Vibrational spectroscopic characterization of the phosphate mineral ludlamite $(Fe,Mn,Mg)_3(PO_4)_2 \cdot 4H_2O$ – A mineral found in lithium bearing pegmatites

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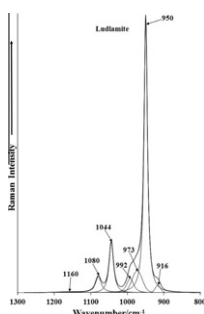[c] Federal University of Itajubá, Campus Itabira, Itabira, MG 35903-087, Brazil

HIGHLIGHTS

▶ We have analyzed the phosphate mineral ludlamite by EMP-WDS.
▶ The mineral is a ferrous phosphate with some minor substitution of Mg and Mn.
▶ Spectroscopic analysis shows the mineral is predominantly a phosphate with some minor hydrogen phosphate units.
▶ The position of the OH bands shows that water is very strongly hydrogen bonded in the ludlamite structure.

GRAPHICAL ABSTRACT

Raman spectrum of ludlamite in the phosphate stretching region.

ARTICLE INFO

ABSTRACT

The objective of this work is to analyze ludlamite $(Fe,Mn,Mg)_3(PO_4)_2 \cdot 4H_2O$ from Boa Vista mine, Galiléia, Brazil and to assess the molecular structure of the mineral. The phosphate mineral ludlamite has been characterized by EMP-WDS, Raman and infrared spectroscopic measurements. The mineral is shown to be a ferrous phosphate with some minor substitution of Mg and Mn.

Raman bands at 917 and 950 cm^{-1} are assigned to the symmetric stretching mode of $HOPO_3^{2-}$ and PO_4^{3-} units. Raman bands at 548, 564, 599 and 634 cm^{-1} are assigned to the ν_4 PO_4^{3-} bending modes. Raman bands at 2605, 2730, 2896 and 3190 cm^{-1} and infrared bands at 2623, 2838, 3136 and 3185 cm^{-1} are attributed to water stretching vibrations. By using a Libowitzky empirical function, hydrogen bond distances are calculated from the OH stretching wavenumbers. Strong hydrogen bonds in the structure of ludlamite are observed as determined by their hydrogen bond distances. The application of infrared and Raman spectroscopy to the study of ludlamite enables the molecular structure of the pegmatite mineral ludlamite to be assessed.

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Introduction

The mineral ludlamite $(Fe,Mn,Mg)_3(PO_4)_2 \cdot 4H_2O$ is an hydrated phosphate mineral found in complex pegmatites and was first identified at the classic Wheal Jane Mine in Cornwall, England. It is characterized by a bright green, usually apple-green color, a vit-reous luster. The mineral is known from a number of other places worldwide [1–9]. The mineral is monoclinic with Point Group: 2/m and space group: P21/a with $a = 10.541$ Å, $b = 4.646$ Å, $c = 9.324$ Å, $\beta = 100.52°$ and $Z = 2$ [10]. The mineral is a common secondary alteration product of earlier phosphates, formed under reducing conditions.

There have been many studies of the magnetic properties of ludlamite [13–17]. Abrahams found the mineral remained monoclinic even at very low temperatures [13]. Using neutron activation

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studies, Abrahams found that the phosphate unit was almost perfectly symmetric [13]. Forsyth et al. [14] refined the magnetic properties of ludlamite. Meijer et al. [18] performed static susceptibility measurements on 2 single crystals of the mineral ludlamite $Fe_3(PO_4)_2 \cdot 4H_2O$. Mossbauer studies were undertaken by Paster et al. [15] and the hyperfine structure determined. Pizarro et al. [16] studied the doping of ludlamite with Co^{2+}.

Raman spectroscopy has proven most useful for the study of secondary minerals. To the best of the authors' knowledge, there have been very few vibrational spectroscopic studies of ludlamite [19] and no Raman studies of this mineral have been forthcoming. Some ludlamite related studies of iron containing phosphate minerals such as vivianite and the so-called metavivianite have been undertaken by the authors [20–23]. The objective of this paper is to report the Raman and infrared spectra of ludlamite and relate the spectra to the molecular chemistry and the crystal chemistry of this phosphate mineral. The paper follows the systematic research on Raman and infrared spectroscopy of secondary minerals containing oxy-anions formed in the oxidation zone.

In this work, samples of a pure ludlamite from the Boa Vista pegmatite, located in the municipality of Galiléia, Minas Gerais, Brazil were analyzed. Studies include chemistry via EMP in the WDS mode, and spectroscopic characterization of the structure with infrared and Raman spectroscopy. We have relate the spectra to the structure and chemistry of the mineral.

Geological setting, occurrence and general appearance

The Boa Vista mine, located in the municipality of Galiléia, Minas Gerais, Brazil is an important source of rare phosphates [11]. Nowadays, the pegmatite is mined for industrial feldspar and with minor importance of gemstones and samples for the collectors market. The pegmatite is heterogeneous with well developed mineralogical and textural zoning. It has asymmetric lens shape with the longer axis trending to NW-SE and body dip about 65° to NE. The maximum extension is of about 80 m and 10 m thickness. The pegmatite is hosted by quartz–mica schist of the São Tomé Formation with tourmalinization in the contact. Hydrothermal and metasomatic processes were responsible for a deep albitization of the pegmatite body [1]. The primary mineral association is represented by quartz, muscovite, microcline, schorl, dravite, beryl, graftonite and triphylite. The secondary association is mainly composed by albite, Li-rich micas, Sn, Nb, W and Ta oxides, sulfides, siderite and a complex association of phosphates formed in the result of alteration of triphylite [1,2,11,12].

Secondary phosphates, namely heterosite, wolfeite, arrojadite, beryllonite, alluaudite, amblygonite, hydroxylherderite, vivianite, ludlamite, rockbridgeite, phosphosiderite and tavorite are common minerals in miarolitic cavities and in massive blocks formed after the aggregates of primary triphylite up to 1.0 m length [11]. Ludlamite single crystals up to 4.0 mm along the c axis and with prismatic shape occur in association with siderite, metavivianite, albite and muscovite. Single crystals of ludlamite were extracted from a massive block in association with metavivianite and siderite.

Experimental

Samples and preparation

Light green ludlamite crystal from granitic pegmatite from Boa Vista mine, Galiléia, Minas Gerais, Brazil was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-091 and SAA-092. The samples are from Boa Vista claim, a lithium bearing

pegmatite located in Conselheiro Pena, Minas Gerais. The crystals were hand selected from a sample in association with metavivianite and siderite. The ludlamite crystals were analyzed by X-ray diffraction and Scanning electron microscopy (SEM).

Electron microprobe analysis (EMP)

EMP was performed on a ludlamite single crystal. The chemical analysis was undertaken using a Jeol JXA8900R with four WDS spectrometers at the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. For each selected element the following standards were applied: Fe (magnetite), Mn (rodhonite), Mg (MgO), Ca ($Ca_2P_2O_7$), Al (Al_2O_3) and P ($Ca_2P_2O_7$). Samples of ludlamite embedded in an epoxy resin were coated with a thin layer of evaporated carbon. The EMP was performed at 15 kV of accelerating voltage and beam current of 10 nA.

Raman microprobe spectroscopy

Crystals of ludlamite 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. Different orientations were collected. The Raman spectra were measured at room temperature (298 K).

Infrared spectroscopy

Infrared spectra of the same crystals used for Raman spectroscopy 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. Infrared spectra were measured at 298 K.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The 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

Chemical characterization

The quantitative chemical analysis of the ludlamite mineral sample (SAA-091) is reported in Table 1. Composition is the average from three spots. H_2O content was calculated by stoichiometry

and the chemical formula was calculated on the basis of 12 oxygen atoms (O, OH, H_2O) in the structure. The chemical composition indicates a partial substitution of Fe^+ cations by Mg^{2+} and Mn^{2+}. Traces of Ca and Al also were found. Chemical formula is thus $(Fe_{2.35}Mn_{0.25}Mg_{0.22})_{\sum 2.82}(PO_4)_{2.08} \cdot 4.0(H_2O)$.

Raman and infrared spectroscopy

The Raman spectra of the two ludlamite mineral samples labeled as SAA-091 and SAA-092 over the complete wavenumber range is shown in Fig. 1a and b. These spectra display the relative intensities of the Raman bands and their position. It is obvious that the two spectra in Fig. 1a and b are almost identical. It is noted that there are large parts of the spectra where no intensity is observed. Thus, the spectra are subdivided into section based upon the type of vibration being studied. The infrared spectra of the two ludlamite samples are displayed in Fig. 2a and b. These spectra display the position and relative intensities of the infrared bands. As with the Raman spectra there are large sections of the spectra where no intensity is observed. Thus, the spectra are subdivided into sections depending upon the type of vibration being studied.

The Raman spectra of ludlamite in the 800–1300 cm^{-1} spectral range are illustrated in Fig. 3a and b. An intense Raman band at around 950 cm^{-1} is assigned to the v_1 PO_4^{3-} symmetric stretching mode. A shoulder band observed at 917 cm^{-1} is assigned to $HOPO_3^{2-}$ symmetric stretching mode. Two low intensity Raman bands are found at around 973 and 992 cm^{-1} (Fig. 3a) and 978 and 993 cm^{-1} (Fig. 3b). These bands are assigned to $(HO)_2PO_2^-$ symmetric stretching mode. Choi et al. [24] published spectra of NaH_2PO_4; however these authors did not tabulate or mark the position of the peaks. Therefore, it is very difficult to make any comparison of the peak positions of ludlamite and that of published data by Choi et al. Casciani and Condrate [25] reported bands assigned to these vibrational modes for $Ca(H_2PO_4)_2$ at 876 and 901 cm^{-1}. The Raman bands at 1044, 1080 and 1160 cm^{-1} (Fig. 3a) and 1044, 1078 and 1121 cm^{-1} (Fig. 3b) are assigned to the phosphate and hydrogen phosphate antisymmetric stretching modes. In the work undertaken on the magnetic properties of ludlamite, it is always stated that the phosphate anion retains its symmetry [10,15,18]. However, in terms of vibrational spectroscopy peaks which are attributed to hydrogen phosphate and dihydrogen phosphate units are observed, thus supporting the concept of loss of symmetry of the phosphate units. It is proposed that the protons from water are very labile and can interact with the phosphate units to for hydrogen phosphate ions. On the picosecond time scale of vibrational spectroscopy, as compared with measurements made with magnetic susceptibility measurements, the proton oscillates between water and the phosphate units, which results in the formation of the hydrogen phosphate units.

The infrared spectra of the two ludlamite samples are reported in Fig. 4a and b. The infrared spectra are very similar. An intense infrared band is observed at 988 cm^{-1} and is assigned to the v_1 PO_4^{3-} symmetric stretching mode. The intense band at 1039 cm^{-1}

with a shoulder at 1098 cm^{-1} is assigned to the v_3 PO_4^{3-} antisymmetric stretching mode. Two other intense infrared bands are observed at 912 and 939 cm^{-1} and are attributed to the stretching vibrations of the $(HO)_2PO_2^-$ units.

The Raman spectra of ludlamite in the 300–800 cm^{-1} spectral region are shown in Fig. 5a and b. This spectral region is where the phosphate bending modes are observed. Raman bands are observed at 548, 564, 599 and 634 cm^{-1} (Fig. 5a) and 549, 565, 600, and 635 cm^{-1} (Fig. 5b). Ardealite $Ca_2(HPO_4)(SO_4) \cdot 4H_2O$ is a mineral which also contains the hydrogen phosphate anion. Intense Raman bands are found at 505 and 528 cm^{-1} for ardealite and are assigned to the v_4 $(HPO_4)2-$ bending modes. It is probable that the bending modes of OPO and HOPO bending modes occur at the same energy, thus two distinct bands are not observed. The mineral newberyite $Mg(PO_3OH) \cdot 3H_2O$ also contains a hydrogen phosphate anion. The Raman spectrum of this mineral has been reported [26]. An intense band was observed for this mineral at 498 cm^{-1}. Rajendran and Keefe [27] reported Raman bands at 521 and 586 cm^{-1} and assigned these bands to $(H—O)P=O$ absorption bands. This assignment is in contrast to the assignment of bands by Ross as reported in Farmer's treatise on the infrared spectra of minerals [28].

The Raman spectrum of ludlamite in the 100–300 cm^{-1} spectral range is reported in Fig. 6a and b. There is a close resemblance between the spectra in this far wavenumber range between the two samples. For sample SAA-091, intense Raman bands are observed at 103, 172 and 199 cm^{-1} and for sample SAA-092, Raman bands are found at 104, 145, 174 and 202 cm^{-1}. Raman bands of lower intensity are observed at 244, 249, 266 and 286 cm^{-1} for SAA-091 and 243, 251, 261, 271 and 287 cm^{-1} for mineral SAA-092. These bands are described as external vibrations or lattice modes.

The Raman spectrum of ludlamite in the OH stretching region over the 2400 to 3800 cm^{-1} spectral range are displayed in Fig. 7a and b. The spectra consist of a series of overlapping bands which may be resolved into component bands. Bands are observed at 2605, 2730, 2896 and 3190 cm^{-1} for sample SAA-091 and at 2621, 2735, 2859 and 3196 cm^{-1} for mineral sample SAA-092. The position of the bands shows that water is involved in very strong bonding to the metal cations. The infrared spectrum of ludlamite in the OH stretching region over the 2400–3800 cm^{-1} spectral range are displayed in Fig. 8a and b. As for the Raman spectra, the spectral profiles may be resolved into component bands. Infrared bands are observed at 2623, 2838, 3136 and 3185 cm^{-1} (sample SAA-091) and at 2634, 2840, 2979, 3131 and 3182 cm^{-1} (sample SAA-092). These bands are assigned to the OH stretching vibrations of water.

Studies have shown a strong correlation between OH stretching frequencies and both $O\cdots O$ bond distances and $H\cdots O$ hydrogen bond distances [29–32]. Libowitzky [33] showed that a regression function can be employed relating the hydroxyl stretching wavenumbers with regression coefficients better than 0.96 using infrared spectroscopy [33]. The function is described as: $v_1 = (3592 - 304) \times 10^{9 \frac{-d(O-O)}{0.1321}} cm^{-1}$. Thus OH---O hydrogen bond

Table 1
Chemical composition of ludlamite from Boa Vista pegmatite (mean of 3 electron microprobe analyses). H_2O calculated by stoichiometry.

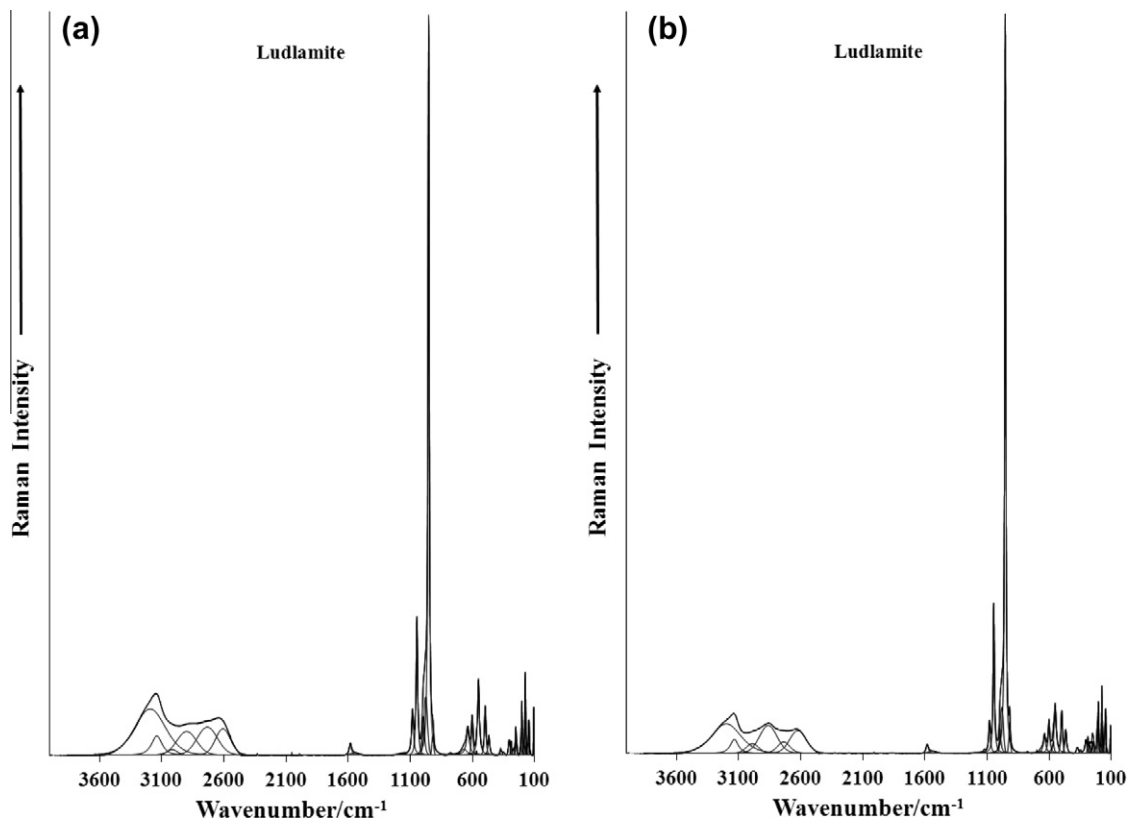| Constituent	wt.%	Range (wt.%)	Number of atoms	Probe standard/crystal
FeO	42.07	40.78–42.82	2.35	Magnetite/TAP
MnO	4.37	3.62–5.48	0.25	Rodhonite/LIF
P_2O_5	36.82	36.41–37.20	2.08	$Ca_2P_2O_7$/PETJ
MgO	2.15	1.96–2.43	0.22	MgO/TAP
CaO	0.01	0.01–0.02	0.00	$Ca_2P_2O_7$/PETJ
Al_2O_3	0.07	0.04–0.12	0.00	Al_2O_3/TAP
H2O	17.98	Calculated by stoichiometry	4.00	
Total	103.47		7.84	

Fig. 1. Raman spectrum of ludlamite (samples SAA-091 and SAA-092) in the 100–4000 cm^{-1} spectral range.
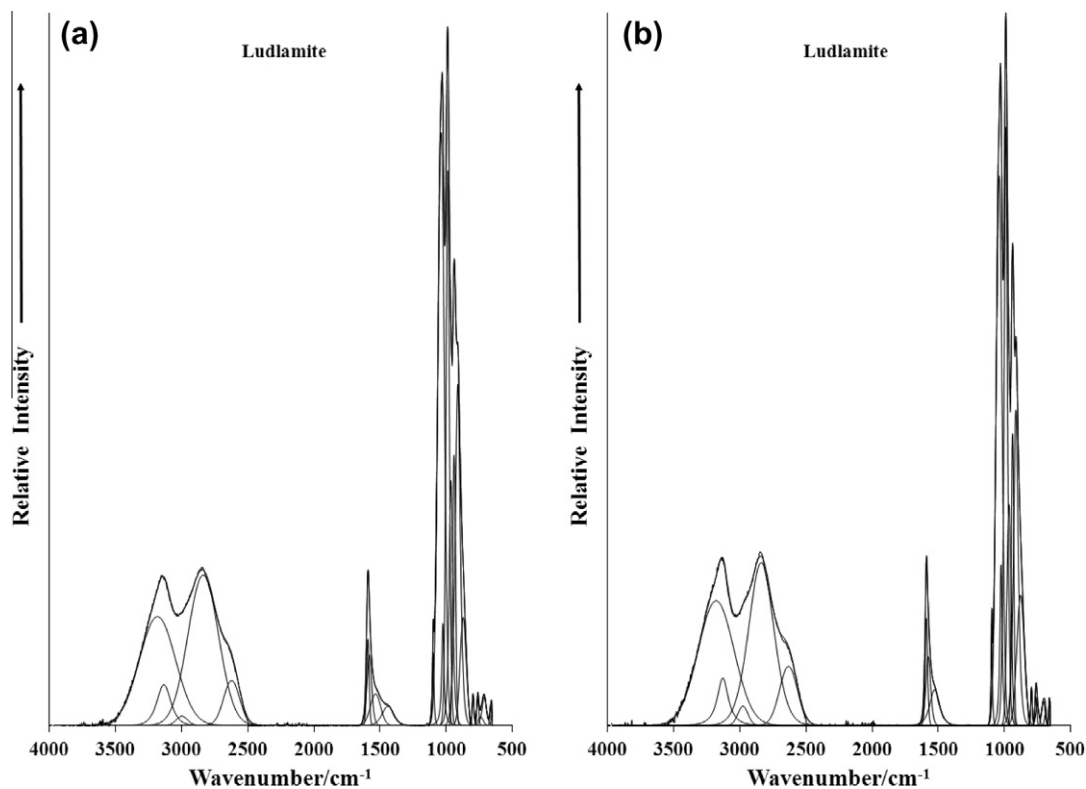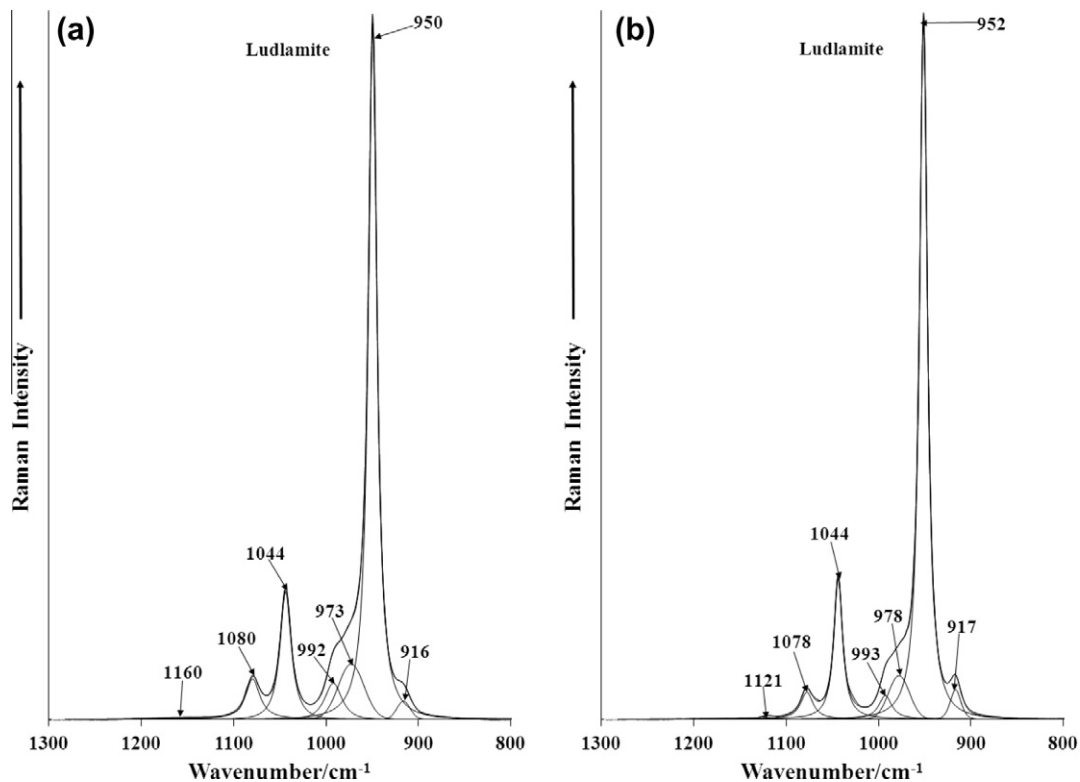

Fig. 2. Infrared spectrum of ludlamite (samples SAA-091 and SAA-092) in the 500–4000 cm^{-1} spectral range.

distances may be calculated using the Libowitzky empirical function. Hydrogen bond distances may be obtained by using the OH stretching wavenumbers as given in Fig. 7a and b.

By using the position of the Raman OH stretching wavenumbers, estimates of the hydrogen bond distances can be made. Here hydrogen bond distances are calculated as 2.582 (2605 cm^{-1}),
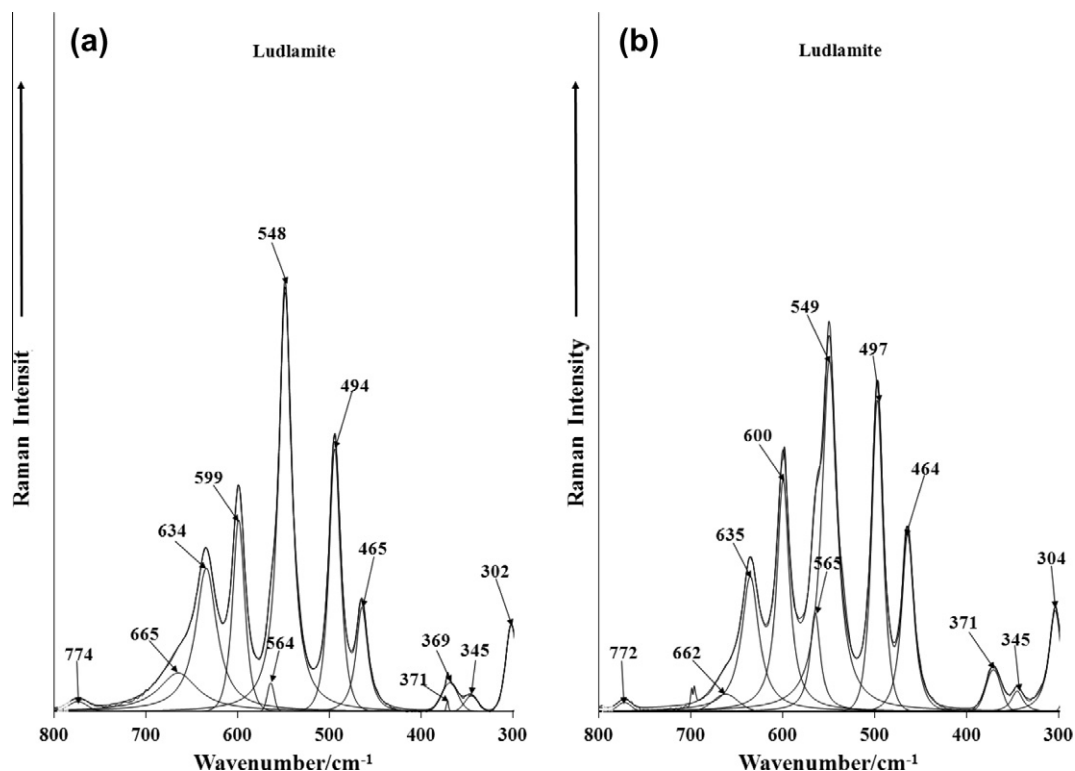
Fig. 3. Raman spectrum of ludlamite (samples SAA-091 and SAA-092) in the 800–1400 cm^{-1} spectral range.

Fig. 4. Infrared spectrum of ludlamite (samples SAA-091 and SAA-092) in the 500–1300 cm^{-1} spectral range.

2.600 Å (2730 cm^{-1}), 2.628 Å (2896 cm^{-1}), 2.652 Å (3013 cm^{-1}), 2.684 Å (3137 cm^{-1}), 2.799 Å (3190 cm^{-1}). It is observed that the hydrogen bond distances calculated from the Raman spectra are in a similar range as calculated from the infrared spectrum. The large hydrogen bond distances which are present in ludlamite can also be seen in other mixed anion minerals such as peisleyite

Fig. 5. Raman spectrum of ludlamite (samples SAA-091 and SAA-092) in the 300–800 cm^{-1} spectral range.
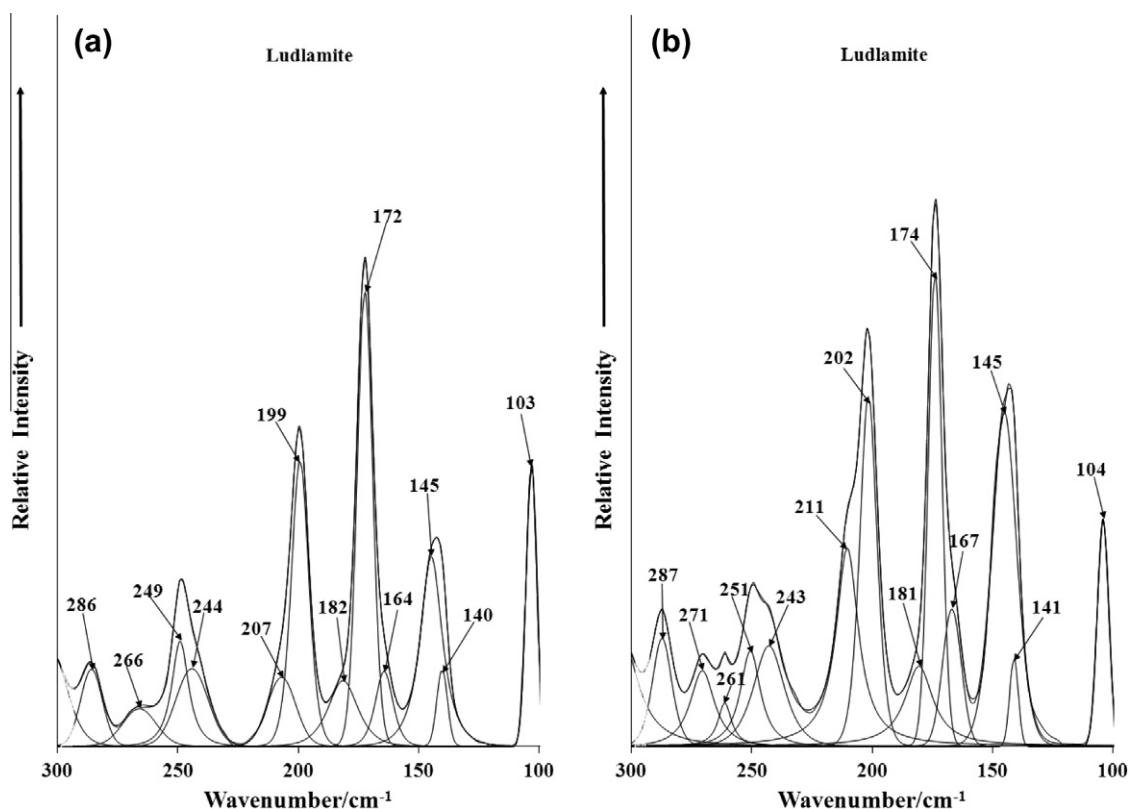

Fig. 6. Raman spectrum of ludlamite (samples SAA-091 and SAA-092) in the 100–300 cm^{-1} spectral range.

and perhamite [34,35] where the distances ranging between 3.052(5) and 2.683(6) Å. Two types of OH units can be identified in the structure of ludlamite. The hydrogen bond distances

previously established can be used to predict the hydroxyl stretching wavenumbers. The spectrum of ludlamite may be divided into two groups of OH stretching wavenumbers; namely
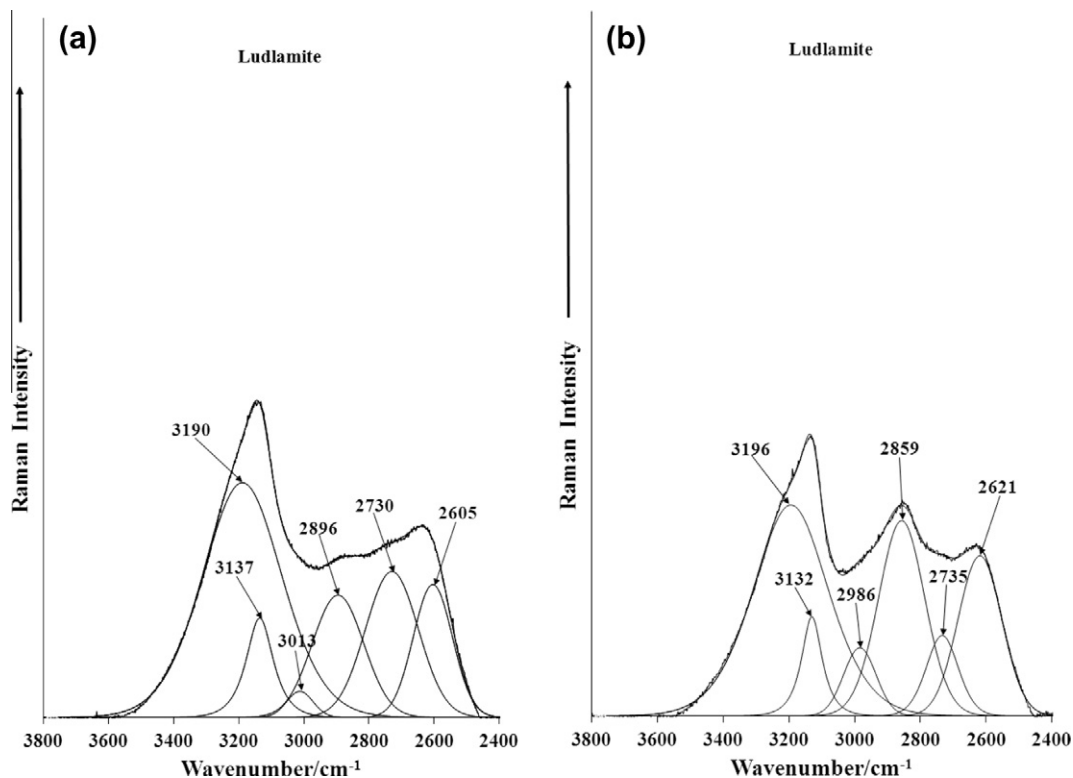
Fig. 7. Raman spectrum of ludlamite (samples SAA-091 and SAA-092) in the 2800–3800 cm^{-1} spectral range.
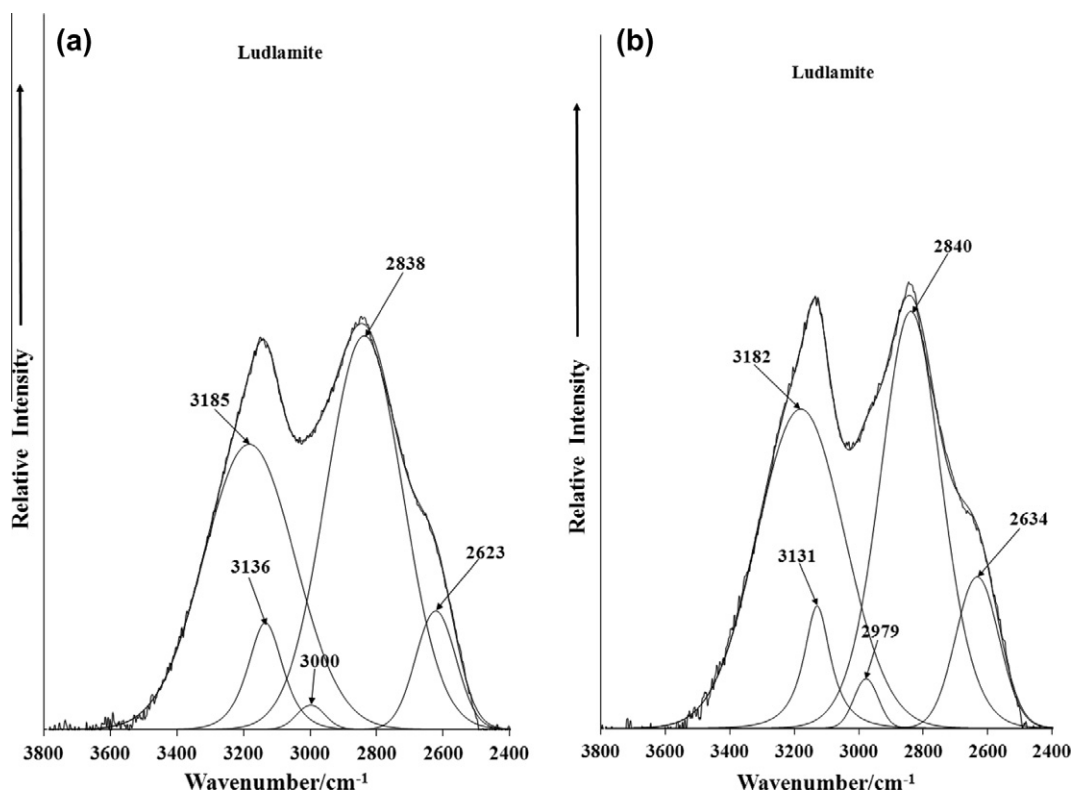

Fig. 8. Infrared spectrum of ludlamite (samples SAA-091 and SAA-092) in the 2800–3800 cm^{-1} spectral range.

2600–3000 cm^{-1} and 3000–3200 cm^{-1}. This distinction suggests that the strength of the hydrogen bonds as measured by the hydrogen bond distances can also be divided into two groups according to the H-bond distances. An arbitrary cut-off point may be 2.649 Å based upon the wavenumber 3000 cm^{-1}. Thus, the bands listed

above occurring above 3000 cm^{-1} may be described as weak hydrogen bonds and the series of bands <3000 cm^{-1} as relatively strong hydrogen bonds. The number and variation of water hydrogen bond distances are important for the stability off the mineral.

Conclusions

The phosphate mineral ludlamite has been characterized by EMP, Raman and infrared spectroscopic measurements. Raman spectroscopy identified an intense sharp band at 950 cm^{-1} attributed to the v_1 PO$_4^{3-}$ symmetric stretching mode. A low intensity shoulder band at 917 cm^{-1} is assigned to HOPO$_3^{2-}$ symmetric stretching mode. It is suggested that this hydrogen phosphate results for the rapid exchange of the proton from water resulting in the formation of hydrogen phosphate. Raman bands at 548, 564, 599 and 634 cm^{-1} are assigned to the v_4 PO$_4^{3-}$ bending modes. Raman bands in the OH stretching region are assigned to water stretching vibrations. The position of these bands provides evidence for strong bonding of the water to the metal cations. Further, the position of the water stretching modes indicates strong hydrogen bonding between the phosphate and water units. The values of the calculated hydrogen bond distances shows the hydrogen bond distances are very short indicating very strong hydrogen bonds between water and the phosphate units.

Acknowledgements

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