Infrared and Raman spectroscopic characterization of the arsenate mineral ceruleite Cu$_2$Al$_7$(AsO$_4$)$_4$(OH)$_{13}$.11.5(H$_2$O)

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Highlights
- We have studied the mineral ceruleite.
- The mineral ceruleite is an hydroxy arsenate of copper and aluminium of formula Cu$_2$Al$_7$(AsO$_4$)$_4$(OH)$_{13}$.11.5(H$_2$O).
- The molecular structure of ceruleite has been assessed using vibrational spectroscopy.
- Hydrogen bond distances were estimated.

Abstract
The molecular structure of the arsenate mineral ceruleite has been assessed using a combination of Raman and infrared spectroscopy. The most intense band observed at 903 cm$^{-1}$ is assigned to the (AsO$_4$)$_3^{3-}$ symmetric stretching vibrational mode. The infrared spectrum shows intense bands at 787, 827 and 886 cm$^{-1}$, ascribed to the triply degenerate $m_3$ antisymmetric stretching vibration. Raman bands observed at 373, 400, 417 and 430 cm$^{-1}$ are attributed to the $m_2$ vibrational mode. Three broad bands for ceruleite found at 3056, 3198 and 3384 cm$^{-1}$ are assigned to water OH stretching bands. By using a Libowitzky empirical equation, hydrogen bond distances of 2.65 and 2.75 Å are calculated. Vibrational spectra enable the molecular structure of the ceruleite mineral to be determined and whilst similarities exist in the spectral patterns with the roselite mineral group, sufficient differences exist to be able to determine the identification of the minerals.

Introduction
The mineral ceruleite is an hydroxy arsenate of copper and aluminium of formula Cu$_2$Al$_7$(AsO$_4$)$_4$(OH)$_{13}$.11.5(H$_2$O) [1–4]. The mineral is found in the oxidized zone of arsenic-rich polymetallic mineral deposits and as a post-mine product [3–5]. The mineral appears to be sky-blue to a pale blue in colour. The mineral is triclinic with space group 1 bar [4,6,7]. The cell dimensions are

\[a = 14.359(3) \quad b = 14.687(3) \quad c = 7.440(3)\]

An infrared spectrum of ceruleite has been published [6]. This work has shown that the water is coordinated to the arsenate anion in the ceruleite structure. The vibrational modes of oxyanions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion ($v_1$) is observed at 810 cm$^{-1}$ and coincides with the position of the antisymmetric stretching mode ($v_2$). The symmetric bending mode ($v_3$) is observed at 342 cm$^{-1}$ and the antisymmetric bending mode ($v_4$) at 398 cm$^{-1}$. The positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring oxyanions. Farmer lists a number of infrared spectra of
arsenates including roselite, annabergite, erythrite, symplecite and köttigite [8]. The effect of reduced site symmetry in the crystal (compared with the free arsenate ion) will remove the degeneracy and allow splitting of the bands according to factor group analysis. Farmer based upon the work of Moenke reported the infrared spectra of roselite [8]. Farmer listed two bands at 985 and 920 cm⁻¹ and assigned these bands to the v₁ (AsO₄)²⁻ symmetric stretching vibrations [8]. The v₃ (AsO₄)²⁻ symmetric stretching vibrations were listed as 870, 850 and 805 cm⁻¹. The assignment of these bands does not appear to correct. The v₄ bending modes were found at 453 and 435 cm⁻¹. No v₂ bands were provided. A band at 535 cm⁻¹ was not assigned but may well be attributed to a water libration mode. No OH stretching vibrations were tabulated. For comparison Farmer listed the v₁ and v₃ bands of annabergite at 832 cm⁻¹ and 795 cm⁻¹. The v₄ bending modes were found at 510, 460 and 427 cm⁻¹ for annabergite. Two OH stretching vibrations were observed at 3430 and 3160 cm⁻¹ for annabergite. A number of bands were listed which were unassigned. To the best of our knowledge, few Raman spectra of the fairfieldite and/or roselite mineral subgroups have been forthcoming [9].

Few comprehensive studies of the fairfieldite and roselite mineral subgroups and related minerals such as divalent cationic arsenates have been undertaken [8]. Most of the infrared data predates the advent of Fourier transform infrared spectroscopy [10–15]. Although some Raman studies of some arsenate minerals have been undertaken [16,17], no Raman spectroscopic investigation of roselite arsenate minerals has been forthcoming. Griffith did report the results of the Raman spectrum of a synthetic annabergite. The symmetric stretching mode of the (AsO₄)²⁻ unit was observed at 859 cm⁻¹; the antisymmetric stretching mode at 880 cm⁻¹, the symmetric bending mode at 438 cm⁻¹ and antisymmetric bending mode at 452 cm⁻¹; other bands were located at 797 and 820 cm⁻¹ [18]. The structural investigation of some arsenates and the nature of the hydrogen bond in these structures have been undertaken [19].

As part of a comprehensive study of the molecular structure of minerals containing oxyanions such as the arsenate anion using of the IR and Raman spectroscopy, we report the vibrational spectroscopic properties of the above named ceruleite and relate the spectra to the structure of the mineral. A comparison is made with other arsenate bearing minerals.

**Experimental**

**Samples description and preparation**

The ceruleite sample studied in this work was collected from Emma Louisa gold mine, Guanaco district, about 100 km east-north-east of Taltal, Antofagasta, Chile. The mineral occurs in the oxidized zone of arsenic-rich polymetallic mineral deposits and as a post mining product. The sample was incorporated into the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-002. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the chemical characterization.

The Guanaco district is well known as an important source of arsenates. The region is the type locality of a number of minerals, including ceruleite.

**Scanning electron microscopy (SEM)**

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br).

Ceruleite crystal aggregate was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analysis in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

**Raman microprobe spectroscopy**

Crystals of ceruleite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× 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 polarized 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 acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

A Raman spectrum of ceruleite is given in the RUFF data base and this spectrum with the marked peak positions is given in the Supplementary information as Fig. S1.

**Infrared spectroscopy**

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4,000,525 cm⁻¹ range were obtained by the co-addition of 128 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. The infrared spectra are given in the Supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracal 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 Lorentzia–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 r² greater than 0.995.

**Results and discussion**

**Vibrational spectroscopy background**

According to Myneni et al. [20,21] and Nakamoto [22], (AsO₄)³⁻ is a tetrahedral unit, which exhibits four fundamental vibrations: the Raman active v₁ symmetric stretching vibration (A₁) at 818 cm⁻¹; the Raman active doubly degenerate v₂ symmetric bending vibration (E) observed at 350 cm⁻¹, the infrared and Raman active triply degenerate v₃ antisymmetric stretching vibration (F₂) found around 786 cm⁻¹, and the infrared and Raman active triply degenerate v₄ bending vibration (F₂) observed at 405 cm⁻¹. Protonation, metal complexation, and/or adsorption on a mineral surface will cause the change in (AsO₄)³⁻ symmetry from T₄ to
lower symmetries, such as \( C_{3v}, C_{2v} \) or even \( C_1 \). This loss of degeneracy causes splitting of degenerate vibrations of \( \text{AsO}_3^2^- \) and the shifting of the As–OH stretching vibrations to different wavenumbers. Such chemical interactions reduce \( \text{AsO}_3^2^- \) tetrahedral symmetry, as mentioned above, to either \( C_{3v}/C_3 \) (corner-sharing), \( C_{2v}/C_2 \) (edge-sharing, bidentate binuclear), or \( C_1/C_1 \) (corner-sharing, edge-sharing, bidentate binuclear, multidentate) \[20,21\]. In association with As–OH stretching vibration and coordination changes, the \( \Gamma \) band may give rise to several new \( \Gamma_1, \Gamma_2, \Gamma_3 \), and/or \( \Gamma_4 \) vibrations \[20,21\]. In the absence of symmetry deviations, \( \text{AsO}_3 \cdot \text{OH} \) and the shift to different wavenumbers and the doubly degenerate \( \Gamma \) and triply degenerate \( \Gamma \) modes may arise to several new \( \Gamma_1, \Gamma_2, \Gamma_3 \), and/or \( \Gamma_4 \) vibrations \[20,21\]. As–OH stretching vibration, \( \delta \) As–OH out-of-plane bending vibration, \( \delta_\text{as} \) (AsO3OH)\(^2^-\) bending vibration \[23–25\]. Keller \[23\] assigned observed the following infrared bands in \( \text{Na}_2\text{AsO}_3\cdot7\text{H}_2\text{O} \) and tri-symmetric stretching vibration and \( \delta_\text{as} \) (AsO3OH)\(^2^-\) bending vibration \[23–25\].

Vibrational spectroscopy

The Raman spectrum of ceruleite in the 100–4000 cm\(^{-1}\) spectral region is displayed in Fig. 1a. This figure shows the position of the Raman bands and the relative intensity of these bands. It is observed that there are large parts of the spectrum where no intensity is found and therefore the spectrum is subdivided into sections based upon the type of vibration being examined. The infrared spectrum over the 500–4000 cm\(^{-1}\) spectral range is illustrated in Fig. 1b. This spectrum shows the position and relative intensities of the infrared bands. In a similar manner to the Raman spectrum, the infrared spectrum is subdivided into sections based upon the type of vibration being studied.

The Raman spectrum of ceruleite in the 800–1200 cm\(^{-1}\) spectral range is shown in Fig. 2a. The infrared spectrum of ceruleite in the 500–1300 cm\(^{-1}\) spectral range is shown in Fig. 2b. A Raman spectrum of ceruleite from the RRUFF data base is reported in Fig. S1. This figure shows the position and intensity of the peaks in the 100–1100 cm\(^{-1}\) spectral range. There is a strong similarity between the spectrum reported in this work and that on the RRUFF data base. The RRUFF spectrum does suffer from a lack of signal; and also the spectrum of the hydroxyl stretching region is not shown. The most intense band is observed at 903 cm\(^{-1}\) and is assigned to the (AsO4)\(^3-\) symmetric stretching vibrational mode.

Thus, the band at 903 cm\(^{-1}\) is shifted from the expected position. Protonation, metal complexation, and/or adsorption on a mineral surface will cause the change in (AsO4)\(^3-\) symmetry from \( T_d \) to lower symmetries, such as \( C_{3v}, C_{2v} \) or even \( C_1 \). This loss of degeneracy causes splitting of degenerate vibrations of AsO4\(^3-\) and the shifting of the As–OH stretching vibrations to different wavenumbers. The Raman spectrum (Fig. 1a) displays three bands at 827, 845
and 870 cm\(^{-1}\). According to Myneni et al. [20,21] and Nakamoto [22], the infrared and Raman active triply degenerate \(v_3\) antisymmetric stretching vibration (\(F_2\)) should be found around 786 cm\(^{-1}\). Again, as for the symmetric stretching mode, the antisymmetric stretching vibrations are observed at higher wavenumbers than might be predicted. Two bands are observed in the RRUFF spectrum at 824 and 869 cm\(^{-1}\) and are attributed to this vibrational mode.

The position of AsO\(_4\) stretching bands appears to vary depending on the cation in the formula of the roselite subgroup mineral. Bands are observed for talmessite (Ca\(_2\)Mg) at 828, 814 and 781 cm\(^{-1}\). For the talmessite (Ca\(_2\)Co) Raman bands are observed at 868, 841 and 824 cm\(^{-1}\). For the mineral roselite two bands are observed at 864 and 798 cm\(^{-1}\). Raman bands have been observed at 854 and 800 cm\(^{-1}\) for annabergite. In the roselite subgroup, Raman spectra do not appear to be any phosphate isomorphic substitution. In the infrared spectra of roselite as reported by Farmer, two infrared bands were reported at 985 and 920 cm\(^{-1}\). These bands were assigned by Farmer to the \(m_1\) symmetric stretching mode of the (AsO\(_4\))\(^{3-}\) anion. Such an assignment in the light of these Raman results for roselite seems unlikely. A more likely assignment is to the \(m_1\) symmetric stretching mode of the (PO\(_4\))\(^{3-}\) anion. This isomorphic substitution of phosphate for arsenate may in itself be unusual as whilst cationic isomorphic substitution is common, it is not known whether the anionic substitution is common. Current literature does not report any anionic isomorphic substitution. Raman spectral studies of the vivianite phosphates show that there is a band at 951 cm\(^{-1}\) for vivianite and bobieriite. The bands are observed at 852 and 792 cm\(^{-1}\) for erythrite and at 875 and 807 cm\(^{-1}\) for hörnesite. No bands are observed in these positions for the roselite minerals. Bands at 841 (talmessite-Co), 828 cm\(^{-1}\) (talmessite) 798 cm\(^{-1}\) (roselite) are assigned to the \(v_1\) symmetric stretching modes of \(A_1\) symmetry. Griffith [26] reported Raman bands for a synthetic annabergite at 880, 859, 820 and 797 cm\(^{-1}\).

The infrared spectrum shows intense infrared bands at 787, 827, 886 cm\(^{-1}\). These bands are ascribed to the triply degenerate \(v_3\) antisymmetric stretching vibration. The infrared band at 909 cm\(^{-1}\) is the equivalent of the Raman band at 903 cm\(^{-1}\) and is attributed to the \(v_1\) symmetric stretching vibration. The fact that this band is observed in the infrared spectrum supports the concept that the symmetry of the arsenate anion is reduced to \(C_{3v}\), \(C_{2v}\) or even \(C_1\). The Raman peaks at 932, 951, and 1042 cm\(^{-1}\) are attributed to phosphate bands. This, perhaps, is not unexpected as phosphate can readily substitute for arsenate in isomorphic substitution. It is thought that phosphate bands are observed in the infrared spectrum at 979, 1038, 1059 and 1114 cm\(^{-1}\).

The Raman spectra of ceruleite in the 300–800 cm\(^{-1}\) and 100–300 cm\(^{-1}\) spectral ranges are given in Fig. 3. The Raman active doubly degenerate \(v_2\) symmetric bending vibration (\(E\)) would be expected to be observed at \(\approx 350\) cm\(^{-1}\). Raman bands are observed at 373, 400, 417 and 430 cm\(^{-1}\) and are attributed to this vibrational mode. In the RRUFF spectrum, Raman bands are observed at 373, 397 and 463 cm\(^{-1}\). The infrared and Raman active triply degenerate \(v_4\) bending vibration (\(F_2\)) is expected at around 405 cm\(^{-1}\). Strong Raman bands for ceruleite are found at 515 and 597 cm\(^{-1}\). In the RRUFF spectrum, the Raman bands are observed at 507 and 594 cm\(^{-1}\). The position of these bands seems high to be assigned to the \(v_4\) bending modes. In association with AsO\(_3\)\(^2-\) symmetry and coordination changes, the triply degenerate \(F\) modes may

Fig. 3. (a) Raman spectrum of ceruleite over the 300–800 cm\(^{-1}\) spectral range and (b) Raman spectrum of ceruleite over the 100 to 300 cm\(^{-1}\) spectral range.

Fig. 4. (a) Raman spectrum of ceruleite over the 2600–4000 cm\(^{-1}\) spectral range and (b) infrared spectrum of ceruleite over the 2600–4000 cm\(^{-1}\) spectral range.
give rise to several new $A_1$, $B_1$, and/or $E$ vibrations, which may occur at higher wavenumbers [20,21]. It is probable that the peaks in the 300 cm$^{-1}$ region are due to metal oxygen stretching vibrations. Raman bands at 299, 316 and 335 cm$^{-1}$ are observed. Quite intense Raman bands are found in the 100–300 cm$^{-1}$ spectral range. Raman bands are found at 208 and 262 cm$^{-1}$ with Raman bands of lesser intensity at 118, 132, 152, 176, 231, 239 and 280 cm$^{-1}$. These bands are due to external vibrations and are simply referred to as lattice vibrations.

The Raman spectrum in the 2600–3800 cm$^{-1}$ spectral range is illustrated in Fig. 4a. This spectral range is where the OH stretching vibrations are found. Two spectral features are observed. Firstly a series of low intensity Raman bands at 3056, 3198 and 3384 cm$^{-1}$. These bands are attributed to water stretching vibrations. The second feature is the sharp Raman bands at 3597 and 3608 cm$^{-1}$ with a shoulder band at 3611 cm$^{-1}$. These bands are assigned to the stretching vibrations of the hydroxyl units. The observation of these multiple bands supports the concept of the non-equivalence of the OH units in the structure of ceruleite.

In contrast, strong infrared bands are observed at 3048, 3159, 3237 and 3360 cm$^{-1}$ and are assigned to water stretching vibrations. These bands are ascribed to water stretching vibrations. An intense, somewhat broad band at 3601 cm$^{-1}$ is assigned to the stretching vibrations of the hydroxyl units.

The Raman spectrum of ceruleite over the 1400–1800 cm$^{-1}$ spectral range is given in Fig. 5a. The spectrum suffers from a lack of signal; nevertheless, a Raman band is identified at 1654 cm$^{-1}$, which is attributed to the bending mode of water. The infrared spectrum over the 1300–1800 cm$^{-1}$ spectral range is reported in Fig. 5b. The water bending mode is again observed at 1649 cm$^{-1}$.

A comparison may be made with the hydrogen bond distances of other arsenate minerals. Four hydrogen bond distances for talc mesite are 2.76 Å, 2.72 Å, 2.71 Å and 2.697 Å. For roselite, hydrogen bond distances of 2.75 and 2.67 Å are calculated. Two types of water molecules are identified in the structure and the known hydrogen bond distances used to predict the hydroxyl stretching frequencies. The data fundamentally distinguishes between two types of water according to the hydrogen bond distances, namely strongly hydrogen bonded water and weakly hydrogen bonded water. However the predicted values do not take into account factor group splitting, accidental degeneracy and in-phase and out-of-phase vibrations. The strong hydrogen bonding would suggest that the thermal decomposition of the minerals would take place at significantly high temperatures. Some thermal studies were performed on collinsite, fairfieldite, and talc mesite, and show the dehydration temperature increased with the strength of H bonds [32].

Conclusions

A combination of Raman spectroscopy at ambient temperatures complimented with infrared spectroscopy has been used to characterize the arsenate mineral known as ceruleite and also arsenites of the roselite mineral subgroup. The fundamental vibrations in the spectra are related to the structure of the minerals.

The ceruleite arsenate mineral is characterized by typical spectra of the $\text{AsO}_4$ units. The symmetric stretching modes are observed in the 800–950 cm$^{-1}$ region; the antisymmetric stretching modes are observed in the 827–870 cm$^{-1}$ region. Some bands are observed around 950 cm$^{-1}$ region and are attributed to water librational modes. The $v_4$ bending modes are observed around 500 cm$^{-1}$ and the $v_3$ bending modes in the 373–430 cm$^{-1}$ region. Multiple bands are observed in these regions indicating a loss of symmetry of the $\text{AsO}_4$ unit. Intense sharp Raman bands at 3597 and 3608 cm$^{-1}$ assigned to the stretching vibrations of the hydroxyl units. The observation of multiple bands offers credence to the non-equivalence of the OH units in the ceruleite structure. Vibrational spectroscopy enables aspects of the molecular structure of ceruleite to be evidenced.

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**Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.07.103.

**References**