A vibrational spectroscopic study of the phosphate mineral zanazziite – $Ca_2(MgFe^{2+})(MgFe^{2+}Al)_4Be_4(PO_4)_6 \cdot 6(H_2O)$

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HIGHLIGHTS

► We have analyzed the phosphate mineral zanazziite and determined its formula.
► The mineral was studied by electron microprobe, Raman and infrared spectroscopy.
► Multiple bands in the bending region supports the concept of a reduction in symmetry of phosphate anion.

GRAPHICAL ABSTRACT
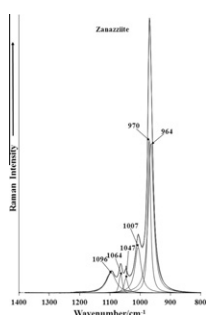
ABSTRACT

Zanazziite is the magnesium member of a complex beryllium calcium phosphate mineral group named roscherite. The studied samples were collected from the Ponte do Piauí mine, located in Itinga, Minas Gerais. The mineral was studied by electron microprobe, Raman and infrared spectroscopy. The chemical formula can be expressed as $Ca_{2.00}(Mg_{3.15},Fe_{0.78},Mn_{0.16},Zn_{0.01},Al_{0.26},Ca_{0.14})Be_{4.00}(PO_4)_{6.09}(OH)_{4.00} \cdot 5.69(H_2O)$ and shows an intermediate member of the zanazziite–greinfeinstenite series, with predominance of zanazziite member.

The molecular structure of the mineral zanazziite has been determined using a combination of Raman and infrared spectroscopy. A very intense Raman band at 970 cm^{-1} is assigned to the phosphate symmetric stretching mode whilst the Raman bands at 1007, 1047, 1064 and 1096 cm^{-1} are attributed to the phosphate antisymmetric stretching mode. The infrared spectrum is broad and the antisymmetric stretching bands are prominent. Raman bands at 559, 568, 589 cm^{-1} are assigned to the v_4 out of plane bending modes of the PO_4 and HPO_4 units. The observation of multiple bands supports the concept that the symmetry of the phosphate unit in the zanazziite structure is reduced in symmetry. Raman bands at 3437 and 3447 cm^{-1} are attributed to the OH stretching vibrations; Raman bands at 3098 and 3256 are attributed to water stretching vibrations. The width and complexity of the infrared spectral profile in contrast to the well resolved Raman spectra, proves that the pegmatitic phosphates are better studied with Raman spectroscopy.

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Introduction

Zanazziite is a calcium and magnesium beryllium hydrated phosphate mineral from the rosherite group. Zanazziite arises as barrel-shaped crystals and can reach up to 4 mm. It grows along

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side quartz or in association with others secondary phosphate minerals, including eosphorite–childrenite, montebrasite, beryllonite, fluorapatite and brazilianite. It was first found in miarolitic cavities in the granitic pegmatite named Lavra da Ilha, near Taquaral, municipality of Itinga, in northeastern Minas Gerais, Brazil. Zanazziite is named after Dr. Pier F. Zanazzi. Zanazziite has an ideal chemical formula of $Ca_2Mg_5Be_4(PO_4)_6(OH)_4 \cdot 6H_2O$ [1].

Zanazziite is one of the members of the roscherite group, which is a complex group of calcium and beryllium phosphates of general formula: $Ca_2(M_1)_2(M_2)_4Be_4(PO_4)_6(OH)_4X_2 \cdot 4H_2O$; where M_1 and M_2 are octahedral sites. M_1 is occupied by Mg, Mn^{2+}, Fe^{2+}, Fe^{3+}, Zn, and Al, however the Al dominant member is unknown. The M_1 can be also partially vacant. The M_2 sites are essentially vacant, their common occupancy usually being 1/3–1/2 per formula unit. X = OH or H_2O. In addition to zanazziite, others minerals in roscherite group are namely atencioite, footemineite, greinfenstenite, guimarãesite, roscherite and ruifrancoite [2]. Due to the complexity of the roscherite group, Rastsvetaeva et al. (2005) general formula as $Ca_2M_5Be_4(PO_4)_6(OH)_4 \cdot n(H_2O)$, where M is occupied by Mn, Fe, Zn, Mg and Al and $n \sim 6$.

Zanazzite belongs to the monoclinic crystal system, space group $C2/c$ [3–5]. The unit cell parameters are: $a = 15.876$ Å, $b = 11.860$ Å, $c = 6.607$ Å, and $\beta = 95.49°$. The axial ratio of zanazziite is $a = 1.3391$, $b = 1$ and $c = 0.5571$. There is uncertainty in analyzing zanazziites distribution of cations on M_1 and M_2 sites. The M_2 site in zanazziite is indistinct; it contains two Me–O bond distances, and two Me–OH bond distances. In X-ray scattering and diffraction models the data presents an approximation of the number of electrons in each atomic site, giving 17.3 e− in the M_2 site and 64.8 e− in the M_1 site. The crystals in zanazziite are prismatic to bladed, usually rough, barrel-shaped, with indices {100}, {110} and {001}. Cleavages are on {100} good, and {010} distinct.

Characterization of beryllium mineral paragenesis is an important tool in the petrogenetic study of granitic and alkaline pegmatites [6]. Be metal is an important element in industry with different applications in metallurgy, especially in the production of copper, aluminum and magnesium alloys. Due to its stiffness, light weight and dimensional stability over a wide temperature range beryllium has also importance for the defense and aerospace industry. Beryllium is also a hazardous element and is responsible to development of chronic beryllium disease (CBD) [7,8], arousing interest in the environmental sciences.

Be phosphates are relatively rare in nature and are related to the hydrothermal and supergene process in granitic pegmatites [9]. A number of 26 phosphate minerals are known in nature and approved by the International Mineralogical Association. Černý [10] and Černá et al. [11] described beryllium phosphates as secondary product of latte alteration of beryl. In recent years, spectroscopic studies concerning phosphate minerals are increasing, especially due to their industrial and technological importance; however, only near-infrared vibrational spectroscopic data are available on zanazziite [12].

Farmer [13] 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 (v_1) at 938 cm^{-1}, the antisymmetric stretching mode (v_3) at 1017 cm^{-1}, the symmetric bending mode (v_2) at 420 cm^{-1} and the v_4 mode at 567 cm^{-1} [14–16]. The value for the v_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavellite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrenite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4 units.

The value for the v_2 symmetric bending vibration of PO_4 units as determined by infrared spectroscopy was given as 438 cm^{-1} (augelite), 452 cm^{-1} (wavellite), 440 and 415 cm^{-1} (rockbridgeite), 455, 435 and 415 cm^{-1} (dufrenite) and 470 and 450 cm^{-1} (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the PO_4 units. This symmetry reduction is also observed through the v_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015 cm^{-1}; wavellite at 1145, 1102, 1062 and 1025 cm^{-1}; rockbridgeite at 1145, 1060 and 1030 cm^{-1}; dufrenite at 1135, 1070 and 1032 cm^{-1}; and beraunite at 1150, 1100, 1076 and 1035 cm^{-1}. In the infrared study of triploidite, a basic manganese phosphate, Farmer reports the infrared spectrum with the (v_1) at 957 cm^{-1}, (v_3) at 1090, 1058, 1030 and 1010 cm^{-1}, (v_2) at 420 cm^{-1} and the v_4 mode at 595, 570, 486 cm^{-1} [12]. A hydroxyl stretching frequency of 3509 cm^{-1} was given. In the spectroscopic study of strengite, in the region below to 400 cm^{-1}, Frost and Weier [17] described the metal stretching vibrations for MnO and also the OMnO bending modes.

In this work, samples of a pure, monomineral zanazziite from the Ponte do Piauí pegmatite, located in the municipality of Itinga, Minas Gerais, Brazil has been carried out. Studies include chemistry via electron microprobe analysis in the WDS mode (EMP), spectroscopic characterization of the structure with infrared and Raman spectroscopy.

Geological setting, occurrence and general appearance

The studied samples were collected from the Ponte do Piauí mine, located in the Piauí valley, municipality of Itinga. The region is well-known as an important source of rare phosphates and gemological minerals. The pegmatite is located in the Araçuaí pegmatite district, one of the subdivisions of the Eastern Brazilian Pegmatite province (EBP) [18]. The Araçuaí pegmatite district covers an area of about 10,000 km^2, in the northern region of Minas Gerais, in the Jequitinhonha River basin, about 560 km north of Belo Horizonte.

The Ponte do Piauí is mined for gemstones and samples for the collectors market. The pegmatite is heterogeneous with well-developed mineralogical and textural zoning. The pegmatite is hosted by cordierite–biotite-quartz schists with minor intercalations of calcsilicate rocks of the Salinas Formation. Tourmalinization is observed in the contact between the pegmatite and the host rock. Hydrothermal and metasomatic fluids were responsible for the development of miarolitic cavities. Primary phosphates were not observed.

The primary mineral association is represented by quartz, muscovite, microcline, schorl and almandine–spessartine. The secondary association is mainly composed by albite, Li bearing micas, cassiterite, elbaite and hydrothermal rose quartz. In the Ponte do Piauí pegmatite, secondary phosphates, namely eosphorite, fluorapatite, zanazziite, occur in miarolitic cavities in association with albite, quartz and muscovite. Zanazziite grows usually along the surface of quartz and albite.

Experimental

Samples description and preparation

For the development of this work, olive-green zanazziite single crystals were chosen for our investigation. Samples were collected in the Ponte do Piauí mine and was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais with sample code SAA-094.
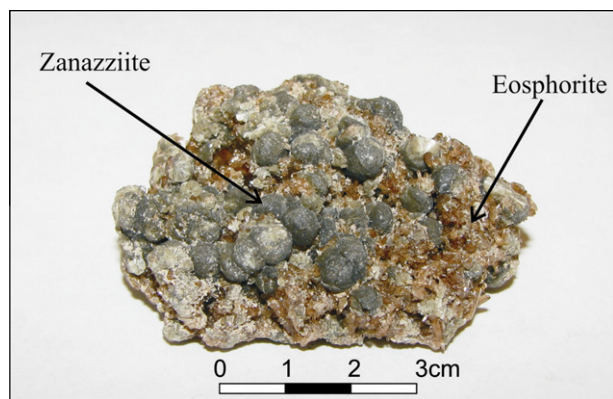
Fig. 1. Aggregate of zanazziite and eosphorite from Ponte do Piauí mine.

The mine is located in Itinga, north of Minas Gerais. To remove contaminated phases, with the support of a Stereomicroscope Leica Model EZ4, zanazziite crystals were hand selected from a sample in association with eosphorite (Fig. 1). The zanazziite crystal aggregates were phase analyzed by X-ray powder diffraction and scanning electron microscopy in the EDS mode (SEM/EDS).

Electron microprobe analysis (EMP)

A quantitative chemical analysis was carried via EMP. Two zanazziite crystals of the same aggregate selected for this study were analyzed. The chemical formula was calculated with medium values obtained in the two crystals.

The chemical analysis was carried out with a Jeol JXA8900R spectrometer from the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. For each selected element was used the following standards: Fe and Mg – olivine, Mn – rodhonite, P and Ca – Apatite Artimex, Al – Corundum, and Zn – ZnS. Beryllium and H_2O were calculated by stoichiometry. The epoxy embedded zanazziite samples were polished in the sequence of 9 μm, 6 μm and 1 μm diamond paste MetaDI® II Diamond Paste – Buhler, using water as a lubricant, with a semi-automatic MiniMet® 1000 Grinder–Polisher – Buehler. Finally, the epoxy embedded zanazziite was coated with a thin layer of evaporated carbon. The electron probe microanalysis in the WDS (wavelength dispersive spectrometer) mode was obtained at 15 kV accelerating voltage and beam current of 10 nA. Chemical formula was calculated on the basis of 34 atoms (O, OH, H_2O).

Thermogravimetric analysis – TG/DTG

Thermogravimetric analysis of the reddingite mineral were obtained by using TA Instruments Inc. Q500 high- resolution TGA operating at a 5 °C/min ramp with 6.0 °C resolution from room temperature to 1000 °C in a high-purity flowing nitrogen atmosphere (40 cm³/min). Approximately 22 mg of finely ground dried sample was heated in an open platinum crucible. The result of the thermal analysis is given in the supplementary information.

Raman microprobe spectroscopy

Fragments of the zanazziite sample 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. The spectra were collected over night. Raman Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. The Raman spectrum of at least 10 fragments was collected to ensure the consistency of the spectra.

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. The infrared spectra are given in the supplementary information.

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 samples is presented in Table 1. Composition is the result of medium values of

Table 1
Chemical composition of zanazziite from Ponte do Piauí pegmatite (mean of chemical analysis of 2 crystals). H_2O measured by mass loss and Be calculated by stoichiometry.

Constituent	wt.%	Number of cations		Range (wt.%)	Probe standard
CaO	10.26	2.14		11.25–11.27	Apatite
MgO	11.82	3.15		11.67–11.96	Olivine
FeO	5.27	0.78		5.08–5.47	Olivine
MnO	1.07	0.16		1.05–1.09	Rodhonite
ZnO	0.04	0.01		0.00–0.07	ZnS
BeO	10.30	4.00		Calculated by stoichiometry	
Al₂O₃	2.53	0.26		2.46–2.60	Corundum
P₂O₅	40.58	6.09		39.99–41.18	Apatite
H₂O (total)	13.00	7.69	OH – 4.00	Measured by mass loss	
			H₂O – 5.69		
Total	95.87	26.34			

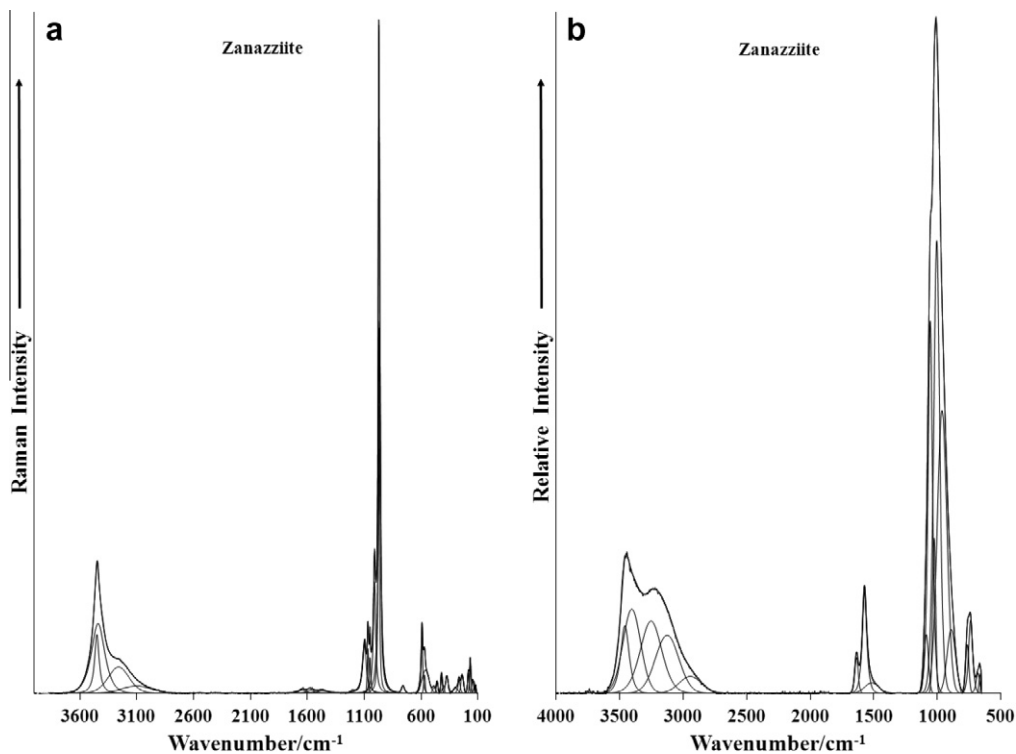**Fig. 2.** (a) Raman spectrum of zanazziite over the 100–4000 cm⁻¹ spectral range. (b) Infrared spectrum of zanazziite over the 500–4000 cm⁻¹ spectral range.
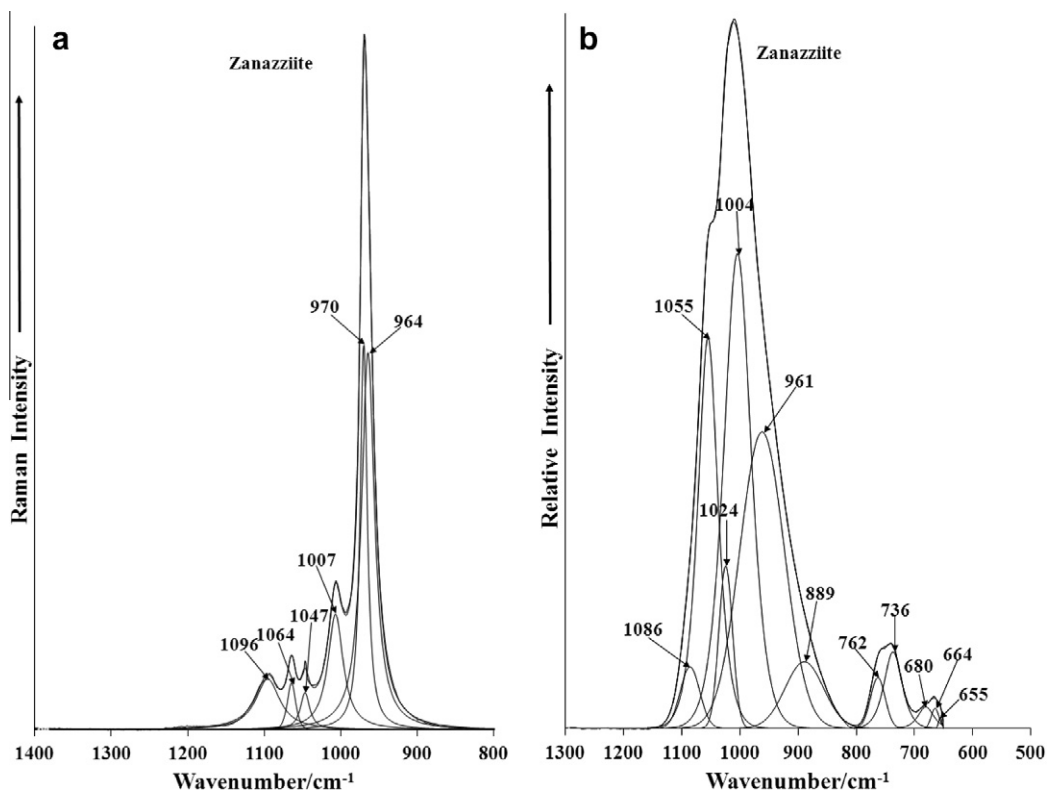

Fig. 3. (a) Raman spectrum of zanazziite over the 800–1400 cm⁻¹ spectral range. (b) Infrared spectrum of zanazziite over the 500–1300 cm⁻¹ spectral range.

measurements in 2 crystals. $H_2O \cdot H_2O$ content was measured by mass loss (ML) observed in the TG curve. The beryllium contents was calculated by stoichiometry according to the zanazziite–greinfeinstenite series and the chemical formula was calculated on the basis of 34 oxygen atoms (O, OH, H_2O) on the structure. The chemical composition indicates an intermediate

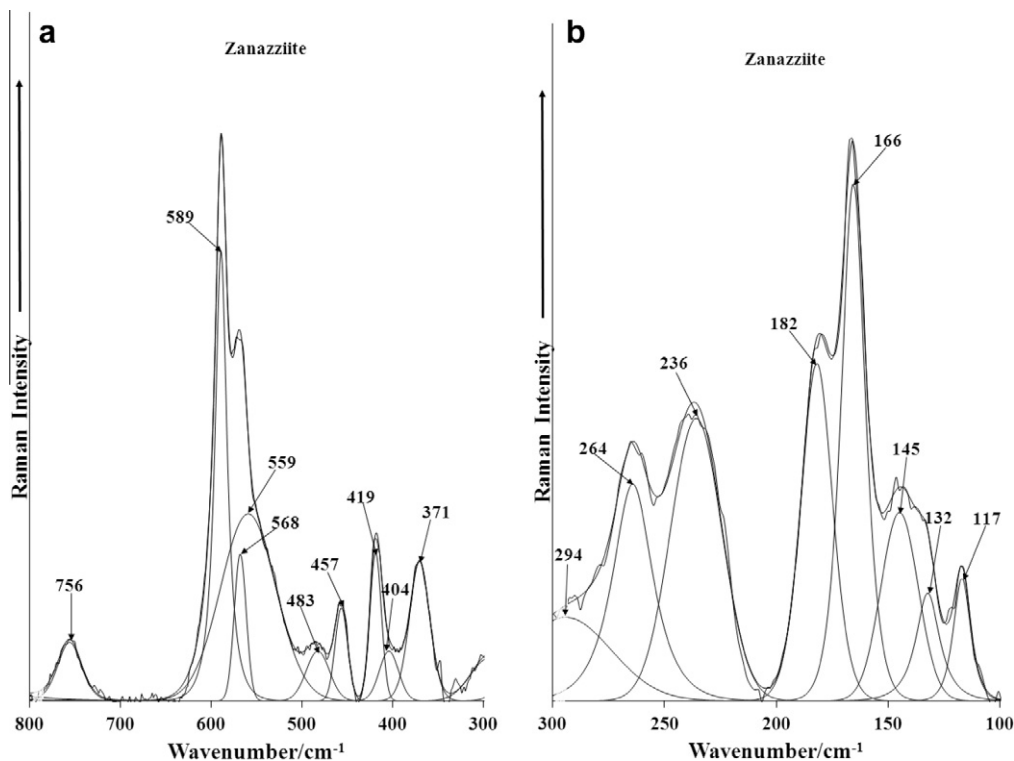**Fig. 4.** (a) Raman spectrum of zanazziite over the 300–800 cm^{-1} spectral range. (b) Raman spectrum of zanazziite over the 100–300 cm^{-1} spectral range.

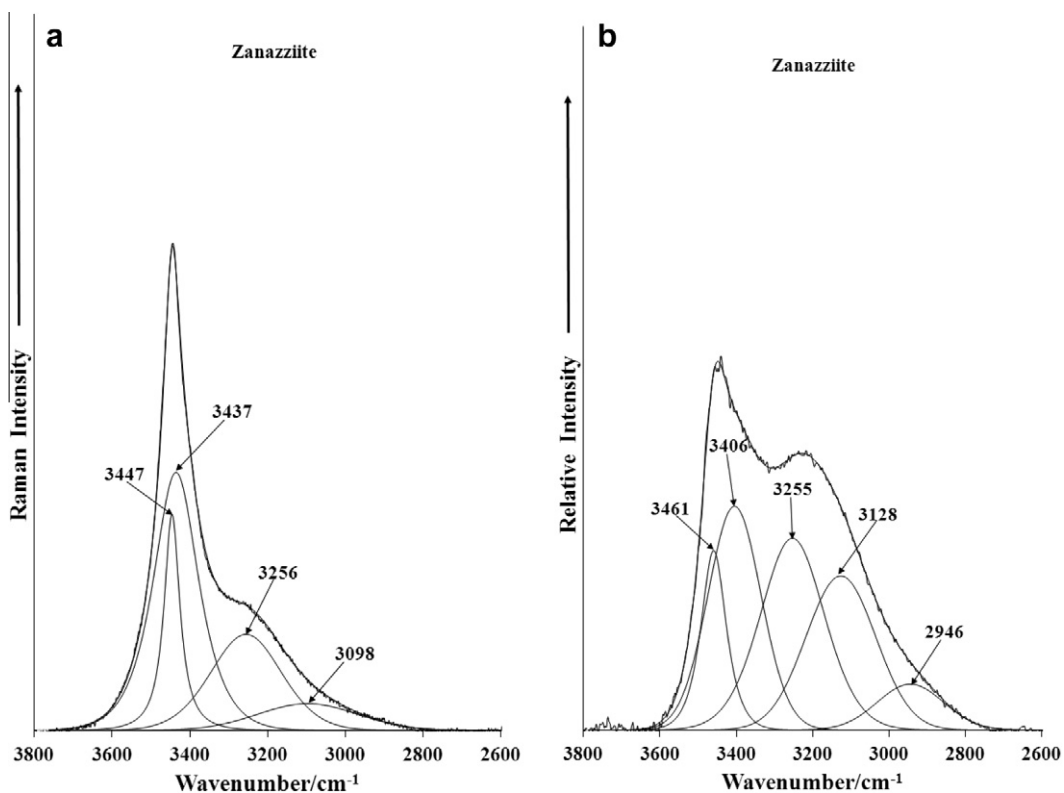**Fig. 5.** (a) Raman spectrum of zanazziite over the 2600–4000 cm^{-1} spectral range. (b) Infrared spectrum of zanazziite over the 2600–4000 cm^{-1} spectral range.

member of the zanazziite–greinfeinstenite series with predominance of zanazziite in relation to the greinfeinstenite end member. Impurities of Mn, Zn and Al were also measured.

The measured Ca amount is higher than the calculated value for the zanazziite–greifeinstenite series, and suggest the presence of Ca in the M site.
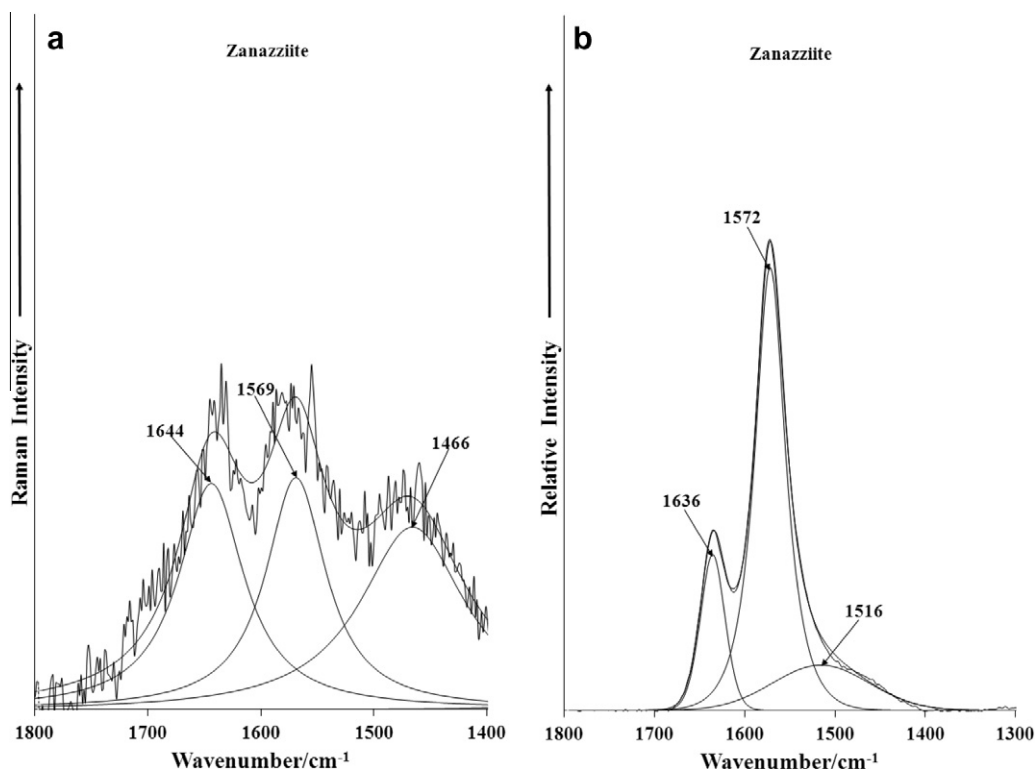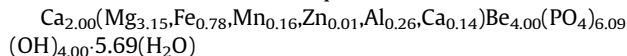
Fig. 6. (a) Raman spectrum of zanazziite over the 1300–1800 cm^{-1} spectral range. (b) Infrared spectrum of zanazziite over the 1300–1800 cm^{-1} spectral range.

Chemical formula can be expressed as:

$Ca_{2.00}(Mg_{3.15},Fe_{0.78},Mn_{0.16},Zn_{0.01},Al_{0.26},Ca_{0.14})Be_{4.00}(PO_4)_{6.09}$
$(OH)_{4.00}\cdot 5.69(H_2O)$

The total occupancy of the M site is 4.5 atoms. In comparison to the general formula where M site is occupied by 5 atoms, the difference can be considered due to vacancy [3].

Spectroscopy

The Raman spectrum of zanazziite in the 100–4000 cm^{-1} spectral range is illustrated in Fig. 2a. This spectrum displays the position and relative intensity of the Raman bands. It is noted and spectral intensity in the 2600–4000 cm^{-1} spectral region is minimal. It is noted that there are large parts of the spectrum where no intensity is observed. Thus, the spectrum is divided into sections according to the type of vibration being observed. The most intense bands are observed in the phosphate stretching region around 1000 cm^{-1}. Significant intensity is found in the hydroxyl stretching region. The infrared spectrum of zanazziite over the 500–4000 cm^{-1} spectral range is shown in Fig. 2b. This figure records the position and relative intensity of the infrared bands. Some strong intensity in the OH stretching region is now observed.

The Raman spectrum of zanazziite in the 800–1400 cm^{-1} spectral region is reported in Fig. 3a. This spectral region is the region of the phosphate stretching vibrations. The most intense band is observed at 964 and 970 cm^{-1}. This band is attributed to the $v_1 PO_4^{3-}$ symmetric stretching vibration. Other Raman bands are observed at 1007, 1047, 1064 and 1096 cm^{-1} and are assigned to the $v_3 PO_4^{3-}$ antisymmetric stretching vibration. The infrared spectrum of zanazziite is reported in Fig. 3b. An intense infrared spectrum is observed. The complex spectral profile may be resolved into component bands with bands resolved at 961, 1004, 1024, 1055 and 1086 cm^{-1}. The infrared band at 1004 is probably the $v_3 PO_4^{3-}$ symmetric stretching vibration. The latter three bands are assigned to the $v_3 PO_4^{3-}$ antisymmetric stretching vibration.

Infrared bands in the 600–800 cm^{-1} spectral region (Fig. 3b) are attributed to hydroxyl deformation modes. This band is also observed in the Raman spectrum at 756 cm^{-1} (Fig. 4a). The Raman spectrum of zanazziite in the 300–800 cm^{-1} spectral range is reported in Fig. 4a. This part of the Raman spectrum may be divided into three regions: (a) bands in the 550–650 cm^{-1} spectral region (b) bands centered around 455 cm^{-1} and (c) bands in the 300–380 cm^{-1} spectral range. The first group of bands at 559, 568, 589 cm^{-1} are assigned to the v_4 out of plane bending modes of the PO_4 and HPO_4 units. The Raman spectrum of NaH_2PO_4 shows Raman bands at 526, 546 and 618 cm^{-1}. The observation of multiple bands in this spectral region supports the concept of symmetry reduction of both the phosphate units. The second group of bands at 404, 419, 457 and 483 cm^{-1} are attributed to the v_2 PO_4 and HPO_4 bending modes. The Raman spectrum of NaH_2PO_4 shows two Raman bands at 460 and 482 cm^{-1}. The observation of multiple Raman bands for the zanazziite mineral supports the concept of symmetry reduction. The third group of bands at 236, 264 and 294 cm^{-1} are attributed to metal–oxygen vibrations.
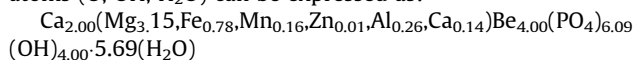
The Raman spectrum over the 2600–3800 cm^{-1} spectral range is displayed in Fig. 5a and the infrared spectrum in the same spectral region in Fig. 5b. In the Raman spectrum, bands are observed at 3098, 3256, 3437 and 3447 cm^{-1}. The bands at 3437 and 3447 cm^{-1} are attributed to the OH stretching vibrations of the OH units in the zanazziite structure. The first two Raman bands are assigned to water stretching modes. The infrared spectrum shows a series of overlapping bands. As for the analysis of the Raman spectrum, the two bands at 3406 and 3461 cm^{-1} are assigned to the stretching vibrations of OH units and the two infrared bands at 3128 and 3255 cm^{-1} are attributed to water stretching vibrations.

Interpretation of the spectra in the OH stretching region is confirmed by the study of the bands in the 1300–1800 cm^{-1} spectral region as is shown in Fig. 6a and b. The Raman spectrum suffers from a lack of signal; nevertheless, three bands may be observed at 1466, 1569 and 1644 cm^{-1}. This latter band is attributed to

the water bending mode and its position indicates that water is involved in strong hydrogen bonding. The position of the water bending mode is normally around 1625 cm^{-1} as in liquid water. Strong water hydrogen bonding gives water bending bands in the order of 1650 cm^{-1}. The Raman spectrum is in harmony with the infrared spectrum (Fig. 6b), where infrared bands are found at 1572 and 1636 cm^{-1}. This latter band is assigned to the water bending mode. The band at 1572 cm^{-1} (infrared) and 1569 cm^{-1} (Raman) is thought to be due to a hydroxyl deformation mode.

Conclusions

Zanazziite – Ca$_2$(Mn, Fe^{2+})(Mg,Fe^{2+},Al)$_4$Be$_4$(PO$_4$)$_6$(OH)$_4$·6(H$_2$O) was studied by electron microprobe in the WDS mode, Raman and infrared spectroscopy. The chemical characterization by electron microprobe shows an intermediate member in the series zanazziite–greinfeinstenite, with predominance of the zanazziite member. The mineral occurs in association with other secondary phosphates such as eosphorite in miarolitic cavities of granitic pegmatites. Chemical formula calculated on the basis of 34 oxygen atoms (O, OH, H$_2$O) can be expressed as:

Ca$_{2.00}$(Mg$_3$.15,Fe$_{0.78}$,Mn$_{0.16}$,Zn$_{0.01}$,Al$_{0.26}$,Ca$_{0.14}$)Be$_{4.00}$(PO$_4$)$_{6.09}$ (OH)$_{4.00}$·5.69(H$_2$O)

Aspects of the structure of zanazziite using vibrational spectroscopy were assessed. Raman and infrared bands associated with hydrogen phosphate and phosphate units were observed. It is apparent that all three anion types exist in the structure of zanazziite and these anionic types are enhanced by the basic nature of the mineral. The proton on the water units is apparently very mobile and enables the formation of the monohydrogen and dihydrogen phosphate units. Vibrational spectroscopy enabled an assessment of the molecular structure of zanazziite to be made.

Acknowledgments

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.2012.11.017.

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