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A Raman and infrared spectroscopic study of the phosphate mineral laueite

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ABSTRACT

A laueite mineral sample from Lavra Da Ilha, Minas Gerais, Brazil has been studied by vibrational spectroscopy and scanning electron microscopy with EDX. Chemical formula calculated on the basis of semi-quantitative chemical analysis can be expressed as $(Mn^{2+}_{0.85},Fe^{2+}_{0.10}Mg_{0.05})_{\sum 1.00}(Fe^{3+}_{1.90},Al_{0.10})_{\sum 2.00}(PO_4)_2(OH)_2{\cdot}8H_2O$.

The laueite structure is based on an infinite chains of vertex-linked oxygen octahedra, with Fe^{3+} occupying the octahedral centers, the chain oriented parallel to the *c*-axis and linked by PO_4 groups. Consequentially not all phosphate units are identical. Two intense Raman bands observed at 980 and 1045 cm^{-1} are assigned to the ν_1 PO_4^{3-} symmetric stretching mode. Intense Raman bands are observed at 525 and 551 cm^{-1} with a shoulder at 542 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4^{3-}. The observation of multiple bands supports the concept of non-equivalent phosphate units in the structure. Intense Raman bands are observed at 3379 and 3478 cm^{-1} and are attributed to the OH stretching vibrations of the hydroxyl units. Intense broad infrared bands are observed. Vibrational spectroscopy enables subtle details of the molecular structure of laueite to be determined.

1. Introduction

The mineral laueite of formula $Mn^{2+}Fe_2^{3+}(PO_4)_2(OH)_2{\cdot}8H_2O$ [1,2] is a hydrated hydroxy phosphate of ferric iron and manganese. The mineral is a member of the homonimous mineral group. Other minerals in this group are césarferreiraite $Fe^{2+}(Fe^{3+})_2(AsO_4)_2(OH)_2{\cdot}8H_2O$, ferrolaueite $Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2{\cdot}8H_2O$, gordonite $MgAl_2^{3+}(PO_4)_2(OH)_2{\cdot}8H_2O$, kastningite $(Mn^{2+}, Fe^{2+},Mg)Al_2(PO_4)_2(OH)_2{\cdot}8H_2O$, laueite $Mn^{2+}Fe_2^{3+}(PO_4)_2(OH)_2{\cdot}8H_2O$, maghrebite $MgAl_2(AsO_4)_2(OH)_2{\cdot}8H_2O$, mangangordonite $Mn^{2+}Al_2^{3+}(PO_4)_2(OH)_2{\cdot}8H_2O$, paravauxite $Fe^{2+}Al_2^{3+}(PO_4)_2(OH)_2{\cdot}8H_2O$ [3], sigloite $Fe^{3+}Al_2^{3+}(PO_4)_2(OH)_2{\cdot}7H_2O$ [4] and ushkovite $MgFe_2^{3+}(PO_4)_2(OH)_2{\cdot}8H_2O$ [5–8].

The mineral was named by Hugo Strunz in 1954 in honor of Max Felix Theodor von Laue (1879–1960). Laue was the first to verify that minerals had a regular atomic arrangement as had been predicted by previous physicists. Laueite was first described from Hagendorf South pegmatite, Bavaria, Germany. Laueite is dimorphous with the mineral gordonite [9]. Crystal structure of laueite was determined by Moore [5–7]. Moore found that there were two isotypes and 3 polymorphs for laueite [5]. The laueite structure is based on an infinite chain of vertex-linked oxygen octahedra, with Fe^{3+} occupying the octahedral centers, the chains oriented parallel to the *c*-axis. The mineral shows triclinic symmetry, space group *P*-1, and unit cell parameters are: a = 5.28 Å, b = 10.66 Å, c = 7.14 Å, α = 107.91°, β = 110.98°, γ = 71.12°.

As paravauxite is isostructural with laueite $Mn^{2+}Fe^{3+}{}_2(PO_4)_2(OH)_2{\cdot}8H_2O$ [3,12], it could be indirectly concluded that the structure of paravauxite is based on an infinite chain of vertex-linked oxygen octahedra, with Al occupying the octahedral centers, the chain oriented parallel to the *c*-axis. Chains are in turn connected to others by PO_4 tetrahedra which also bridge through isolated octahedra (with Fe^{2+} as centers). The laueite structural formula is $Mn^{2+}Fe^{3+}{}_2(OH)_2(PO_4)_2(H_2O)_6{\cdot}2H_2O$ [3], and according to analogy, the paravauxite structural formula is then $Fe^{2+}Al_2(OH)_2(PO^4)_2(H_2O)_6{\cdot}2H_2O$ and the non-octahedrally bonded waters appearing in a cavity left in the structure. In detailed description, in analogy with laueite structure [3], the chains of Al-octahedra decorated by flanking PO_4^{3-} groups (which extend in *c*-direction) meld in the *a*-direction by sharing one quarter of the flanking PO_4 vertices with octahedra of adjacent chains to form an $[Al_2(PO_4)_2(OH)_2(H_2O)_2]$ sheet. In the resulting sheet, the PO_4

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tetrahedra are three-connected. There are two distinct octahedra in these sheets, one of which is six-connected within the sheet, and the other of which is only four-connected and has (H_2O) at two vertices.

Raman spectroscopy has proven very useful for the study of minerals, especially minerals containing oxyanions such as phosphate [3,4]. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. The objective of this research is to report the Raman and infrared spectra of laueite and to relate the spectra to the molecular structure of the mineral.

2. Experimental

2.1. Samples description and preparation

The mineral laueite 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 SAE-025. The laueite originated from the Cigana mine, Conselheiro Pena, Minas Gerais, Brazil. The mineral occurs in association with frondelite in a paragenesis related to the hydrothermal alteration of triphylite in Li-bearing pegmatites. Crystals of laueite can make nice specimens with their colorless or light green color and glassy luster. The mineral is an uncommon species in complex zoned pegmatites.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the mineral chemistry.

2.2. Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the NanoLab, REDEMAT, School of Mines, Universidade Federal de Ouro Preto, Ouro Preto, Minas Gerais, Brazil. Laueite crystals were coated with a 5 nm layer of evaporated carbon. Secondary electron image was obtained using a TESCAN VEGA 3 equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with an Oxford spectrometer and were applied to support the mineral characterization.

Raman spectroscopy

Crystals of laueite 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 polarised 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 4000 and 100 cm^{-1}. Some of these phosphate minerals fluoresced badly at 633 nm; as a consequence other laser excitation wavelengths were used especially the 785 nm laser. The power at the sample was 0.1 mW.

Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

A Raman spectrum of laueite is provided in the RRUFF data base. The spectrum only covers the 1200–100 cm^{-1} spectral range. This spectrum is provided in Supplementary information as Fig. S1.

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 4000–600 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 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.

5. Results and discussion

5.1. Chemical characterization

The BSI image of laueite sample studied in this work is shown in Fig. 1. Qualitative and semi-quantitative chemical composition shows a Fe and Mn phosphate phase with minor amounts of Mg and Al. The chemical analysis is represented as an EDX spectrum in Fig. 2. On the basis of semiquantitative chemical analyses the

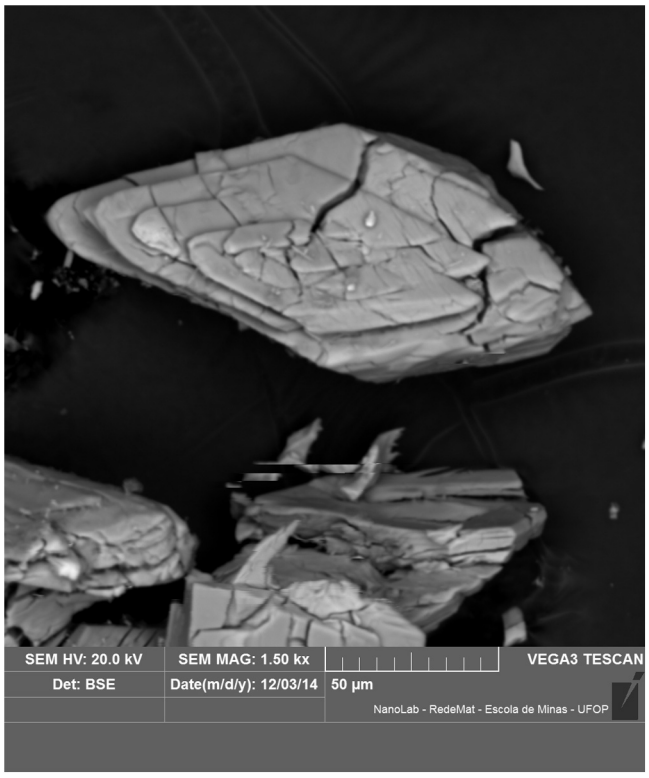

Fig. 1. SEM image of Brazilian laueite.

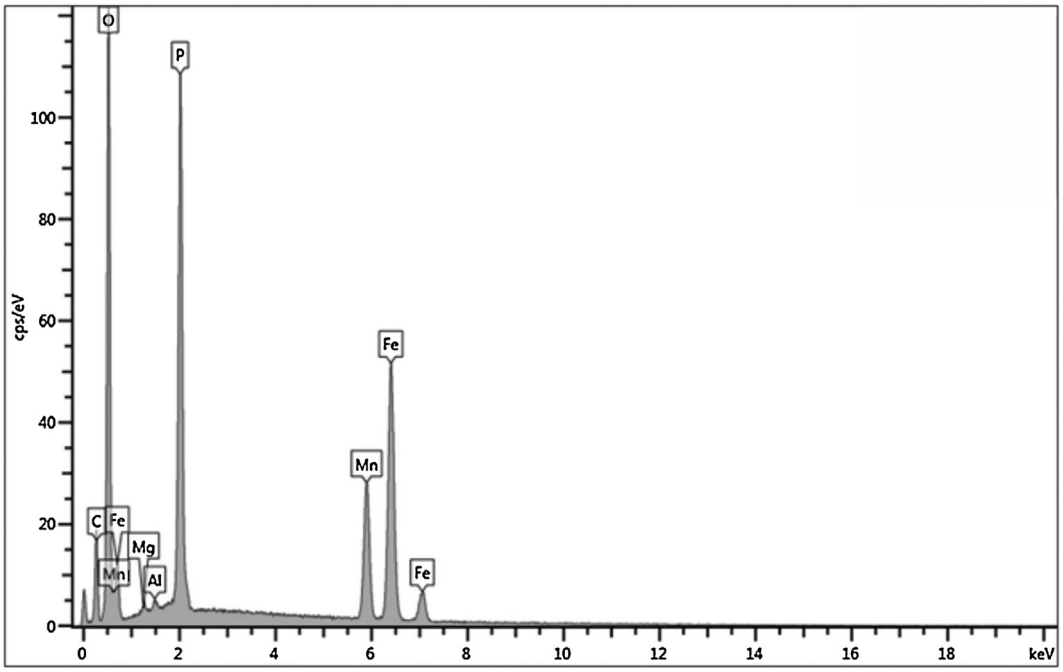

Fig. 2. EDX analysis of Brazilian laueite.

chemical formula was calculated and can be expressed as $(Mn^{2+}_{0.85},Fe^{2+}_{0.10}Mg_{0.05})_{\sum 1.00}(Fe^{3+}_{1.90},Al_{0.10})_{\sum 2.00}(PO_4)_2(OH)_2{\cdot}8H_2O$.

Vibrational spectroscopy

The Raman spectrum of laueite over the 4000–100 cm^{-1} spectral range is reported in Fig. 3a. This spectrum was obtained using the 633 nm laser. The spectrum shows complexity with many bands being observed. This figure shows the position and relative intensities of the Raman bands. It is noteworthy that there are large parts of the spectrum where no intensity is observed. The Raman spectrum is therefore, subdivided into sections depending upon the type of vibration being analysed. The infrared spectrum of laueite over the 4000–600 cm^{-1} spectral range is displayed in Fig. 3b. The spectrum is not shown below 600 cm^{-1}. The reason for this is that we are using a reflection technique and the ATR cell absorbs all incident radiation below this wavenumber. There are parts of this infrared spectrum where little or no intensity is observed. This spectrum may be thus subdivided into sections depending upon the type of vibration being analyzed. A summary of the spectroscopic data is given in Table 1 .

The Raman spectrum of the laueite mineral sample over the 3800–2500 cm^{-1} spectral range is reported in Fig. 4a. Intense Raman bands are observed at 3478, 3430 and 3379 cm^{-1} and are assigned to the stretching vibration of the hydroxyl units. The bands at 3080 and 3297 cm^{-1} are assigned to water stretching vibrations. The infrared spectrum over the 3800–2500 cm^{-1} spectral range is reported in Fig. 4b. The infrared spectrum is complex with overlapping bands observed. Band component analysis enables component bands to be resolved. Infrared bands are observed at 3532, 3470, 3387, 3241 and 3035 cm^{-1} are attributed to the OH stretching vibrations of the hydroxyl units, although the band at 3035 cm^{-1} may assigned to water stretching vibration. Breitinger et al. studied he mineral wardite. Although the structure of wardite is different to that of laueite, it is not unreasonable to make a comparison. Breitinger et al. [10] found infrared bands at 3520 (vw), 3545 (s), 3585 (sh) and 3613 cm^{-1} (m). Breitinger et al. states that the ν(OH) modes in the two

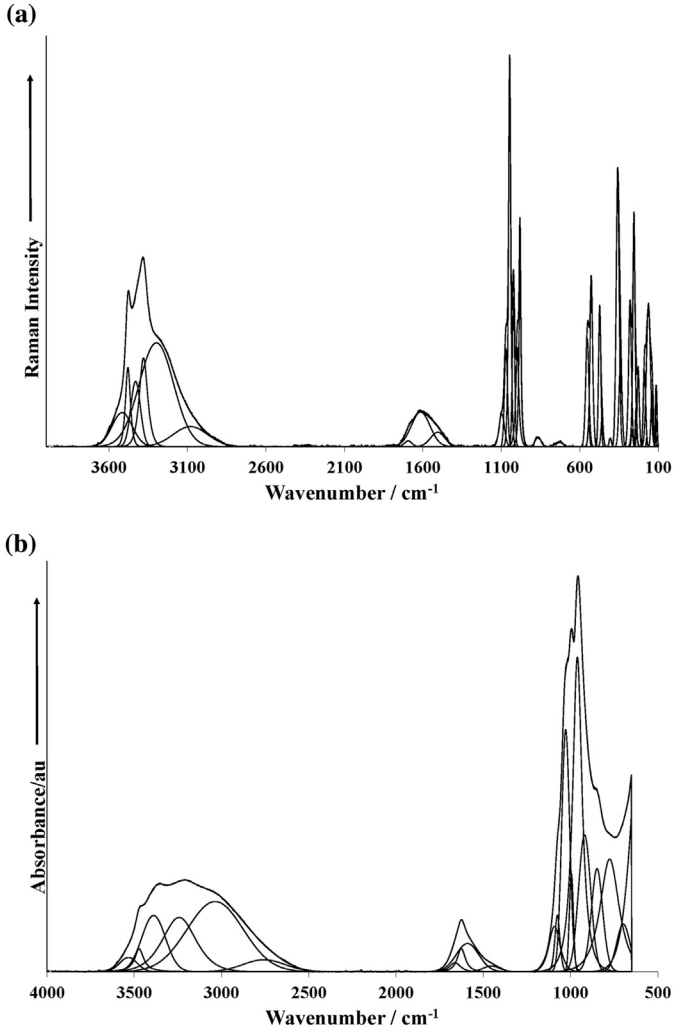

Fig. 3. (a) Raman spectrum of laueite over the 4000–100 cm^{-1} spectral range (b) infrared spectra of laueite over the 4000–500 cm^{-1} spectral range.

Table 1
Vibrational spectroscopic data of laueite (lattice modes not listed).

Laueite Raman	Laueite Infrared	Probable assignment
3515	3532	$\nu_{(OH)}$
3478	3470	$\nu_{(OH)}$
3430		$\nu_{(H_2O)}$
3379	3387	$\nu_{(H_2O)}$
3297		$\nu_{(H_2O)}$
3080	3035	$\nu_{(H_2O)}$
1692	1650	$\delta_{(H_2O)}$
1613	1624	$\delta_{(H_2O)}$
1096	1090	$\nu_{3(PO_4)}$
1064	1074	$\nu_{3(PO_4)}$
1045	1026	$\nu_{3(PO_4)}$
1021	993	$\nu_{1(PO_4)}$
997	959	$\nu_{1(PO_4)}$
980	918	$\gamma_{(H_2O)}$
864	864	$\gamma_{(H_2O)}$
	774	$\gamma_{(H_2O)}$
731	669	$\gamma_{(H_2O)}$
551		$\gamma_{4(PO_4)}$
542		$\gamma_{4(PO_4)}$
525		$\gamma_{4(PO_4)}$
472		$\nu_{2(PO_4)}$
456		$\nu_{2(PO_4)}$
404		$\nu_{2(PO_4)}$
357		$\nu_{1(FeO)}$
335		$\nu_{1(FeO)}$

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 [10]. The ν(OH) region of IR spectra of laueite shows two sharp bands (3241 and 3387 cm^{-1}) with two weak shoulders or satellites (3470 and 3532 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 Fe–OH–Fe groups.

These bands at 3241 and 3387 cm^{-1} are assigned to water stretching vibrations. It is probable that some of the component bands are due to overtones and combination of the water bending and librational modes. The position of the water stretching vibration provides evidence for strong hydrogen bonding and that water is involved in different hydrogen bonding arrangements. The bands provide an indication that water is very strongly hydrogen bonded in the laueite structure. It is possible that the bands reflect the two isotypes of laueite as demonstrated by Moore [5].

The Raman spectrum of the laueite in the 1800–1300 cm^{-1} spectral range is illustrated in Fig. 5a. Two Raman bands are found at 1633 and 1692 cm^{-1}. These bands are ascribed to water bending modes. The infrared spectrum of the laueite mineral sample over the 1800–1300 cm^{-1} spectral range is shown in Fig. 5b. Infrared bands are observed at 1589 and 1624 cm^{-1}. The bands in this region result from correlation splitting as a result of the short distance and orientation of the H_2O molecules.

The Raman spectrum of laueite in the 1250–650 cm^{-1} region is displayed in Fig. 6a. The spectrum is dominated by two intense bands at around 980 and 1045 cm^{-1}. These two bands are assigned to the ν_1 PO_4^{3-} symmetric stretching vibrations. The Raman spectrum of laueite from the RRUFF data base is provided in the supplementary information as Fig. S1. Two intense bands are observed at 976 and 1089 cm^{-1} with a shoulder band at 1003 cm^{-1}. This spectrum differs from our spectrum as shown in Fig. 6a. Two intense bands are observed reflecting two non-equivalent phosphate units in the laueite structure, as was demonstrated by Moore [5]. Galy [11] first studied the polarized Raman spectra of the $H_2PO_4^-$ anion. Choi et al. reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [12] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($Ca(H_2PO_4)_2$), monocalcium dihydrogen phosphate hydrate ($Ca(H_2PO_4)_2{\cdot}H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6{\cdot}5H_2O$). These authors determined band assignments for $Ca(H_2PO_4)$ and reported bands at 1002 and 1011 cm^{-1} as POH and PO stretching vibrations, respectively. The two Raman bands at 1086 and 1167 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [12] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P—O symmetric and the P—O antisymmetric stretching vibrations.

Breitinger et al. used FT-Raman to obtain their spectra of wardite and found overlapping Raman bands at 999 and 1033 cm^{-1} and assigned these bands to the ν_1 PO_4^{3-} symmetric stretching and ν_3 PO_4^{3-} antisymmetric stretching modes. The difference in the spectra between our work and that of Breitinger et al. may be attributed to the improved technology of the spectrometer with greater resolution. Other bands of lesser intensity are observed at 997, 1021, 1069 and 1096 cm^{-1}. These latter two bands are assigned to the ν_3 PO_4^{3-} antisymmetric stretching vibrations. The first two bands are attributed to ν_1 $HOPO_3^{3-}$ stretching vibrations.

Breitinger et al. assigned the band at 999 cm^{-1} in the Raman spectrum of wardite to AlOH deformation modes. In this work the band at 997 cm^{-1} is quite sharp and well resolved. A group of low

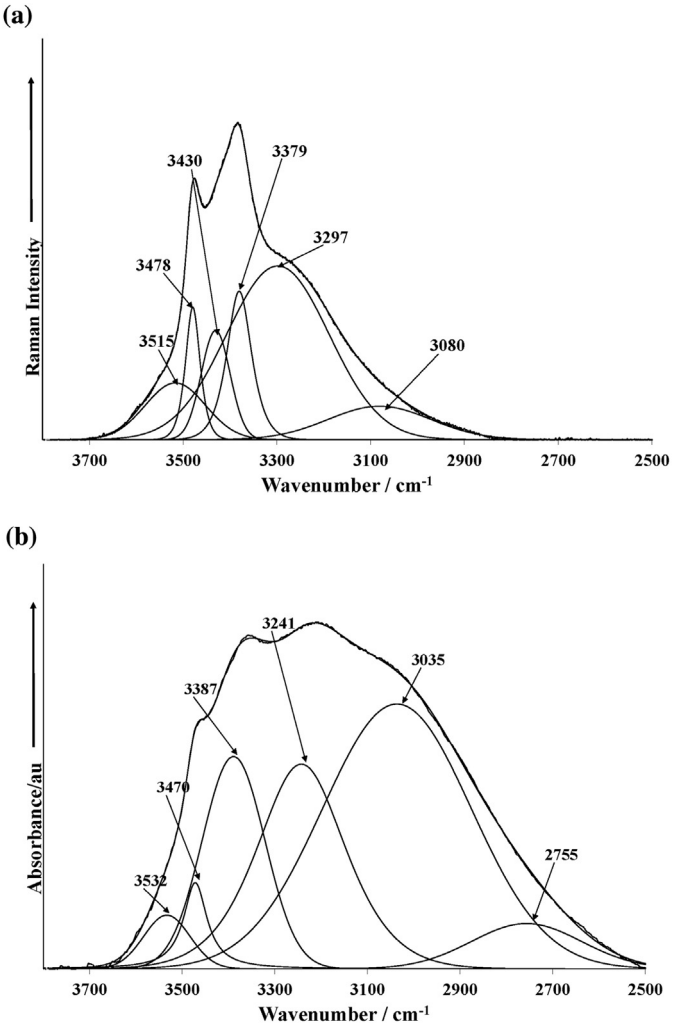

Fig. 4. (a) Raman spectrum of laueite over the 3800–2600 cm^{-1} spectral range (b) Infrared spectrum of laueite over the 3800–2500 cm^{-1} range.

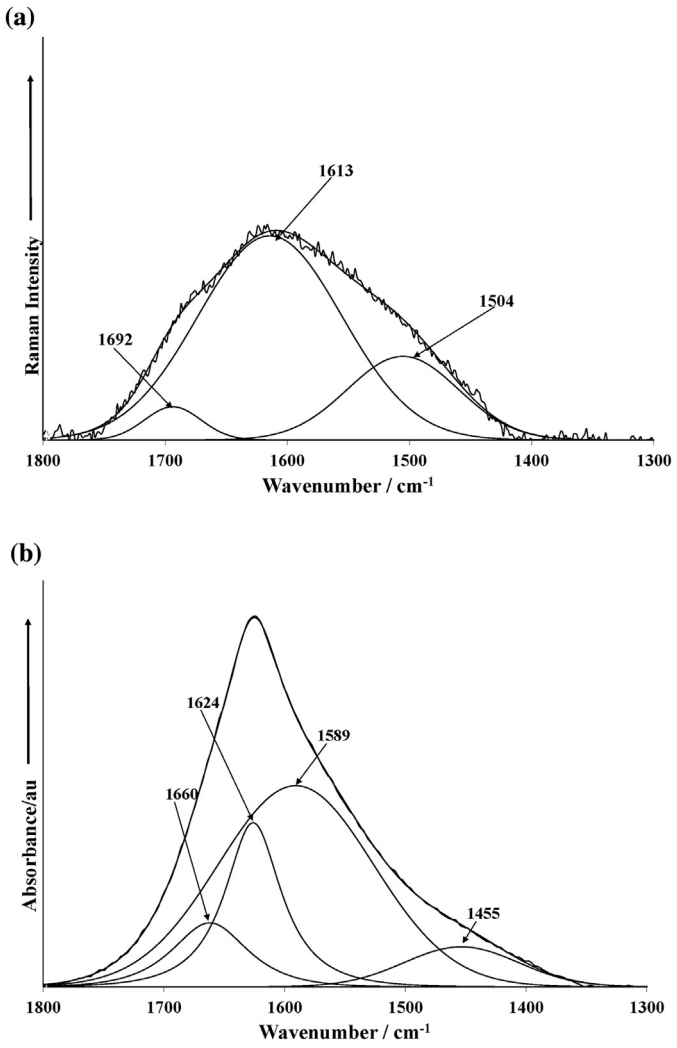

Fig. 5. (a) Raman and (b) infrared spectrum of laueite, both over the 1800–1300 cm^{-1} range.

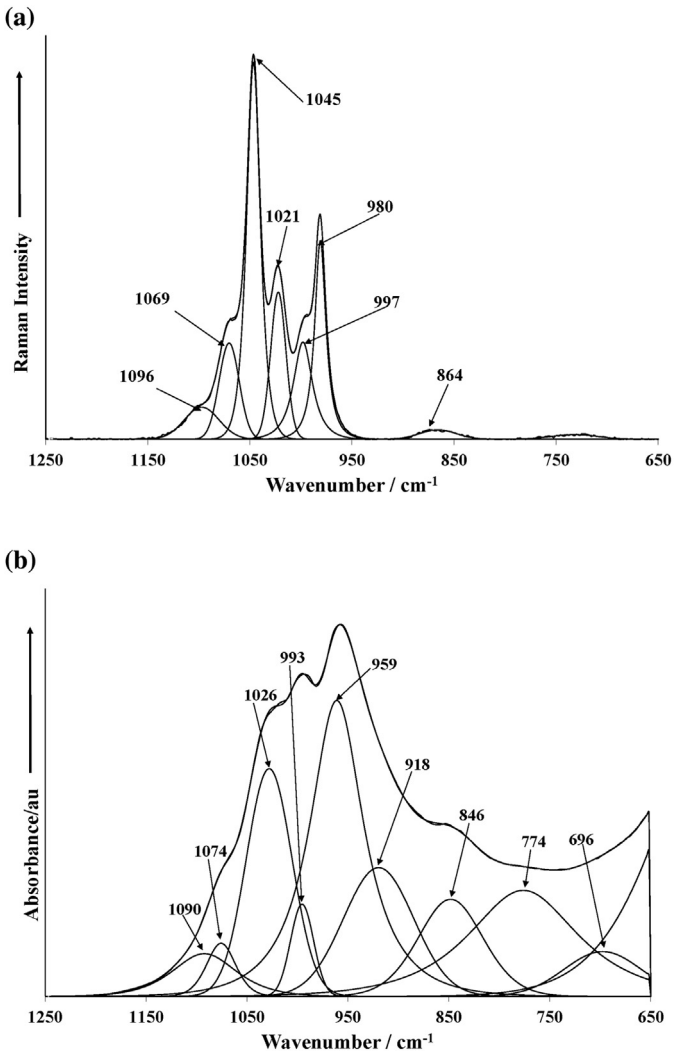

Fig. 6. (a) Raman and (b) infrared spectrum of laueite, both over the 1250–650 cm^{-1} range.

intensity bands at 1069 and 1096 cm^{-1} and are assigned to the ν_3 PO_4^{3-} antisymmetric stretching modes. Breitinger et al. did not report any bands in these positions in the Raman spectrum of wardite. These workers reported infrared bands at 1058 (strong) with shoulders at 1129 and 1168 cm^{-1} and assigned these bands to δAl_2OH deformation modes. A low intensity broad band at 864 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 also attributed to water librational modes.

The infrared spectrum of laueite over the 1250–650 cm^{-1} spectral range is displayed in Fig. 6b. The infrared spectrum shows some similarity to that of the Raman spectrum. The infrared band at around 1026 cm^{-1} is attributed to the ν_1 PO_4^{3-} symmetric stretching mode. The infrared bands at 1072 and 1090 cm^{-1} are attributed to the ν_3 PO_4^{3-} antisymmetric stretching modes. The series of infrared bands at 774, 846 and 918 cm^{-1} are assigned to the water librational modes. Some of these bands may also be due to the δFe_2OH deformation modes, in harmony with the assignment of Breitinger et al. He and co-workers stated that the deceptively simple strong IR band centered at 1059 cm^{-1} for wardite contains at least four components of $\nu(PO_4)$ generated by lifting of the originally threefold degeneracy of $\nu_3(PO_4)$ and activation of $\nu_1(PO_4)$ due to the general position of PO_4 and again at least four components of the deformation modes $\delta(Al_2OH)$ involving the two pairs of the non-equivalent OH groups. In this work we have obtained much greater resolution and these components are resolved into the component bands.

The Raman spectral region of the phosphate bending modes over the 800–100 cm^{-1} spectral range is reported in Fig. 7. Intense

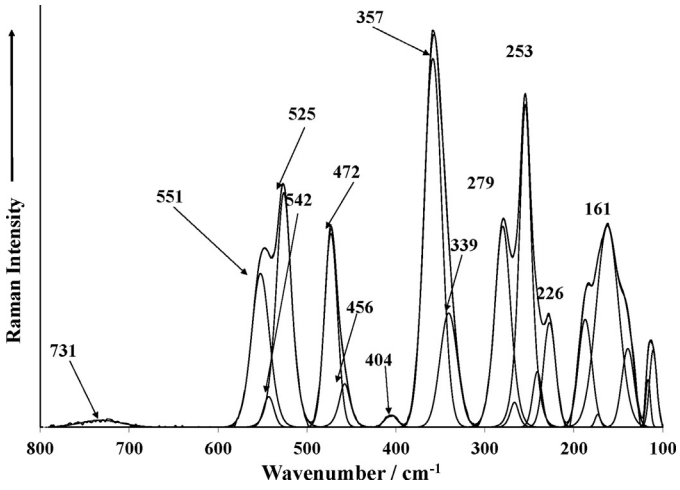

Fig. 7. Raman spectrum of laueite over the 800 to 100 cm^{-1} range.

Raman bands are observed at 551, 542 and 525 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4^{3-} and $HOPO_3^{2-}$ units. In the RRUFF spectrum of laueite, Raman bands are found at 462, 516 and 577 cm^{-1}.

The Raman band at 993 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the POH units, whereas the Raman band at 1009 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the PO_4^{3-} units. Galy [11] first studied the polarized Raman spectra of the $H_2PO_4^-$ anion. Choi et al. reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [12] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($Ca(H_2PO_4)_2$), monocalcium dihydrogen phosphate hydrate ($Ca(H_2PO_4)_2{\cdot}H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6{\cdot}5H_2O$). These authors determined band assignments for $Ca(H_2PO_4)$ and reported bands at 1002 and 1011 cm^{-1} as POH and PO stretching vibrations, respectively. The two Raman bands at 1086 and 1167 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [12] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P—O symmetric and the P—O antisymmetric stretching vibrations.

Breitinger et al. assigned these bands at 551, 542 and 525 cm^{-1} to $\nu(Al(O/OH)_6)$ stretching vibrations. No phosphate bending modes in the work of Breitinger et al. 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). A series of bands for laueite are observed at 472 and 456 cm^{-1}. These bands 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 482 and 460 $cm^{-1}$and are attributed to the ν_2 PO_4^{3-} bending modes. Raman bands at 317, 446 and 515 cm^{-1} reported by Breitinger et al. were assigned to vibrational modes of the $AlO_6/AlOH_6$ units. Intense Raman bands at 357 and 339 cm^{-1} are assigned to the FeO and MnO ν_1 stretching vibrations. The low intensity Raman band at 731 cm^{-1} may be a second water librational mode. In the RRUFF spectrum, intense Raman bands are observed at 257 and 335 cm^{-1}.

In the infrared spectrum (Fig. 6b) a series of bands are observed at 696, 643 and 620 cm^{-1}. These bands are attributed to the ν_4 out of plane bending modes of the PO_4^{3-} units. Breitinger et al. assigned bands in this region to $\nu(Al(O/OH)_6)$ stretching vibrations. In harmony with Breitinger et al. assignments, the infrared bands observed at 732, 795 and 893 cm^{-1} are attributed to water librational modes. The Raman spectrum of laueite in the 300–100 cm^{-1} region is shown in Fig. 7. Intense Raman bands observed at 253 cm^{-1} for the laueite are related to the O—Fe—O skeletal stretching vibrations. Other bands in this part of the spectrum are noted at 226, 240, 265 and 279 cm^{-1}. The intense band in all the spectra at 161 cm^{-1} is considered to be due to H—OH hydrogen bonds. Other Raman bands are observed at 110, 115, 138, 172 and 186 cm^{-1}. These bands are simply assigned to lattice vibrations.

7. Conclusions

Raman spectroscopy complemented with infrared spectroscopy has been used to study the molecular structure of mineral laueite from Brazil. The mineral specimen was also analysed using SEM with EDX technology. Chemical formula calculated on the basis of semi-quantitative chemical analysis of the studied sample can be expressed as $(Mn^{2+}_{0.85},Fe^{2+}_{0.10}Mg_{0.05})_{\sum 1.00}(Fe^{3+}_{1.90},Al_{0.10})_{\sum 2.00}(PO_4)_2(OH)_2{\cdot}8H_2O$.

The laueite structure is based on an infinite chains of vertex-linked oxygen octahedra, with Fe^{3+} occupying the octahedral centers, the chain oriented parallel to the *c*-axis and linked by PO_4 groups. Two intense Raman bands observed at 980and 1045 cm^{-1} are assigned to the ν_1 PO_4^{3-} symmetric stretching mode. Intense Raman bands are observed at 525 and 551 cm^{-1} with a shoulder at 542 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4^{3-}. The observation of multiple bands supports the concept of non-equivalent phosphate units in the structure. As a consequence at the molecular level non-equivalent phosphate units exist in the structure and multiple phosphate vibrational modes are observed.

Acknowledgments

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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.vibspec.2015.12.001.

References

[1] W.H. Baur, Comparison of the crystal structures of pseudolaueite and laueite, Am. Mineral. 54 (1969) 1310–1321.
[2] P.J. Dunn, New occurrences for ushkovite and comments on laueite, Mineral. Rec. 16 (1985) 463–464.
[3] R.L. Frost, R. Scholz, A. Lopes, Y. Xi, Z.Z. Gobac, L.F.C. Horta, Raman and infrared spectroscopic characterization of the phosphate mineral paravauxite $Fe^{2+}Al_2(PO_4)_2(OH)_2{\cdot}8H_2O$, Spectrochim. Acta A 116 (2013) 491–496.
[4] R.L. Frost, Y. Xi, R. Scholz, F.M. Belotti, M. Candido Filho, The phosphate mineral sigloite $Fe^{3+}Al+(PO_4)_2(OH)_3{\cdot}7(H_2O)$, an exception to the paragenesis rule—a vibrational spectroscopic study, J. Mol. Struct. 1033 (2013) 258–264.
[5] P.B. Moore, The crystal structure of laueite, $Mn^{2+}Fe_2^{3+}(OH)_2(PO_4)_2(H_2O)$ $6.2H_2O$, Am. Mineral. 50 (1965) 1884–1892.
[6] P.B. Moore, Laueite, pseudolaueite, stewartite, and metavauxite. Combinatorial polymorphism, Neues Jb. Miner. Abh. 123 (1975) 148–159.
[7] P.B. Moore, T. Araki, Stewartite, $Mn^{2+}Fe_2^{3+}(OH)_2(H_2O)_6[PO_4]2.2H_2O$. Its atomic arrangement, Am. Mineral. 59 (1974) 1272–1276.
[8] M.A. Galliski, F.C. Hawthorne, Refinement of the crystal structure of ushkovite from Nevados de Palermo, Republica Argentina, Can. Mineral. 40 (2002) 929–937.
[9] P.B. Leavens, A.L. Rheingold, Crystal structures of gordonite, $MgAl_2(PO_4)_2(OH)_2(H_2O)6.2H_2O$, and its manganese analog, Neues Jb. Miner. Monat. (1988) 265–270.
[10] D.K. Breitinger, H.H. Belz, L. Hajba, V. Komlosi, J. Mink, G. Brehm, D. Colognesi, S.F. Parker, R.G. Schwab, Combined vibrational spectra of natural wardite, J. Mol. Struct. 706 (2004) 95–99.
[11] A. Galy, J. Phys. Radium 12 (1951) 827.
[12] F.S. Casciani, R.A. Condrate Sr., Proceedings International Congress on Phosphorus Compounds, 2nd edition, (1980) 175–190.