A Raman and infrared spectroscopic study of the sulphate mineral aluminite Al$_2$(SO$_4$)(OH)$_4$·7H$_2$O

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HIGHLIGHTS

- We have studied the mineral aluminite.
- Using SEM, EDX and vibrational spectroscopy.
- Bands due to OH and water stretching vibrations are observed.
- The observation of multiple bending modes supports the concept of reduction of symmetry of the sulphate anion.

GRAPHICAL ABSTRACT

ABSTRACT

The mineral aluminite has been studied using a number of techniques, including scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDX) and Raman and infrared spectroscopy. Raman spectroscopy identifies multiple sulphate symmetric stretching modes in line with the three sulphate crystallographically different sites. Raman spectroscopy also identifies a low intensity band at 1069 cm^{-1} which may be attributed to a carbonate symmetric stretching mode, indicating the presence of thaumasite. The observation of multiple bands in this $v_{4\ \text{spectral}}$ region offers evidence for the reduction in symmetry of the sulphate anion from T_d to C_{2v} or even lower symmetry. The Raman band at 3588 cm^{-1} is assigned to the OH unit stretching vibration and the broad feature at around 3439 cm^{-1} to water stretching bands. Water stretching vibrations are observed at 3157, 3294, 3378 and 3439 cm^{-1}. Vibrational spectroscopy enables an assessment of the molecular structure of aluminite to be made.

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Introduction

Aluminite is a hydrous aluminium sulphate with formula Al$_2$SO$_4$(OH)$_4$·7H$_2$O [1,2]. It is an earthy white to grey-white monoclinic mineral which almost never exhibits a crystal form. It forms botryoidal to mammillary clay-like masses. It forms in clay and lignite deposits as an oxidation product of pyrite and marcasite along with aluminium silicates [3,4]. It is a mineral that is likely formed in Bayer liquors and forms along with other aluminium compounds during the sea water neutralisation of red mud [5–7]. It occurs in volcanic sublimates, in sulphur deposits and also in caves [8]. Aluminite was described from a number of localities such as Sussex in England [9]; Styria, Austria [10]; Kazakhstan [11] and USA [12] among others. Aluminite crystallises with monoclinic symmetry. Unit cell parameters are: $a = 7.440$ (1) Å, $b = 15.583$ (2) Å, $c = 11.700$ (2) Å, $\beta = 110.18$ (2)°, $V = 1273.7$ Å^3 and $Z = 4$ [13,14].

The objective of this work is to undertake a Raman and infrared spectroscopic study of aluminite. This mineral is found in our red

mud samples, a by-product of the alumina industry. Also, we detect the mineral in Bayer liquors. The authors have undertaken extensive studies of red mud and the products of the reaction of red mud with sea water. It is of fundamental importance to be able to recognise this mineral especially when found in complex mixtures of minerals as is found in red mud and Bayer liquors. There have been very few vibrational spectroscopic studies of this mineral. No Raman spectra have been reported even though some infrared studies have been undertaken. Raman spectroscopy has proven most useful for the study of mineral structure. The objective of this research is to report the Raman and infrared spectra of aluminite and to relate the spectra to the mineral structure.

Experimental

Samples description and preparation

The aluminite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-199. The mineral originated from Newhaven, East Sussex, England, United Kingdom. Description of the locality has been published [9].

The mineral sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The aluminite studied in this work occurs as a massive aggregate composed by single crystals with prismatic form up to 30 μm. Scanning electron microscopy (SEM) in the EDS mode was applied to support the mineral characterisation.

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). Aluminite crystals were coated with a 5 nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterisation.

Raman microprobe spectroscopy

Crystals of aluminite 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 100 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. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra. Raman Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over 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.

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 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.

Results and discussion

Mineral characterisation

The SEM image of aluminite sample studied in this work is shown in Fig. 1. The image shows an aluminite crystal aggregate. Individual crystals up to 30 μm in length are observed. Crystals shows prismatic habitus. Qualitative chemical analysis shows a homogeneous phase, composed by S, Al. Carbon was also observed and occurs due to C coating (Fig. 2).

Spectroscopy

Background

Spectroscopy of the sulphate anion in solids

The Raman spectroscopy of the aqueous sulphate tetrahedral oxyanion yields the symmetric stretching (v_1) vibration at 981 cm^{-1}, the in-plane bending (v_2) mode at 451 cm^{-1}, the antisymmetric stretching (v_3) mode at 1104 cm^{-1} and the out-of-plane bending (v_4) mode at 613 cm^{-1} [15]. Ross reports the interpretation of the infrared spectra for potassium alum as v_1, 981 cm^{-1}; v_2, 465 cm^{-1}; v_3, 1200, 1105 cm^{-1}; v_4, 618 and 600 cm^{-1} [16]. Water stretching modes were reported at 3400 and 3000 cm^{-1}, bending modes at 1645 cm^{-1}, and librational modes at 930 and 700 cm^{-1} [17]. The Raman spectrum of the mineral chalcanthite shows a single symmetric stretching mode at
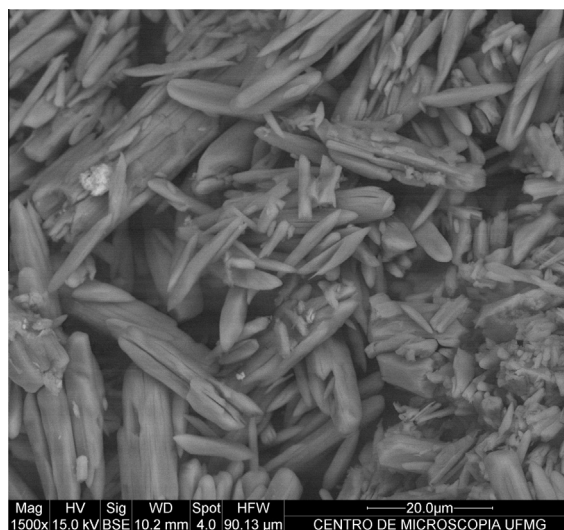

Fig. 1. Shows a backscattered electron image (BSI) of a aluminite crystal aggregate. Individual crystals up to 30 μm in length. Crystals shows prismatic habitus.
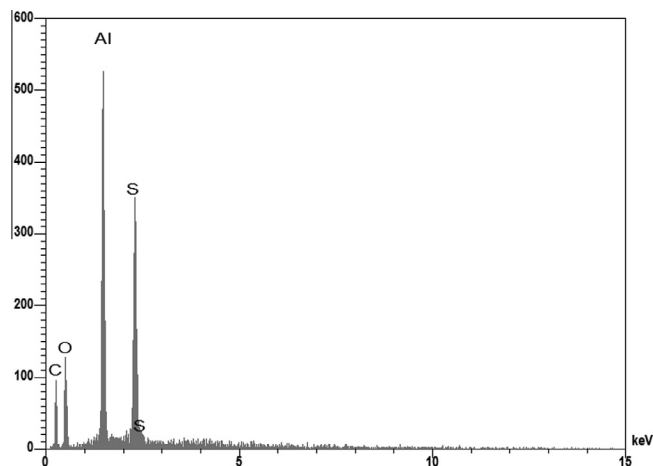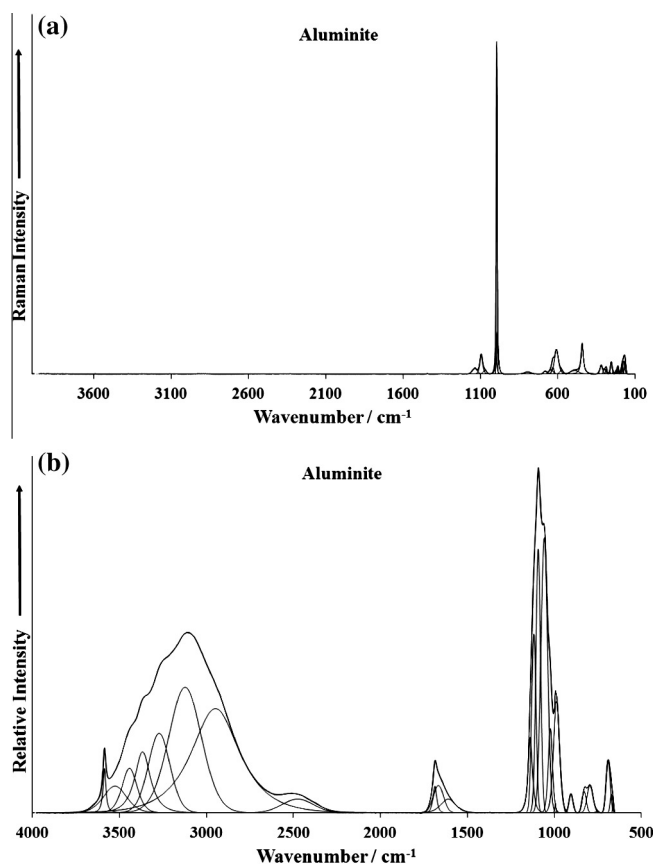
Fig. 2. EDS spectra of aluminite.

Fig. 3. (a) Raman spectrum of aluminite (upper spectrum) over 100–4000 cm^{-1} spectral range and (b) infrared spectrum of aluminite (lower spectrum) over 500–4000 cm^{-1} spectral range.

984.7 cm^{-1}. Two v_2 modes are observed at 463 and 445 cm^{-1} and three v_3 modes at 1173, 1146 and 1100 cm^{-1}. The v_4 mode is observed as a single band at 610 cm^{-1}. A complex set of overlapping bands is observed in the low wavenumber region at 257, 244, 210 136 and 126 cm^{-1}. Recently, Raman spectra of four basic copper sulphate minerals, namely antlerite, brochiantite, posnjakite and langite, were published [18]. The SO symmetric stretching modes for the four basic copper sulphate minerals are observed at 990, 985, 974 and 972 cm^{-1}. Only the mineral brochantite showed a single band in this region. Multiple bands were observed for these minerals in the antisymmetric stretching region.
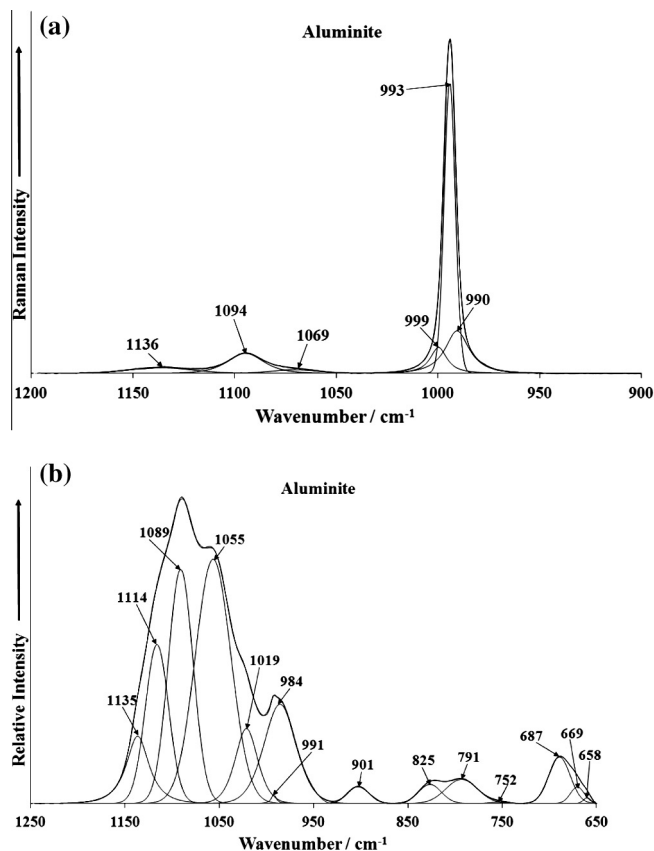

Fig. 4. (a) Raman spectrum of aluminite (upper spectrum) in 900–1200 cm^{-1} spectral range and (b) infrared spectrum of aluminite (lower spectrum) in 650–1250 cm^{-1} spectral range.

Ross [16] also lists the infrared spectra of the pseudo-alums formed from one divalent and one trivalent cation. Halotrichite has infrared bands at v_1, 1000 cm^{-1}; v_2, 480 cm^{-1}; v_3, 1121, 1085, 1068 cm^{-1}; v_4, 645, 600 cm^{-1}. Pickeringite the Mg end member of the halotrichite–pickeringite series has infrared bands at v_1, 1000 cm^{-1}; v_2, 435 cm^{-1}; v_3, 1085, 1025 cm^{-1}; v_4, 638, 600 cm^{-1} [16]. These minerals display infrared water bands in the OH stretching, 3400 and 3000 cm^{-1} region; OH deformation, 1650 cm^{-1} region; OH libration, 725 cm^{-1} region. Ross also reports a weak band at ∼960 cm^{-1} which is assigned to a second OH librational vibration [16]. As with the infrared spectra, Raman spectra of alums are based on the combination of the spectra of the sulphate and water. Sulphate typically is a tetrahedral oxyanion with Raman bands at 981 (v_1), 451 (v_2), 1104 (v_3) and 613 (v_4) cm^{-1} [19]. Some sulphates have their symmetry reduced through acting as monodentate and bidentate ligands [19]. In the case of bidentate behaviour both bridging and chelating ligands are known. This reduction in symmetry is observed by the splitting of the v_3 and v_4 into two components under C_{3v} symmetry and three components under C_{2v} symmetry.

Vibrational spectroscopy

The Raman spectrum of aluminite over 100–4000 cm^{-1} spectral range is shown in Fig. 3a. The infrared spectrum of aluminite over 500–4000 cm^{-1} spectral range is shown in Fig. 3b. These figures display the position and relative intensity of the Raman and infrared bands of aluminite. The Raman spectrum may be subdivided into subsections based upon the type of vibration being studied. It is noted that the intensity in the Raman spectrum of aluminite over 3000–3800 cm^{-1}, the region of the OH stretching vibrations,
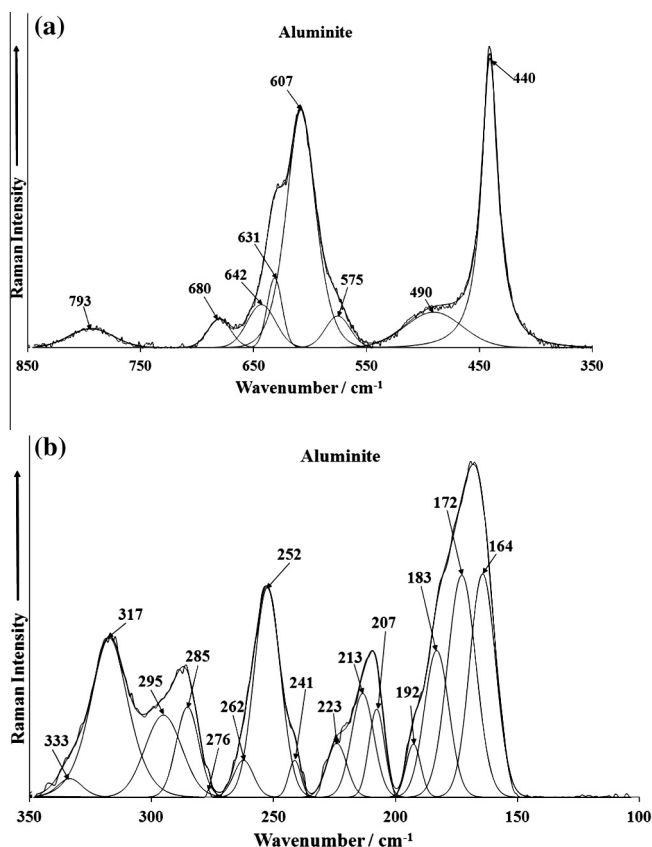
Fig. 5. (a) Raman spectrum of aluminite (upper spectrum) in 500–750 cm^{-1} spectral range and (b) Raman spectrum of aluminite (lower spectrum) in 100–300 cm^{-1} spectral range.
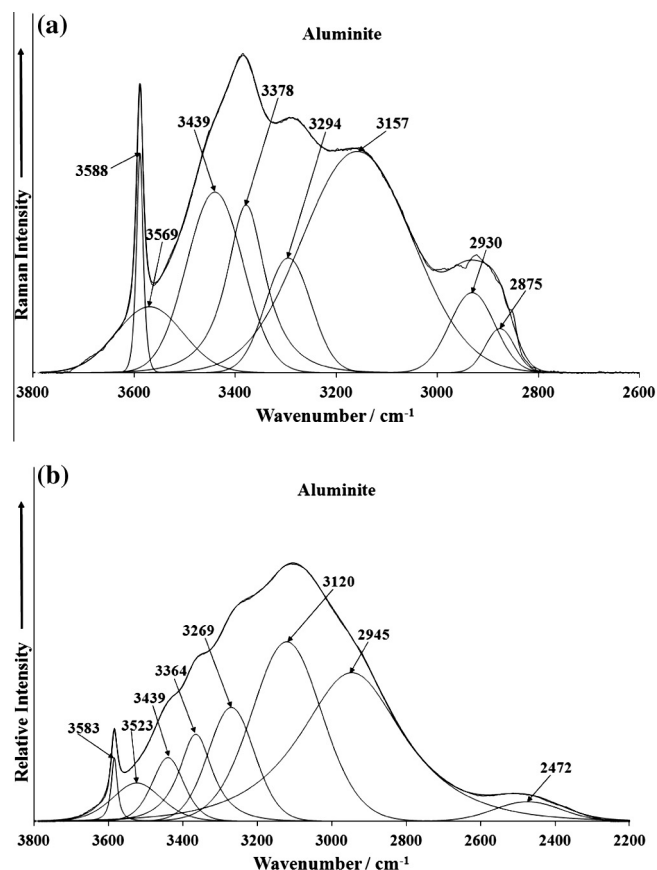

Fig. 6. (a) Raman spectrum of aluminite (lower spectrum) in 2600–3800 cm^{-1} spectral range and (b) infrared spectrum of aluminite (lower spectrum) in 2600–3800 cm^{-1} spectral range.

is very low. Yet, considerable intensity is observed in this spectral region the infrared spectrum.

The Raman spectrum of aluminite over 900–1200 cm^{-1} spectral range is displayed in Fig. 4a. The spectrum is dominated by a very sharp intense band at 993 cm^{-1}. Some low intensity shoulders are observed at 990 and 999 cm^{-1}. This band is assigned to the SO_4^{2-} v_1 symmetric stretching mode. The position of this band is very typical of a sulphate unit [20–25]. Several low intensity Raman bands are noted at 1069, 1094 and 1136 cm^{-1}. These bands are attributed to the SO_4^{2-} v_3 antisymmetric stretching mode. Again, the position of these bands is very typical of the sulphate anion in minerals.

In contrast, the infrared spectrum over 650–1250 cm^{-1} spectral range is reported in Fig. 4b. The infrared spectrum shows broad overlapping peaks which may be resolved into component bands. The infrared band at 984 cm^{-1} is attributed to the SO_4^{2-} v_1 symmetric stretching mode and is of much lower intensity compared with the equivalent Raman band. A series of infrared bands are observed at 1055, 1089, 1114 and 1135 cm^{-1} and are ascribed to the SO_4^{2-} v_3 antisymmetric stretching mode. Infrared bands below 900 cm^{-1} are related to the sulphate bending and water librational modes.

The Raman spectrum of aluminite over 350–850 cm^{-1} spectral range is displayed in Fig. 5a, whilst the Raman spectrum of aluminite over 100–350 cm^{-1} spectral range is displayed in Fig. 5b. The first spectrum is where the sulphate bending modes are to be found together with water librational modes. The series of Raman bands at 575, 607, 631, 642 and 680 cm^{-1} are assigned to the v_4 SO_4^{2-} bending modes. Ross [17] investigated the infrared spectra of selected sulphate minerals and reported v_4 SO_4^{2-} bending modes at 595, 618 and 680 cm^{-1} and v_2 (SO$_4$)$^{2-}$ bending modes at 460 and 494 cm^{-1}. The infrared spectrum (Fig. 4b) shows a series

of bands at 658, 669 and 687 cm^{-1} which are assigned to the v_4 SO_4^{2-} bending modes. The two Raman bands for aluminite at 440 and 490 cm^{-1} are assigned to the v_2 (SO$_4$)$^{2-}$ bending modes. The observation of multiple bands supports the concept of a reduction in symmetry of the sulphate anion in aluminite from T_d to C_{3v} or even C_{2v}. The low intensity Raman band at 793 cm^{-1} may be a water librational mode. The infrared bands at 752, 791 and 825 cm^{-1} are attributed to water librational modes (Fig. 4b). The infrared band at 901 cm^{-1} may be due to a hydroxyl deformation mode.

The assignment of bands in Fig. 5b is difficult. One way is simply to describe the bands as due to external vibrations. It is tempting to suggest that the Raman bands at 285, 317 and 333 cm^{-1} are due to metal oxygen vibrations. Other bands in this spectral region are simply described as lattice vibrations.

The formula of aluminite Al$_2$(SO$_4$)(OH)$_4$·7H$_2$O is such that it contains both hydroxyl and water units. The Raman spectrum of aluminite over 2600–3800 cm^{-1} spectral range is provided in Fig. 6a. Two features may be observed: firstly a sharp intense band at 3588 cm^{-1} assigned to the stretching vibration of the OH units and secondly a broad feature which may be decomposed into component bands at 3930, 3429, 3378, 3294 and 3157 cm^{-1} attributed to water stretching vibrations. The infrared spectrum (Fig. 6b) shows a similar spectral profile; however the intensity of the OH stretching vibration at 3583 cm^{-1} is of lesser intensity. A series of infrared bands at 2945, 3120, 3269, 3364, 3439 and 3523 cm^{-1} are ascribed to water stretching vibrations. The Raman spectrum of aluminite over 1350–1550 cm^{-1} spectral range is reported in Fig. 7a. Two low intensity Raman bands are observed
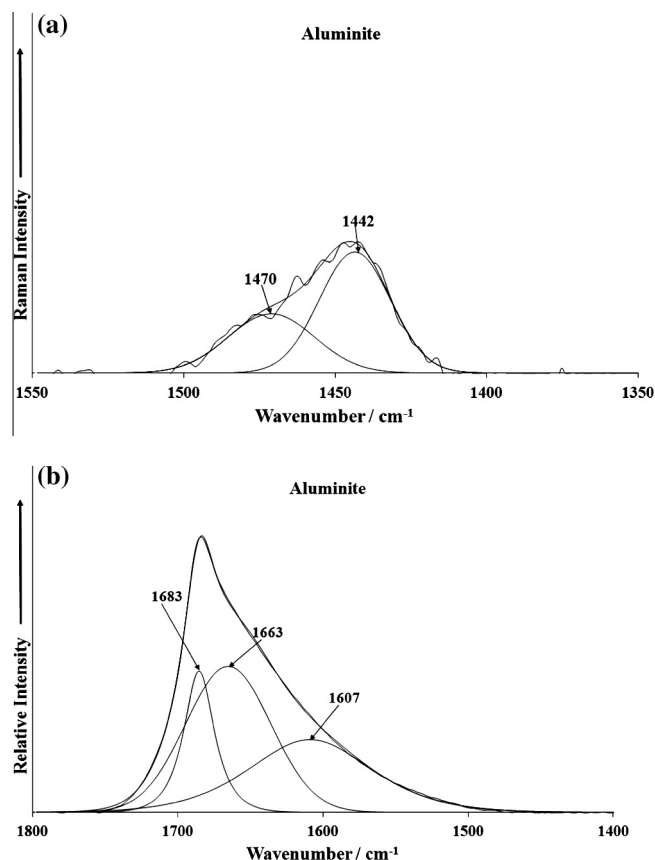
Fig. 7. (a) Raman spectrum of aluminite in 1350–1550 cm^{-1} spectral range (b) infrared spectrum of aluminite in 1400–1800 cm^{-1} spectral range.

at 1442 and 1470 cm^{-1}. The infrared spectrum of aluminite over 1400–1800 cm^{-1} spectral region is shown in Fig. 7b. The spectrum is broad with a low wavenumber tail; two infrared bands are resolved at 1663 and 1683 cm^{-1}. These bands are attributed to the water bending modes. The position of these bands is such that strong hydrogen bonding of these water molecules in the aluminite structure is noted.

Conclusions

Aluminite is a hydrated hydroxy sulphate of aluminium of formula $Al_2(SO_4)(OH)_4 \cdot 7H_2O$, and as such lends itself to analysis by vibrational spectroscopic techniques. SEM with EDX shows a homogenous mineral which analyses perfectly. This mineral is difficult to identify by X-ray diffraction, thus making Raman and infrared spectroscopy very useful tools for identifying this mineral. This study will assist with the identification of aluminate in red mud and products of red mud formed through the reaction of red mud and sea water and also Bayer liquors.

The Raman spectrum is dominated by a single intense band at 993 cm^{-1} with low intensity bands at 1069, 1094 and 1136 cm^{-1} assigned to the SO_4^{2-} stretching vibrations. In contrast, the infrared spectrum shows broad overlapping peaks which may be resolved into component bands. The series of Raman bands at 575, 607, 631, 642 and 680 cm^{-1} are assigned to the v_4 SO_4^{2-} bending modes, whilst and v_2 $(SO_4)^{2-}$ bending modes at 460 and 494 cm^{-1}. The observation of multiple bands supports the concept of a reduction in symmetry of the sulphate anion in aluminite from T_d to C_{3v} or even C_{2v}.

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