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Vibrational spectroscopic study of poldervaartite $\text{CaCa}[\text{SiO}_3(\text{OH})](\text{OH})$

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HIGHLIGHTS

- We have studied the structure of the mineral poldervaartite $\text{CaCa}[\text{SiO}_3(\text{OH})](\text{OH})$.
- It forms a series with its manganese analogue olmiite $\text{CaMn}[\text{SiO}_3(\text{OH})](\text{OH})$.
- We used scanning electron microscopy, thermogravimetric analysis, Raman and infrared spectroscopy.
- Thermogravimetric analysis proves the mineral decomposes at 485 °C with a mass loss of 7.6%.
- Vibrational spectroscopy enables a detailed assessment of the molecular structure of poldervaartite.

GRAPHICAL ABSTRACT



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ABSTRACT

We have studied the mineral poldervaartite $\text{CaCa}[\text{SiO}_3(\text{OH})](\text{OH})$ which forms a series with its manganese analogue olmiite $\text{CaMn}[\text{SiO}_3(\text{OH})](\text{OH})$ using a range of techniques including scanning electron microscopy, thermogravimetric analysis, Raman and infrared spectroscopy. Chemical analysis shows the mineral is reasonably pure and contains only calcium and manganese with low amounts of Al and F. Thermogravimetric analysis proves the mineral decomposes at 485 °C with a mass loss of 7.6% compared with the theoretical mass loss of 7.7%. A strong Raman band at 852 cm^{-1} is assigned to the SiO stretching vibration of the $\text{SiO}_3(\text{OH})$ units. Two Raman bands at 914 and 953 cm^{-1} are attributed to the antisymmetric vibrations. Intense prominent peaks observed at 3487, 3502, 3509, 3521 and 3547 cm^{-1} are assigned to the OH stretching vibration of the $\text{SiO}_3(\text{OH})$ units. The observation of multiple OH bands supports the concept of the non-equivalence of the OH units. Vibrational spectroscopy enables a detailed assessment of the molecular structure of poldervaartite.

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Introduction

The mineral poldervaartite $\text{CaCa}[\text{SiO}_3(\text{OH})](\text{OH})$ is a silicate mineral of calcium [1]. Sometimes, the formula is written as $(\text{Ca},\text{Mn}_{2}^{2+})\text{SiO}_3(\text{OH})_2$. The Mn dominant analogue of poldervaartite is olmiite [2].

The mineral poldervaartite $\text{CaCa}[\text{SiO}_3(\text{OH})](\text{OH})$, forms a series with olmiite, ideally $\text{CaMn}[\text{SiO}_3(\text{OH})](\text{OH})$, its Mn analogue – [1,3]. The chemical formula of olmiite [4] is correctly calculated from the EPMA data ($\text{Mn} > 0.5$ and $\text{Ca} < 1.5$ atom per formula unit (a.p.f.u.)). For the mineral chemistry of poldervaartite ($\text{Ca} > 1.5$ and $\text{Mn} < 0.5$ a.p.f.u.). This mineral was first found in South Africa at the N'Chwaning II mine of the Kalahari manganese fields and occurs as a product of hydrothermal alteration of primary sedimentary and low-grade

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metamorphic ores in a temperature range from 250 °C to 400 °C. Usually, poldervaartite occurs in association with celestine, bultfonteinite, olmiite, sturmanite and hematite [1,3].

The mineral is orthorhombic with point group: $2/m\ 2/m\ 2/m$. The mineral occurs as wheat-sheaf aggregates with a crystal length reaching up to 7 mm. The space group is $Pbca$ with $a = 9.398(1)$, $b = 9.139(2)$, $c = 10.535(2)$ Å and $Z = 8$. Olmiite crystallizes in the orthorhombic crystal system, with unit cell parameters $a = 9.243(3)$, $b = 9.076(9)$, $c = 10.342(9)$ Å. $V = 868(1)$ Å³ [1,3]. The atomic arrangement of poldervaartite is similar to that of olmiite. Variations in bond distances and angles are related to the pronounced difference in the Ca and Mn content. The structure of both poldervaartite and olmiite can be schematically described, for convenience, as a sequence along [010] of alternating layers containing $M2 + Si$ and $M1$ polyhedra, respectively. Nonetheless, the strong three-dimensional linkage among the polyhedral units results in a rather isotropic framework, as pointed out by Dai [1,3]. Olmiite consists of isolated $SiO_3(OH)$ tetrahedra continuously connected along the [100] direction to two M_2O_7 polyhedra by sharing edges. The $M2-Si$ chains are linked together by corner sharing to form waved sheets parallel to (010). Alternating sheets are linked together by $M1$ octahedra and hydrogen bonds, resulting in a strongly bonded polyhedral network [1,3].

Recently, the authors undertook a study of the mineral olmiite [4]. In this work, we have studied the mineral poldervaartite $CaCa [SiO_3(OH)(OH)]$ using scanning electron microscopy, thermogravimetric analyses and vibrational spectroscopy. The combination of scanning electron microscopy (SEM) and vibrational spectroscopy has proven a success for the study of the chemistry and molecular structure of minerals [5–10]. In this work we also related the Raman and FTIR spectra of poldervaartite to the structure of the mineral.

Experimental

Samples description and preparation

The poldervaartite 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 SAD-041. The sample is from the type locality in N' Chwaning II mine of the Kalahari manganese fields, South Africa. The mineral occurs in association with calcite and manganese oxides.

The compositions have been reported by Anthony et al. (page 192) [11]. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Qualitative and semiquantitative chemical analysis via SEM/EDS were applied to the mineral characterization.

Scanning electron microscopy (SEM)

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

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

Thermogravimetric analysis – TG/DTG

Thermogravimetric analysis of the poldervaartite mineral was obtained by using TA Instruments Inc. Q50 high-resolution TGA

operating at a 10 °C/min ramp with data sample interval of 0.50 s/pt from room temperature to 1000 °C in a high-purity flowing nitrogen atmosphere (100 cm³/min). A total mass of 41.92 mg of finely ground samples was heated in an open platinum crucible.

Raman microprobe spectroscopy

Crystals of poldervaartite 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.

An image of the poldervaartite crystals measured is shown in the graphical abstract. Clearly the crystals of poldervaartite are readily observed, making the Raman spectroscopic measurements readily obtainable.

Infrared spectroscopy

Infrared spectra of poldervaartite were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 500–4000 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 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 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

Chemical characterization

The SEM image of poldervaartite sample studied in this work is shown in Fig. 1. The image shows a poldervaartite crystal aggregate. The mineral occurs in association with small amounts of manganese oxides. Qualitative chemical analysis shows a Ca and Mn silicate (Fig. 2). Traces of Al and F were noted. No other elements were detected. The chemical analysis of olmiite shows a Ca and Mn silicate [4].

Thermal analysis

The thermal analysis of poldervaartite is given in the supplementary information as Fig. S1. Two mass loss steps are observed at 485 °C and 722 °C with mass losses of 5.4 and 1.3%.

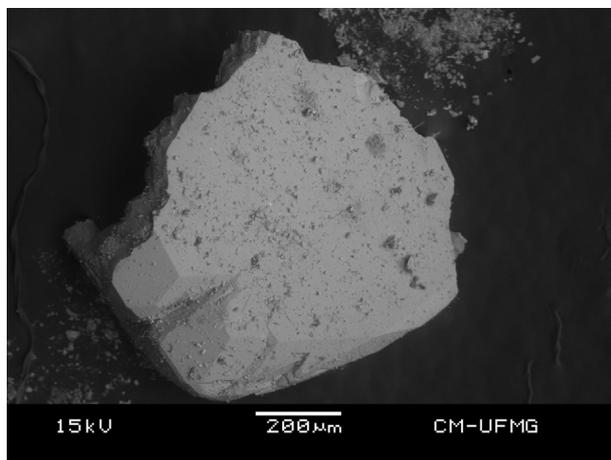


Fig. 1. Backscattered electron (BSE) image of a poldervaartite crystal aggregate up to 0.5 mm in length.

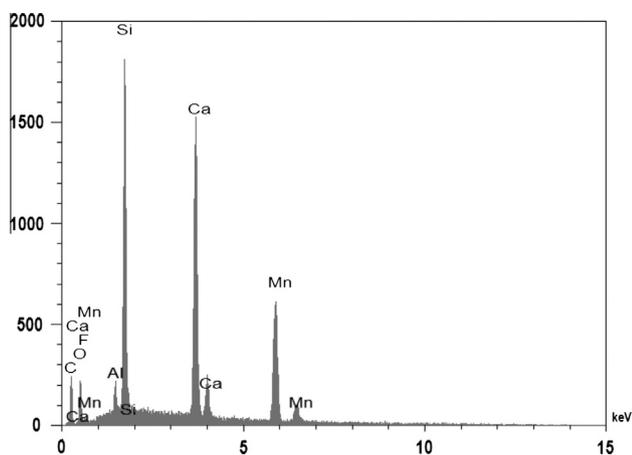
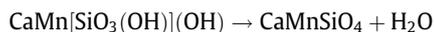


Fig. 2. EDS analysis of poldervaartite.

The temperature range for the mass loss is very narrow. The following chemical reaction is proposed for the thermal decomposition of poldervaartite:



Vibrational spectroscopy

Vibrational spectroscopy of poldervaartite

The Raman spectrum of poldervaartite 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 poldervaartite in the 500–4000 cm^{-1} spectral region is shown 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.

The Raman spectrum of poldervaartite over the 700–1000 cm^{-1} spectral range is shown in Fig. 4a. The Raman spectrum is dominated by an intense peak at 852 cm^{-1} . Dowty showed that the SiO_3 units had a unique band position of 980 cm^{-1} [12] (see Figs. 2 and 4 of this

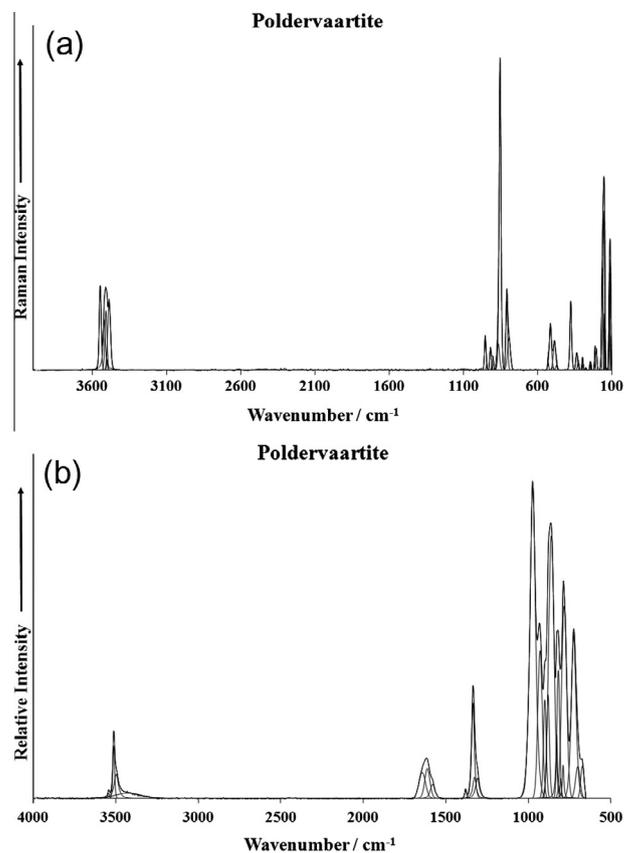


Fig. 3. (a) Raman spectrum of poldervaartite over the 100–4000 cm^{-1} spectral range (upper spectrum). (b) Infrared spectrum of poldervaartite over the 500–4000 cm^{-1} spectral range (lower spectrum).

reference). Dowty also showed that Si_2O_5 units had a Raman peak at around 1100 cm^{-1} . Poldervaartite consists of isolated $\text{SiO}_3(\text{OH})$ tetrahedra continuously connected along the [100] direction to two M_2O_7 polyhedra by sharing edges. The M2–Si chains are linked together by corner sharing to form waved sheets parallel to (010). Alternating sheets are linked together by M1 octahedra and hydrogen bonds, resulting in a strongly bonded polyhedral network [1,3]. Thus, the Raman peak at 852 cm^{-1} is assigned to the SiO stretching vibration of the $\text{SiO}_3(\text{OH})$ units. In the Raman spectrum of olmiite [4] the band position was found at 853 cm^{-1} . The two bands of poldervaartite at 900 and 917 cm^{-1} with a low intensity shoulder at 907 cm^{-1} are attributed to the antisymmetric vibrations of the $\text{SiO}_3(\text{OH})$ units. The position of these bands for olmiite [4] were found at 914 and 953 cm^{-1} . The two Raman bands of poldervaartite at 792 and 807 cm^{-1} are attributed to the SiOH deformation modes. These two bands were found for olmiite [4] at 799 and 811 cm^{-1} .

The infrared spectrum of poldervaartite over the 650 to 1050 cm^{-1} spectral range is shown in Fig. 4b. Strong infrared bands are observed at 858 and 970 cm^{-1} . This latter band together with the infrared bands at 877, 897 and 926 cm^{-1} are assigned to the SiO antisymmetric stretching vibrations. The infrared band at 858 cm^{-1} is ascribed to the SiO symmetric stretching band. Other infrared bands are observed at 780, 786, 800 and 815 cm^{-1} . If we follow the assignment of the Raman bands, then these bands are due to hydroxyl deformation modes.

The Raman spectra over the 400–600 cm^{-1} spectral range and over the 100–250 cm^{-1} spectral range are presented in Fig. 5. Raman bands noted at 485 and 513 cm^{-1} are assigned to OSiO bending modes. Dowty calculated the band position of these bending modes for different siloxane units [12] and demonstrated the

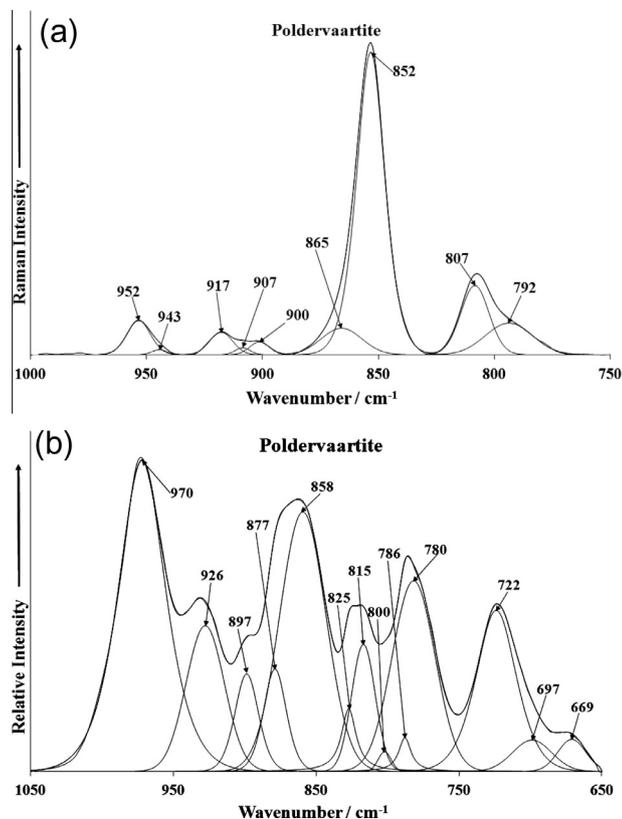


Fig. 4. (a) Raman spectrum of poldervaartite (upper spectrum) over the 1000–1150 cm^{-1} spectral range and (b) infrared spectrum of poldervaartite (lower spectrum) over the 650–1150 cm^{-1} spectral range.

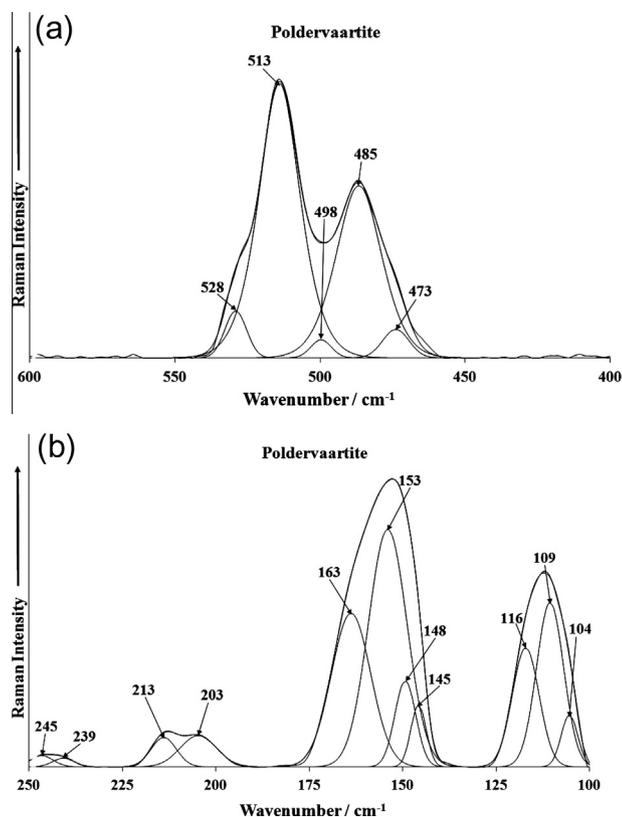


Fig. 5. (a) Raman spectrum of poldervaartite (upper spectrum) over the 400–800 cm^{-1} spectral range and (b) Raman spectrum of poldervaartite (lower spectrum) over the 100–400 cm^{-1} spectral range.

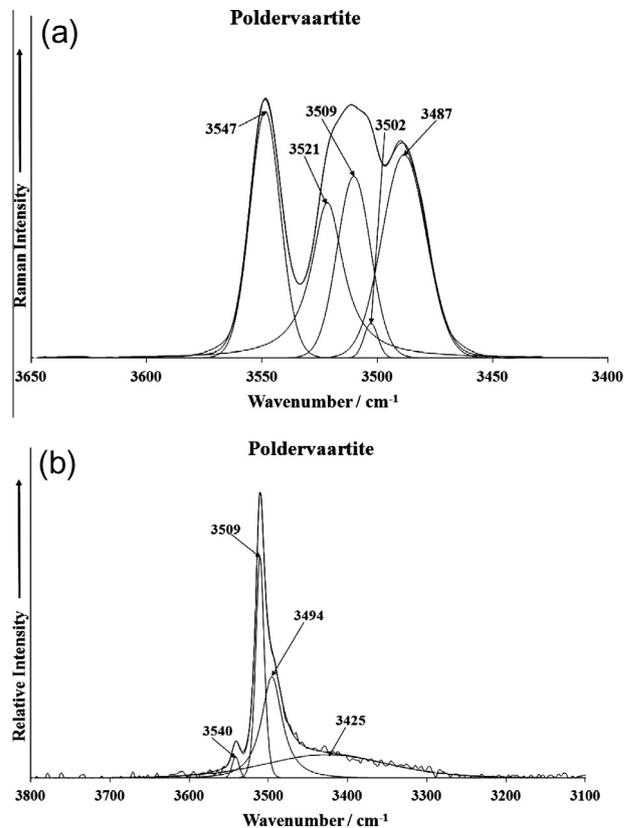


Fig. 6. (a) Raman spectrum of poldervaartite (upper spectrum) over the 2800–4000 cm^{-1} spectral range and (b) infrared spectrum of poldervaartite (lower spectrum) over the 2800–3800 cm^{-1} spectral range.

band position of the bending modes for SiO_3 units is located at around 650 cm^{-1} . This calculated value is in harmony with the higher wavenumber band observed at 663 cm^{-1} as calculated by Dowty. According to Adams et al. [13], the band at 432 cm^{-1} is due to the coincidence of both the B_{2g} and E_g modes. Raman bands are observed in the far low wavenumber region at 104, 109, 116, 145, 148, 153, 163, 203, 213 cm^{-1} . These bands are simply described as lattice vibrations.

The Raman spectrum of poldervaartite over the 3400–3650 cm^{-1} spectral range is reported in Fig. 6a. Prominent peaks are observed at 3487, 3502, 3509, 3521 and 3547 cm^{-1} . These bands are assigned to the OH stretching vibration of the SiO_3 (OH) units. The observation of multiple bands proves that the OH groups are not equivalent

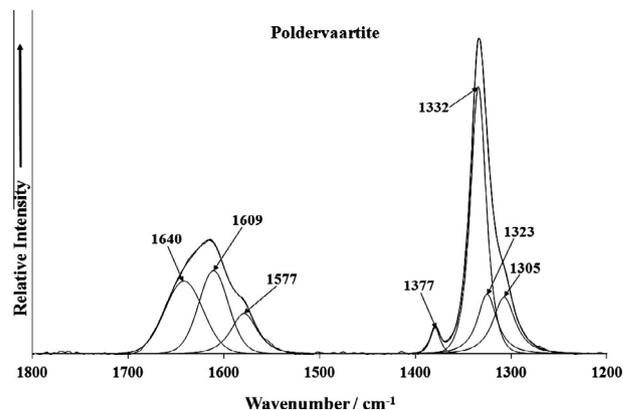


Fig. 7. Infrared spectrum of poldervaartite over the 1200–1800 cm^{-1} spectral range.

in the poldervaartite structure. The infrared spectrum of poldervaartite over the 3000–3800 cm^{-1} spectral range is shown in Fig. 6b. Infrared bands are found at 3494, 3509 and 3540 cm^{-1} with a broad shoulder at 3425 cm^{-1} . The infrared bands support the concept of the non-equivalence of the OH units in the poldervaartite structure. The broad feature may be ascribed to water stretching modes; however, no water bending mode was observed in the infrared spectrum in the 1500–1800 cm^{-1} spectral range. Some infrared bands were observed in the 1200–1800 cm^{-1} spectral range (Fig. 7). Infrared bands are observed at 1305, 1323, 1332 and 1377 cm^{-1} . These bands are all related to SiO vibrations. Infrared bands are observed at 1609 and 1640 cm^{-1} and are probably due to water bending modes.

Conclusions

We have studied the mineral poldervaartite $\text{CaCa}[\text{SiO}_3(\text{OH})](\text{OH})$ which forms a continuous series with its manganese analogue olmiite $\text{CaMn}[\text{SiO}_3(\text{OH})](\text{OH})$ using a combination of electron microscopy with EDS analysis, thermogravimetric analysis, infrared and Raman spectroscopy. These temperatures are below the thermal decomposition of poldervaartite of 502 °C.

Raman spectroscopy identifies a peak at 852 cm^{-1} assigned to the SiO stretching vibration of the $\text{SiO}_3(\text{OH})$ units. Strong infrared bands observed at 858 and 970 cm^{-1} are assigned to this vibration. Prominent peaks are observed at 3487, 3502, 3509, 3521 and 3547 cm^{-1} and are assigned to the OH stretching vibration of the $\text{SiO}_3(\text{OH})$ units. The equivalent infrared bands found at 3494, 3509 and 3540 cm^{-1} supports the concept of the non-equivalence of the OH units in the poldervaartite structure. Vibrational spectroscopy enables a detailed assessment of the molecular structure of poldervaartite to be attained.

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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.2014.09.017>.

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