

Vibrational spectroscopic characterization of the phosphate mineral phosphophyllite – $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, from Hagendorf Süd, Germany and in comparison with other zinc phosphates

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HIGHLIGHTS

- ▶ Chemical analysis of phosphophyllite was carried out by Scanning Electron Microscope in the EDS mode.
- ▶ The chemical formula was determined to be: $\text{Zn}_2(\text{Fe}_{0.65}, \text{Mn}_{0.35})_{\Sigma 1.00}(\text{PO}_4)_2 \cdot 4(\text{H}_2\text{O})$.
- ▶ The mineral was characterized by both Raman and infrared spectroscopy.
- ▶ An assessment of the molecular structure was made.
- ▶ A comparison is made with the spectra of other zinc phosphate minerals.

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ABSTRACT

This research was undertaken on phosphophyllite sample from the Hagendorf Süd pegmatite, Bavaria, Germany. Chemical analysis was carried out by Scanning Electron Microscope in the EDS mode and indicates a zinc and iron phosphate with partial substitution of manganese, which partially replaced iron. The calculated chemical formula of the studied sample was determined to be: $\text{Zn}_2(\text{Fe}_{0.65}, \text{Mn}_{0.35})_{\Sigma 1.00}(\text{PO}_4)_2 \cdot 4(\text{H}_2\text{O})$. The intense Raman peak at 995 cm^{-1} is assigned to the $\nu_1 \text{ PO}_4^{3-}$ symmetric stretching mode and the two Raman bands at 1073 and 1135 cm^{-1} to the $\nu_3 \text{ PO}_4^{3-}$ antisymmetric stretching modes. The $\nu_4 \text{ PO}_4^{3-}$ bending modes are observed at 505 , 571 , 592 and 653 cm^{-1} and the $\nu_2 \text{ PO}_4^{3-}$ bending mode at 415 cm^{-1} . The sharp Raman band at 3567 cm^{-1} attributed to the stretching vibration of OH units brings into question the actual formula of phosphophyllite. Vibrational spectroscopy enables an assessment of the molecular structure of phosphophyllite to be assessed.

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1. Introduction

Phosphophyllite is a rare Zn and Fe hydrous phosphate with general chemical formula expressed by $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ [1,2]. It was first described in pegmatites in Hagendorf, Bavaria, by Laubmann and Steinmetz [3]. The mineral crystallizes in the monoclinic crystal system, $P2_1/c$ space group with unit cell parameters given as: $a = 10.378 \text{ \AA}$, $b = 5.084 \text{ \AA}$, $c = 10.553 \text{ \AA}$, $\beta = 121.14^\circ$ and $Z = 2$ [2,4,5]. Several studies have suggested similarity between the crystal structure of phosphophyllite and that of hopeite [6–8] and parahopeite [2,9–11]. The framework consists of $[\text{Zn}_2\text{P}_2\text{O}_7]$ tetrahedral sheets identical to those in hopeite, interleaved with $[\text{FeO} \cdot 4\text{H}_2\text{O}]$ octahedral sheets similar to those in parahopeite. The phospho-

phyllite is a secondary mineral derivative from primary iron-manganese phosphates and sphalerite [3,12]. At the type locality, the phosphophyllite occurs associated with natrolite, triplite, triphylite, triplioide and apatite [3]. The mineral occurs in granitic pegmatites and in hydrothermal deposits. Despite the type locality, other occurrences were reported from Reaphook Hill, Australia [13]; Cerro de Potossi, Bolivia [14] and from East Kemptville Tin Mine Canada [15], among others.

Farmer [16] divided the vibrational spectra of phosphates according to the presence, or absence of water and hydroxyl units in the minerals. 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} . The value for the ν_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was also

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described. 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} (dufrenite) and 470 and 450 cm^{-1} (beranite). 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 was also described by Frost and Weier [17].

To the best knowledge of the authors, data about vibrational spectroscopic characterization of phosphophyllite are restricted to the database of the University of Arizona (ruff.info) and no interpretation is given, however, in recent years, the application of spectroscopic techniques to understand the structure of phosphates has been increasing. In this work, a sample of the rare mineral phosphophyllite from the type locality was studied. Characterization includes chemistry via scanning electron microscopy (SEM) in the EDS mode and spectroscopic characterization of the structure with infrared and Raman.

2. Experimental

2.1. Occurrence, samples description and preparation

The phosphophyllite 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-098. The sample is from the Hagendorf pegmatite, Germany, and can be considered a reference material. The Hagendorf pegmatite was an important feldspar–quartz deposit in Europe. It is located in the NE Bavarian basement [18] and despite the industrial minerals it is an important source of rare phosphates such as hagedorfite [19], scholzite [20] and keckite [21]. The studied sample occurs in association with siderite and vivianite. The sample was gently crushed and prepared to be analyzed by different methods. Scanning electron microscopy (SEM) was applied to support the mineral characterization.

2.2. 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 fragment of a phosphophyllite single crystal was prepared in a carbon tape. Due to the low vacuum conditions the sample does not was metalized. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analysis in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

2.3. Raman microprobe spectroscopy

A phosphophyllite crystal was 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 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between 200 and 4000 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 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

2.4. 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.

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.

3. Results and discussion

3.1. Chemical characterization

The BSE image of the phosphophyllite sample studied in this work is shown in Fig. 1. Qualitative and semi-quantitative chemical composition shows a Zn, Fe and Mn phosphate. The semi-quantitative chemical data was recalculated considering 16.07% of H_2O in the structure, as expected for stoichiometric phosphophyllite. According to the crystal structure, 100% of Fe was considered as Fe^{2+} . The chemical analysis is shown in Fig. 2. The chemical formula was calculated on the basis of 12 O atoms and can be expressed as:

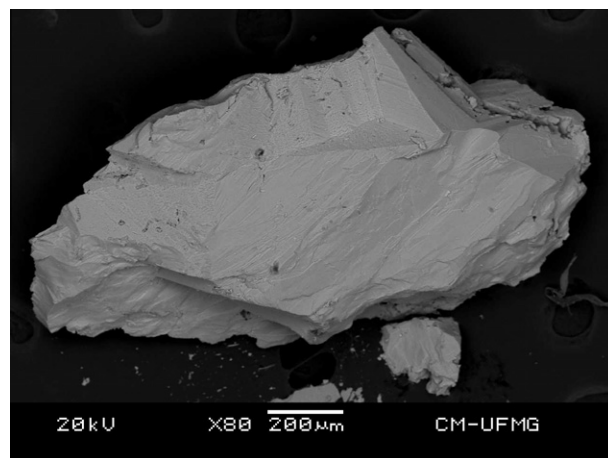
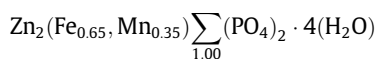


Fig. 1. Backscattered electron image (BSI) of a phosphophyllite fragment up to 2.0 mm in length.

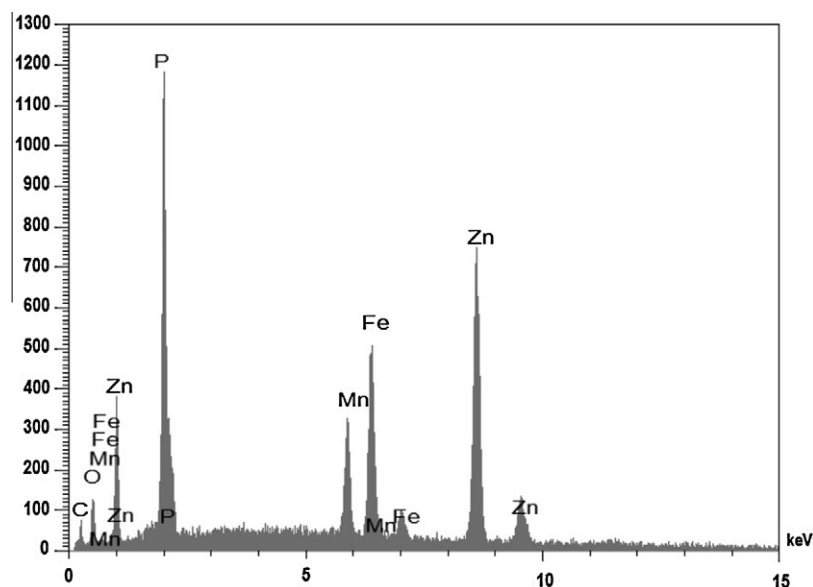


Fig. 2. EDS spectra of phosphophyllite.

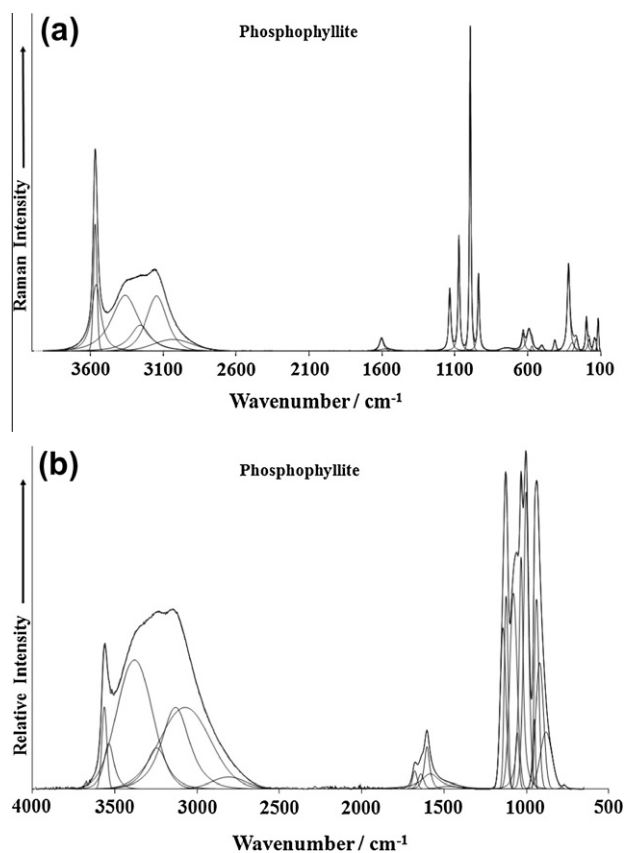


Fig. 3. (a) Raman spectrum of phosphophyllite over the 100–4000 cm^{-1} spectral range. (b) Infrared spectrum of phosphophyllite over the 500–4000 cm^{-1} spectral range.

3.2. Vibrational spectroscopy

The Raman spectrum of phosphophyllite in the 4000–100 cm^{-1} spectral region is displayed in Fig. 3a. This spectrum shows the position of the Raman bands and their relative intensities. Observed, there are large parts of the spectrum where no intensity is

observed and therefore, the spectrum is subdivided into sections according to the types of vibration being examined. The infrared spectrum over the 4000–500 cm^{-1} spectral range is reported in Fig. 3b. This spectrum shows the position and relative intensities of the infrared bands. There are large parts of the spectrum where no intensity is observed, and therefore, the spectrum is subdivided into sections depending upon the type of vibration being studied.

The Raman spectrum in the 1400–800 cm^{-1} spectral range is illustrated in Fig. 4a. The Raman spectrum appears to be quite simple in this spectral region when compared to the Raman spectra of many pegmatitic phosphates. The intense Raman peak at 995 cm^{-1} is assigned to the $\nu_1 \text{PO}_4^{3-}$ symmetric stretching mode. The two Raman bands at 1073 and 1135 cm^{-1} are ascribed to the $\nu_3 \text{PO}_4^{3-}$ antisymmetric stretching modes. The Raman band at 939 cm^{-1} is thought to be due to a PO stretching vibration of hydrogen phosphate units. This band appears at 938 cm^{-1} in the infrared spectrum and is of great intensity with shoulder bands at 919 and 950 cm^{-1} . The infrared band at 1002 cm^{-1} is defined as the $\nu_1 \text{PO}_4^{3-}$ symmetric stretching mode. The infrared bands at 1032, 1078, 1123 and 1141 cm^{-1} are attributed to the $\nu_3 \text{PO}_4^{3-}$ antisymmetric stretching modes.

A comparison may be made with the vibrational spectroscopy of other zinc phosphate minerals. For hopeite, a Raman band is observed at 940 cm^{-1} and is assigned to the ν_1 symmetric stretching vibration. This band was previously reported at 941 cm^{-1} in excellent agreement with the results reported in this work [22]. In the infrared spectrum of hopeite, an intense band is observed at 995 cm^{-1} with other low intensity bands at 1150, 1059 and 1000 cm^{-1} , all of which are ascribed to the ν_3 antisymmetric stretching modes. Pawlig et al. reported bands at 1150, 1055 and 997 cm^{-1} [22]. In the infrared spectrum of hopeite, bands at 948 and 922 cm^{-1} are observed and are attributed to the ‘forbidden’ symmetric stretching modes. A previous study reported a band at 943 cm^{-1} [22]; however the band was strongly asymmetric on the low wavenumber side. Other infrared bands are observed at 1137, 1096, 1059, 1019 and 995 cm^{-1} . A previous study reported bands at 1127, 1104, 1069, 1011 and 994 cm^{-1} with the last band observed after partial deuteration [22].

The Raman spectrum of parahopeite shows a band centered upon 959 cm^{-1} which is assigned to the symmetric stretching mode. Three antisymmetric stretching bands are observed at

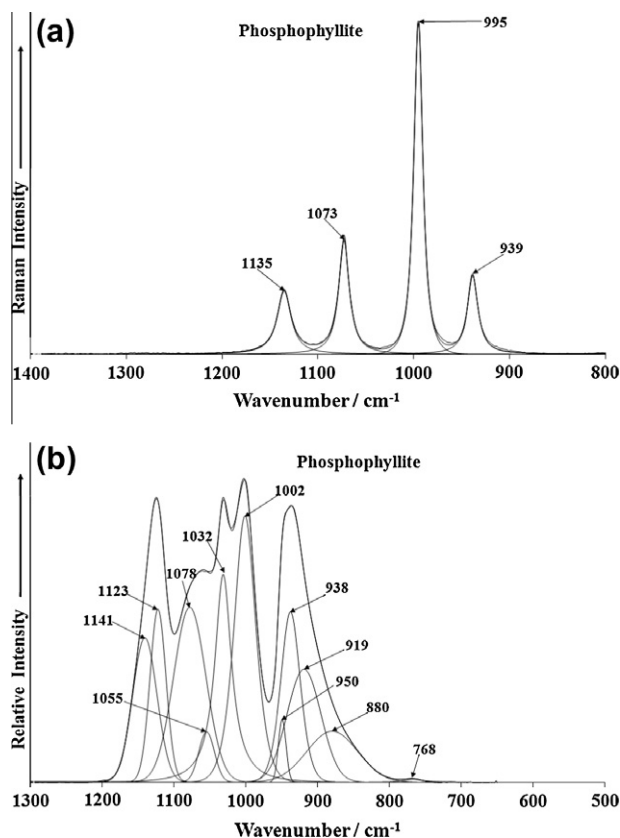


Fig. 4. (a) Raman spectrum of phosphophyllite over the 800–1400 cm^{-1} spectral range. (b) Infrared spectrum of phosphophyllite over the 500–1300 cm^{-1} spectral range.

1053, 1033 and 1003 cm^{-1} . Parahopeite is triclinic as compared with hopeite which is orthorhombic. The infrared spectrum of parahopeite shows two bands at 951 and 919 cm^{-1} . Three bands are observed at 1106, 1045 and 1002 cm^{-1} . It should be noted that the spectra both Raman and infrared of parahopeite is different from that of hopeite, which is not unexpected since the two minerals have different crystal structures. To our knowledge no vibrational spectra of parahopeite have been reported; Castagnola and Dutta [23] showed some Raman spectra of ion exchanged zinc phosphates and some resemblance of the spectra of the films corresponds to the spectrum of parahopeite [23]. The Raman spectrum of spencerite displays a low intensity band as a shoulder on the main peak at 999 cm^{-1} at 952 cm^{-1} . This band is attributed to the symmetric stretching mode. Other Raman bands are observed at 1095, 1019, 999 and 989 cm^{-1} . These bands are attributed to the ν_3 antisymmetric stretching modes. Infrared bands are observed at 940 and 842 cm^{-1} ; and also at 1048, 1010 and 987 cm^{-1} . The Raman spectrum of tarbuttite shows an intense band centered at 965 cm^{-1} assigned to the ν_1 symmetric stretching mode and at 1069, 1051 and 1011 cm^{-1} assigned to the ν_3 antisymmetric stretching modes. The infrared spectrum of tarbuttite shows two bands at 954 and 902 cm^{-1} and also at 1088, 1056 and 990 cm^{-1} . In comparison the Raman spectrum of scholzite shows an intense band at 923 cm^{-1} with an even more intense band at 1000 cm^{-1} . Other Raman bands are observed at 1171, 1115, 1088, 1053, and 1026 cm^{-1} . The infrared spectrum of scholzite is complex with multiple overlapping bands. IR bands are observed at 1107, 1047, 999, 956 and 929 cm^{-1} . The Raman spectrum of parascholzite is similar to but not the same as that

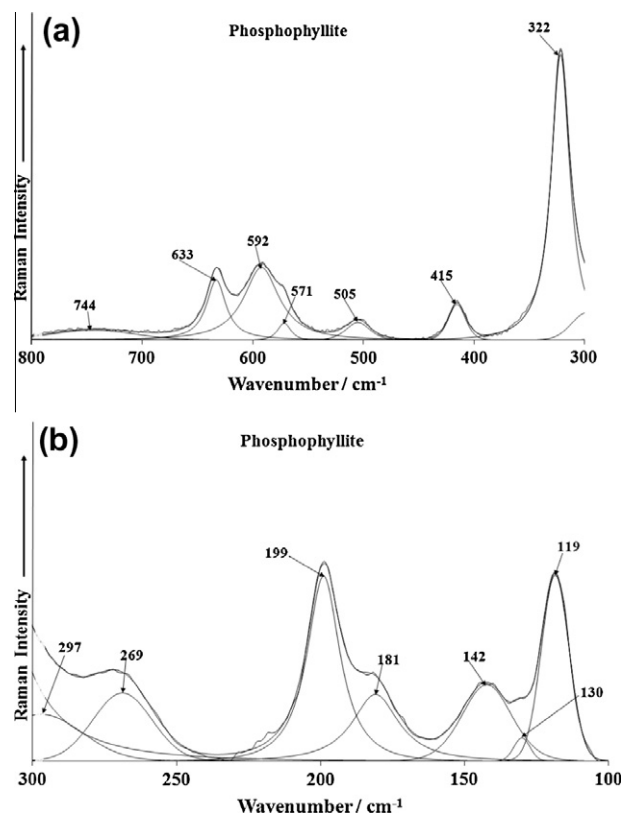


Fig. 5. (a) Raman spectrum of phosphophyllite over the 300–800 cm^{-1} spectral range. (b) Raman spectrum of phosphophyllite over the 100–300 cm^{-1} spectral range.

of scholzite. The ν_1 band is observed at 925 cm^{-1} and ν_3 modes at 1170, 1115, 1086 and 999 cm^{-1} .

The Raman spectrum in the 800–300 cm^{-1} spectral range is reported in Fig. 5a. The most prominent band is the intense band at 322 cm^{-1} . This band is assigned to metal-oxygen vibrations (ZnO, FeO, MnO). The Raman band at 415 cm^{-1} is assigned to the ν_2 PO_4^{3-} bending modes. The series of Raman bands at 505, 571, 592 and 633 cm^{-1} are attributed to the ν_4 PO_4^{3-} bending modes. The broad Raman band at 744 cm^{-1} is likely to be due to the water librational mode. The Raman spectrum in the far low wavenumber region over the 300–100 cm^{-1} spectral range is reported in Fig. 5b. The two bands at 269 and 297 cm^{-1} may be due to MO stretching vibrations. The other Raman bands at 119, 142, 181 and 199 cm^{-1} are simply described as lattice vibrations and are due to external vibrations.

A comparison may be made with the vibrational spectra of the other zinc phosphate minerals in this spectral region. The Raman spectrum of hopeite shows a broad band centered upon 372 cm^{-1} . This band is assigned to the PO_4 ν_2 symmetric bending mode. A second intense band is observed at 313 cm^{-1} . Both bands are assigned to the ν_2 bending modes. A previous study of the Raman spectrum of hopeite gave bands at 366 and 310 cm^{-1} [22]. A set of three bands are observed at 634, 596 and 569 cm^{-1} and are attributed to the ν_4 bending modes. Pawlig et al. reported bands at 637, 598 and 565 cm^{-1} [22]. Just as with the PO_4^{3-} stretching region, the low wavenumber region of parahopeite is very different from that of hopeite. An intense band is observed at 326 cm^{-1} with a second band at 362 cm^{-1} . These bands are assigned to the ν_2 bending modes. Raman bands are also observed at 645, 568, 563 and 504 cm^{-1} and are ascribed to the ν_4 bending modes of para-

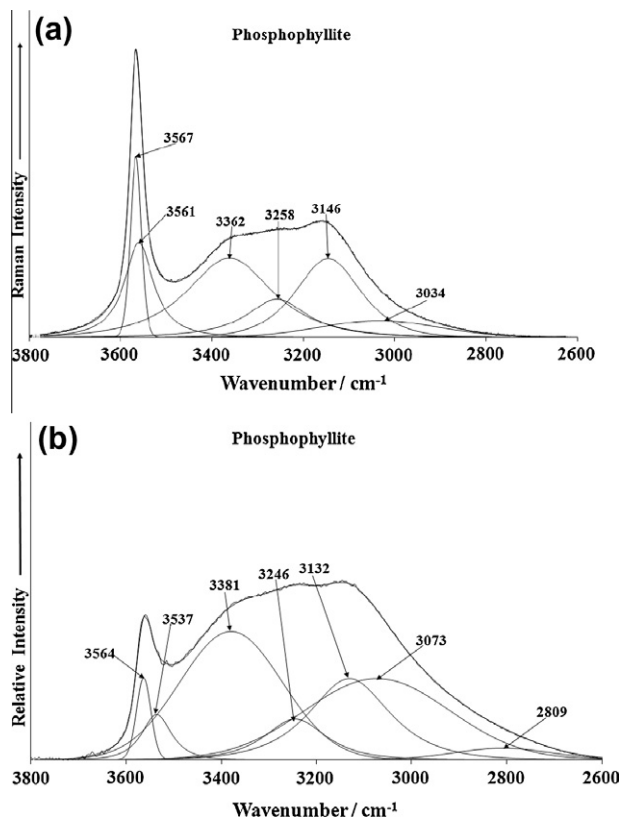


Fig. 6. (a) Raman spectrum of phosphophyllite over the 2600–4000 cm^{-1} spectral range. (b) Infrared spectrum of phosphophyllite over the 2600–4000 cm^{-1} spectral range.

hopeite. Infrared bands of parahopeite are observed at 567 and 543 cm^{-1} . The Raman spectrum of the low wavenumber region of spencerite shows more complexity. A set of bands assigned to the ν_2 bending modes are observed at 396, 376 and 350 cm^{-1} . A second set of bands are observed at 596, 588, 510 and 488 cm^{-1} and are assigned to the ν_4 bending modes. There is a strong resemblance between the low wavenumber spectra of spencerite and tarbuttite. A set of bands are observed at 382, 339 and 302 cm^{-1} and are assigned to the ν_2 bending modes. An intense band is observed in the Raman spectrum at 410 cm^{-1} (scholzite) and 409 cm^{-1} (parascholzite). This band is assigned to the ν_2 bending mode. Other bands are observed at 340, 309, 287 and 273 cm^{-1} for scholzite and at 302, 286, 271 and 236 cm^{-1} for parascholzite. A set of low intensity bands are observed at 664, 634, 600, 551 and 510 cm^{-1} for scholzite and are attributed to the ν_4 bending modes. For parascholzite an intense band was found at 553 cm^{-1} and is assigned to the ν_4 bending mode. Other low intensity bands are observed at 662, 637, 599 and 511 cm^{-1} . It is likely these bands are also due to the ν_4 bending modes.

The Raman spectrum in the 3800–2600 cm^{-1} spectral range is illustrated in Fig. 6a. Two spectral features are observed. The sharp Raman band at 3567 cm^{-1} which is attributed to the stretching vibration of OH units. The observation of this peak brings into question the actual formula of the mineral $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. The second feature is the broad spectral profile over the ~3400 to 2600 cm^{-1} spectral range. Raman bands may be resolved at 3034, 3146, 3258 and 3362 cm^{-1} . These bands are assigned to water stretching vibrations. The intensity of these bands are significantly higher in the infrared spectrum (Fig. 6b). The infrared bands at 3073, 3132, 3246, 3381 and 3537 cm^{-1} are assigned to water stretching vibrations.

The unit cells of the zinc phosphate minerals all contain multiple units of water except for tarbuttite which has no water but has a hydroxyl unit. Thus multiple OH stretching vibrations would be expected in both the Raman and infrared spectra. For hopeite two Raman bands in the hydroxyl stretching region are observed at 3456 and 3247 cm^{-1} . Pawlig et al. reported the infrared spectrum of hopeite and its deuterium-analogs [22]. They reported infrared bands at 3537, 3410, 3263 and 3181 cm^{-1} [22]. The structure of hopeite consists of $\text{ZnO}_2(\text{H}_2\text{O})_4$ octahedra, ZnO_4 tetrahedra, and PO_4 tetrahedra, none of which are regular; these polyhedra share corners and edges [24]. It is likely that the two water molecules are non-equivalent, thus giving rise to in-phase and out-of-phase behavior. Hence two Raman bands and two infrared bands would be expected.

In contrast the crystal structure of parahopeite is subtly different from that of hopeite [11]. The crystal structure of parahopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, is similar to those of phosphophyllite and hopeite in that one of the 2 Zn atoms is 6-coordinated and the other is 4-coordinated. Parahopeite differs from the other 2 minerals because one of the P–O tetrahedral O atoms is bonded to both the 6- and 4-coordinated Zn in parahopeite. In phosphophyllite and hopeite, only 3 of the O atoms are so bonded. Consequently the vibrational spectra of parahopeite would be predicted to be different from that of hopeite.

The Raman spectra of parahopeite in the hydroxyl stretching region shows four bands centered at 3439, 3293, 3163 and 3027 cm^{-1} . Four bands are observed in the infrared spectrum at 3451, 3311, 3143 and 3043 cm^{-1} . It is predicted that there are two non-equivalent water molecules in the unit cell of parahopeite. These water OH stretching vibrations will show in-phase and out-of-phase behavior resulting in the prediction of four bands in the Raman and infrared spectrum. A similar structure exists for spencerite as for parahopeite [25]. The atomic arrangement in spencerite consists of complex sheets of coordination octahedra and tetrahedra around Zn and P atoms connected by layers of water molecules. Four Raman bands are observed at 3548, 3516, 3469 and 3146 cm^{-1} .

Spencerite has one hydroxyl unit and consequently the higher wavenumber band (at 3548 cm^{-1} in the Raman spectrum and at 3520 cm^{-1} in the infrared spectrum) is assigned to the symmetric stretching vibration. The other three lower wavenumber bands are assigned to water stretching bands. The mineral tarbuttite is triclinic with a 5.499, b 5.654, c 6.465 Å, α 102 Deg51', β 102 Deg46', and γ 86 Deg50' [26]. The space group is P1. The unit cell contains $2\text{Zn}_2(\text{OH})\text{PO}_4$. The atoms around Zn ions form a regular trigonal bipyramid with a Zn–O distance of 2.04 Å. The P–O bond length in the PO_4 tetrahedron varies from 1.52 to 1.55 Å [27]. The Raman spectrum of the hydroxyl stretching region of tarbuttite consists of a single sharp band centered at 3446 cm^{-1} . Scholzite is orthorhombic with space group D2h5 – Pbcm (or D2h16 – Pbnm) and a = 17.14, b = 22.19, c = 6.61 Å, $a:b:c$ = 0.772:1:0.298, Z = 12, d = 3.11 [28]. Scholzites have apparent stacking disorders. Thus several polytypes can exist and one of these is parascholzite [29]. It is no doubt caused by variation in the moles of water of crystallization [30]. The Raman spectrum of scholzite in the hydroxyl stretching region shows four bands at 3437, 3343, 3283 and 3185 cm^{-1} . Three bands were observed in the infrared spectrum of the hydroxyl stretching region at 3425, 3310 and 3204 cm^{-1} . Bands are observed in similar positions in the Raman and infrared spectrum of parascholzite.

The Raman spectrum over the 1800–1400 cm^{-1} spectral range is provided in Fig. 7a. The spectrum displays a single band at 1603 cm^{-1} . This band is attributed a water bending mode. Greater complexity is shown in this spectral region in the infrared spectrum (Fig. 7b). The infrared bands at 1603, 1641 and 1678 cm^{-1}

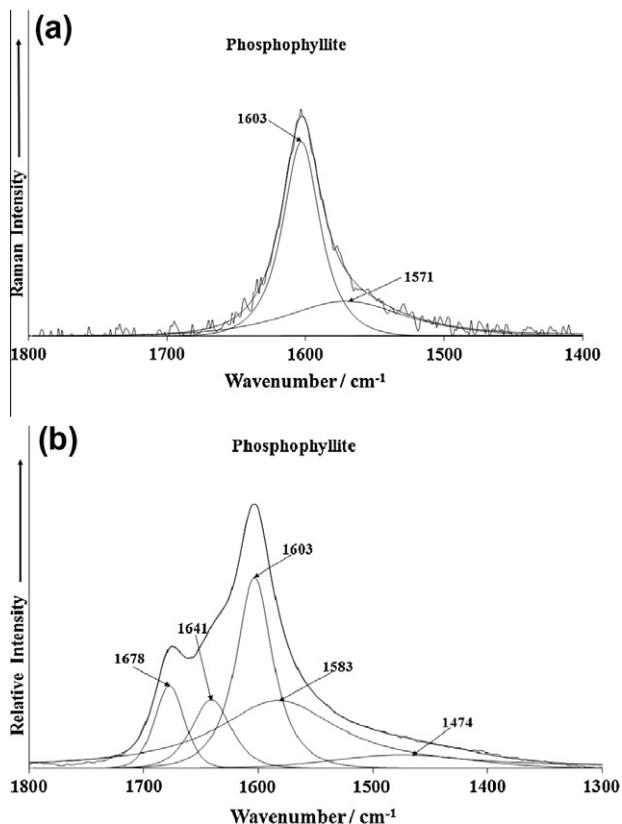


Fig. 7. (a) Raman spectrum of phosphophyllite over the 1300–1800 cm^{-1} spectral range. (b) Infrared spectrum of phosphophyllite over the 1300–1800 cm^{-1} spectral range.

are attributed to water bending modes. The observation of water bending modes supports the concept of water in different molecular environments with different hydrogen bond strengths.

4. Conclusions

A phosphophyllite sample was studied by Electron Microscope in the EDS mode, Raman and infrared spectroscopy. The chemical analysis shows chemical formula expressed by $\text{Zn}_2(\text{Fe}_{0.65}, \text{Mn}_{0.35})_{\Sigma=1.00}(\text{PO}_4)_2 \cdot 4(\text{H}_2\text{O})$, that indicate predominance of phosphophyllite end member in a series with an unknown Zn and Mn phosphate.

Aspects of the structure of phosphophyllite using vibrational spectroscopy were assessed. The intense Raman peak at 995 cm^{-1} is assigned to the $\nu_1 \text{ PO}_4^{3-}$ symmetric stretching mode and the two Raman bands at 1073 and 1135 cm^{-1} to the $\nu_3 \text{ PO}_4^{3-}$ antisymmetric stretching modes. The $\nu_4 \text{ PO}_4^{3-}$ bending modes are observed at 505 , 571 , 592 and 653 cm^{-1} and the $\nu_2 \text{ PO}_4^{3-}$ bending mode at 415 cm^{-1} . The sharp Raman band at 3567 cm^{-1} attributed

to the stretching vibration of OH units brings into question the actual formula of phosphophyllite. A comparison is made with the vibrational spectra of other zinc containing phosphate minerals.

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