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Infrared and Raman spectroscopic characterisation of the sulphate mineral creedite – $Ca_3Al_2SO_4(F,OH)\cdot 2H_2O$ – and in comparison with the alums

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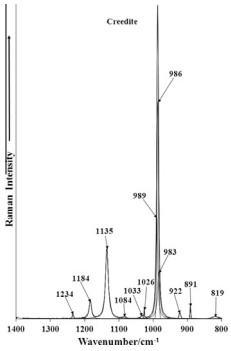
HIGHLIGHTS

- We have studied the sulphate mineral creedite.
- A comparison is made with the spectroscopy of the alums.
- Multiple bands in the antisymmetric stretching region support the concept of a reduction in symmetry of the sulphate anion.
- Sulphate is coordinated to the water bonded to the Al^{3+} in the creedite structure.

GRAPHICAL ABSTRACT



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ABSTRACT

The mineral creedite is a fluorinated hydroxy hydrated sulphate of aluminium and calcium of formula $Ca_3Al_2SO_4(F,OH)\cdot 2H_2O$. The mineral has been studied by a combination of electron probe analysis to determine the molecular formula of the mineral and the structure assessed by vibrational spectroscopy. The spectroscopy of creedite may be compared with that of the alums. The Raman spectrum of creedite is characterised by an intense sharp band at 986 cm^{-1} assigned to the SO_4^{2-} ν_1 (A_g) symmetric stretching mode. Multiple bands of creedite in the antisymmetric stretching region support the concept of a reduction in symmetry of the sulphate anion. Multiple bands are also observed in the bending region with the three bands at 601, 629 and 663 cm^{-1} assigned to the SO_4^{2-} ν_4 (A_g) bending modes. The observation of multiple bands at 440, 457 and 483 cm^{-1} attributed to the SO_4^{2-} ν_2 (B_g) bending modes supports the concept that the symmetry of the sulphate is reduced by coordination to the water bonded to the Al^{3+} in the creedite structure. The splitting of the ν_2, ν_3 and ν_4 modes is attributed to the reduction of symmetry of the SO_4 and it is proposed that the sulphate coordinates to water in the hydrated aluminium in bidentate chelation.

Introduction

The mineral creedite [1] is a rather rare sulphate mineral of formula $Ca_3Al_2SO_4(F,OH)\cdot 2H_2O$, found in the very highly oxidised zone of metal ore bodies. The colour of the mineral can vary from clear to white to reddish brown and purple. The reddish-brown coloured creedite contains Fe^{3+} where some of the Al^{3+} has been replaced by Fe^{3+}. The mineral is found in many localities worldwide [2–7]. A picture of the mineral is provided in the supplementary information. The mineral has been found in ancient slag dumps [8]. Creedite was named after the location where it was discovered in 1916 in the Colorado Fluorspar Co. Mine at Wagon Wheel Gap, located at Creede Quadrangle, USA [1]. Creedite is a rare hydroxylhalide mineral and usually forms from the oxidation of fluorite

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ore deposits. Creedite is monoclinic [9] with point group 2/m and space group: $C2/c$ and cell dimensions $a = 13.936(1)$, $b = 8.606(1)$, $c = 9.985(1)$, $\beta = 94.39(1)$ and $Z = 4$ [10].

Background

Creedite shows a resemblance in formula to the alums. The infrared spectra of alums based upon one monovalent and one trivalent cation have been published [11]. Of the three known alum structures (α,β,γ), only the α structure occurs naturally. The different structures result from small differences in the cation sizes. Small cations give the γ structure, middle sized cations, the α structure and the large cations the β structure. The kalinite and tschermigite mineral structures are known. Tschermigite has a cubic structure with a space group T_h^6. Kalinite has a monoclinic structure with space group 2/m. The sulphate ions occupy the C_3 or C_2 sites. Farmer [11] has reported the interpretation of the infrared spectra for potassium alum as ν_1, 981 cm^{-1}; ν_2, 465 cm^{-1}; ν_3, 1200, 1105 cm^{-1}; ν_4, 618 and 600 cm^{-1}. Water stretching modes were reported at 3400 and 3000 cm^{-1}; bending mode at 1645 cm^{-1}; and librational modes at 930 and 700 cm^{-1}. In the structure of alums, six water molecules surround each of the two cations. This means the sulphate ions are distant from the cations and coordinate to the water molecules.

The Raman spectra of alums are based on the combination of the vibrations of sulphate and water. Sulphate typically is a tetrahedral oxyanion of T_d symmetry with (theoretical) bands at 981 (ν_1), 451 (ν_2), 1104 (ν_3) and 613 (ν_4) cm^{-1} [11,12]. Some sulphates have their symmetry reduced through the formation of monodentate and bidentate ligands. In the case of bidentate formation both bridging and chelating ligands are known [12,13]. The structure of alums is such that the sulphates are distant from the cations. This means that for symmetry reduction, the sulphate must coordinate to the water molecules in the hydration sphere of the cations. If bidentate bridging occurs, then the sulphate may bridge across two water molecules, which may be from the two hydration spheres of the two cations. This reduction in symmetry is observed by the splitting of the ν_3 and ν_4 into two components under C_{3v} symmetry and into three components under C_{2v} symmetry. A synthetic alum, ammonium indium sulphate, shows bidentate chelation. The Raman spectrum showed the ν_1 band observed at 1011 cm^{-1}, ν_2 at 462 cm^{-1}, and three ν_3 modes at 1174, 1115 and 1050 cm^{-1}. Five ν_4 modes were observed at 668, 659, 653, 614, 601 cm^{-1}. The observation of the five ν_4 modes suggests that both bidentate chelation and bidentate bridging is present. The Raman spectroscopy of synthetic alums containing hexa-aquo coordinated trivalent ions has been extensively studied [14]. Raman spectroscopy of single crystals of synthetic alums has also been reported [15].

However little attention has been applied to the Raman spectroscopy of naturally occurring creedite. Significant changes in intensity, position and bandwidth result when hydrated sulphates are studied by Raman spectroscopy [16–18]. Raman spectroscopy of gypsum at liquid nitrogen temperature showed bands for ν_2 at 494 and 416 cm^{-1}, and for ν_4 at 673, 626 and 622 cm^{-1} [16–18]. The Raman spectrum of basic aluminium sulphate shows two broad bands, which are assigned to the ν_2 and ν_4 sulphate triplets at 446, 459 and 496 cm^{-1} and 572, 614 and 630 cm^{-1} [16–18]. The ν_1 band for basic aluminium sulphate is observed as a single band at 990 cm^{-1} overlapped by the ν_3 triplet at 979, 1009 and 1053 cm^{-1}. In the study of basic aluminium sulphate, coordinated water bands were reported at 3035, 3138 and 3256 cm^{-1}. The study of alums is related to the studies of hydrotalcites and other aluminium based minerals such as creedite, which are being researched by the authors. The objective of this research is to analyse the vibrational spectra of creedite and relate the spectra to the structure of the mineral. A comparison with the spectroscopy of alums is also made.

Experimental

Samples description and preparation

The creedite sample studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-136. The sample is from the Santa Eulalia mining district, Chihuahua Province, Mexico, and occurs in association with gypsum, in aggregates up to 5 cm. Colourless creedite single crystals show prismatic form. An iron hydroxide coating gives an orange colour. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The creedite sample was phase analysed by X-ray diffraction. Scanning electron microscopy (SEM) was applied to support the mineralogical chemical.

Raman microprobe spectroscopy

Crystals of creedite 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 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 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.

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 4000–525 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 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

Chemical characterisation

The SEM image of creedite sample studied in this work is shown in Fig. 1. The crystal is prismatic with euhedric form. Qualitative

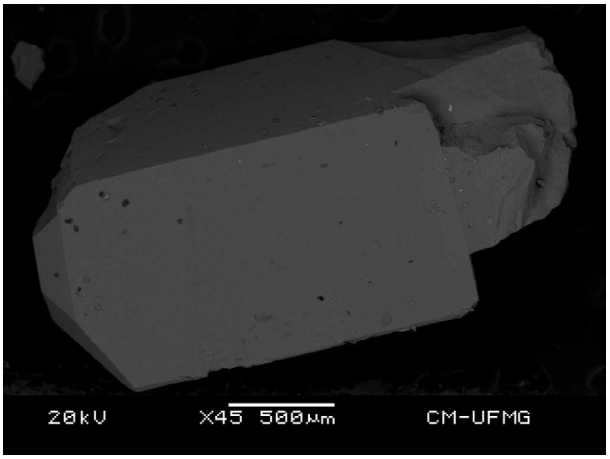

Fig. 1. A backscattered electron image (BSI) of a creedite crystal up to 3.0 mm in length.

chemical composition shows a homogeneous composition, with S, Ca, Al and F as expected for creedite.

Fig. 1 shows a backscattered electron image (BSI) of a creedite crystal up to 3.0 mm in length. Fig. 2 shows an EDS spectra of creedite.

Vibrational spectroscopy

The Raman spectrum of creedite in the 100–4000 cm^{-1} spectral range is displayed in supplementary information as Fig. S1a. This figure clearly shows that the position of the peaks and the relative intensities of the Raman bands. The spectrum in the 2600–3800 cm^{-1} displays significant intensity compared with the sulphate spectral region around 1000 cm^{-1}. Clearly there are parts of the spectrum where no Raman intensity is observed. Thus, the Raman spectrum is subdivided into subsections depending upon the type of vibrations being observed. In comparison, the infrared spectrum of creedite as shown in supplementary information as Fig. S1b shows significantly more intensity in the 2500–3600 cm^{-1} spectral range. Again there are parts of the spectrum where no intensity is found, and as a consequence the spectrum is divided into sections for further analysis, based upon the type of vibration being studied.

The Raman spectrum in the 800–1400 cm^{-1} spectral range is illustrated in Fig. 3a. The infrared spectrum in the 500–1300 cm^{-1} spectral range is illustrated in Fig. 3b. The Raman spectrum is dominated by a very sharp intense band at 986 cm^{-1} with shoulder bands at 983 and 989 cm^{-1}. The width of the ν_1 sulphate mode of creedite is 5.5 cm^{-1}; i.e. the band is very sharp. This band is assigned to the SO_4^{2-} symmetric stretching mode. The width of the ν_1 band at 990 cm^{-1} for potash alum is 6.4 cm^{-1}. The width of the ν_1 sulphate mode of the ammonium alum was 6.4 cm^{-1}. The bandwidth of the ν_1 mode for Fe alum was 5.7 cm^{-1}. The ν_1 mode of aluminium sulphate $[Al_2(SO_4)_3{\cdot}xH_2O]$ is observed at 991 cm^{-1} with a bandwidth of 9.9 cm^{-1}. The band is also observed in the infrared spectrum as a sharp band at 985 cm^{-1}. The position of the band is in an identical position as for other aluminium sulphates [16–18]. The band was found at 990 cm^{-1} for the alums: kalinite, and tschermigite. The observation of multiple bands gives credence to the fact that there are non-equivalent sulphates in the creedite structure. The sulphate ions are distant from the cations and the reason why two ν_1 sulphate modes are obtained is attributed to the position of the sulphate relative to the two cations.

This concept is supported by the number of bands in the 1000–1200 cm^{-1} region. Raman bands are observed at 1026, 1033, 1084, 1135 and 1184 cm^{-1}. These bands are attributed to the SO_4^{2-} antisymmetric stretching modes. Multiple bands are also observed for this vibrational mode in the infrared spectrum with great intensity at 1043, 1081, 1137 and 1166 cm^{-1}. Two bands are observed in the infrared spectrum at 765 and 798 cm^{-1} and are attributed to water librational modes. In comparison, the two Raman bands at 891 and 922 cm^{-1} are assigned to hydroxyl deformation modes. Ross [12] reports the ν_3 mode at 1104 cm^{-1}. The Raman spectrum of the kalinite at 298 K shows two bands at 1132 and 1104 cm^{-1}. Upon cooling to 77 K four bands at 1137, 1131, 1107 and 1093 cm^{-1} are observed. The Raman spectrum of sodium sulphate displays three antisymmetric vibrations at 1101, 1131 and 1152 cm^{-1} [17,18].

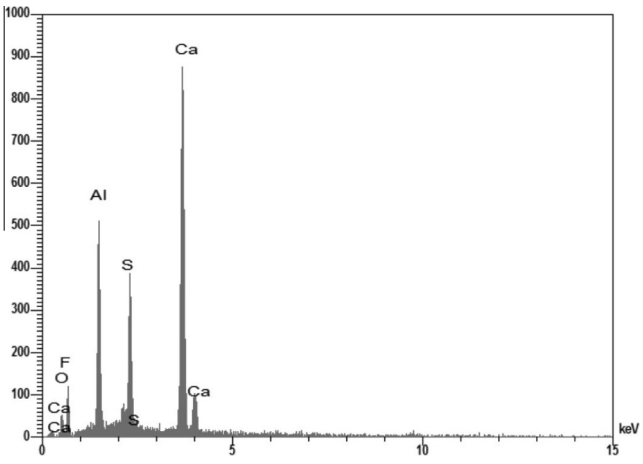

Fig. 2. EDS spectra of creedite.

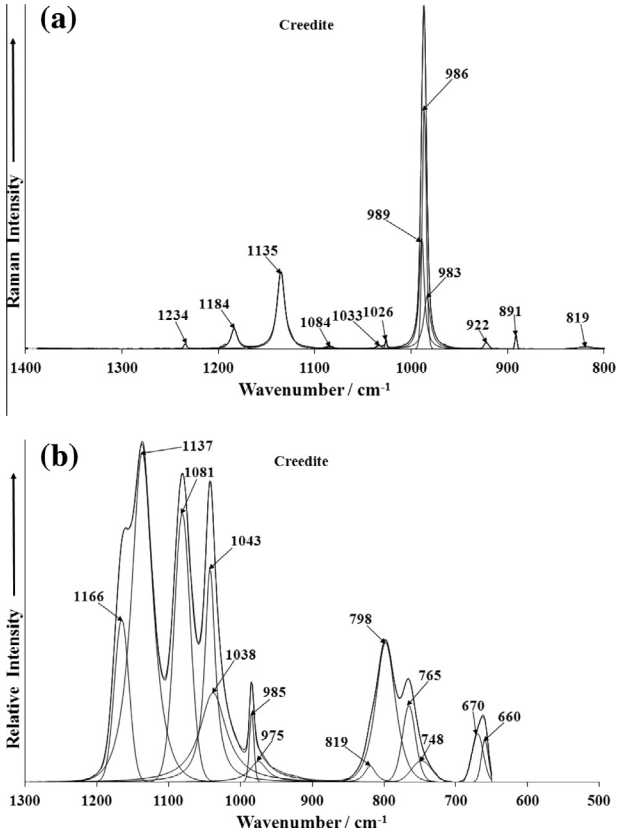

Fig. 3. (a) Raman spectrum of creedite over the 800–1400 cm^{-1} spectral range. (b) Infrared spectrum of creedite over the 500–1300 cm^{-1} spectral range.

Gypsum also showed three bands at 1140, 1135 and 1109 in the 298 K spectrum [16]. The Raman spectrum of basic aluminium sulphate showed two bands at 1053 and 1009 cm^{-1} [17,18]. The observation of two bands in the 298 K spectrum supports the concept that the symmetry of the sulphate is reduced. The T_d sulphate symmetry is reduced to C_{2v}. This reduction in symmetry is observed by the splitting of the ν_3 into two components under C_{3v} symmetry and into three components under C_{2v} symmetry. One possibility is that the four bands are indicative of bidentate bridging of the sulphate to water surrounding the Al^{3+} cation. A second possibility is that the four bands result from twice two bands. In that case there are two different sulphates with C_{3v} symmetry. For the ammonium alum, two bands are observed at 1102 and 1132 cm^{-1} in the 298 K spectrum. Again it is suggested that the symmetry is reduced to C_{2v}. Upon cooling to liquid nitrogen temperature four bands are observed at 1136, 1112, 1102 and 1087 cm^{-1}. This observation suggests that the symmetry is reduced to C_{2v}. In the case of lonecreekite, bands are observed at 1134, 1112 and 1099 cm^{-1}. In a similar fashion to the alums, creedite displays multiple bands in the SO_4^{2-} antisymmetric stretching region. There are several possibilities (a) three bands is indicative of reduction to C_{2v} symmetry (b) one band is T_d and two bands belong to a C_{3v} symmetry.

The Raman spectra of creedite in the 300–800 cm^{-1} and in the 100–300 cm^{-1} spectral ranges are shown in Fig. 4a and b. Two sets of bands are observed: (a) bands between 600 and 700 cm^{-1} and (b) bands in the 400–500 cm^{-1} spectral region. According to Ross [12], the ν_4 mode of sulphate occurs at around 613 cm^{-1}. Thus, the three bands at 601, 629 and 663 cm^{-1} are assigned to the SO_4^{2-} ν_4 (A_g) bending modes. A number of Raman bands of low intensity are observed at 311, 322, 348, 371 and 394 cm^{-1}. These bands are assigned to the ν_g (A_g) H_2O vibration. In the Raman spectra of alums, a band is observed at 330 cm^{-1} which splits into two bands at 342 and 321 cm^{-1} at 77 K. In the Raman spectra of the low wavenumber region of ammonium alum, the band is observed at 331 cm^{-1} at 298 K and at 341 cm^{-1} at 77 K. A single band is also observed in the Raman spectra of ammonium ferric alum at 307 cm^{-1}.

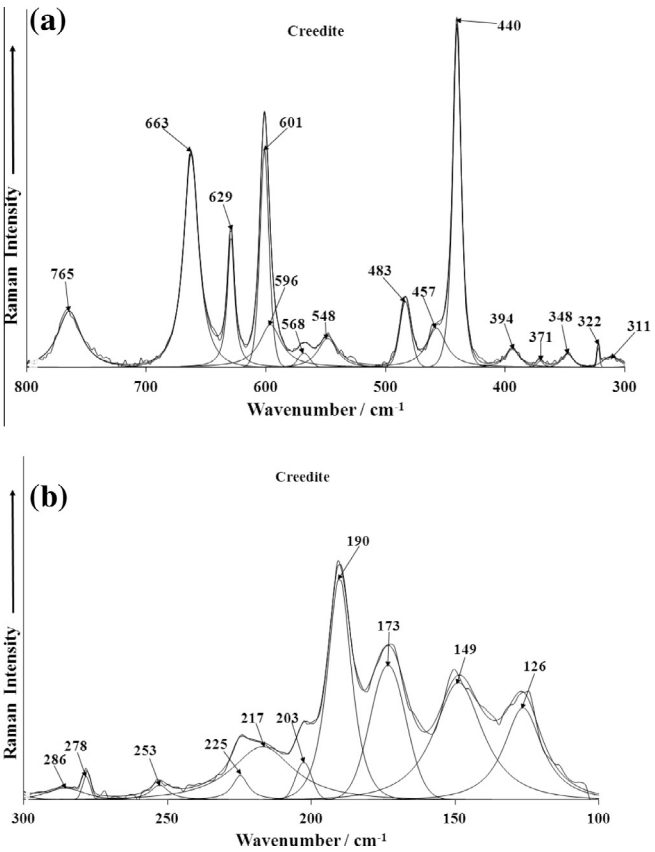

Fig. 4. (a) Raman spectrum of creedite over the 300–800 cm^{-1} spectral range. (b) Raman spectrum of creedite over the 100–300 cm^{-1} spectral range.

The splitting of this ν_4 vibrational mode supports the concept of reduction in symmetry of the sulphate to C_{2v}. Previous studies have suggested bands in this position can be assigned to the ν_4 mode. By means of a comparison, the Raman spectrum of sodium sulphate shows three bands at 621, 633 and 650 cm^{-1}. Also basic aluminium sulphate has three bands at 572, 614 and 630 cm^{-1}. For tschermigite, a single band is observed at 618 cm^{-1} and which resolves into three bands at 643, 629 and 615 cm^{-1} at liquid nitrogen temperature. The Raman spectrum of creedite displays two bands at 548 and 568 cm^{-1}. Bands are also observed at 534 and 499 cm^{-1}. Bands in similar positions were observed for kalinite at 547 and 517 cm^{-1}. The attribution of these bands is difficult and the bands may be assigned to either the ν_T (B_g) H_2O or the ν_4 (B_g) SO_4 mode. The 542 cm^{-1} band for tschermigite shows considerable reduction in bandwidth combined with an increase in intensity upon cooling to liquid nitrogen temperature. Ross [12] reports the observation of four ν_4 modes to the sulphate bidentate coordination to the water surrounding the aluminium cation. Lonecreekite shows three bands in the 77 K spectrum at 596, 616 and 634 cm^{-1} with an intense band at 527 cm^{-1}. The intensity of this band suggests that the band may be more readily assignable to the ν_T (B_g) mode of H_2O.

The three bands for creedite at 440, 457 and 483 cm^{-1} are attributed to the SO_4^{2-} ν_2 (B_g) bending modes. The observation of multiple bands supports the concept that the symmetry of the sulphate is reduced though coordination to the water bonded to the Al^{3+} in the creedite structure. A comparison may be made with the spectroscopy of selected alums. The Raman spectrum of ammonium alum shows a single very broad ν_2 band at 456 cm^{-1} at 298 K which splits into three bands 439, 462 and 473 cm^{-1} at 77 K. The Raman spectrum of lonecreekite (ammonium ferric sulphate) at 77 K shows two bands at 435 and 463 cm^{-1}. The spectrum in the ~450 cm^{-1} region for kalinite may be resolved into three component bands at 440, 462 and 472 cm^{-1} with band widths of 7.3, 13.5, 10.6 cm^{-1}. The observation of the three ν_2 bands for the tschermigite suggests that the sulphate coordinates to the water as a bidentate ligand. The lonecreekite shows two bands at 435 and 463 cm^{-1}. The observation of two bands is indicative of a reduction of symmetry to C_{3v}. The role of the sulphate in coordinating the water coordinating the Fe^{3+} is apparently different from that of water in the coordination sphere of Al^{3+}. It is suggested that the sulphate coordinates the water surrounding the Al^{3+} in a bidentate structure and coordinates Fe^{3+} in a monodenate structure.

The Raman spectrum of creedite in the 3000–3800 cm^{-1} spectral range is illustrated in Fig. 5a. In comparison, the infrared spectrum in the 2600–3800 cm^{-1} spectral range is reported in Fig. 5b. The Raman band at 3524 cm^{-1} and the infrared band at 3521 cm^{-1} are assigned to the OH stretching vibrational mode of the hydroxyl units. A small shoulder band at 3584 cm^{-1} is also found. This band is also attributed to the stretching vibration of the hydroxyl units. The observation of two bands supports the concept that the OH units are not all equivalent in the creedite structure. Water plays a significant role in the structure of creedite as for the alums and is observed through the bands associated with the hydroxyl vibrations. Water bands occur around 3400 cm^{-1} region (the OH stretching region), around 1630 cm^{-1} (the hydroxyl deformation region), around 500 cm^{-1}, (the water librational region) and at around 300 cm^{-1}, the water torsional mode. Distinct water Raman bands are observed at 3248, 3349 and 3458 cm^{-1}.

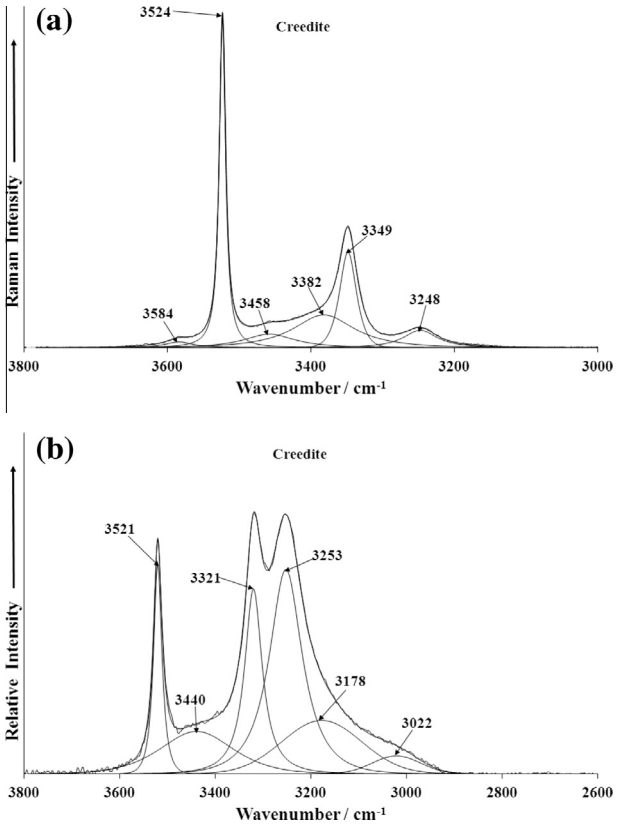

Fig. 5. (a) Raman spectrum of creedite over the 2600–4000 cm^{-1} spectral range. (b) Infrared spectrum of creedite over the 2600–4000 cm^{-1} spectral range.

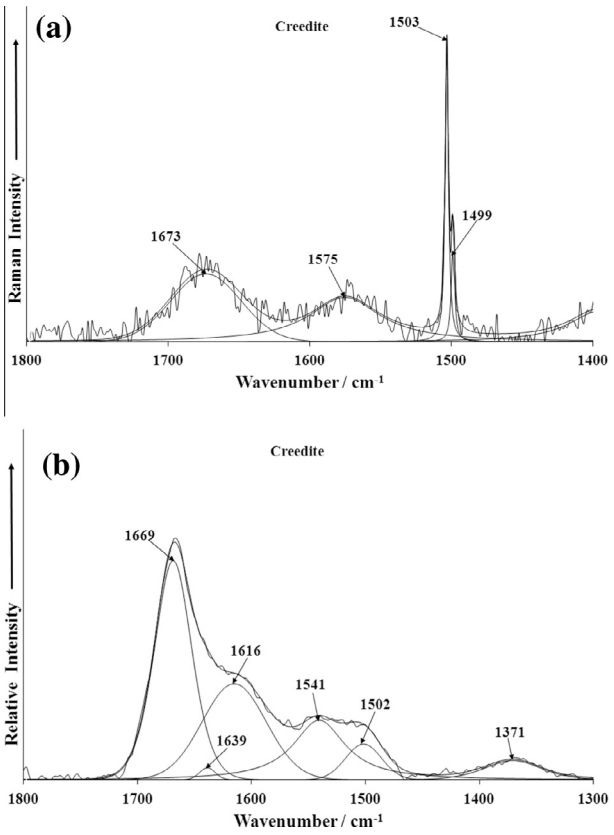

Fig. 6. (a) Raman spectrum of creedite over the 1300–1800 cm^{-1} spectral range. (b) Infrared spectrum of creedite over the 1300–1800 cm^{-1} spectral range.

In the infrared spectrum distinct bands are observed at 3253 and 3321 cm^{-1} with minor components at 3178 and 3440 cm^{-1}. Two broad bands are observed for the potash alum at 298 K at 3379 and 3528 cm^{-1}. For both the ammonium alum and ferric alums, the NH stretching modes overlap with the OH stretching vibrations, making the band component analysis and assignment of the bands difficult. The spectra for the potash alum shows two types of water present (a) adsorbed water observed as the bands at 3528 cm^{-1} and (b) coordinated water observed as bands at 3379 cm^{-1} and at 3350 and 3379 cm^{-1} (77 K). The observation of very strongly bonded water is also confirmed by the position of the water bending mode at 1673 cm^{-1} (Fig. 6a) and the band position in the infrared spectrum at 1669 cm^{-1} (Fig. 6b).

Conclusions

The vibrational spectrum of creedite is compared with that of the alums. A strong resemblance is observed. It is proposed that the symmetry of the sulphate as observed by the number of bands in the ν_2 and ν_4 modes, is reduced to C_{2v}. The sulphate coordinates to the aluminium in the minerals through bidentate chelation. The splitting of the ν_2, ν_3 and ν_4 modes in the vibrational spectrum of creedite is attributed to the reduction of symmetry of the SO_4^{2-} and it is proposed that the sulphate coordinates to water in the hydrated aluminium and calcium in bidentate chelation.

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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.2013.02.029.

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