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Raman spectroscopy of hydrogen-arsenate group (AsO$_3$OH) in solid-state compounds: cobalt mineral phase burgessite Co$_2$(H$_2$O)$_4$[AsO$_3$OH]$_2$·H$_2$O

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Raman spectrum of burgessite, Co$_2$(H$_2$O)$_4$[AsO$_3$OH]$_2$·H$_2$O was studied, interpreted and compared with its infrared spectrum. The stretching and bending vibrations of (AsO$_3$) and As-OH units together with the stretching, bending and libration modes of water molecules and hydroxyl ions were assigned. The range of O-H...O hydrogen bond lengths was inferred from the Raman and infrared spectra of burgessite. The presence of (AsO$_3$OH)$_2^-$ units in the crystal structure of burgessite was proved in agreement with its recently solved crystal structure. Raman and infrared spectra of erythrite inferred from the RRUFF database are used for comparison.

KEYWORDS: burgessite, hydrogenarsenate, Raman spectroscopy, infrared spectroscopy, hydrogen bonds

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INTRODUCTION

The role of the hydrogen-arsenate group \((\text{AsO}_3\text{OH})^{2-}\) in synthetic solid-state compound and natural minerals indicates their specific conditions of origin and formation, especially substantial acid environment. [1-4] Detailed research of such solid-state compounds in natural environment brings therefore much information on the behaviour of arsenic and other elements (especially cations such as Cu, Co, Ni, Zn, Fe, Ca, Mg, etc.) under conditions, which enable their large mobility and influence also natural environment [1].

Burgessite, \(\text{Co}_2(\text{H}_2\text{O})_4[\text{AsO}_3(\text{OH})]_2\cdot\text{H}_2\text{O}\), is a monoclinic member of large group of the chemically related minerals, containing \((\text{AsO}_3\text{OH})^{2-}\) anions [1-3]. Burgessite was described as rare mineral species of supergene origin, from the Keely mine, South Lorrain Township, Timiskaming District, Ontario, Canada in association with primary minerals skutterudite, cobaltite and bismuth, and supergene minerals arsenolite, bismutoferrite and erythrite [5]. It is chemically similar to hydrated cobalt arsenate, erythrite \(\text{Co}_3(\text{AsO}_4)\cdot 8\text{H}_2\text{O}\) but its crystal structure is different [5,6].

The crystal structure of burgessite has been solved by Cooper and Hawthorne [6]. According to these researchers, burgessite is monoclinic of the space group \(P2_1/n\), \(a = 4.7058(12)\), \(b = 9.299(3)\), \(c = 12.738(4)\) Å, \(\beta = 98.933(8)\)°, \(Z = 2\) [6] and it is not isostructural with any other mineral or inorganic compound [6]. According to the results of the single-crystal study, there is one unique As site that is four-coordinated by oxygen atoms and occupied by \(\text{As}^{5+}\). The bond-valence analysis of the final crystal structure [6] indicates three oxygen atoms \((\text{O})^{2-}\), one hydroxyl \((\text{OH})^-\) and three water molecules \((\text{H}_2\text{O})\) in the asymmetric unit-cell. The hydroxyl anion is bonded to the \(\text{As}^{5+}\) cation thus forming an hydrogen-arsenate group \((\text{AsO}_3\text{OH})^{2-}\). In the crystal structure, there are chains of the form \([\text{Co}_2(\text{H}_2\text{O})_4][\text{AsO}_3(\text{OH})]_2\). These chains are linked into three-dimensional structure by hydrogen bonds that involve hydroxyls bonded to \(\text{As}^{5+}\), water molecules bonded to \(\text{Co}^{2+}\), and water molecules held in the structure solely by hydrogen bonds. The crystal structure of erythrite is formed from chains of the same bond-topology as was found in burgessite [6,7].

Sejkora et al. [5] described and tentatively interpreted the infrared spectrum of burgessite. Raman and infrared spectra of chemically similar erythrite are presented e.g. in RRUFF data base (R050073) without any interpretation. Martens et al. [8,9] discussed
vibrational spectra of erythrite, its synthetic analogue, deuteroanalogue and partly dehydrated analogue.

The aim of this paper is to report the Raman spectra of burgessite, and to relate the spectra to the molecular and crystal chemistry of this hydrogen-arsenate mineral. The paper follows the systematic research of the large group of supergene minerals \cite{10-13} and especially molecular structure of minerals containing oxyanions using IR and Raman spectroscopy \cite{14-25}.

**EXPERIMENTAL**

**Mineral**

The studied samples of the mineral burgessite were found in the Keeley mine, South Larrain Township, Timiskaming District, Ontario, Canada \cite{5}. The samples were checked for the phase purity by the X-ray powder diffraction and no significant impurities were found. The refined unit-cell parameters for the monoclinic space group $P2_1/n$ are: $a = 4.6982(7)$, $b = 9.262(1)$, $c = 12.702(1)$ Å, $\beta = 98.95(1)^\circ$, $V = 546.0(1)$ Å$^3$. These values are similar with data from the crystal structure refinement \cite{6}.

The burgessite sample was quantitatively analysed by Cameca SX 100 microprobe system in wavelength dispersion mode for its chemical composition. Studied sample was mounted into the epoxide resin and polished, then it was coated with carbon layer 250 Å thick. An acceleration voltage of 15 kV, a specimen current of 4 - 10 nA and a beam diameter of 5-20 μm were applied. The following lines and standards were used: $K_\alpha$: andradite (Ca), baryte (S), CoO (Co), fluorapatite (P), NiO (Ni), ZnO (Zn); $L_\alpha$: InAs (As). Peak counting times (CT) were 20 s for main elements and 60 s for minor ones, CT of each background was ½ of peak time. The raw intensities were converted to the concentrations using automatic PAP matrix correction software package. The results (mean of 8 point analyses) are CaO 0.18, NiO 3.52, CoO 27.31, ZnO 0.04, $P_2O_5$ 0.03, $As_2O_5$ 47.91, $SO_3$ 0.13, $H_2O$ 22.65, the sum 101.77 wt. % and empirical formula on the basis of 13 (O,OH,H$_2$O) anions is $(Co_{1.75}Ni_{0.23}Ca_{0.02})_{\Sigma2.00}(AsO_3OH)_{2.00}(H_2O)_{5.00}$. The presence and quantity of (OH) and H$_2$O groups were established by the crystal structure refinement \cite{6}. The observed chemical composition of burgessite sample is close to the ideal composition $Co_2(H_2O)_4[AsO_3(OH)]_2H_2O$ given for this compound \cite{5,6}.
Crystals of burgessite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm\(^{-1}\) and a precision of ± 1 cm\(^{-1}\) in the range between 200 and 4000 cm\(^{-1}\). Repeated acquisition on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm\(^{-1}\) line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation\(^{[24-32]}\). Infrared-absorption spectrum of pulverized burgessite sample in KBr disk was recorded with a Nicolet 740 spectrophotometer in the range 4000 - 400 cm\(^{-1}\).

Spectral manipulation of Raman and infrared spectra such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package 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 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**

**Arsenate vibrations**
(AsO₄)³⁻ tetrahedral unit exhibits four fundamental vibrations: the \( \nu_1 \) symmetric stretching vibration \( (A_1) \) 818 cm⁻¹, Raman active; the doubly degenerate \( \nu_2 \) symmetric bending vibration \( (E) \) 350 cm⁻¹, Raman active; the triply degenerate \( \nu_3 \) antisymmetric stretching vibration \( (F_2) \) 786 cm⁻¹, Raman and infrared active; and the triply degenerate \( \nu_4 \) bending vibration \( (F_2) \) 405 cm⁻¹, Raman and infrared active \[^{33-35}\]. Protonation, metal complexation and/or adsorption on a mineral surface should cause a change in the (AsO₄)³⁻ symmetry from \( T_d \) to lower symmetries, such as \( C_{3v}, C_{2v} \) or \( C_1 \). This loss of degeneracy causes splitting of degenerate vibrations of (AsO₄)³⁻ units and the shifting of the As-OH stretching vibrations to different wavenumbers. Such chemical interactions reduce the (AsO₄)³⁻ tetrahedral symmetry to either \( C_{3v}/C_3 \) (corner sharing), \( C_{2v}/C_2 \) (edge-sharing, bidentate binuclear), or \( C_1/C_s \) (corner-sharing, edge-sharing, bidentate binuclear, multidentate) \[^{33, 34}\]. In association with the (AsO₄)³⁻ symmetry and coordination changes, the \( A_1 \) band may shift to different wavenumbers and the doubly degenerate \( E \) and triply degenerate \( F \) modes may give rise to several new \( A_1, B_1 \) and/or \( E \) vibrations. Arsenate group bending modes are not discussed in these papers \[^{33, 34}\].

In the absence of symmetry deviations, (AsO₃OH)²⁻ in \( C_{3v} \) symmetry exhibits the \( \nu_{\text{symmetric}} \) As-OH and \( \nu_{\text{antisymmetric}} \) (AsO₃) together with \( \delta \) As-OH and \( \delta \) (AsO₃) bending vibrations \[^{36-38}\]. In the Raman spectrum of Na₂(AsO₃OH) \( \cdot \) 7H₂O, the observed bands were attributed to the following vibrations: 55, 94, 116 and 115 cm⁻¹ to the lattice modes, 210 cm⁻¹ to the \( \nu \) (OH...O) stretching mode, 315 cm⁻¹ to the (AsO₃OH)²⁻ rocking mode, 338 cm⁻¹ to the \( \delta_{\text{symmetric}} \) (AsO₃OH)²⁻ bending mode, 381 cm⁻¹ to the \( \delta_{\text{antisymmetric}} \) (AsO₃OH)²⁻ bending mode, 737 cm⁻¹ to the \( \nu_{\text{symmetric}} \) As-OH stretching mode \( (A_1) \) and 866 cm⁻¹ to the \( \nu_{\text{antisymmetric}} \) (AsO₃OH)²⁻ stretching mode \( (E) \) \[^{37}\] and infrared bands at 450 and 360 cm⁻¹ to the \( \delta_{\text{antisymmetric}} \) (AsO₃OH)²⁻ bending vibration \( (E) \), 580 cm⁻¹ to the \( \delta \) As-OH out-of-plane bending vibration, 715 cm⁻¹ to the \( \nu \) As-OH stretching vibration \( (A_1) \), 830 cm⁻¹ to the \( \nu_{\text{antisymmetric}} \) (AsO₃OH)²⁻ stretching vibration \( (E) \), and 1165 cm⁻¹ to the \( \delta \) As-OH in-plane bending vibration \[^{36}\]. Keller et al. \[^{39}\] interpreted the infrared spectrum of koritnigite, Zn(H₂O)(AsO₃OH) as follows (cm⁻¹): \( \nu \) OH stretching vibrations 3480, 3200, 2770, 2420 and 2280 cm⁻¹; \( \delta \) H₂O bending vibrations 1645 and 1560 cm⁻¹; \( \delta \) As-OH in-plane bending vibration (??); \( \nu_{\text{antisymmetric}} \) AsO₃ antisymmetric stretching vibration \( (E) \) 845 and 815 cm⁻¹; \( \nu \) As-OH stretching vibration \( (A_1) \) 760 cm⁻¹; \( \delta \) As-OH out-of-plane bending vibration (??) 650
cm$^{-1}$, $\delta_{\text{antisymmetric AsO}_3}$ bending vibrations ($E$) 388 and 378 cm$^{-1}$; $\delta$ AsO$_3$ bending vibration 320 cm$^{-1}$; bands at 495 and 445 cm$^{-1}$ and a shoulder at 350 cm$^{-1}$ remained unassigned.

Infrared and Raman spectra of the hydrogen-arsenate ion are recently also discussed by Drozd et al. [40]. They assigned bands in the 550-400 cm$^{-1}$ and 400-300 cm$^{-1}$ wavenumber region to the $\nu_4$ and $\nu_2$ bending vibrations of the hydrogen-arsenate ion.

Raman and infrared spectroscopy of burgessite

The Raman bands and shoulders at 3591, 3395, 3328, 3204 and 3185 cm$^{-1}$ (Fig. 1) and the infrared bands and shoulders at 3593, 3516, 3410, 3245, 2952 and 2415 cm$^{-1}$ (Fig. S1) are assigned to the $\nu$ OH stretching vibrations. The Raman band at 3591 cm$^{-1}$ and an infrared shoulder at 3593 cm$^{-1}$ may be connected with $\nu$ OH stretching vibrations of relatively free or weakly hydrogen bonded hydroxyl ion of the (AsO$_3$OH)$_2^-$ units. According to Libowitzky [41], O-H...O hydrogen bond lengths vary in the range from 2.7 to $>3.2$ Å (Raman) and 2.57 to $>3.2$ Å (infrared). This range is well comparable with distances obtained from the solved crystal structure [6]. Infrared bands of erythrite are at 3043 and 3169 cm$^{-1}$ assigned to the $\nu$ OH stretching vibrations of hydrogen bonded water molecules. A infrared sharp band at 3458 cm$^{-1}$ is attributed to weakly hydrogen bonded or free hydroxyl ions (inferred from RUFF database R050073). Martens et al. [9] observed in synthetic erythrite corresponding Raman bands at 3009, 3218, 3333, 3449 and 3479 cm$^{-1}$.

The infrared bands at 1707 and 1636 cm$^{-1}$ (Fig. S2) are attributed to the $\delta$ H$_2$O bending vibrations, however, the band at 1707 cm$^{-1}$ may be related to a combination band. A complex set of bands in the range from 1512 to 1008 cm$^{-1}$ is assigned to the $\delta$ As-OH vibrations and overtones and combination bands. Observed infrared bands are comparable with those inferred from RRUFF database and burgessite original description by Sejkora et al. [5], and other hydrogen-arsenate minerals, e.g. geminite [1], haidingerite and brassite [2], pharmacolite [3] and dussertite [4]. Raman bands of synthetic erythrite observed at 1571, 1621, 1641 and 1682 cm$^{-1}$ [9] and infrared bands of erythrite at 1579, 1649 and 1684 cm$^{-1}$ (inferred from RRUFF R050073) are assigned to the $\delta$ ($\nu_2$) bending vibrations of structurally nonequivalent water molecules.
The Raman bands at 852, 830 and 806 cm\(^{-1}\) (Fig. 2) and the infrared bands at 868, 836 and 802 cm\(^{-1}\) (Fig. S3) are assigned to the \(v_3\) and \(v_1\) (AsO\(_3\)) stretching vibrations. The Raman band at 740 and the infrared band at 741 cm\(^{-1}\) are attributed to the \(\nu\) As-OH stretching vibrations. The infrared bands at 726, 697, 679, 655 and 619 cm\(^{-1}\) are assigned to libration modes of water molecules and hydroxyl ions. The infrared bands at 589 and 557 cm\(^{-1}\) are connected with \(\delta\) As-OH bending vibrations, at 492, 470, 437 and 431 cm\(^{-1}\) to the split triply degenerate \(\delta\) (AsO\(_3\)) bending vibrations. The Raman band at 447 cm\(^{-1}\) (Fig. 3) is assigned to the triply degenerate \(\delta\) (AsO\(_3\)) and the Raman bands at 383, 353 and 322 cm\(^{-1}\) to the split doubly degenerate \(\delta\) (AsO\(_3\)) bending vibrations. However, according to Vansant [37], the Raman band at 322 cm\(^{-1}\) may be assigned to the \(\rho\) (AsO\(_3\)) rocking vibration. The Raman bands at 233 and 215 cm\(^{-1}\) are assigned to the \(\nu\) (O-H...O) stretching vibrations [37] and that at 162 cm\(^{-1}\) to the lattice mode. In the spectra of erythrite, Martens et al. [9] assigned a Raman band at 850 cm\(^{-1}\) and an infrared band at 821 cm\(^{-1}\) to the \(v_1\) (AsO\(_4\))\(^3\) symmetric stretching vibrations and the Raman bands at 788, 796 and 803 cm\(^{-1}\) to the split triply degenerate (AsO\(_4\))\(^3\)- antisymmetric stretching vibrations, the Raman bands at 441, 446 and 457 cm\(^{-1}\), and those at 375 and 385 cm\(^{-1}\) are connected with the triply degenerate \(\nu_3\) and doubly degenerate \(\nu_2\) (AsO\(_4\))\(^3\)- bending vibrations, respectively. From the RRUFF Raman spectrum (R050073) may be inferred, that the most intensive band is that at 797 cm\(^{-1}\). This band may be therefore assigned to the \(v_1\) (AsO\(_4\))\(^3\)- symmetric stretching vibration. This does not agree, however with the attribution by Martens et al. [9]. Raman bands at 864 and 963 cm\(^{-1}\) and infrared bands at 777, 824 and 881 cm\(^{-1}\) are assigned to the split triply degenerate \(v_3\) (AsO\(_4\))\(^3\)-. The Raman band at 568 cm\(^{-1}\) and the infrared bands at 569, 594 and 640 cm\(^{-1}\) are attributed to the libration modes of structurally nonequivalent water molecules. The infrared bands at 415, 444 and 484 cm\(^{-1}\) are assigned to the split triply degenerate \(\nu_4\) (AsO\(_4\))\(^3\)- bending vibrations. The Raman bands at 441 and 372 cm\(^{-1}\) are attributed to the triply degenerate \(\nu_4\) and doubly degenerate \(\nu_2\) (AsO\(_4\))\(^3\)- bending vibrations, respectively. The Raman bands at 243 and 264 cm\(^{-1}\) may be connected with the \(\nu\) (OH...O) stretching vibrations [37], and those at 110, 117, 146, 155 and 203 cm\(^{-1}\) are related to the lattice vibrations.

CONCLUSIONS
(a) Raman and infrared spectra of hydrated copper hydrogen-arsenate mineral burgessite from a type locality at Canada were studied. Raman and infrared spectra of erythrite taken from RRUFF database (R050073) are discussed for comparison.

(b) Vibrational (stretching and bending) bands related to \((\text{AsO}_3\text{OH})^2-\) units \((\text{AsO}_3), (\text{As-OH}),\text{ stretching, bending and libration modes of water molecules and hydroxyl ions were observed and assigned.}\)

(c) The range of O-H...O hydrogen bond lengths inferred from the Raman (2.7 to > 3.2 Å) and infrared (2.57 to > 3.2 Å) spectra are comparable with the data from X-ray single crystal structure refinement.

(d) Observed Raman and/or infrared spectra of burgessite are comparable with those of other hydrogen-arsenate minerals, containing \((\text{AsO}_3\text{OH})^2-\) units in their crystal structures \([1-4]\).

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REFERENCES


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Fig. S2  Infrared spectrum of burgessite in the range from 950 to 1900 cm\(^{-1}\).

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Fig. 1 Raman spectrum of burgessite in the range from 2800 to 3700 cm\(^{-1}\).
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