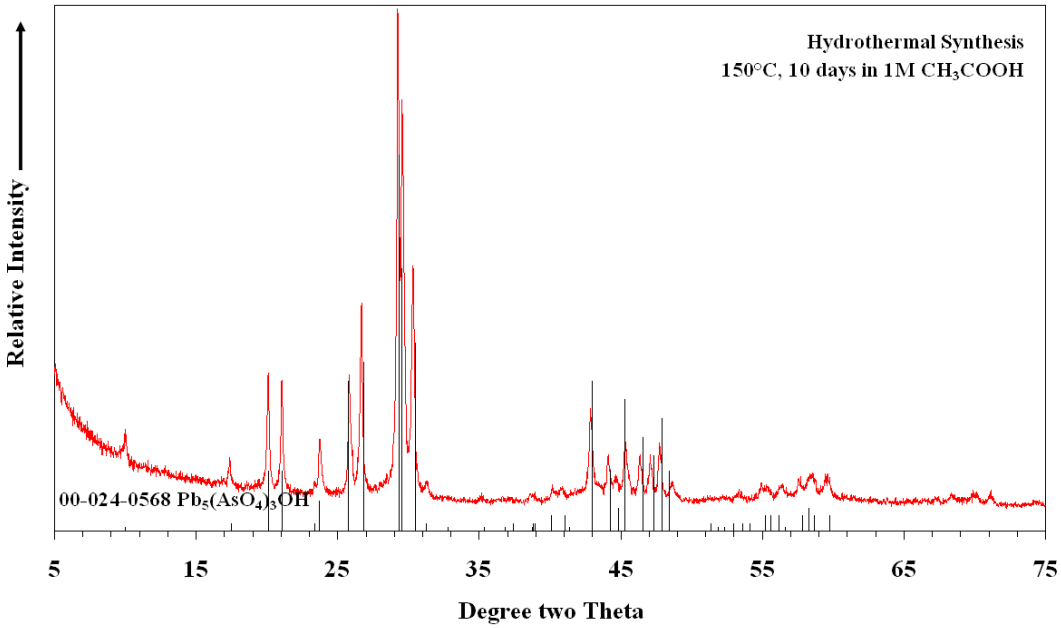


Fig. 2 XRD pattern of the product of reaction P3

399



400

401 **Fig. 3 XRD pattern of the product of reaction H1**

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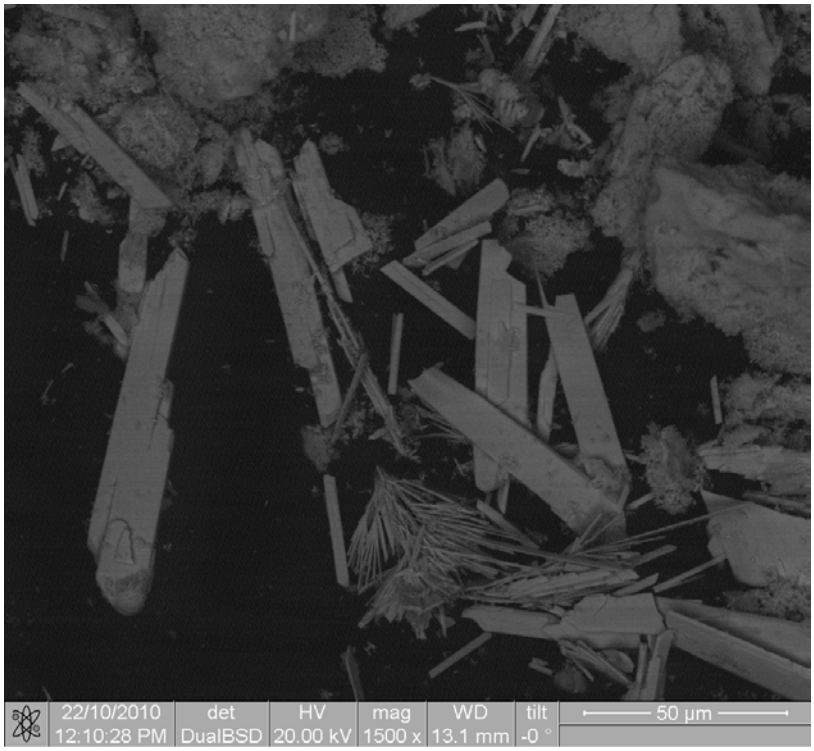


Fig. 4a SEM micrograph of product of reaction W1

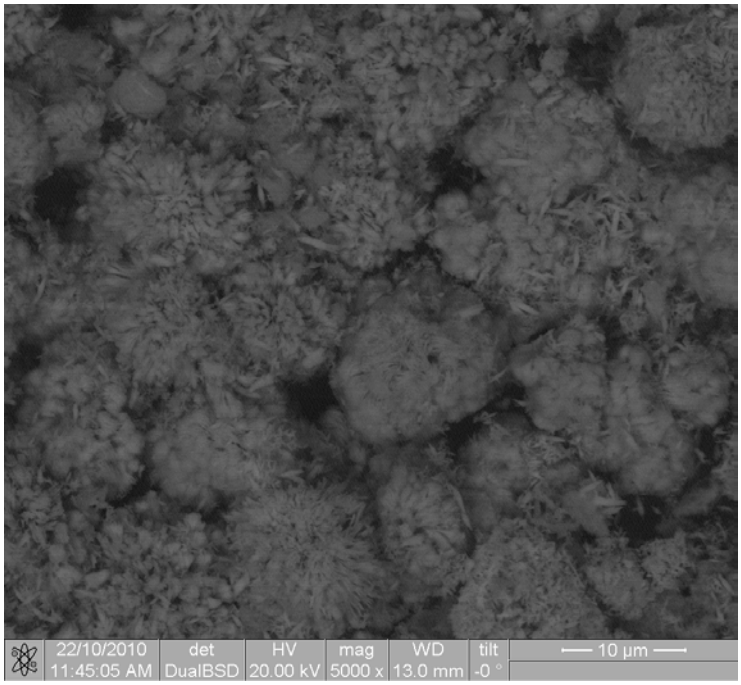
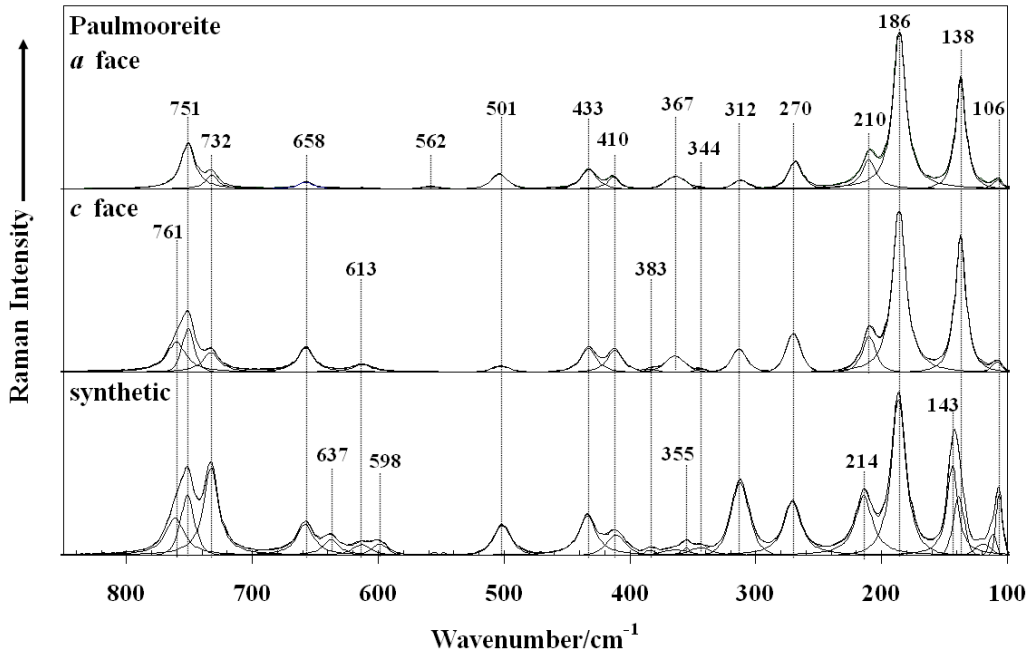


Fig. 4b SEM micrograph of product of reaction W2



413

414 **Fig. 5 Raman spectra of natural and synthetic paulmooreite in the 800 – 100 cm^{-1} region**

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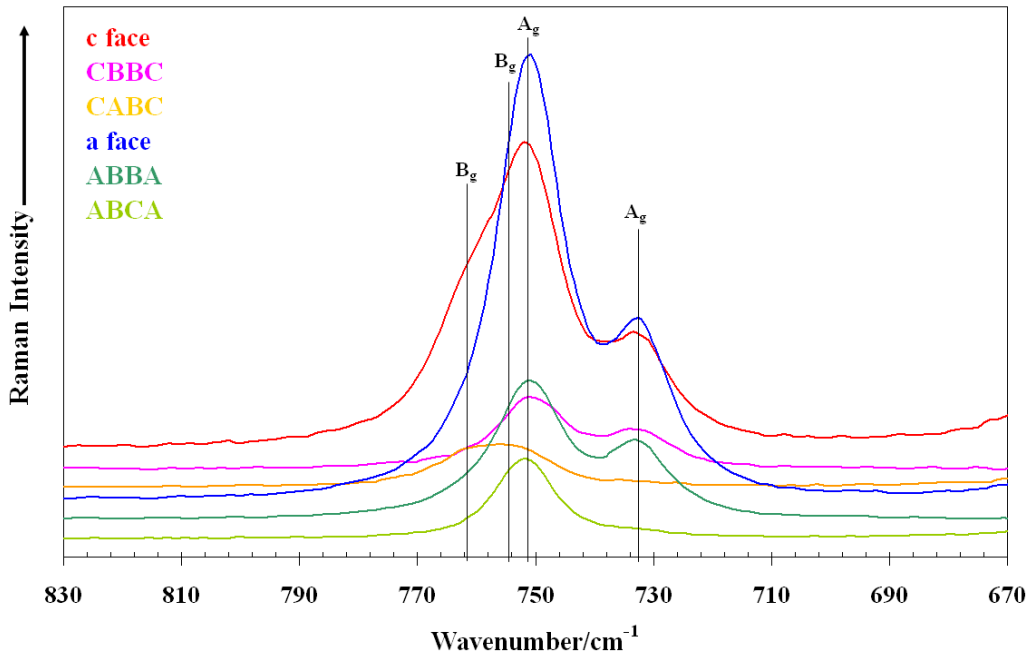

Fig. 6 Oriented single crystal spectra of natural paulmooreite in the 830 – 670 cm^{-1} region

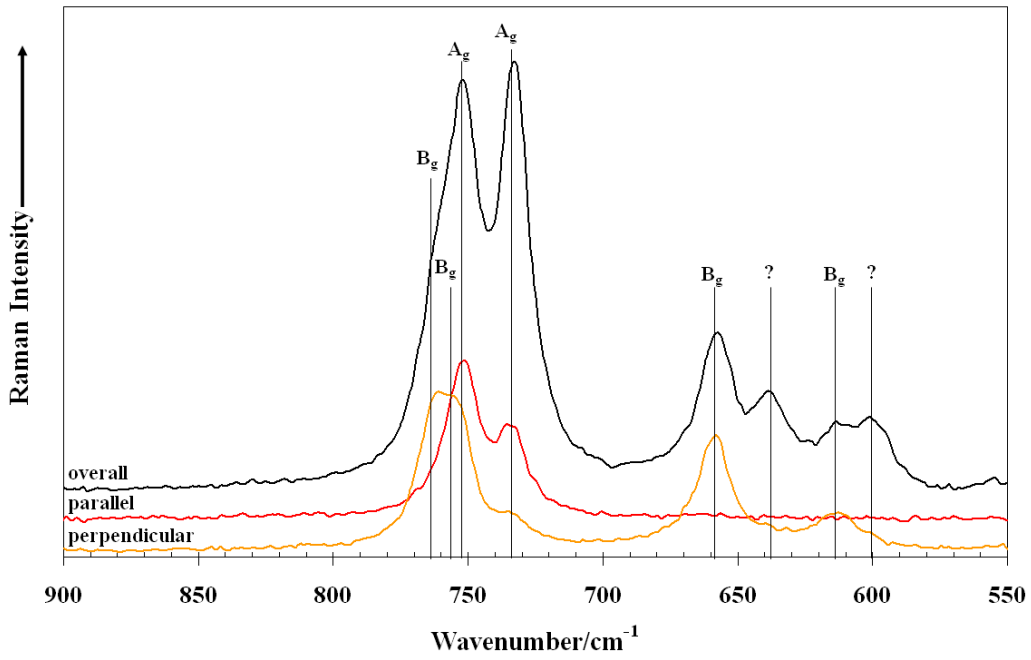

Fig. 7 Oriented single crystal spectra of synthetic paulmooreite in the 900 – 550 cm^{-1} region.

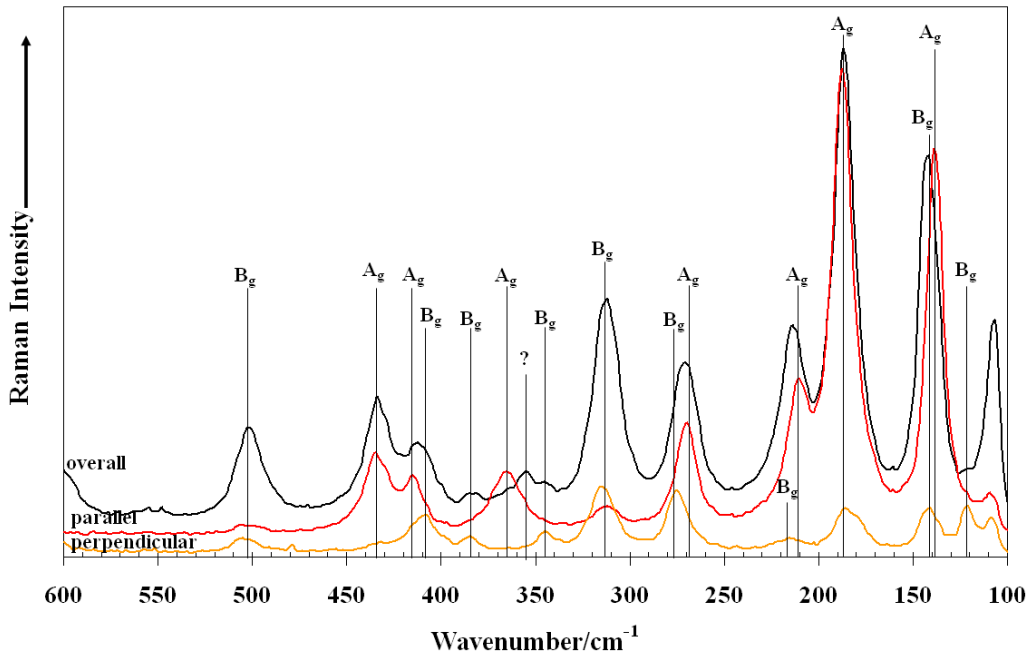

Fig. 8 Oriented single crystal spectra of synthetic paulmooreite in the 600 – 100 cm^{-1} region.

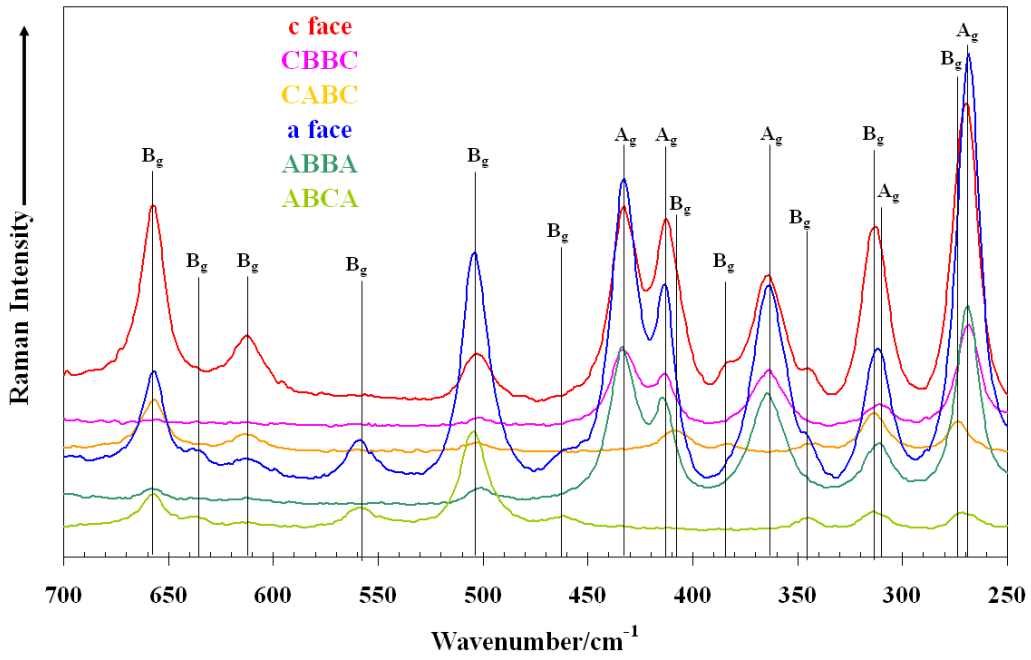

Fig. 9 Oriented single crystal spectra of natural paulmooreite in the 700 – 250 cm^{-1} region.

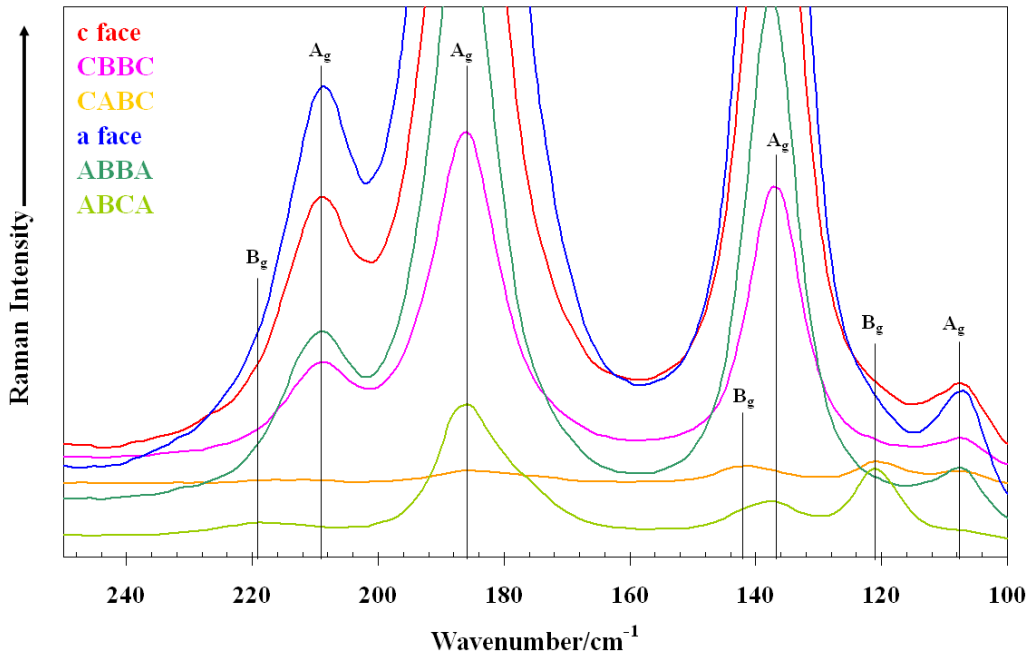

Fig. 10 Oriented single crystal spectra of natural paulmooreite in the 250 – 100 cm^{-1} region.

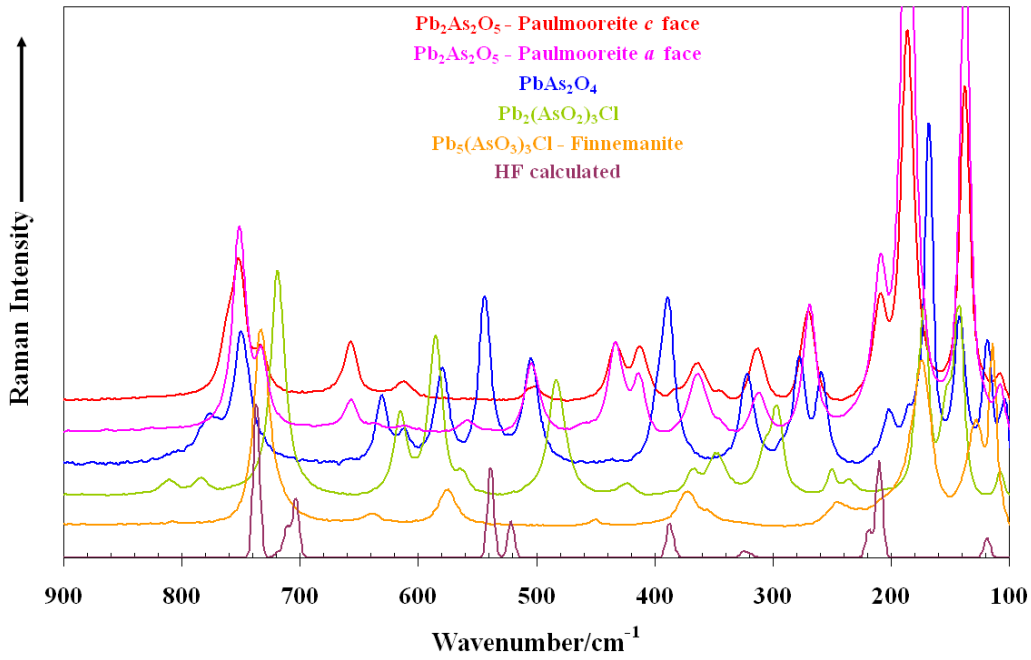

Fig. 11 Stacked Raman spectra of paulmooreite,$Pb_5(AsO_3)_3Cl$, $PbAs_2O_4$, $Pb_2(AsO_2)_3Cl$, and HF calculated Raman spectrum of paulmooreite