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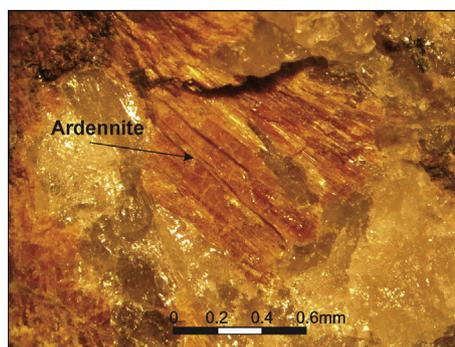
## A vibrational spectroscopic study of the silicate mineral ardennite-(As)

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### HIGHLIGHTS

- We have studied the mineral ardennite-(As).
- Qualitative chemical analysis shows a homogeneous phase, composed by Si, Mn, Al and As.
- Raman bands at 3041, 3149, 3211 and 3298  $\text{cm}^{-1}$  are attributed to the stretching vibrations of water.
- Bands attributable to OH units were found.
- Water adsorbed on the surfaces of mineral ardennite-(As) was identified.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We have used a combination of scanning electron microscopy with EDX and vibrational spectroscopy to study the mineral ardennite-(As). The mineral ardennite-(As) of accepted formula  $\text{Mn}_4^{2+}(\text{Al,Mg})_6(\text{Si}_3\text{O}_{10})(\text{SiO}_4)_2(\text{AsO}_4,\text{VO}_4)(\text{OH})_6$  is a silicate mineral which may contain arsenate and/or vanadates anions. Because of the oxyanions present, the mineral lends itself to analysis by Raman and infrared spectroscopy. Qualitative chemical analysis shows a homogeneous phase, composed by Si, Mn, Al and As. Ca and V were also observed in partial substitution for Mn and As. Raman bands at 1197, 1225, 1287 and 1394  $\text{cm}^{-1}$  are assigned to SiO stretching vibrations. The strong Raman bands at 779 and 877  $\text{cm}^{-1}$  are assigned to the  $\text{AsO}_4^{3-}$  antisymmetric and symmetric stretching vibrations.

The Raman band at 352  $\text{cm}^{-1}$  is assigned to the  $\nu_2$  symmetric bending vibration. The series of Raman bands between 414 and 471  $\text{cm}^{-1}$  are assigned to the  $\nu_4$  out of plane bending modes of the  $\text{AsO}_4^{3-}$  units. Intense Raman bands observed at 301 and 314  $\text{cm}^{-1}$  are attributed to the MnO stretching and bending vibrations. Raman bands at 3041, 3149, 3211 and 3298  $\text{cm}^{-1}$  are attributed to the stretching vibrations of OH units. There is vibrational spectroscopic evidence for the presence of water adsorbed on the ardennite-(As) surfaces.

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### Introduction

The mineral ardennite-(As) of formula  $\text{Mn}_4^{2+}(\text{Al,Mg})_6(\text{Si}_3\text{O}_{10})(\text{SiO}_4)_2(\text{AsO}_4,\text{VO}_4)(\text{OH})_6$  is a silicate mineral which may contain arsenate and/or vanadates anions [1]. This mineral originally was referred to as ardennite, which was named for the type locality in the Ardennes Mountains in Belgium; it has since been redefined

as ardennite-(As), as there is also a vanadate ( $\text{VO}_4$ ) analogue of the mineral [1]. The two minerals form a continuous solid solution. Ardennite-(As) is a rare mineral that occurs in pegmatites, quartz veins, and highly oxidized manganese and aluminum rich sediments [2–5].

The mineral is orthorhombic [6–8] of point group:  $2/m\ 2/m\ 2/m$  and space group:  $\text{Pnmm}$ :  $a = 8.7126(8)$ ,  $b = 18.5124(11)$ ,  $c = 5.8108(8)$ , and  $Z = 2$ . According to Donnay and Allman [9], the crystal structure of ardennite-(As) can be derived from that of epidote by Ito-type twinning; it leads to the  $\text{Si}_3\text{O}_{10}$  groups, which

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strengthen the bond chains along *c*. As in epidote, chains of octahedra sharing edges extend along *b*. These chains are connected by the  $\text{SiO}_4$  and  $\text{Si}_3\text{O}_{10}$  groups.  $(\text{As},\text{V})\text{O}_4$  tetrahedra do not share corners with  $\text{SiO}_4$  tetrahedra [9].

There is an apparent lack of information on the vibrational spectra of ardeninite-(As). The reason for such a lack of information is not known; yet the mineral contains OH units, siloxane units and arsenate and/or vanadates units. Such units lend themselves to vibrational spectroscopy. Raman spectroscopy has proven most useful for the study of mineral structures especially at the molecular level. The objective of this research is to report the Raman and infrared spectra of ardeninite-(As) and to relate the spectra to the mineral structure.

## Experimental

### Samples description and preparation

The ardeninite-(As) sample studied in this work occurs as single crystals with tabular habitus up to 1 cm in association with quartz. The sample is from the Salmchâteau, Vielsalm, Stavelot Massif, Luxembourg Province, Belgium, the type locality for the mineral [1]. Ardeninite-(As) occurs in association with quartz. The mineral shows yellow color and vitreous to sub-adamantine luster. An image of ardeninite-(As) is provided in the Supplementary information 1.

The mineral has been analyzed by X-ray diffraction. The XRD pattern of our ardeninite-(As) matches the standard exactly. The XRD pattern of our ardeninite-(As) is given in the Supplementary information.

The sample is part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-088. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The ardeninite-(As) sample studied in this work was analyzed by scanning electron microscopy (SEM) in the EDS mode to support the mineral characterization.

### Scanning electron microscopy (SEM)

Experiments and analyzes 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>). Ardeninite-(As) 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 analyzes in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

### Raman microprobe spectroscopy

Crystals of ardeninite-(As) were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10 $\times$ , 20 $\times$ , and 50 $\times$  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  $\text{cm}^{-1}$  and a precision of  $\pm 1 \text{ cm}^{-1}$  in the range between 200 and 4000  $\text{cm}^{-1}$ . Repeated acquisitions on the crystals using the highest magnification (50 $\times$ ) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5  $\text{cm}^{-1}$  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 ardeninite-As is given in the RRUFF data base at [http://rruff.info/Ardennite-\(As\)](http://rruff.info/Ardennite-(As)). No assignment of the bands was provided. This spectrum is included in the Supplementary information 2. This RRUFF spectrum does not show bands above 1100  $\text{cm}^{-1}$ ; no water bands or OH stretching vibrations are provided when at least the latter could be expected. In the RRUFF spectrum of ardeninite-As, some very intense Raman bands are observed between 4000  $\text{cm}^{-1}$  and 5000  $\text{cm}^{-1}$ . These bands may be caused by fluorescence.

### 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  $\text{cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of 4  $\text{cm}^{-1}$  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 Spectralcalc 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

### Mineral characterization

The SEM image of ardeninite-(As) sample studied in this work is shown in Fig. 1. The image shows a crystal fragment up to 1 mm. A perfect cleavage is observed on 010. Qualitative chemical analysis shows a homogeneous phase, composed by Si, Mn, Al and As. Ca and V were also observed in partial substitution of Mn and As, respectively. Semiquantitative chemical analysis shows an As/V ratio equal to 89/11. Zonation of the crystal was not observed and the sample can be considered as a single phase (Fig. 2).

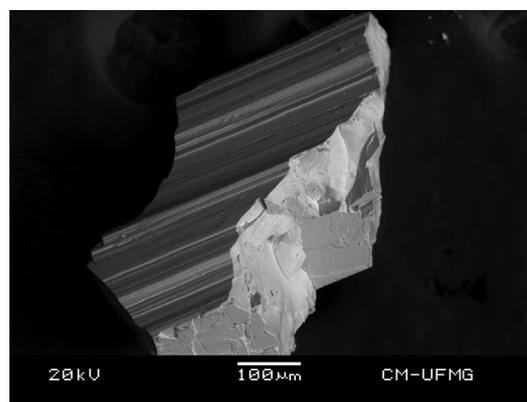


Fig. 1. Backscattered electron image (BSI) of an ardeninite-(As) crystal fragment up to 1.0 mm in length.

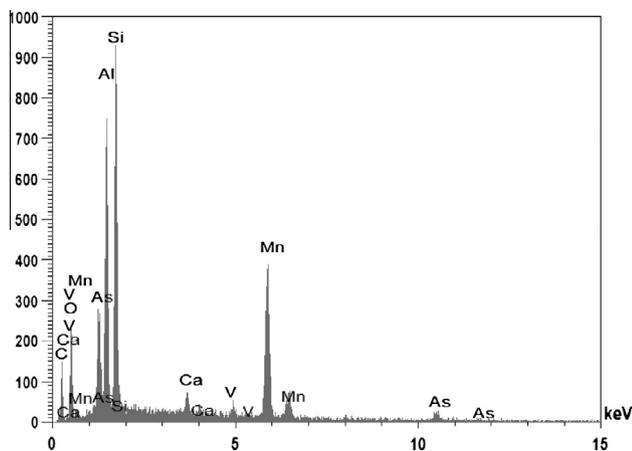


Fig. 2. EDS spectrum of ardennite-(As).

### Vibrational spectroscopy

The Raman spectrum of ardennite-(As) over the 3600–100  $\text{cm}^{-1}$  spectral range is reported in Fig. 3a. This spectrum displays the band positions and relative intensities of these Raman bands. There are large parts of the spectrum where little or no intensity is observed. Therefore, the spectrum is divided into subsections depending upon the type of vibration being studied. It is noted that there is an apparent lack of intensity in the OH stretching region. The spectrum is dominated by Raman bands in the 1400–1100  $\text{cm}^{-1}$  region. The infrared spectrum of ardennite-(As)

over the 4000–500  $\text{cm}^{-1}$  spectral range is illustrated in Fig. 3b. The position of the infrared bands and their relative intensities are observed. There are parts of the spectrum where little or no intensity is observed. The infrared spectrum is subdivided into sections based upon the type of vibration being analyzed.

The formula of the mineral ardennite-(As) is  $\text{Mn}_4^{2+}(\text{Al,Mg})_6(\text{Si}_3\text{O}_{10})(\text{SiO}_4)_2(\text{AsO}_4, \text{VO}_4)(\text{OH})_6$  and it is expected that there would be Raman and infrared bands dominated by  $\text{SiO}_4$  and  $\text{Si}_3\text{O}_{10}$  peaks. The Raman spectrum of ardennite-(As) over the 1100–1800  $\text{cm}^{-1}$  spectral range is shown in Fig. 4a. This spectrum shows strong Raman bands between 1100 and 1400  $\text{cm}^{-1}$  with band components resolved at 1197, 1225, 1287 and 1394  $\text{cm}^{-1}$ . These bands are assigned to  $\text{SiO}$  antisymmetric stretching vibrations. Because of the complexity of bonded silicate polyhedra, it is difficult to assign the  $\text{SiO}$  bands.

The Raman band at 1605  $\text{cm}^{-1}$  is due to a water bending mode. Dowty showed that the  $-\text{SiO}_3$  units had a unique band position of 980  $\text{cm}^{-1}$  [10] (see Figs. 2 and 4 of this reference). Dowty also showed that  $\text{Si}_2\text{O}_5$  units had a Raman peak at around 1100  $\text{cm}^{-1}$ . The bands at around 1200  $\text{cm}^{-1}$  are assigned to the  $\text{SiO}$  stretching vibration of these  $\text{Si}_2\text{O}_5$  units. The infrared spectrum of ardennite-(As) over the 1450–1800  $\text{cm}^{-1}$  spectral range is shown in Fig. 4b. The infrared band at 1650  $\text{cm}^{-1}$  is assigned to the water bending mode of strongly hydrogen bonded water molecules. The observation of bands at 1605  $\text{cm}^{-1}$  (Raman) and 1650  $\text{cm}^{-1}$  (infrared) gives credence to the adsorption of water on the ardennite-(As) surfaces.

The Raman spectrum of ardennite-(As) over the 1000–700  $\text{cm}^{-1}$  spectral range is reported in Fig. 5a. This spectrum shows well-resolved bands with Raman peaks observed at 713, 779, 877 and 935  $\text{cm}^{-1}$ . The Raman spectrum of ardennite-(As) from the

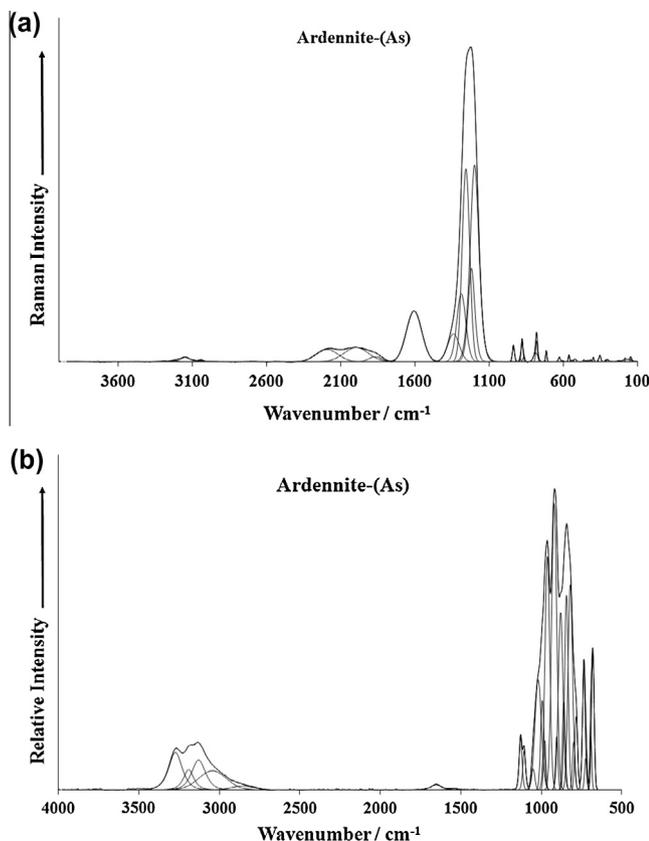


Fig. 3. (a) Raman spectrum of ardennite-(As) over the 4000–100  $\text{cm}^{-1}$  spectral range and (b) infrared spectrum of ardennite-(As) over the 4000–500  $\text{cm}^{-1}$  spectral range.

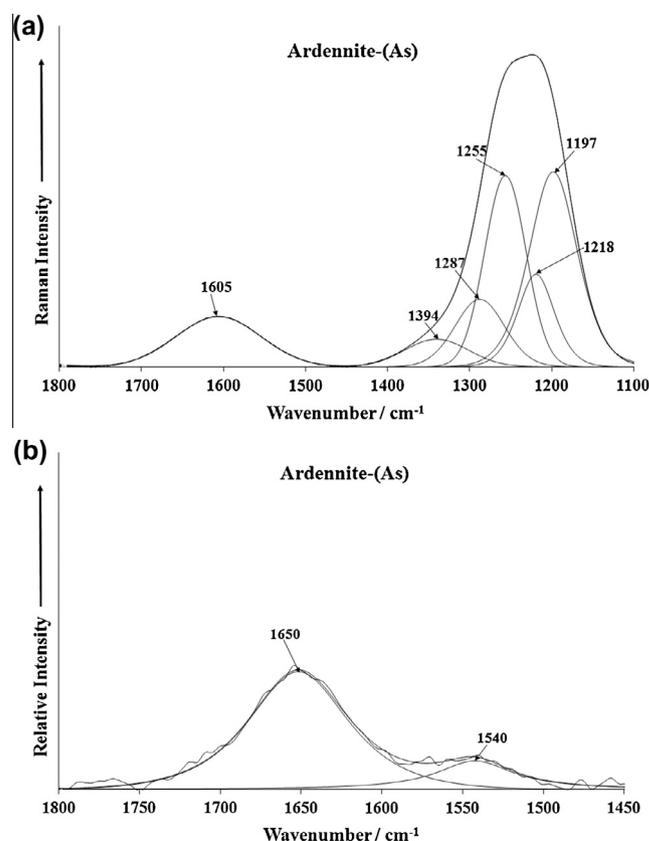
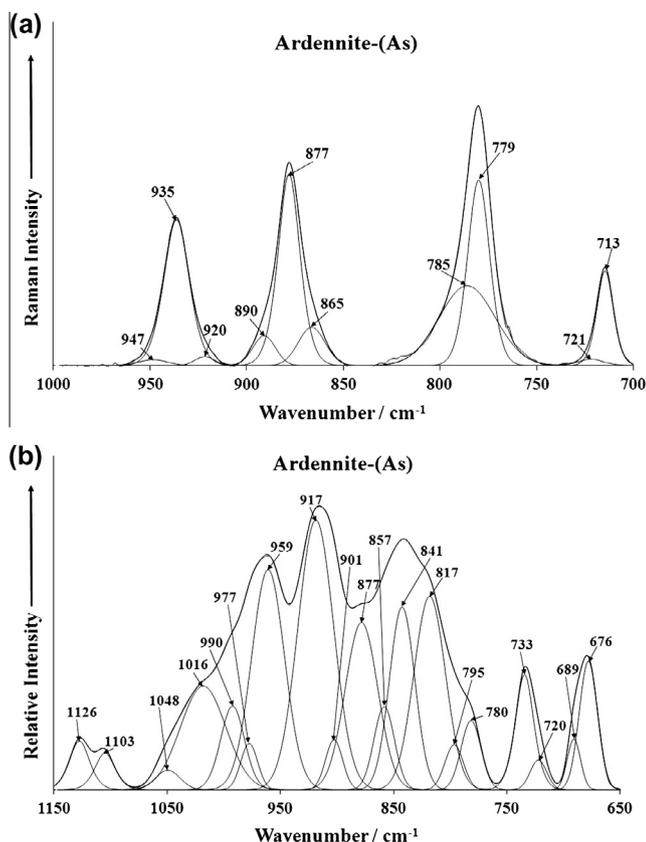


Fig. 4. (a) Raman spectrum of ardennite-(As) over the 1800–1100  $\text{cm}^{-1}$  spectral range and (b) infrared spectrum of ardennite-(As) over the 1800–1450  $\text{cm}^{-1}$  spectral range.

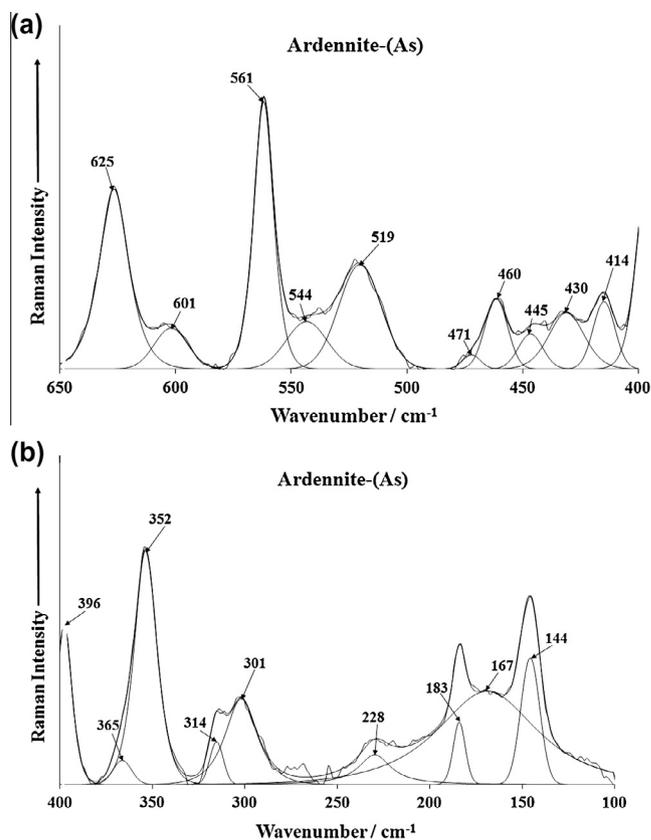


**Fig. 5.** (a) Raman spectrum of ardennite-(As) over the 1400–800 cm<sup>-1</sup> spectral range and (b) infrared spectrum of ardennite-(As) over the 1300–800 cm<sup>-1</sup> spectral range.

RRUFF data base (provided in the Supplementary information) shows a very strong peak at 875 cm<sup>-1</sup> and two other intense bands at 713, 780 and 932 cm<sup>-1</sup>. The values detailed here are in excellent agreement with our data in Fig. 5a. One possible interpretation of this Raman spectrum is to assign the band at 877 (875 RUFF) cm<sup>-1</sup> to the AsO<sub>4</sub><sup>3-</sup> ν<sub>1</sub> symmetric stretching mode and the band at band at 779 (780 RRUFF) cm<sup>-1</sup> to the AsO<sub>4</sub><sup>3-</sup> ν<sub>3</sub> antisymmetric stretching mode. The semi-quantitative analysis of the ardennite-As sample shows the ratio of As to V is about 89/11. The Raman band at 935 (932 RRUFF) is due to the VO<sub>4</sub><sup>3-</sup> ν<sub>1</sub> symmetric stretching mode. Some low intensity shoulders are also observed. These bands are thought to be related to the Si–O stretching and bending vibrations. Dowty calculated the band position of these bending modes for different siloxane units [10]. Dowty demonstrated the band position of the bending modes for SiO<sub>3</sub> units at around 650 cm<sup>-1</sup>. This calculated value is in harmony with the higher wavenumber band observed at 625 cm<sup>-1</sup> (628 cm<sup>-1</sup> in the RRUFF spectrum).

The infrared spectrum of ardennite-(As) over the 1150–650 cm<sup>-1</sup> spectral range is reported in Fig. 5b. The spectrum shows great complexity with multiple overlapping bands. This complexity shows why the Raman spectroscopy is more advantageous to collect data on ardennite-(As) than infrared spectroscopy. Infrared bands are found at 1103 and 1126 cm<sup>-1</sup> and are assigned to the SiO antisymmetric stretching vibrations. The series of bands observed at 780, 817, 841, 877, 901, 917, 959, 977, 990 and 1016 cm<sup>-1</sup> are related to the stretching and bending vibrations of the Si<sub>3</sub>O<sub>10</sub> and SiO<sub>4</sub> units. Knowing which band is due to which vibration is difficult to assess.

The Raman spectra of ardennite-(As) in the 650–400 cm<sup>-1</sup> and 400–100 cm<sup>-1</sup> spectral range are shown in Fig. 6. There are three



**Fig. 6.** (a) Raman spectrum of ardennite-(As) over the 800–300 cm<sup>-1</sup> spectral range and (b) Raman spectrum of ardennite-(As) over the 300–100 cm<sup>-1</sup> spectral range.

sections in the first figure: (a) the bands at 601 and 625 cm<sup>-1</sup> (b) the bands at 519, 544 and 561 cm<sup>-1</sup> (c) the series of bands at 414, 430, 445, 460 and 471 cm<sup>-1</sup>. In the RRUFF spectrum of ardennite-(As) Raman bands are observed at 350, 398, 462, 522, 557 and 628 cm<sup>-1</sup>. The position of these peaks are in harmony with the bands determined in this work as displayed in Fig. 6a. The series of Raman bands between 414 and 471 cm<sup>-1</sup> are assigned to the ν<sub>4</sub> out of plane bending modes of the AsO<sub>4</sub><sup>3-</sup> units. The band at 352 cm<sup>-1</sup> (Fig. 6b) is assigned to the ν<sub>2</sub> symmetric bending vibration. Griffith who reported bands at 324 and 310 cm<sup>-1</sup> for the bending modes of olivenite.

Dowty calculated the band position of these bending modes for different silicate units [10]. Dowty demonstrated the band position of the bending modes for SiO<sub>3</sub> units at around 650 cm<sup>-1</sup>. Thus, the two bands at 601 and 623 cm<sup>-1</sup> are assigned to this vibrational mode. This calculated value is in harmony with the higher wavenumber band observed at 625 cm<sup>-1</sup>. According to Adams et al. [11] the band at 430 cm<sup>-1</sup> is due to the coincidence of both the B<sub>2g</sub> and E<sub>g</sub> modes. Thus the series of bands between 414 and 471 cm<sup>-1</sup> are due to this bending mode vibration. Intense bands are observed at 301, 314, 352 and 396 cm<sup>-1</sup>. These bands are due to the MnO stretching and bending vibrations. The other bands in Fig. 5b at 144, 183 and 228 cm<sup>-1</sup> are simply described as lattice bands.

The Raman spectrum of ardennite-(As) over the 3400–2900 cm<sup>-1</sup> spectral range is illustrated in Fig. 7a. This figure shows resolved bands at 3041, 3149, 3211 and 3298 cm<sup>-1</sup>. The position of these bands is such that they are assigned to water stretching vibrations. The position of these bands suggests that water is strongly hydrogen bonded to the arsenate anions in the ardennite-(As) structure. The formula of the mineral Mn<sub>4</sub><sup>2+</sup>(Al,Mg)<sub>6</sub>(Si<sub>3</sub>O<sub>10</sub>)(SiO<sub>4</sub>)<sub>2</sub>(AsO<sub>4</sub>,VO<sub>4</sub>)(OH)<sub>6</sub> is such that no water is expected in

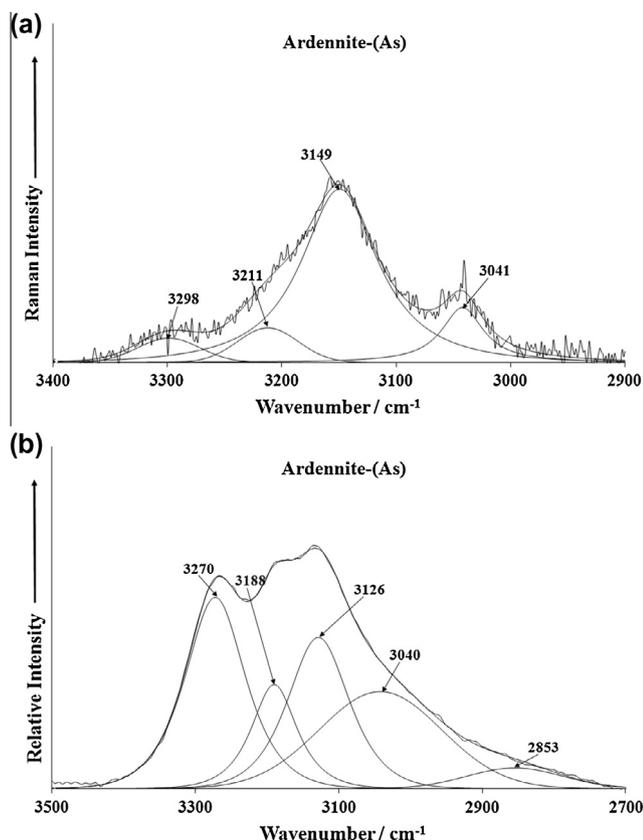


Fig. 7. (a) Raman spectrum of ardenite-(As) over the 4000–2600  $\text{cm}^{-1}$  spectral range and (b) infrared spectrum of ardenite-(As) over the 4000–2600  $\text{cm}^{-1}$  spectral range.

the formula. Thus, if the formula is not correct as it is written, then some water should be expected in the formula of ardenite-(As). Otherwise these bands are due to the OH units in the ardenite-(As) structure. The infrared spectrum of ardenite-(As) in the 1800–1450  $\text{cm}^{-1}$  region, shows a strong band at 1650  $\text{cm}^{-1}$  which is assigned to water bending modes (Fig. 4b). The presence of this band proves that water is adsorbed on the surfaces of ardenite-(As). The infrared spectrum of ardenite-(As) in the 3500–2700  $\text{cm}^{-1}$  spectral range is reported in Fig. 7b. Infrared bands are found at 3126, 3188 and 3270  $\text{cm}^{-1}$ . A broad tail is observed with resolved bands at 2853 and 3040  $\text{cm}^{-1}$ . These bands are ascribed to the stretching vibrations of the water units, probably adsorbed on the hydroxyl surface of ardenite-(As). These bands are assigned to the stretching vibrations of the OH units.

Both Raman and infrared bands in the OH stretching region, indicate the presence of water on the surface of ardenite-(As). However, the accepted formula has only OH units; thus bringing into question the formula of ardenite-(As). The formula of the mineral is given as  $\text{Mn}_4^{2+}(\text{Al,Mg})_6(\text{Si}_3\text{O}_{10})(\text{SiO}_4)_2(\text{AsO}_4, \text{VO}_4)(\text{OH})_6$ .

However, the bands which could be assigned to OH stretching or deformation modes could be identified.

## Conclusions

A study of the rare mineral ardenite-(As) was made using a combination of SEM with EDX and infrared and Raman spectroscopy. Qualitative chemical analysis shows a homogeneous phase, composed by Si, Mn, Al and As. Some minor substitution of V for As and Ca for Mn was observed. Raman bands were assigned to the stretching vibrations of the siloxane and arsenate units. Both Raman and infrared bands in the OH stretching region, indicate the presence of water in the structure of ardenite-(As). However, the accepted formula has only OH units; thus bringing into question the formula of ardenite-(As). The formula of the mineral is given as  $\text{Mn}_4^{2+}(\text{Al,Mg})_6(\text{Si}_3\text{O}_{10})(\text{SiO}_4)_2(\text{AsO}_4, \text{VO}_4)(\text{OH})_6$ . The position of the OH stretching vibrations provides strong evidence for bonding of water to the hydroxyl surfaces of ardenite-(As). Vibrational spectroscopy offers new information on the molecular structure of ardenite-(As) which might not be readily obtained by other methods.

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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.2013.09.148>.

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