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A vibrational spectroscopic study of the phosphate mineral vantasselite $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 9\text{H}_2\text{O}$



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HIGHLIGHTS

- We have studied the phosphate mineral vantasselite $\text{Al}_2(\text{PO}_4)(\text{OH})_3 \cdot 3\text{H}_2\text{O}$.
- Using a combination of SEM with EDX and Raman and infrared spectroscopy.
- Chemical analysis shows a mineral containing Al, Fe and P.
- A comparison is made with other aluminum containing phosphate minerals.
- Vibrational spectroscopy offers a mechanism for the study of the molecular structure of vantasselite.

GRAPHICAL ABSTRACT



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ABSTRACT

We have studied the phosphate mineral vantasselite $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 9\text{H}_2\text{O}$ using a combination of SEM with EDX and Raman and infrared spectroscopy. Qualitative chemical analysis shows Al, Fe and P. Raman bands at 1013 and 1027 cm^{-1} are assigned to the PO_4^{3-} ν_1 symmetric stretching mode. The observation of two bands suggests the non-equivalence of the phosphate units in the vantasselite structure. Raman bands at 1051, 1076 and 1090 cm^{-1} are attributed to the PO_4^{3-} ν_3 antisymmetric stretching vibration. A comparison is made with the spectroscopy of wardite. Strong infrared bands at 1044, 1078, 1092, 1112, 1133, 1180 and 1210 cm^{-1} are attributed to the PO_4^{3-} ν_3 antisymmetric stretching mode. Some of these bands may be due to $\delta\text{Al}_2\text{OH}$ deformation modes. Vibrational spectroscopy offers a mechanism for the study of the molecular structure of vantasselite.

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Introduction

Vantasselite is a rare aluminum phosphate mineral with chemical formula given as $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 9\text{H}_2\text{O}$. The mineral crystallizes with orthorhombic symmetry, Point Group: 222, unit cell parameters are: Space Group: *Pm*am, *Pma*2 or *P2*₁am; *a* = 10.528(4),

b = 16.541(3), *c* = 20.373(6) and *Z* = 8. The crystals occur with lamellar habitus, elongated along 100. The crystal aggregates forms rosettes up to 5 mm. Vantasselite was first described from Bihain, Vielsalm, Stavelot Massif, Belgium [1]. The mineral occurs on dumps in a quartzite quarry in quartz veinlets or lining schistosity planes. The associated minerals are wavellite, cacoxenite, variscite, turquoise, lithiophorite, cryptomelane, quartz, clinocllore and muscovite. There is no crystal structure determination for vantasselite. The only scientific publication about this mineral is the

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original description [1]. Due to the cleavage and the type of fragment like plates, the unit cell refinement is not useful, or is very complicated to be used for the determination of the crystal structure. Thus, it seems appropriate in order to determine aspects of the molecular structure of vantasselite to use vibrational spectroscopic techniques.

Interestingly Farmer in his book on the infrared spectra of minerals divided the vibrational spectra of phosphates according to the presence, or absence of water and hydroxyl units in the minerals [2]. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} [3–5]. Farmer reported the infrared spectra of berlinite (AlPO_4) with PO_4 stretching modes at 1263 , 1171 , 1130 and 1114 cm^{-1} ; bending modes at 511 , 480 , 451 , 379 and 605 cm^{-1} . Al–O modes were found at 750 , 705 , 698 and 648 cm^{-1} . On hydration of the mineral as with variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), PO_4 stretching modes were found at 1160 , 1075 , 1050 and 938 cm^{-1} ; bending modes at 515 , 450 and 420 cm^{-1} ; in addition H_2O stretching bands were found at 3588 , 3110 , 2945 cm^{-1} . For the mineral augelite ($\text{AlPO}_4(\text{OH})_3$), infrared bands were observed at 930 (ν_1), 438 (ν_2), 1205 , 1155 , 1079 , 1015 (ν_3) and 615 , 556 cm^{-1} (ν_4). For augelite, OH stretching modes were not observed.

There are a couple of minerals the chemistry of which may be compared with vantasselite. These include wardite and cyrilovite. There have been some studies of the vibrational spectroscopy of wardite [6,7]. Tarte et al. collected the infrared spectra of five samples of cyrilovite $\text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$ [8] and wardite [7]. Cyrilovite is analogous to wardite, with ferric iron replacing the aluminum in the structure. It is likely that solid solutions of the two minerals are formed with varying amounts of ferric ion and aluminum in the structure. The mineral wardite is capable of crystallizing in a similar form to that of cyrilovite because of their closely related chemical compositions. Between wardite's composition, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$, and cyrilovite composition, $\text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$, these minerals are able to form end members of a series of solid solutions. Either of the two minerals can occur in various proportions in a series of solid solutions in the wardite mineral group. Cyrilovite is a rare accessory mineral in some oxidizing phosphate-bearing granite pegmatites and iron deposits. The vibrational spectrum is dependent upon the ratio of the Al/Fe. Tarte et al. found that the two minerals wardite and cyrilovite can be distinguished by the spectral patterns of the OH stretching region in the infrared spectrum [7]. These workers did

not interpret the spectra of the phosphate because of complexity and no detailed assignments were given. Breiteringer et al. reported the combined vibrational spectra of a natural wardite. Breiteringer et al. used a full array of techniques including inelastic neutron scattering, infrared, Raman and near infrared techniques [6]. These workers used a natural wardite with significant amounts of ferric iron in the structure. In other words, the sample analyzed was fundamentally a solid solution of wardite and cyrilovite, but at the wardite end. The original papers on the infrared spectrum of isolated phosphate units was published by Lazarev [9]. Of course, phosphates structures are different. Usually they have rather low symmetry: orthorhombic, monoclinic, or even triclinic [10]. Farmer based upon the work of Petrov et al. [11–13] made a comparison of the results of the vibrational spectrum of a series of phosphates.

Raman spectroscopy has proven most useful for the study of mineral structures [14–19]. The objective of this research is to report the Raman and infrared spectra of vantasselite and to relate the spectra to the molecular structure of the minerals. The mineral vantasselite may be described as an environmental mineral in that it is formed in waste dumps and mining wastes, as such the mineral is often small in crystal size and difficult to measure by X-ray diffraction. The number of vantasselite occurrences is limited [20]. This is the first report of a systematic vibrational spectroscopic study of vantasselite from Belgium.

Experimental

Mineral

The vantasselite sample studied in this work was collected from the Bihain, Vielsalm, Stavelot Massif, Luxembourg Province, Belgium. The sample is incorporated into the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-085. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Zeiss Stemi DV4 from the Museu de Ciência e Técnica of the Federal University of Ouro Preto. Scanning electron microscopy (SEM) was applied to support the mineral characterization.

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>).

A vantasselite crystal aggregate up to 0.5 mm was coated with a 5 nm layer of evaporated carbon. Backscattering Electron images was 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 characterization.

Raman spectroscopy

Crystals of vantasselite were placed on a polished metal surface on the stage of an Olympus BSM 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 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between 100 and 4000 cm^{-1} . Repeated

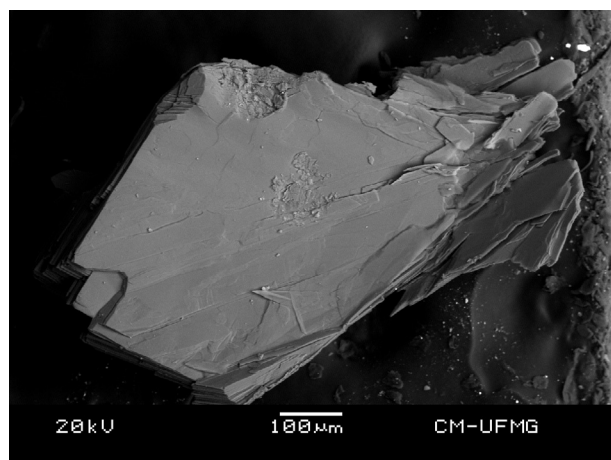


Fig. 1. Backscattered electron image (BSI) of a vantasselite fragment up to 0.5 mm in length.

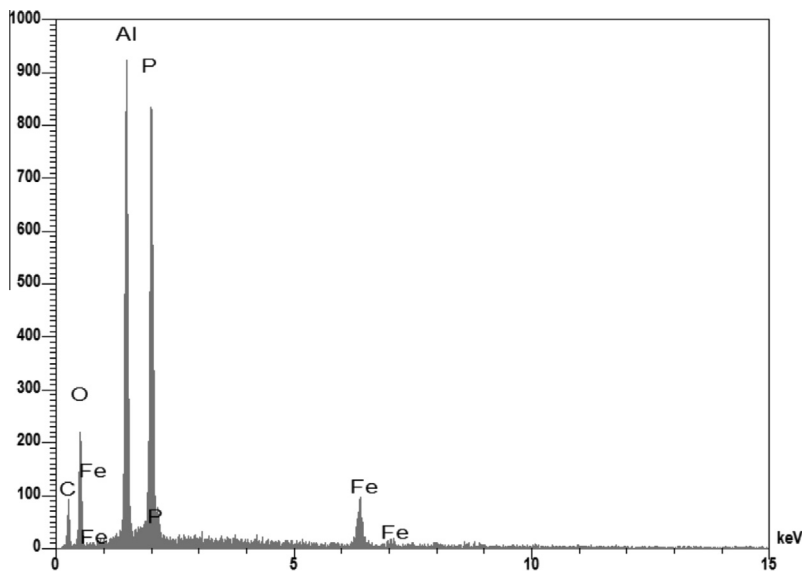


Fig. 2. EDS spectra of vantasselite.

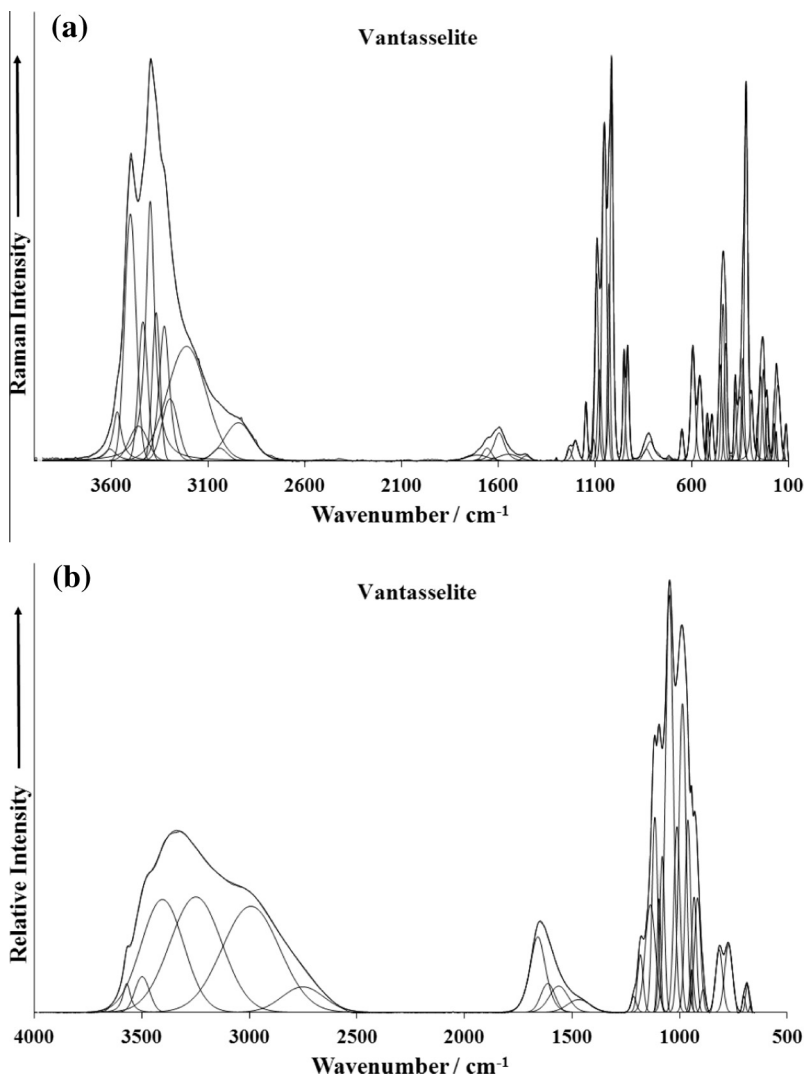


Fig. 3. (a) Raman spectrum of vantasselite over the 100–4000 cm⁻¹ spectral range. (b) Infrared spectrum of vantasselite over the 500–4000 cm⁻¹ spectral range.

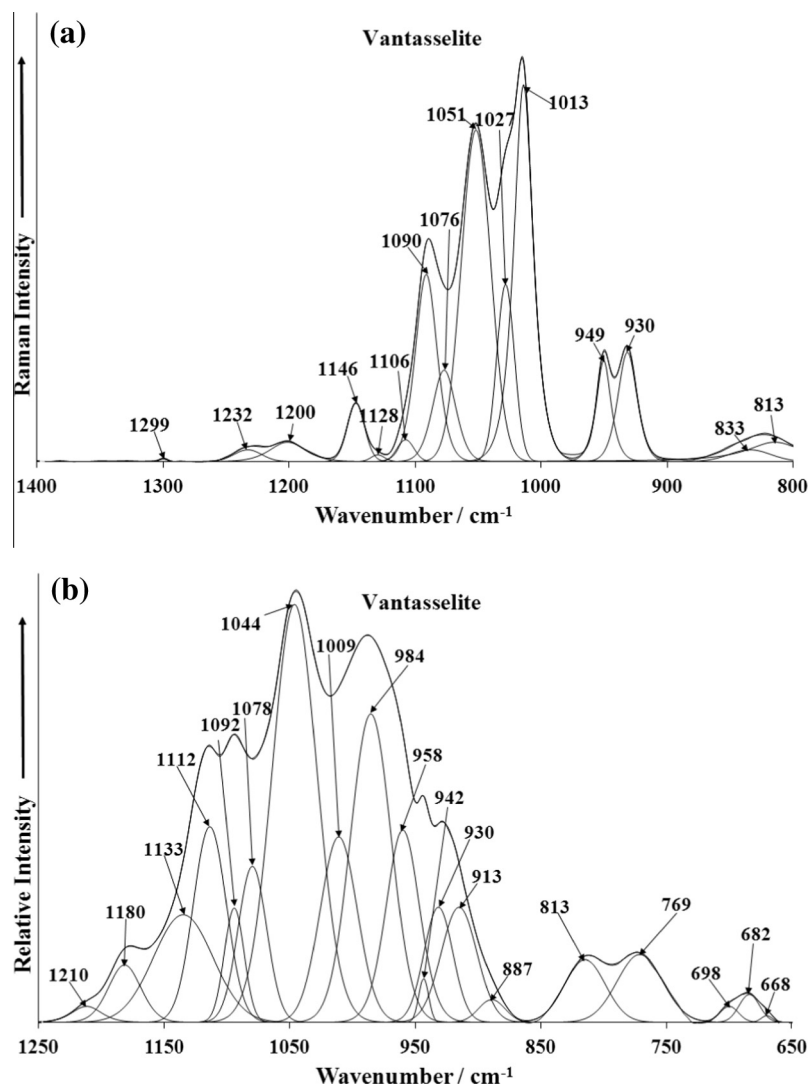


Fig. 4. (a) Raman spectrum of vantasselite (upper spectrum) in the 800–1400 cm⁻¹ spectral range and (b) infrared spectrum of vantasselite (lower spectrum) in the 650–1250 cm⁻¹ spectral range.

acquisition on the crystals using the highest magnification (50×) was 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.

A Raman spectrum of vantasselite is given in the RRUFF data base (<http://rruff.info/Vantasselite>). This spectrum is provided in [supplementary information as Fig. S1](#). No assignment of the bands is given and the high wavenumber part of the vantasselite spectrum was not recorded.

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.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number

of component bands used for the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting is undertaken with the minimum number of fitted bands. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

Results and discussion

Chemical characterization

The SEM image of vantasselite sample studied in this work is shown in [Fig. 1](#). Vantasselite crystal aggregates show tabular habitus. A perfect cleavage on (001) is observed. Qualitative chemical analysis shows Al, Fe and P ([Fig. 2](#)). The presence of C in the EDS spectra is due to the influence of carbon tape and coating.

Vibrational spectroscopic background

Farmer [2] divided the vibrational spectra of phosphates according to the presence, or absence of water and/or hydroxyl units in the minerals. In aqueous systems, Raman spectra of

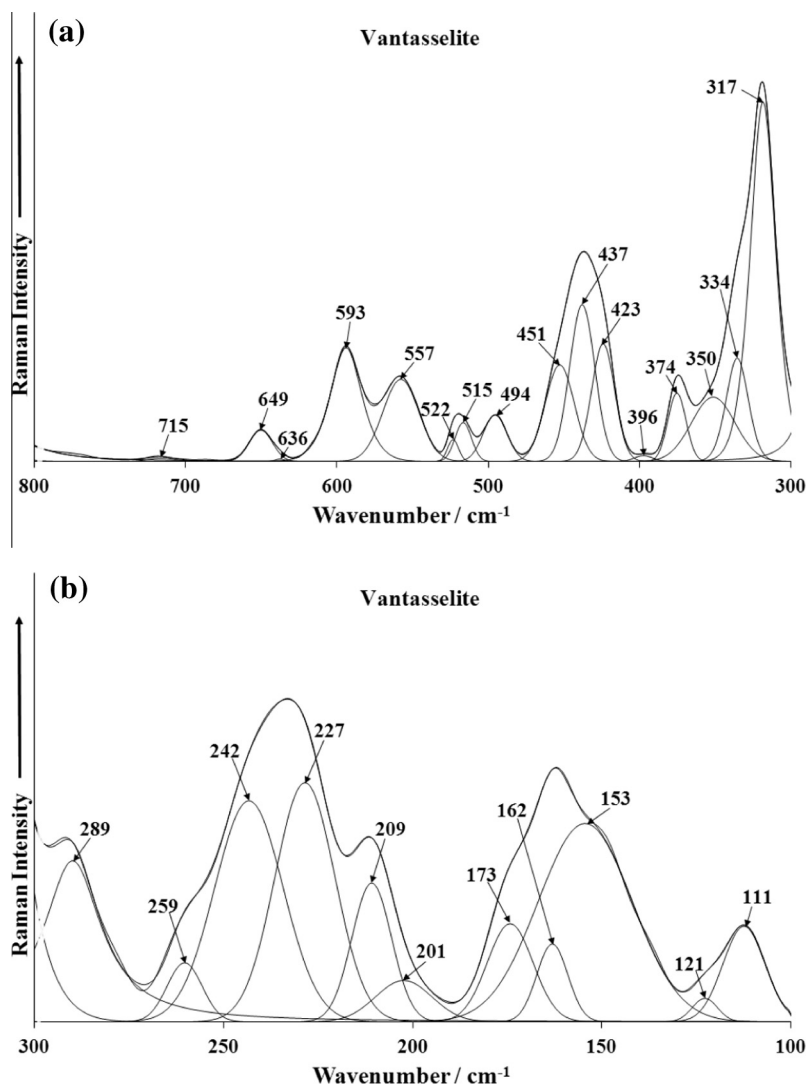


Fig. 5. (a) Raman spectrum of vantasselite (upper spectrum) in the 300–800 cm^{-1} spectral range and (b) Raman spectrum of vantasselite (lower spectrum) in the 100–300 cm^{-1} spectral range.

phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the (ν_4) mode at 567 cm^{-1} [3–5,21]. The value for the ν_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavelite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrénite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4 units.

The value for the ν_2 symmetric bending vibration of PO_4 units as determined by infrared spectroscopy was given as 438 cm^{-1} (augelite), 452 cm^{-1} (wavelite), 440 and 415 cm^{-1} (rockbridgeite), 455, 435 and 415 cm^{-1} (dufrénite) and 470 and 450 cm^{-1} (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the PO_4 units. This symmetry reduction is also observed through the ν_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015 cm^{-1} [22,23]; wavelite at 1145, 1102, 1062 and 1025 cm^{-1} ; rockbridgeite at 1145, 1060 and 1030 cm^{-1} ; dufrénite at 1135, 1070 and 1032 cm^{-1} ; and beraunite at 1150, 1100, 1076 and 1035 cm^{-1} .

Vibrational spectroscopy

The Raman spectrum of vantasselite in the 100–4000 cm^{-1} spectral range is displayed in Fig. 3a. This spectrum shows the position and relative intensities of the Raman bands. It is noted that there are large parts of the spectrum where no intensity or minimal intensity is observed. Thus, the spectrum is subdivided into subsections depending upon the type of vibration being studied. The infrared spectrum of vantasselite in the 500–4000 cm^{-1} spectral region is reported in Fig. 3b. This figure shows the position of the infrared bands and their relative intensities. As for the Raman spectrum, there are parts of the spectrum where little or no intensity is observed; thus the spectrum is subdivided into sections based upon the type of vibration being analyzed.

The Raman spectrum of vantasselite over the 800–1400 cm^{-1} spectral range is shown in Fig. 4a. A number of intense Raman bands are observed at 1013, 1027 and 1051 cm^{-1} . The first band is assigned to the PO_4^{3-} ν_1 symmetric stretching mode. A strong shoulder band is noted at 1027 cm^{-1} and is also assigned to this vibrational mode. The observation of multiple symmetric stretching modes supports the concept of non-equivalent phosphate units in the structure of vantasselite. The Raman bands at 1051, 1076 and 1090 cm^{-1} are attributed to the PO_4^{3-} ν_3 antisymmetric

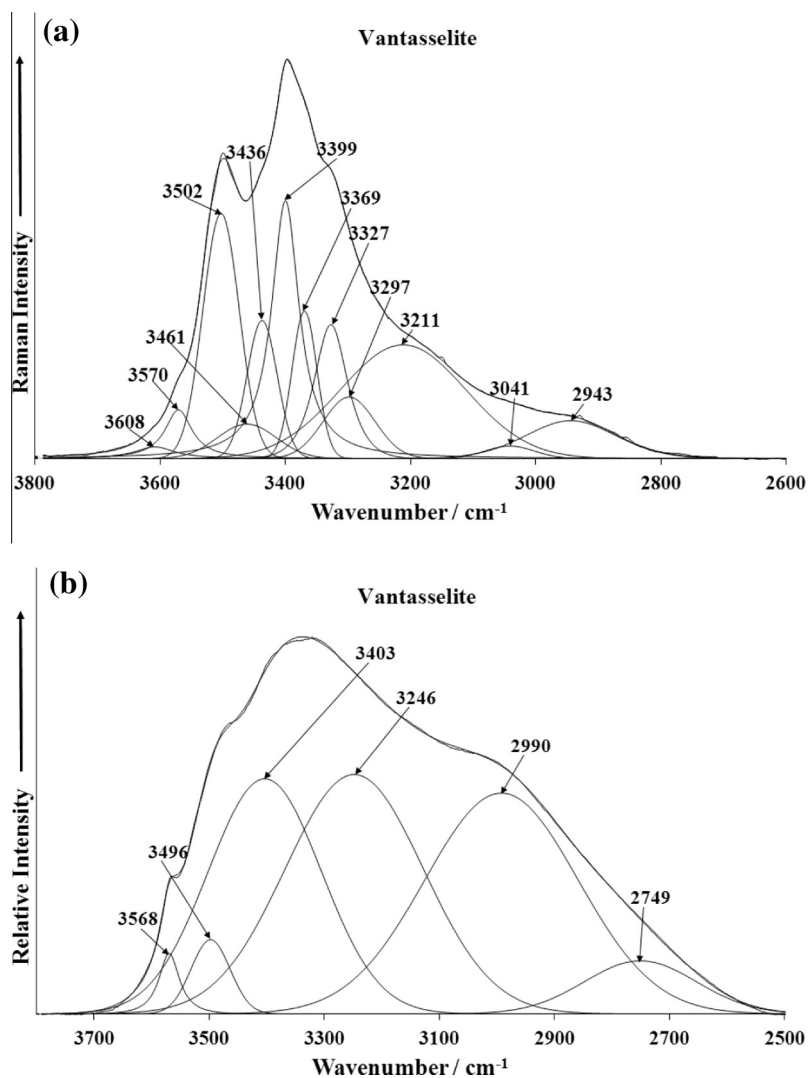


Fig. 6. (a) Raman spectrum of vantasselite (upper spectrum) in the 2600–3800 cm^{-1} spectral range and (b) infrared spectrum of vantasselite (lower spectrum) in the 2500–3800 cm^{-1} spectral range.

stretching vibration. Other lower intensity Raman bands at 1106, 1128 and 1146 cm^{-1} may also be also assigned to this vibration. The multiplicity of the Raman bands supports the concept of a reduction in symmetry of the phosphate units. It is possible that some of these bands are due to the PO stretching vibrations of HOPO_3^{2-} units. The two Raman bands at 930 and 949 cm^{-1} are assigned to AlOH deformation modes. The low intensity Raman bands at 813 and 833 cm^{-1} are assigned to water librational modes. A Raman spectrum of vantasselite is given in the RRUFF data base. Sharp Raman bands are noted at 1009, 1051 and 1090 cm^{-1} which are in agreement with this work. The spectrum looks identical with our spectrum.

Breitinger et al. [6] assigned the band at 999 cm^{-1} for wardite to AlOH deformation modes. It is possible that the strong Raman bands for vantasselite at 1051 cm^{-1} is due to $\delta\text{Al}_2\text{OH}$ deformation modes. In our work on the spectroscopy of wardite, the band at 995 cm^{-1} is very sharp and well resolved. The band at 1051 cm^{-1} is ever so slightly asymmetric on the low wavenumber side and a component may be resolved at 1045 cm^{-1} . A group of low intensity bands are observed at 1084, 1108, 1120, 1140 and 1186 cm^{-1} assigned to the $\nu_3 \text{PO}_4^{3-}$ antisymmetric stretching modes. Breitinger et al. [6] did not report any bands in these positions in the Raman spectrum. They reported infrared bands at 1058 (strong) with

shoulders at 1129 and 1168 cm^{-1} and assigned these bands to $\delta\text{Al}_2\text{OH}$ deformation modes. A low intensity broad band at 884 cm^{-1} is assigned to a water librational mode. In the work of Breitinger et al. a broad low intensity band was found at around 800 cm^{-1} and was attributed to water librational modes.

The infrared spectrum of vantasselite over the 650–1250 cm^{-1} spectral range is shown in Fig. 4b. The spectrum is complex with a number of overlapping bands which may be resolved into component bands. The broadish infrared band at 984 cm^{-1} assigned to the $\text{PO}_4^{3-} \nu_1$ symmetric stretching mode and is the equivalent of the Raman band at 1013 cm^{-1} . The infrared band at 1009 cm^{-1} may also be ascribed to this vibration. The strong infrared bands at 1044, 1078, 1092, 1112, 1133, 1180 and 1210 cm^{-1} are attributed to the $\text{PO}_4^{3-} \nu_3$ antisymmetric stretching mode. The infrared spectra of wardite also show a great deal more complexity than the Raman spectra of wardite. The band for wardite at around 994 cm^{-1} is attributed to the $\nu_1 \text{PO}_4^{3-}$ symmetric stretching mode. The cluster of bands at 1039, 1056, 1069, 1084, 1102, 1135 and 1165 cm^{-1} are attributed to the $\nu_3 \text{PO}_4^{3-}$ antisymmetric stretching modes. Some of these bands may also be due to the $\delta\text{Al}_2\text{OH}$ deformation modes, in harmony with the assignment of Breitinger et al. [6]. He and his co-workers stated that the deceptively simple strong IR band centered at 1059 cm^{-1} for wardite contains at least

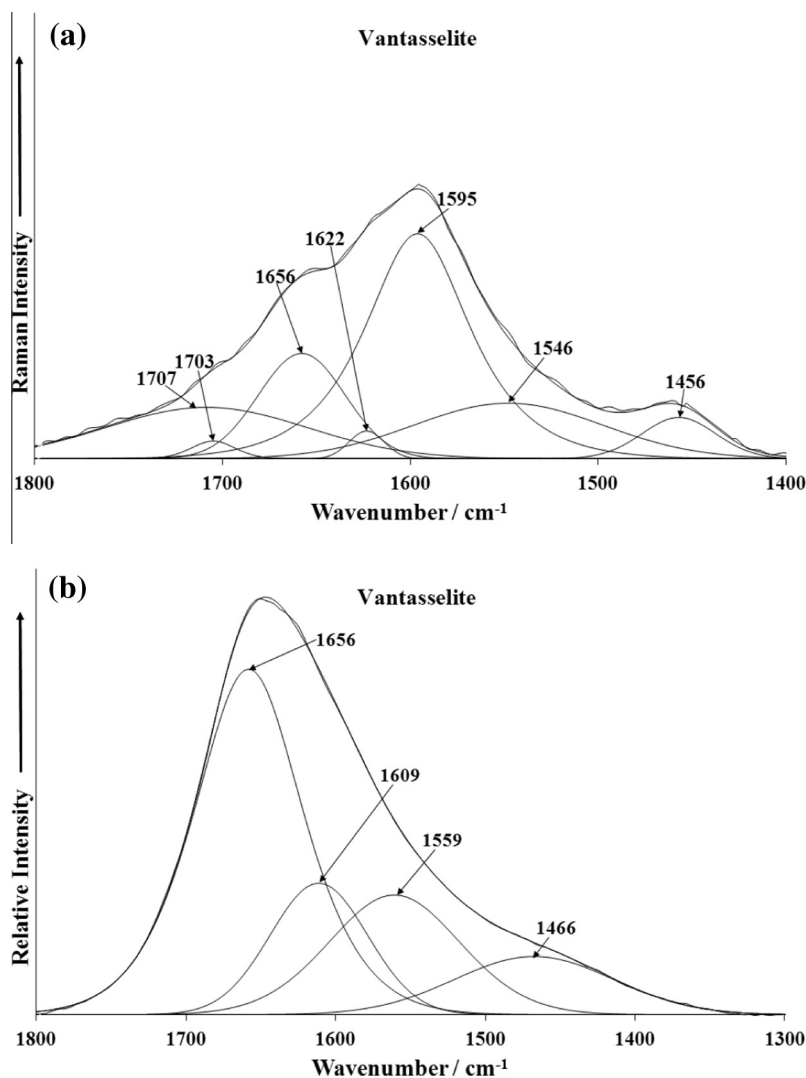


Fig. 7. (a) Raman spectrum of vantasselite (upper spectrum) in the 1400–1800 cm^{-1} spectral range and (b) infrared spectrum of vantasselite (lower spectrum) in the 1300–1800 cm^{-1} spectral range.

four components of $\nu(\text{PO}_4)$ generated by lifting of the originally threefold degeneracy of $\nu_3(\text{PO}_4)$ and activation of $\nu_1(\text{PO}_4)$ due to the general position of PO_4 and again at least four components of the deformation modes $\delta(\text{Al}_2\text{OH})$ involving the two pairs of the non-equivalent OH groups [6]. It is likely that same conclusions may be drawn for the spectra of vantasselite.

The Raman spectrum of vantasselite over the 300–800 cm^{-1} spectral range is reported in Fig. 5a. The strong Raman bands at 557, 593, 636 and 649 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4^{3-} and HOPO_3^{2-} units. Raman bands are found in the RRUFF spectrum at 491, 515, 555, 596 and 651 cm^{-1} . Raman bands for wardite are observed at 605 and 618 cm^{-1} with shoulders at 578 and 589 cm^{-1} and are assigned to the ν_4 out of plane bending modes of the PO_4^{3-} and HOPO_3^{2-} units. Breitingner et al. [6] assigned these bands to $\nu(\text{Al}(\text{O}/\text{OH})_6)$ stretching vibrations. No phosphate bending modes in the work of Breitingner et al. on the studies of wardite including synthetic wardites were reported. The Raman spectrum of crystalline NaH_2PO_4 shows Raman bands at 526, 546 and 618 cm^{-1} (data obtained by the authors). The Raman bands at 423, 437, 451 and 494 cm^{-1} are assigned to the ν_2 PO_4^{3-} and H_2PO_4 bending modes. A series of bands for wardite are observed at 396, 416, 444, 464, and 489 cm^{-1} and are attributed to the ν_2 PO_4^{3-} and H_2PO_4 bending

modes. The Raman spectrum of NaH_2PO_4 shows Raman bands at 460 and 482 cm^{-1} . Thus, the series of Raman bands for wardite at 388, 400, 455, 478 and 502 cm^{-1} are attributed to the ν_2 PO_4^{3-} bending modes. Raman bands at 317, 446 and 515 cm^{-1} reported by Breitingner et al. for wardite were assigned to vibrational modes of the $\text{AlO}_6/\text{AlOH}_6$ units. In the infrared spectrum of wardite, a series of bands are observed at 620, 643 and 673 cm^{-1} . These bands are attributed to the ν_4 out of plane bending modes of the PO_4^{3-} units. Breitingner et al. assigned bands in this region to $\nu(\text{Al}(\text{O}/\text{OH})_6)$ stretching vibrations. In harmony with Breitingner et al. [6] assignments, the infrared bands observed at 732, 795 and 893 cm^{-1} are attributed to water librational modes. Infrared bands are observed at 573, 578 and 588 cm^{-1} are attributed to $\gamma(\text{Al}_2\text{OH})$ vibrations. The Raman spectrum of vantasselite over the 100–300 cm^{-1} spectral range is shown in Fig. 5b. Raman bands are observed at 111, 153, 209, 227 and 242 cm^{-1} with bands of lower intensity at 121, 162, 173, 201, 259 and 289 cm^{-1} . These bands are simply described as lattice vibrations.

The Raman spectrum of vantasselite over the 2600–3800 cm^{-1} spectral range is shown in Fig. 6a. Strong Raman bands are observed at 3211, 3297, 3327, 3369, 3399, 3436, cm^{-1} and are assigned to water stretching vibrations. The Raman band at 3502 cm^{-1} is assigned to the AlOH stretching vibration. The

infrared spectrum of vantasselite over the 2500–3800 cm^{-1} spectral range is shown in Fig. 6b. The spectrum is broad with a series of overlapping bands observed at 2749, 2990, 3246, 3403, 3496 and 3568 cm^{-1} . This latter band is assigned to the stretching vibration of OH units while the remainder of the bands is assigned to water stretching vibrations. The position of the water stretching vibration provides evidence for strong hydrogen bonding and that water is involved in different hydrogen bonding arrangements. Sharp infrared bands for wardite are observed at 3544 and 3611 cm^{-1} and are attributed to the OH stretching vibrations of the hydroxyl units. Two shoulder bands are observed at 3532 and 3601 cm^{-1} are also assigned to the OH stretching vibrations. Breiting et al. [6] found infrared bands at 3520 (vw), 3545 (s), 3585 (sh) and 3613 cm^{-1} (m). Breiting et al. [6] states that the $\nu(\text{OH})$ modes in the two independent pairs of symmetry-correlated OH groups classify as $2a+2b$; with the correlation splitting between a and b species depending on the distances in each of the pairs [6]. The $\nu(\text{OH})$ region of IR spectra of wardite shows two sharp bands (3613 and 3545 cm^{-1}) with two weak shoulders or satellites (3580 and 3520 cm^{-1}). It is likely that the two sharp infrared bands are due to two independent and non-equivalent OH units. The two sharp shoulder bands may be attributed to the Al–OH–Fe groups.

The Raman spectrum of vantasselite over the 1400–1800 cm^{-1} spectral range is shown in Fig. 7a. The spectral profile is broad. Raman bands are noted at 1595, 1622, 1656 cm^{-1} and these bands are ascribed to water bending modes. The number of bands observed in this spectral region is in harmony with the number of bands observed in the water stretching region. The infrared spectrum of vantasselite over the 1300–1800 cm^{-1} spectral range is shown in Fig. 7b. Infrared bands are observed at 1609 and 1656 cm^{-1} and are ascribed to water bending vibrations.

Conclusions

We have studied a sample of the phosphate mineral vantasselite from the Bihain, Vielsalm, Stavelot Massif, Luxembourg Province, Belgium. The chemical characterization via SEM/EDS shows a homogeneous phase, composed of Al and P. The SEM image of vantasselite sample shows a cleavage fragment with tabular habitus.

Vantasselite is one of many aluminum phosphate minerals, including wardite, wavellite, variscite and augelite. The mineral can be successfully analyzed by Raman spectroscopy and a comparison of the Raman spectrum made with that of wardite and augelite. The Raman spectrum is dominated by an intense band at 1029 cm^{-1} assigned to the PO_4^{3-} ν_1 symmetric stretching mode. Raman bands at 545, 559, 581, 616 and 635 cm^{-1} are assigned to the ν_4 PO_4^{3-} bending modes. The Raman bands at 417, 444, 462, 477 and 480 cm^{-1} are due to the ν_2 PO_4^{3-} bending modes. The observation of multiple bending modes offers strong support for the reduction in symmetry of the phosphate anion in the vantasselite structure. Strong Raman bands are observed at 3211, 3297, 3327, 3369, 3399, 3436, cm^{-1} and are assigned to water stretching

vibrations. The Raman band at 3502 cm^{-1} is assigned to the AlOH stretching vibration. Vibrational spectroscopy offers a unique means of studying the molecular structure of vantasselite.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2015.03.090>.

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