Molecular structure of the arsenate mineral chongite from Jáchymov – a vibrational spectroscopy study

Jiří SEJKORA1*, Jakub PLÁŠIL2, Jiří ČEJKA1, Zdeněk DOLNÍČEK1, Radim PAVLÍČEK3

1 Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, 193 00 Prague 9 – Horní Počernice, Czech Republic; jiri_sejkora@nm.cz
2 Institute of Physics ASCR, v.v.i., Na Slovance 1999/2, 182 21 Prague 8, Czech Republic
3 Havlíčkova 388, Unhošť 27351, Czech Republic
* Corresponding author

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1. Introduction

Hureaulite group minerals comprise monoclinic arsenates and phosphates of generalized composition M1M2M3(TIO4)2(T2O7·2H2O)·4H2O (Tab. 1). The M1 site (Fig. 1) is occupied mainly by Ca2+, Mn2+ or Cd2+; the M2 is the preferred site for the smallest octahedrally coordinated cations, as Mg2+, Mn2+, Ca2+ or Zn2+. According to Kampf (2009), vacancy may also occur at this site. The M3 site is then occupied by larger cations as Ca2+, Mn2+ or Zn2+. Elliot et al. 2009; Kampf 2009; Kampf et al. 2016; Meissner et al. 2019. Arsenate members of this mineral group have the tetrahedrally coordinated T1 and T2 sites occupied by (AsO4)3− and (AsO4·OH)2− groups with only minor documented contents of the phosphate component.

Chongite, the Ca–Mg–Ca–As dominant member of the hureaulite group, has been described recently by Kampf et al. (2016) as a new mineral from the Torrecillas mine, Iquique Province, Chile. An unnamed mineral phase “Mg-villyaellenite”, described from Jáchymov (Czech Republic) by Ondruš et al. (1997b), is most probably identical with chongite (Kampf et al. 2016).

Although the description of chongite and refinement of its crystal structure has been published recently (Kampf et al. 2016), vibrational (Raman and infrared) spectroscopic studies have not been undertaken so far. Moreover, Raman spectroscopy has been proven as an excellent technique for the study of molecular structure of minerals containing complex oxyanions (e.g., Čejka et al. 2009; Jirásek et al. 2017; Dufresne et al. 2018). Therefore, we have undertaken a vibrational spectroscopy study of chongite, recently found at the second locality in the world, Jáchymov. This paper aims to summarize results of the complex mineralogical study of this arsenate mineral.

We have undertaken a study of a new arsenate mineral chongite from the second world occurrence, which is Jáchymov (Czech Republic). Chongite occurs as colourless to white crystalline spherical and hemispherical aggregates up to 0.3 mm across composed of rich crusts on strongly weathered fragments of rocks and gangue. The chemical composition of chongite agrees well with the general stoichiometry of the hureaulite group of minerals and corresponds to the molecular structure of chongite as follows: Ca1.84Mg1.00Mn4.00. Chongite is monoclinic, space group C2/c, with the unit-cell parameters refined from X-ray powder diffraction data: a 18.618(5), b 9.421(2), c 9.988(2) Å, β 96.86(2)° and V 1739.4(7) Å3. Raman bands at 3456, 3400, 3194 cm−1 and infrared bands at 3450, 3348, 3201 and 3071 cm−1 are assigned to the νOH stretching structurally distinct differently hydrogen bonded water molecules. Raman bands at 2887, 2416 cm−1 and infrared bands at 2904, 2783 cm−1 are connected to νOH stretching in hydrogen bonded (AsO4·OH)2− units. Raman bands at 1656, 1578 cm−1 and infrared bands at 1652, 1601 cm−1 are assigned to the νδ(H2O) bending vibrations of structurally distinct hydrogen bonded water molecules bonded in the structure through H-bonds of various strength. A Raman band at 1284 cm−1 and infrared bands at 1091 and 1061 cm−1 may be connected to the δ As–OH bending vibrations. The most prominent Raman bands at 902, 861, 828, 807, 758 cm−1 and infrared bands at 932, 899, 863, 815, 746 cm−1 are attributed to overlapping ν As(Nb) antisymmetric stretching, ν As(Ob) antisymmetric stretching, ν As(Oc) symmetric stretching, and ν As(OH) asymmetric stretching vibrations. Raman band at 693 cm−1 and infrared bands at 721, 634 cm−1 are assigned to δ AsOH bend and molecular water libration modes. Raman bands 506, 469, 451, 436 cm−1 and infrared bands at 503, 466 and 417 cm−1 are connected with the νδ(AsO4) antisymmetric stretching vibrations. Raman bands at 389, 360, 346 and 302 cm−1 are related to the νγ(AsO4) and (HOAsO4) bending vibrations. Raman bands at 275 and 238 cm−1 are assigned to the ν(OH−−O) stretching vibrations and those at 190, 162, 110 and 75 cm−1 to lattice modes.

* Corresponding author.
2. Material and methods

2.1. Occurrence and specimen description

Chongite was found on several specimens originating from the Jáchymov ore district (formerly St. Joachimsthal), Krušné hory (Erzgebirge) Mountains, approximately 20 km north of Karlovy Vary (Carlsbad), northwestern Bohemia, Czech Republic. Material originates from the Geschieber vein at the 2nd level of the Svornost mine located in the central part of this ore district (finds were made in April and October 2018).

The Jáchymov ore district is a classic example of Ag + As + Co + Ni + Bi and U vein-type hydrothermal mineralization. The ore veins cut a complex of medium-grade metasedimentary rocks of Cambrian to Ordovician age, in the envelope of a Variscan Karlovy Vary granite pluton (Ondruš et al. 2003a). The majority of the ore minerals were deposited during Variscan mineralization from mesothermal fluids (Ondruš et al. 2003a, b, c). Primary and supergene mineralization in this district resulted in extraordinarily varied associations; more than 440 mineral species have been reported from there up till now (Ondruš et al. 1997a, b, 2003c, d; Hloušek et al. 2014).

Chongite forms rich crusts composed of hemispherical crystalline aggregates having up to 0.3 mm across (Fig. 2); locally were observed also isolated spherical crystalline aggregates up to 0.2 mm (Fig. 3) on strongly weathered fragments of rocks and gangue. Chongite aggregates are colourless to white (some with slight yellow or pink tints), translucent, with vitreous lustre and white streak. It is brittle without visible cleavage and has a conchoidal fracture. Chongite is a supergene mineral formed by alteration of As-bearing hypogene minerals (namely native As and nickelskutterudite) in post-mining conditions of an abandoned mining adit.

2.2. Electron-probe microanalysis

Samples of chongite were analysed with a Cameca SX-100 electron microprobe (National Museum, Prague) operated in the wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 5 nA, and a beam diameter of 10–20 μm. The following lines and standards were used: Kα: diopside (Mg), rhodonite (Mn), fluorapatite (Ca, P); Lα: clinoclase (As). Peak counting times (CT) were 20 s for main elements and 60 s for minor elements; CT for each background was one-half of the peak counting time. The raw intensities were converted to the concentrations automatically.

Tab. 1 Ideal occupation of crystal-structure sites of hureaulite group minerals

| Mineral        | M1 (1 apfu) | M2 (2 apfu) | M3 (2 apfu) | T1 | T2 | Structure reference |
|----------------|-------------|-------------|-------------|----|----|---------------------|
| hureaulite     | Mn          | Mn          | Mn          | P  | P  | Moore and Arakai (1973) |
| miguelromerioite| Mn          | Mn          | Mn          | As | As | Kampf (2009)        |
| villyaellenite | Mn          | Mn          | Ca          | As | As | Kampf (2009)        |
| sainfeldite    | Ca          | Ca          | Ca          | As | As | Ferraris and Abbona (1972) |
| chongite       | Ca          | Mg          | Ca          | As | As | Kampf et al. (2016)  |
| giftgrubeite   | Ca          | Mn          | Ca          | As | As | Meisser et al. (2019) |
| nyholmte       | Cd          | Zn          | Cd          | As | As | Elliot et al. (2009) |

M1, M2, M3, T1 and T2 – sites of general formula of hureaulite group minerals \(M1M2M3(T1O_4)\) \([T2O_3(OH)]_2\cdot4H_2O\)

Fig. 1 The crystal structure of As-bearing members of hureaulite group of minerals viewed down \(c\). The As\(^{5+}\)-tetrahedra are green, the \(M1\) site can be occupied by Mn, Ca or Cd, the \(M2\) by Mn, Mg, Ca, and Zn, the \(M3\) by Mn, Ca or Cd. The unit-cell edges are shown in solid black lines. For clarity, only a half of the cell content along \(c\) is drawn.
using \textit{PAP} (Pouchou and Pichoir 1985) matrix-correction software. The elements Al, Co, F, Fe, K, Na, Ni, S, Si and V were sought (by WDS analysis), but found to be below their respective detection limits (\( \text{c.} \) 0.05–0.10 wt. \%). Water content could not be analysed directly because of the minute amount of material available. The \( \text{H}_2\text{O} \) content was confirmed by Raman and infrared spectroscopy and calculated by stoichiometry of ideal formula.

### 2.3. Powder X-ray diffraction

Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer (National Museum, Prague) with a solid-state 1D LynxEye detector (width 2.05\(^\circ\)) using CuK\(_\alpha\) radiation and operating at 40 kV and 40 mA. The powder patterns were collected using Bragg–Brentano geometry in the range 3–60\(^\circ\) 2\(\theta\), in 0.01\(^\circ\) steps with a counting time of 30 s per step. Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš 1993) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). The experimental powder pattern was indexed in line with the calculated intensities obtained by Lazy Pulverix program (Yvon et al. 1977) from the crystal structure of chongite (Kampf et al. 2016).

### 2.4. Raman and infrared spectroscopy

The Raman spectra of studied sample were collected in the range 4000–50 cm\(^{-1}\) using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by an unpolarised 633 nm He–Ne gas laser and detected by a CCD detector (size 1650 \(\times\) 200 mm, Peltier cooled.

Fig. 2 Chongite crust formed by hemispherical aggregates, Jáchymov; width of image 1.3 mm.

Fig. 3 Spherical crystalline aggregates of chongite on weathered rock, Jáchymov; width of image 0.8 mm.
3. Results and discussion

3.1. Chemical characterization

Chemical composition of chongite sample (Tab. 2) agrees well with the general formula of the hureaulite group minerals $M1M2_{2}M3_{2}(T1O)_{2}_{2}(T2O)OH)_{4}H_{2}O$. The $M1$ and $M3$ sites are occupied only by Ca; $M2$ site is dominated by Mg (1.10–1.47 apfu) accompanied by Ca (0.45–0.81 apfu) and only minor Mn (up to 0.02 apfu). The results suggest that $M2$ site is not fully occupied and vacancies are also present there (0.03–0.09 apfu). The tetrahedral T1 and T2 sites are dominated by As and only partly substituted by P (0.01–0.05 apfu). The empirical formula of chongite (mean of 19 analyses) on the basis of $As + P = 4$ apfu is $Ca_{0.06}(Mg_{0.12}Ca_{0.69}Mn_{0.01})_{2}O_{4} \cdot 4H_{2}O$.

In comparison with the type material (Kampf et al. 2016), chongite from Jáchymov is practically Mn-free and at the $M2$ site contains significant Ca besides dominant Mg (Fig. 4). This suggests an existence of possible solid solution between chongite and saindiifieldite ($Ca_{x}(AsO_{3})_{2}OH)_{y}(AsO_{4})_{z} \cdot 4H_{2}O$).

3.2. Powder X-ray diffraction (XRD)

The experimental powder data for chongite given in Tab. 3 agree well with the theoretical pattern calculated from the single-crystal data; experimental intensities are slightly lower than calculated ones.

| Tab. 2 Chemical composition of chongite from Jáchymov (wt. %) | CaO | MgO | MnO | As$_2$O$_3$ | P$_2$O$_5$ | H$_2$O* | total | Ca | Mg | Mn | $\Sigma$M | As$_2$O$_3$OH | As$_2$O$_4$ | PO$_4$ | H$_2$O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mean | 25.42 | 6.11 | 0.10 | 56.00 | 0.29 | 11.20 | 99.13 | 3.691 | 1.235 | 0.012 | 4.937 | 2.125 | 1.842 | 0.033 | 4 |
| 1 | 26.05 | 5.44 | 0.15 | 56.10 | 0.12 | 11.22 | 99.08 | 3.793 | 1.102 | 0.017 | 4.931 | 2.175 | 1.811 | 0.014 | 4 |
| 2 | 26.18 | 5.47 | 0.02 | 55.55 | 0.44 | 11.19 | 98.85 | 3.814 | 1.109 | 0.002 | 4.925 | 2.149 | 1.800 | 0.051 | 4 |
| 3 | 26.09 | 5.64 | 0.09 | 55.89 | 0.21 | 11.11 | 98.30 | 3.803 | 1.144 | 0.010 | 4.958 | 2.085 | 1.891 | 0.024 | 4 |
| 4 | 25.86 | 5.69 | 0.12 | 55.86 | 0.26 | 11.18 | 98.97 | 3.766 | 1.153 | 0.014 | 4.933 | 2.134 | 1.837 | 0.030 | 4 |
| 5 | 25.71 | 5.73 | 0.08 | 55.64 | 0.34 | 11.18 | 98.68 | 3.751 | 1.163 | 0.009 | 4.923 | 2.154 | 1.806 | 0.039 | 4 |
| 6 | 25.73 | 5.77 | 0.17 | 56.04 | 0.32 | 11.28 | 99.31 | 3.729 | 1.164 | 0.019 | 4.912 | 2.176 | 1.787 | 0.037 | 4 |
| 7 | 25.85 | 5.86 | 0.06 | 56.00 | 0.25 | 11.15 | 99.20 | 3.758 | 1.187 | 0.009 | 4.954 | 2.092 | 1.879 | 0.029 | 4 |
| 8 | 25.74 | 5.88 | 0.19 | 56.00 | 0.21 | 11.13 | 99.15 | 3.745 | 1.190 | 0.022 | 4.957 | 2.086 | 1.890 | 0.024 | 4 |
| 9 | 25.82 | 5.88 | 0.19 | 55.90 | 0.28 | 11.11 | 99.18 | 3.756 | 1.190 | 0.022 | 4.968 | 2.065 | 1.903 | 0.032 | 4 |
| 10 | 25.74 | 5.89 | 0.13 | 55.79 | 0.40 | 11.18 | 99.13 | 3.738 | 1.190 | 0.015 | 4.944 | 2.113 | 1.841 | 0.046 | 4 |
| 11 | 25.32 | 6.14 | 0.10 | 56.03 | 0.30 | 11.25 | 99.14 | 3.672 | 1.239 | 0.011 | 4.923 | 2.154 | 1.811 | 0.034 | 4 |
| 12 | 25.43 | 6.15 | 0.06 | 56.29 | 0.21 | 11.26 | 99.40 | 3.681 | 1.239 | 0.007 | 4.926 | 2.147 | 1.829 | 0.024 | 4 |
| 13 | 25.42 | 6.21 | 0.09 | 56.12 | 0.27 | 11.20 | 99.31 | 3.684 | 1.252 | 0.010 | 4.947 | 2.106 | 1.863 | 0.031 | 4 |
| 14 | 25.24 | 6.29 | 0.15 | 55.93 | 0.36 | 11.19 | 99.16 | 3.661 | 1.269 | 0.017 | 4.948 | 2.105 | 1.854 | 0.041 | 4 |
| 15 | 25.18 | 6.32 | 0.00 | 56.15 | 0.27 | 11.26 | 99.18 | 3.647 | 1.274 | 0.000 | 4.921 | 2.157 | 1.812 | 0.031 | 4 |
| 16 | 25.08 | 6.50 | 0.15 | 56.20 | 0.30 | 11.22 | 99.45 | 3.627 | 1.308 | 0.017 | 4.952 | 2.097 | 1.869 | 0.034 | 4 |
| 17 | 24.30 | 6.96 | 0.15 | 56.32 | 0.27 | 11.31 | 99.23 | 3.509 | 1.399 | 0.008 | 4.916 | 2.168 | 1.801 | 0.031 | 4 |
| 18 | 24.35 | 6.99 | 0.00 | 55.81 | 0.36 | 11.15 | 98.66 | 3.539 | 1.414 | 0.000 | 4.953 | 2.094 | 1.865 | 0.041 | 4 |
| 19 | 23.93 | 7.34 | 0.11 | 56.41 | 0.25 | 11.27 | 99.31 | 3.453 | 1.473 | 0.013 | 4.939 | 2.123 | 1.849 | 0.029 | 4 |

Mean of 19 point analyses; 1–19 individual point analyses; $apfu$ on the basis of $As + P = 4$; $H_2O^*$ contents were calculated on the basis of $(AsO_3OH)^2$ contents (charge balance) and $4H_2O$ molecules in ideal formula.
partly affected by the preferred orientation as well as by the small amount of material available for the study. The refined unit-cell parameters of chongite (Tab. 3) are close to the data published for this mineral from original locality (Kampf et al. 2016). Similarly, as found Meisser et al. (2019) for Mn–Ca members of this group, an increasing portion of Ca$^{2+}$ entering the structure of Mg–Ca members leads to an increasing of unit-cell volume. Considering their ionic radii (Shannon 1976), the [6]-coordinated Ca$^{2+}$ is larger (1.00 Å) than [6]-coordinated Mg$^{2+}$ (0.72 Å) or Mn$^{2+}$ (0.83 Å).

3.3. Raman and infrared spectroscopy

In the asymmetric part of the monoclinic (space group C2/c, Z = 4) chongite unit cell (Kampf et al. 2016), there are three symmetrically distinct $M$ cations (two Ca and one Mg + Ca), one (AsO$_4$)$^{3-}$ and one (AsO$_5$OH)$^{2-}$ group, and two independent H$_2$O molecules. The crystal structure of chongite, as same as other members of hureaulite group (Kampf et al. 2016), is based on an octahedral edge-sharing pentamer formed by $M_1$ (Ca), $M_2$ (Mg + Ca) and $M_3$ (Ca) octahedra. Pentamers are linked into a loose framework by sharing corners with octahedra in adjacent pentamers and are further linked via AsO$_4$ and AsO$_5$OH tetrahedra (Kampf et al. 2016).

The (AsO$_4$)$^{3-}$ anion, the point symmetry $T_d$, $\Gamma = A_g + E + 2F_g$, is characterized by four fundamental modes of vibrations, $v_1$ ($A_g$, $\sim 837$ cm$^{-1}$), symmetric stretching vibration, $v_2$ ($E$), ($\sim 349$ cm$^{-1}$), doubly degenerate bending vibration, $v_3$ (F$_g$, $\sim 878$ cm$^{-1}$), triply degenerate antisymmetric stretching vibration, and $v_4$ (F$_g$, $\sim 463$ cm$^{-1}$) triply degenerate bending vibration. The $v_1$ vibration is Raman active, $v_2$ (δ) vibration is also Raman active, and $v_3$ and $v_4$ (δ) vibrations are Raman and infrared active (Mielke and Ratajczak 1972; Drozd et al. 2005; Nakamoto 2009). The $T_d$ symmetry of the free (AsO$_4$)$^{3-}$ units is only very rarely preserved e.g. in the structure of minerals because of its strong affinity to protons, hydrate and also complex formation with metal cations. The tetrahedral AsO$_4$ symmetry may be therefore reduced to either $C_s/C_s$, $C_3v$ or $C_s/C_s$. This loss of degeneracy may cause splitting of degenerate vibrations of (AsO$_4$)$^{3-}$ and the shifting of the As–OH stretching vibrations to different wavenumbers (Myneni et al. 1998).

| $l$ | $d_{abc}$ | $d_{abc}$ | $h$ | $k$ | $l$ |
|----|---------|---------|-----|-----|-----|
| 20.7 | 9.238 | 9.242 | 2 | 0 | 0 |
| 18.3 | 8.414 | 8.394 | 1 | 1 | 0 |
| 7.2 | 6.596 | 6.585 | 1 | 1 | –1 |
| 5.7 | 6.248 | 6.242 | 1 | 1 | 1 |
| 13.1 | 4.770 | 4.775 | 3 | 1 | –1 |
| 9.6 | 4.709 | 4.710 | 0 | 2 | 0 |
| 29.3 | 4.626 | 4.621 | 4 | 0 | 0 |
| 53.0 | 4.605 | 4.605 | 2 | 0 | –2 |
| 31.4 | 4.397 | 4.399 | 3 | 1 | 1 |
| 8.4 | 4.255 | 4.255 | 0 | 2 | 1 |
| 5.7 | 4.165 | 4.167 | 2 | 0 | 2 |
| 7.1 | 3.934 | 3.942 | 2 | 2 | –1 |
| 7.1 | 3.787 | 3.792 | 2 | 2 | 1 |
| 2.8 | 3.440 | 3.441 | 5 | 1 | 0 |
| 30.7 | 3.410 | 3.415 | 0 | 2 | 2 |
| 100.0 | 3.369 | 3.369 | 5 | 1 | –1 |
| 51.7 | 3.300 | 3.299 | 4 | 2 | 0 |
| 57.8 | 3.290 | 3.293 | 2 | 2 | –2 |
| 26.5 | 3.214 | 3.213 | 4 | 2 | –1 |
| 49.9 | 3.126 | 3.121 | 2 | 2 | 2 |
| 6.4 | 3.080 | 3.081 | 6 | 0 | 0 |
| 19.5 | 3.020 | 3.020 | 1 | 1 | 3 |
| 8.8 | 2.918 | 2.919 | 3 | 1 | –3 |
| 4.5 | 2.861 | 2.861 | 4 | 2 | –2 |
| 2.0 | 2.797 | 2.798 | 3 | 3 | 0 |
| 2.4 | 2.771 | 2.769 | 6 | 0 | –2 |
| 4.9 | 2.698 | 2.706 | 0 | 2 | 3 |
| 7.1 | 2.684 | 2.690 | 5 | 1 | 2 |
| 3.8 | 2.655 | 2.655 | 3 | 3 | 1 |
| 2.9 | 2.554 | 2.558 | 6 | 2 | –1 |
| 7.4 | 2.533 | 2.534 | 7 | 1 | –1 |
| 7.5 | 2.4793 | 2.4792 | 0 | 0 | 4 |
| 7.4 | 2.4390 | 2.4367 | 6 | 2 | 1 |
| 16.3 | 2.3971 | 2.3975 | 7 | 1 | 1 |
| 18.0 | 2.3904 | 2.3934 | 5 | 3 | 0 |
| 7.1 | 2.3744 | 2.3762 | 7 | 1 | –2 |
| 11.4 | 2.3126 | 2.3105 | 8 | 0 | 0 |
| 23.8 | 2.3036 | 2.3023 | 4 | 0 | –4 |
| 7.7 | 2.2805 | 2.2825 | 1 | 3 | –3 |
| 4.4 | 2.2361 | 2.2386 | 2 | 4 | –1 |

Table 3 Powder X-ray diffraction data and refined unit-cell parameters of chongite from Jáchymov

refined unit-cell parameters: $a = 18.618(5); b = 9.421(2); c = 9.988(2)$ Å, $\beta = 96.86(2)^\circ$ and $\gamma = 1739.4(7)$ Å$^3$
According to Mielke and Ratajczak (1972), \((\text{AsO}_3\text{OH})^2-\) ion belongs to the point group \(C_{3v}\). For the modes involving arsenic and oxygen, the total representation reduces to \(\Gamma = 3 A_1 + 3E\). One should expect in the Raman spectrum six fundamental vibrations; however, only four bands have been observed in the Raman studies of aqueous solution of \((\text{AsO}_3\text{OH})^2-\). The Raman and infrared spectra for some synthetic compounds containing \((\text{AsO}_3\text{OH})^2-\) group were published e.g. by Keller (1971), Vansant et al. (1973), Mihajlović et al. (2004), Drozd et al. (2005), Đorđević and Karanović (2008, 2010), Đorđević et al. (2015, 2018). Raman spectra of some hydrogen–arsenate ions-containing minerals were studied, e.g. burgessite (Čejka et al. 2011), pharmacolite (Frost et al. 2010), geminite (Sejkora et al. 2010) and gifigrubeite (Meisser et al. 2019). Raman and infrared spectra of štěpite have been interpreted in detail by Plášil et al. (2013). Makreski et al. (2018) presented a paper on vibrational spectra of complex hydrogen–arsenate minerals pharmacolite, picropharmacolite and vladimirite including DFT (Density Functional Theory) calculation of theoretical spectra.

Summarizing these data, as indicated, it is possible to use them generally for tentative interpretation of the Raman spectra of synthetic and mineral compounds containing \((\text{AsO}_3\text{OH})^2-\) units. When comparing published Raman spectra, however, dispersion of observed related wavenumbers of studied spectra may be significant. Raman bands at \(~3465–3050\) cm\(^{-1}\) are related to the \(\nu_{\text{OH}}\) of hydrogen bonded OH in \((\text{AsO}_3\text{OH})^2-\) units, bands at \(~2250–2325\) cm\(^{-1}\) to the strongly hydrogen bonded OH in \((\text{AsO}_3\text{OH})^2-\), bands at \(~1090–1300\) cm\(^{-1}\) to \(\delta \text{As–OH}\) vibrations. Raman bands at \(~870–958\) cm\(^{-1}\) to the \(\nu_3\) \((\text{AsO}_3\text{OH})^2-\) antisymmetric stretch, bands at \(~846–872\) cm\(^{-1}\) to the \(\nu_1\) \((\text{AsO}_3\text{OH})^2-\) symmetric stretch, bands at \(~825–855\) cm\(^{-1}\) to the \(\delta \text{AsOH}\) bend and \(\nu_3\) \((\text{AsO}_3\text{OH})^2-\) symmetric stretch vibrations. Raman bands at \(700–760\) cm\(^{-1}\), and \(~434–555\) cm\(^{-1}\) to the \(\text{As–OH}\), 435–470 cm\(^{-1}\).

Fig. 4 Section of ternary graph Ca–Mn–Mg \((\text{apfu})\) in the M2 site of chongite.

Fig. 5a – Raman spectrum of chongite over the 50–4000 cm\(^{-1}\) spectral range; b – Infrared spectrum of chongite over 400–4000 cm\(^{-1}\); both spectra are split at 2000 cm\(^{-1}\).
The full-range Raman and infrared spectra of the studied mineral chongite are given in Fig. 5a–b, tabularized values in Tab. 4. Raman bands of chongite at 3456, 3400, 3194, 2887 and 2416 cm\(^{-1}\) (Fig. 6a) and infrared bands at 3450, 3348, 3201, 3071, 2904 and 2783 cm\(^{-1}\) (Fig. 7a) are assigned to the \(\nu \text{ OH stretch of hydrogen bonded water molecules}\). The bands in the range 3500–3000 cm\(^{-1}\) are connected with vibrations of structurally distinct and differently strong hydrogen-bonded water molecules. According to Libowitzky’s empirical relation (Libowitzky 1999) O–H...O hydrogen bond lengths vary approximately in the ranges ~2.85 to ~2.74 Å (Raman) and ~2.85 to ~2.67 Å (infrared). These values are comparable to hydrogen bond lengths of water molecules, inferred from the single-crystal structure data (2.99 to 2.71 Å) of chongite (Kampf et al. 2016). The bands in this range may be also related to the \(\nu \text{ OH of hydrogen bonded OH in (AsO}_2\text{OH})^2\) units. The bands of the \(\nu \text{ OH stretching vibration of (AsO}_2\text{OH})^2\) units are assumed at 2900 cm\(^{-1}\) as mentioned by Mielke and Ratajczak (1972), and at 3200, 2800 and 2250 cm\(^{-1}\) as published by Keller (1971). The calculated O–H...O hydrogen bond lengths ~2.63 to ~2.57 Å (Raman) and ~2.64 to ~2.61 Å (infrared) for these more strongly bonded OH units agree with distance 2.638 Å from single-crystal structure data (Kampf et al. 2016).

Raman bands at 1656 and 1578 cm\(^{-1}\) (Fig. 6b) as well as very broad infrared band with the maxima at 1652 and 1601 cm\(^{-1}\) (Fig. 5b) are connected with the \(\nu_2 (\delta)\) bending vibrations of differently strong hydrogen bonded water molecules. A Raman band at 1462 cm\(^{-1}\) may probably be related to an overtone or a combination band. A Raman band at 1284 cm\(^{-1}\) (Fig. 6b) and two infrared bands at 1091 and 1061 cm\(^{-1}\) (Fig. 7b) may be connected to the \(\delta \text{ As–OH bend}\) (Plášil et al. 2013).

The most prominent Raman bands at 902, 861, 828, 807 and 758 cm\(^{-1}\) (Fig. 6c) and infrared bands at 932, 899, 863, 828 and 807 cm\(^{-1}\) (Fig. 7b) are attributed to overlapping \(\nu_3 \text{ (AsO}_2\text{OH})^2\) antisymmetric stretching, split \(\nu_2 \text{ (AsO}_2\text{OH})^2\) bend, and \(\nu_2 \text{ (AsO}_2\text{OH})^2\) symmetric stretching vibrations. The bands of the higher wavenumbers can be assigned more favourably to the protonated \(\text{(AsO}_2\text{OH})^2\) group (Makreski et al. 2018), but due to presence of both \(\text{(AsO}_2\text{OH})^2\) and \(\text{(AsO}_2\text{OH})^2\) groups in crystal structure of chongite more detailed tentative assignments would be

\begin{table}[h]
\centering
\caption{Tentative interpretation of Raman and infrared spectra for chongite}
\begin{tabular}{cccc}
\hline
\textbf{position} [cm\(^{-1}\)] & \textbf{FWHM} [cm\(^{-1}\)] & \textbf{I} \(_{\text{rel.}}\) [cm\(^{-1}\)] & \textbf{position} [cm\(^{-1}\)]
\hline
3456 & 72 & 5 & 3450
3400 & 166 & 4 & 3348
3194 & 268 & 24 & 3201
& & & 3071
2887 & 305 & 6 & 2904
2416 & 164 & 2 & 2783
1656 & 39 & 1 & 1652
1578 & 110 & 1 & 1601
1462 & 101 & 1 & \text{ovetone or combination band}
1284 & 59 & 1 & 1291
& & & \text{As–OH bend}
902 & 19 & 46 & 899
861 & 30 & 100 & 863
828 & 25 & 43 & \text{As–OH bend, As–OH bend, As–OH bend}
807 & 23 & 5 & 815
758 & 24 & 40 & 746
693 & 79 & 7 & 721
& & & \text{As–OH bend, molecular water libration modes}
506 & 18 & 1 & 503
469 & 22 & 5 & 466
451 & 16 & 3 & 417
436 & 19 & 16 & \text{As–OH bend, As–OH bend, As–OH bend}
389 & 25 & 29 & \text{As–OH bend, As–OH bend, As–OH bend}
360 & 14 & 12 & \text{As–OH bend, As–OH bend, As–OH bend}
346 & 18 & 13 & \text{As–OH bend, As–OH bend, As–OH bend}
302 & 22 & 10 & \text{As–OH bend, As–OH bend, As–OH bend}
275 & 20 & 3 & \text{As–OH bend, As–OH bend, As–OH bend}
238 & 33 & 15 & \text{As–OH bend, As–OH bend, As–OH bend}
190 & 29 & 11 & \text{As–OH bend, As–OH bend, As–OH bend}
162 & 24 & 4 & \text{As–OH bend, As–OH bend, As–OH bend}
110 & 31 & 9 & \text{As–OH bend, As–OH bend, As–OH bend}
100 & 14 & 5 & \text{As–OH bend, As–OH bend, As–OH bend}
75 & 19 & 4 & \text{As–OH bend, As–OH bend, As–OH bend}
\hline
\end{tabular}
\end{table}
only speculative. A Raman band at 693 cm$^{-1}$ and infrared bands at 721 and 634 cm$^{-1}$ are assigned to $\delta$ AsOH bend and molecular water libration modes (Yukhnevich 1973; Plášil et al. 2013).

Raman bands in the range from 550 to 400 cm$^{-1}$ (506, 469, 451 and 436 cm$^{-1}$ – Fig. 6d) and infrared bands at 503, 466 and 417 cm$^{-1}$ (Fig. 5b) are connected with the split triply degenerate $\nu_4 (\delta)$ (AsO$_4$)$^{3-}$ vibrations and
the split triply degenerate $v_4 (\delta) (\text{HOAsO}_3)^2^-$ vibrations (Plašil et al. 2013). Sharp bands of the medium intensity at 389, 360, 346 and 302 cm$^{-1}$ (Fig. 6d) are related to the split doubly degenerate $v_4 (\delta) (\text{AsO}_4)^3^-$ and the split doubly degenerate $v_4 (\delta) (\text{HOAsO}_3)^2^-$ vibrations, respectively (Drozd et al. 2005; Čejka et al. 2011; Plašil et al. 2013). Raman bands at 275 and 238 cm$^{-1}$ (Fig. 6d) are assigned to the $v(OH \cdots O)$ stretching vibrations and those at 190, 162, 110, 100 and 75 cm$^{-1}$ to lattice modes (Plašil et al. 2013).

4. Conclusions

Molecular structure of well-defined sample of chongite from Jáchymov (the second world occurrence) was constrained using the vibrational spectroscopy. Raman and infrared spectroscopy shows the presence of both (AsO$_4$)$^{3-}$ and (AsO$_3$OH)$^{2-}$ units in the crystal structure of chongite. Multiple bands related to vibrations of water molecules prove the presence of differently strong hydrogen bonded and structurally distinct water molecules in the structure of chongite.

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