

# Assessment of the Molecular Structure of an Intermediate Member of the Triplite-Zwieselite Mineral Series: A Raman and Infrared Study

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**ABSTRACT** The mineral series triplite-zwieselite with theoretical formula  $(\text{Mn}^{2+})_2(\text{PO}_4)(\text{F})-(\text{Fe}^{2+})_2(\text{PO}_4)(\text{F})$  from the El Criolo granitic pegmatite, located in the Eastern Pampean Ranges of Córdoba Province, was studied using electron microprobe, thermogravimetry, and Raman and infrared spectroscopy. The analysis of the mineral provided a formula of  $(\text{Fe}_{1.00}, \text{Mn}_{0.85}, \text{Ca}_{0.08}, \text{Mg}_{0.06})_{\Sigma 2.00}(\text{PO}_4)_{1.00}(\text{F}_{0.80}, \text{OH}_{0.20})_{\Sigma 1.00}$ . An intense Raman band at  $981 \text{ cm}^{-1}$  with a shoulder at  $977 \text{ cm}^{-1}$  is assigned to the  $\text{PO}_4^{3-} \nu_1$  symmetric stretching mode. The observation of two bands for the phosphate symmetric stretching mode offers support for the concept that the phosphate units in the structure of triplite-zwieselite are not equivalent. Low-intensity Raman bands at 1012, 1036, 1071, 1087, and  $1127 \text{ cm}^{-1}$  are assigned to the  $\text{PO}_4^{3-} \nu_3$  antisymmetric stretching modes. A set of Raman bands at 572, 604, 639, and  $684 \text{ cm}^{-1}$  are attributed to the  $\text{PO}_4^{3-} \nu_4$  out-of-plane bending modes. A single intense Raman band is found at  $3508 \text{ cm}^{-1}$  and is assigned to the stretching vibration of hydroxyl units. Infrared bands are observed at 3018, 3125, and  $3358 \text{ cm}^{-1}$  and are attributed to water stretching vibrations.

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**KEYWORDS** infrared spectroscopy, phosphate, Raman spectroscopy, triplite, triploidite, zwieselite

## INTRODUCTION

Triplite and zwieselite are two members of the triplite mineral group, which also includes magniotriplite. The general chemical formula of this group can be expressed as  $\text{A}_2(\text{TO}_4) \text{Z}$ , where  $\text{A} = \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}$ ;  $\text{T} = \text{P}$ , and  $\text{As}$  and  $\text{Z} = \text{F}, \text{OH}$ . Triplite and zwieselite are the  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  end members of the solid solutions. Triplite and zwieselite are common minerals in granitic pegmatites and can be also found in high-temperature hydrothermal veins. In granitic pegmatites, these minerals occur as primary minerals.<sup>[1]</sup>

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Wolfe and Heinrich<sup>[2]</sup> suggest triplite as a hydrothermal mineral from Mica Lode pegmatite, Fremont County, Colorado.

Despite the pseudocubic habitus, triplite and zwieselite crystallize in the monoclinic crystal system. The crystal structure of triplite was first determined by Waldrop.<sup>[3]</sup> The unit cell parameters are  $a = 12.065 \text{ \AA}$ ;  $b = 6.454 \text{ \AA}$ ;  $c = 9.937 \text{ \AA}$ ;  $\alpha = 90.0^\circ$ ;  $\beta = 107.093^\circ$ ;  $\gamma = 90.0^\circ$ , Space Group  $I2/a$ . The crystal structure of zwieselite was determined by Yakubovich et al.<sup>[4]</sup> and the unit cell parameters are  $11.999 \text{ \AA}$ ;  $9.890 \text{ \AA}$ ;  $6.489 \text{ \AA}$ ;  $90.0^\circ$ ;  $107.72^\circ$ ; Space Group  $I2/a$ .

Raman spectroscopy has proven most useful for the study of mineral structure. Raman spectroscopy is an important tool in the characterization of phosphates in pegmatite rocks.<sup>[5]</sup> In recent years, spectroscopic studies of phosphate minerals have been increasing, especially due to their industrial and technological importance. Published data of triplite are restricted to the RRUFF Project database (<http://rruff.info/triplite/display=default/R050614>).

Farmer<sup>[6]</sup> 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 ( $\nu_1$ ) at  $938 \text{ cm}^{-1}$ , an antisymmetric stretching mode ( $\nu_3$ ) at  $1017 \text{ cm}^{-1}$ , a symmetric bending mode ( $\nu_2$ ) at  $420 \text{ cm}^{-1}$ , and a bending mode  $\nu_4$  mode at  $567 \text{ cm}^{-1}$ .<sup>[7-9]</sup> The value for the  $\nu_1$  symmetric stretching vibration of  $\text{PO}_4$  units as determined by infrared spectroscopy was given as  $930 \text{ cm}^{-1}$  (augelite),  $940 \text{ cm}^{-1}$  (wavellite),  $970 \text{ cm}^{-1}$  (rockbridgeite),  $995 \text{ cm}^{-1}$  (dufrenite), and  $965 \text{ cm}^{-1}$  (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  $\text{PO}_4$  units.

The value for the  $\nu_2$  symmetric bending vibration of  $\text{PO}_4$  units as determined by infrared spectroscopy in Fe and Mn phosphates was given as  $440$  and  $415 \text{ cm}^{-1}$  (rockbridgeite);  $455$ ,  $435$ , and  $415 \text{ cm}^{-1}$  (dufrenite); and  $470$  and  $450 \text{ cm}^{-1}$  (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the  $\text{PO}_4$  units. This symmetry reduction is also observed through the  $\nu_3$  antisymmetric stretching vibrations.

In the infrared study of triplite, a basic manganese phosphate, Farmer reports the infrared spectrum

with the ( $\nu_1$ ) at  $957 \text{ cm}^{-1}$ ; ( $\nu_3$ ) at  $1090$ ,  $1058$ ,  $1030$ , and  $1010 \text{ cm}^{-1}$ ; ( $\nu_2$ ) at  $420 \text{ cm}^{-1}$ ; and the  $\nu_4$  mode at  $595$ ,  $570$ , and  $486 \text{ cm}^{-1}$ . A hydroxyl stretching frequency of  $3509 \text{ cm}^{-1}$  was given. In the spectroscopic study of strengite, in the region below  $400 \text{ cm}^{-1}$ , Frost and Weier<sup>[10]</sup> described the metal stretching vibrations for MnO and also the OMnO bending modes.

In this work, a sample of a member of triplite-zwieselite mineral series from the El Criolo mine, located in Córdoba Province, Argentina, was selected for analysis. Studies include chemistry via electron microprobe in the WDS mode and spectroscopic characterization of the structure with infrared and Raman spectroscopy. Thermogravimetric study was carried out to determine the thermal stability of the mineral.

## EXPERIMENTAL

### Samples Description and Preparation

A member of the triplite-zwieselite mineral series (Tr-Zw) was obtained from the collection of mineralogist Nelson Valenzuela, from Córdoba, Argentina. The sample was incorporated into the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, with sample code SAB-004. The El Criolo granitic pegmatite belongs to the Cerro Blanco pegmatite group, located in the Eastern Pampean Ranges of Córdoba Province.<sup>[11]</sup>

Tr-Zw occurs as massive blocks with reddish brown color. The fragments are transparent to translucent and the mineral occurs in association with bermanite and phosphosiderite. A fragment of a single crystal of Tr-Zw up to  $2 \text{ cm}$  was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4 (Leica, Tokyo, Japan). Scanning electron microscopy (SEM) was applied to support the mineral characterization and indicate the elements to be analyzed by electron microprobe (EMP).

### Chemical Characterization

A quantitative chemical analysis was carried out via EMP. Tr-Zw fragment selected for this study was analyzed with the performance of eight spots. The chemical analysis was carried out with a JEOL JXA8900R spectrometer (JEOL, Tokyo, Japan) from the Physics Department of the Federal University of

Minas Gerais, Belo Horizonte. For each selected element the following standards were used: Fe—Magnetite, Mn—Rodhonite, F—Fluorite, P and Ca—Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, Sr—Celestite, Al—Al<sub>2</sub>O<sub>3</sub>, and Mg—MgO. The epoxy-embedded Tr-Zw sample was polished in the sequence of 9 μm, 6 μm, and 1 μm diamond paste MetaDI II Diamond Paste (Buehler, Joinville, Brazil), using water as a lubricant, with a semiautomatic MiniMet 1000 Grinder-Polisher (Buehler, Joinville, Brazil). Finally, the epoxy-embedded Tr-Zw 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 five oxygen atoms (considering O and F).

## Thermogravimetric Analysis—TG/DTG

Thermogravimetric analysis of the Tr-Zw mineral was obtained by using a TA Instruments Inc. Q500 high-resolution TGA (New York, New York, USA) operating at a 10°C/min ramp with data sample interval of 0.50 s/pt from room temperature to 1000°C in a high-purity flowing nitrogen atmosphere (100 cm<sup>3</sup>/min). A total mass of 38.13 mg of finely ground sample was heated in an open platinum crucible.

## Raman Microprobe Spectroscopy

Crystals of Tr-Zw were placed on a polished metal surface on the stage of an Olympus BHSM microscope (Olympus, Tokyo, Japan), which is equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system (Renishaw, London, UK), 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 (Spectra-Physics, London, UK) producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm<sup>-1</sup> and a precision of ±1 cm<sup>-1</sup> in the range between 200 and 4000 cm<sup>-1</sup>. 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<sup>-1</sup> line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

## Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer (Thermo Scientific, Sydney, Australia) with a smart endurance single-bounce diamond ATR cell. Spectra over the 4000–525 cm<sup>-1</sup> range were obtained by the coaddition of 128 scans with a resolution of 4 cm<sup>-1</sup> and a mirror velocity of 0.6329 cm/s. Spectra were coadded 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 Spectralcalc software package GRAMS (Galactic Industries Corporation, Salem, New Hampshire, USA). Band component analysis was undertaken using the Jandel “Peakfit” software package that enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Lorentzian-Gaussian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of *r*<sup>2</sup> greater than 0.995.

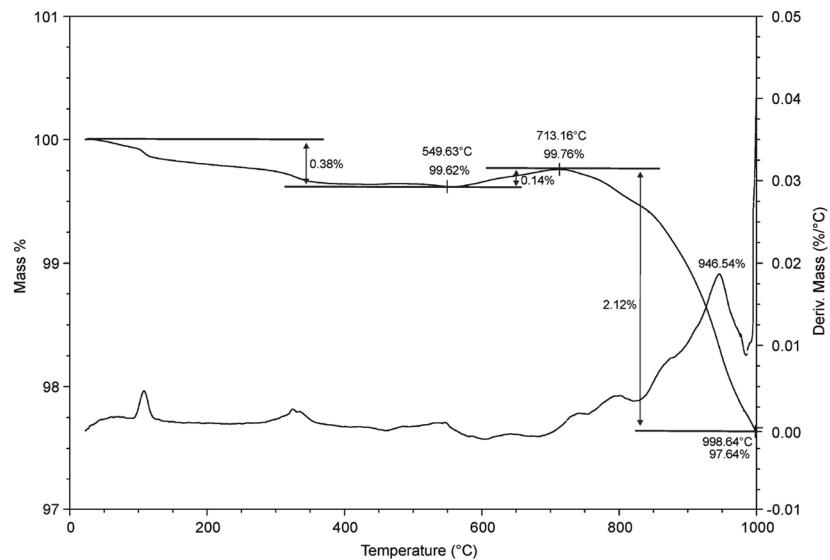
## RESULTS AND DISCUSSION

### Chemical Characterization

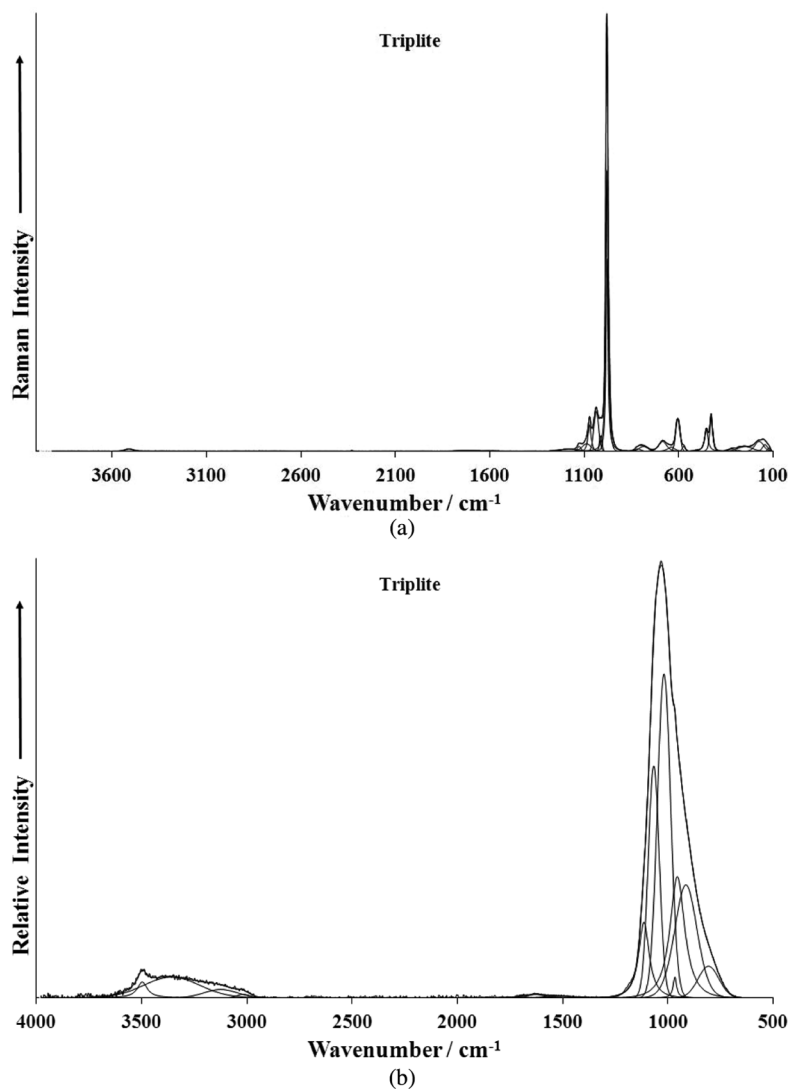
The quantitative chemical analysis of Tr-Zw is presented in Table 1. The composition was calculated

**TABLE 1** Chemical Composition of Tr-Zw from the El Criolo Pegmatite (Mean of 10 Electron Microprobe Analyses; H<sub>2</sub>O Calculated by Stoichiometry)

Constituent	Wt%	Range (wt%)	Number of atoms	Probe standard
FeO	31.49	30.76–32.36	1.00	Magnetite
MgO	0.99	0.86–1.05	0.06	MgO
Al <sub>2</sub> O <sub>3</sub>	0.02	0.00–0.77	0.00	Al <sub>2</sub> O <sub>3</sub>
P <sub>2</sub> O <sub>5</sub>	32.86	32.15–33.37	1.00	Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
MnO	26.60	26.00–27.67	0.85	Rodhonite
CaO	2.06	0.26–2.88	0.08	Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
SrO	0.05	0.00–0.13	0.00	Celestite
F	7.49	6.87–8.15	0.80	Fluorite
H <sub>2</sub> O	0.93	Calculated by stoichiometry	0.20	
O = F	–3.16			
Total	99.33		3.99	



**FIGURE 1** Thermogravimetric analysis of triplite-zwieselite mineral series.



**FIGURE 2** (a) Raman spectrum of Tr-Zw (upper spectrum) over the 100–4000  $\text{cm}^{-1}$  spectral range. (b) Infrared spectrum of Tr-Zw (lower spectrum) over the 500–4000  $\text{cm}^{-1}$  spectral range.

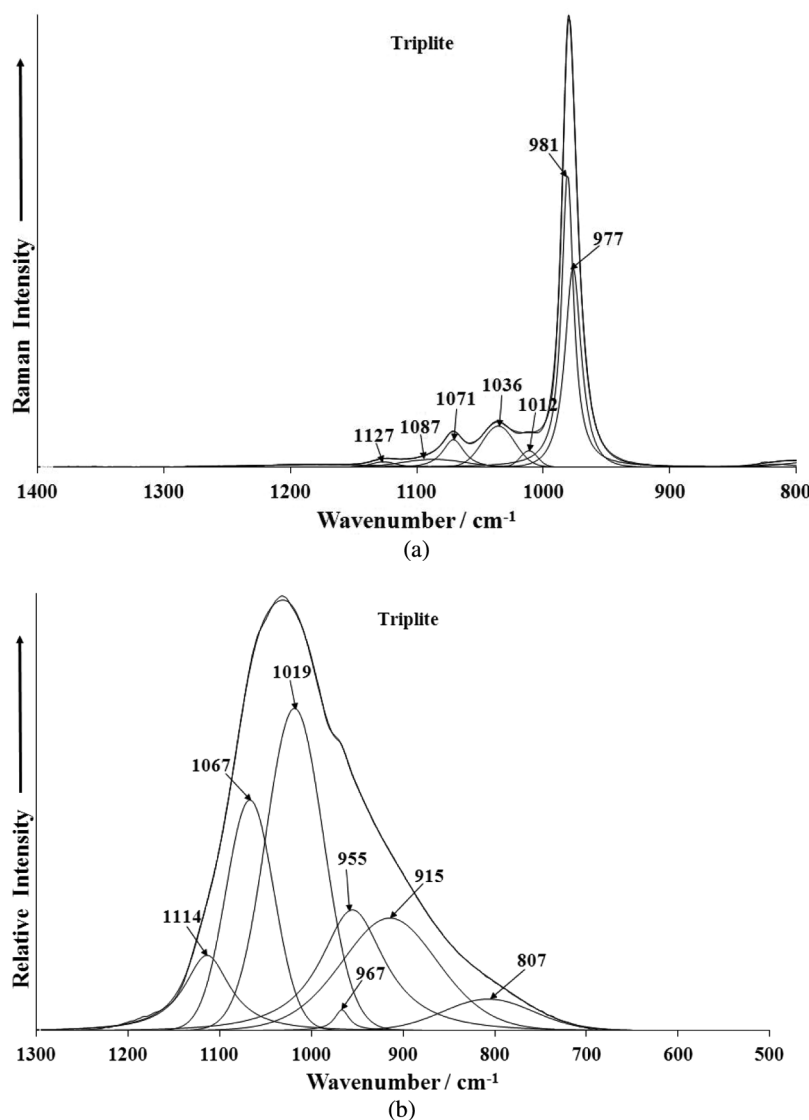
as mean values in 10 spots. The range of the chemical analysis is also presented and shows no significant variance.  $\text{H}_2\text{O}$  content was calculated by stoichiometry considering  $\text{F} + \text{OH} = 1$ . The chemical formula was calculated on the basis of 5 oxygen atoms (O, F) in the structure. The chemical composition indicates an iron-rich phase with partial substitution of manganese and minor calcium and magnesium. The chemical formula of the studied sample can be expressed as:  $(\text{Fe}_{1.00}, \text{Mn}_{0.85}, \text{Ca}_{0.08}, \text{Mg}_{0.06})_{\Sigma 2.00}(\text{PO}_4)_{1.00}(\text{F}_{0.80}, \text{OH}_{0.20})_{\Sigma 1.00}$ .

The solid-solution member of the triplite-zwieselite series has an  $\text{Fe}/(\text{Fe} + \text{Mn})$  ratio of 0.54 and an  $\text{F}/(\text{F} + \text{OH})$  ratio of 0.80. The results are similar with data published by Keller and von Knorring.<sup>[1]</sup> The pattern for the thermogravimetric analysis is presented in

Fig. 1. The TG curve shows a total mass loss of about 2.36% on heating to  $1000^\circ\text{C}$  and resulting in the melting of sample. In the temperature range of  $25^\circ\text{C}$  to around  $550^\circ\text{C}$  is observed a mass loss of around 0.38%. From a temperature up to  $550\text{--}713^\circ\text{C}$  is observed a slight increase of mass of about 0.14%. In the range of  $713\text{--}1000^\circ\text{C}$  was observed a mass loss of about 2.12%, resulting in a total mass loss of 2.36%. This result is in agreement with data published by Mandarino et al.<sup>[12]</sup> An exothermic reaction was observed at  $946.5^\circ\text{C}$ .

## VIBRATIONAL SPECTROSCOPY

Vibrational spectroscopy is most useful for the assessment of the molecular structure of triplite.

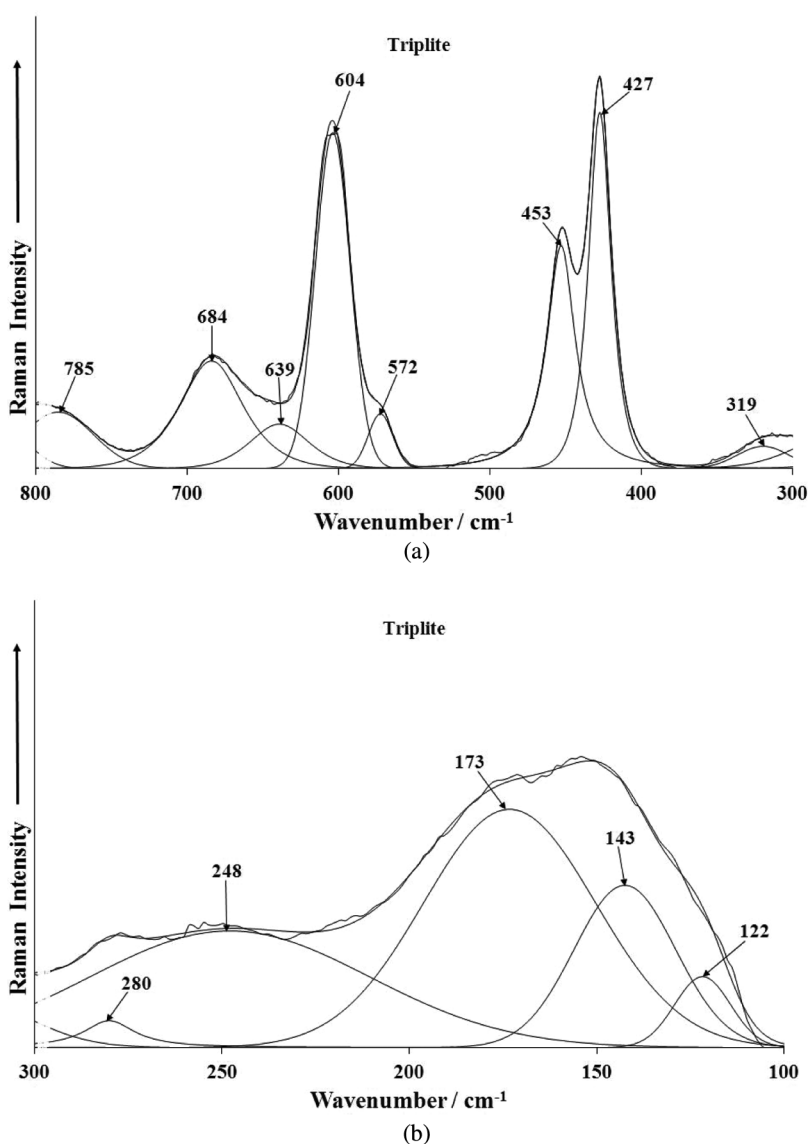


**FIGURE 3** (a) Raman spectrum of Tr-Zw (upper spectrum) over the  $800\text{--}1400\text{ cm}^{-1}$  spectral range. (b) Infrared spectrum of Tr-Zw (lower spectrum) over the  $500\text{--}1300\text{ cm}^{-1}$  spectral range.

Figure 2 shows the Raman and infrared spectra of the triplite-zwieselite mineral sample. The Raman spectrum of triplite-zwieselite over the  $4000\text{--}100\text{ cm}^{-1}$  spectral range is shown in Fig. 2a. This spectrum displays the position and intensity of the Raman bands. It is obvious that there are large parts of the spectrum where no intensity is observed. Consequently, the Raman spectrum is subdivided into sections depending on the type of vibration being studied. The infrared spectrum of triplite-zwieselite over the  $4000\text{--}500\text{ cm}^{-1}$  spectral range is reported in Fig. 2b. As for the Raman spectrum, there are large parts of the infrared spectrum where no intensity is found and therefore the spectrum is subdivided into

sections depending on the type of vibration being examined.

The Raman spectrum of triplite-zwieselite over the  $1400\text{--}800\text{ cm}^{-1}$  spectral range is illustrated in Fig. 3a. The Raman spectrum is dominated by an intense sharp band at  $981\text{ cm}^{-1}$ . This band is assigned to the  $\text{PO}_4^{3-} \nu_1$  symmetric stretching mode. The band shows some asymmetry and a second band may be resolved at  $977\text{ cm}^{-1}$ . The observation of two bands for the phosphate symmetric stretching mode offers support for the concept that the phosphate units in the structure of triplite-zwieselite are not equivalent. Farmer<sup>[6]</sup> reports the infrared spectra of a wide range of phosphate minerals (see, for example, Table 1

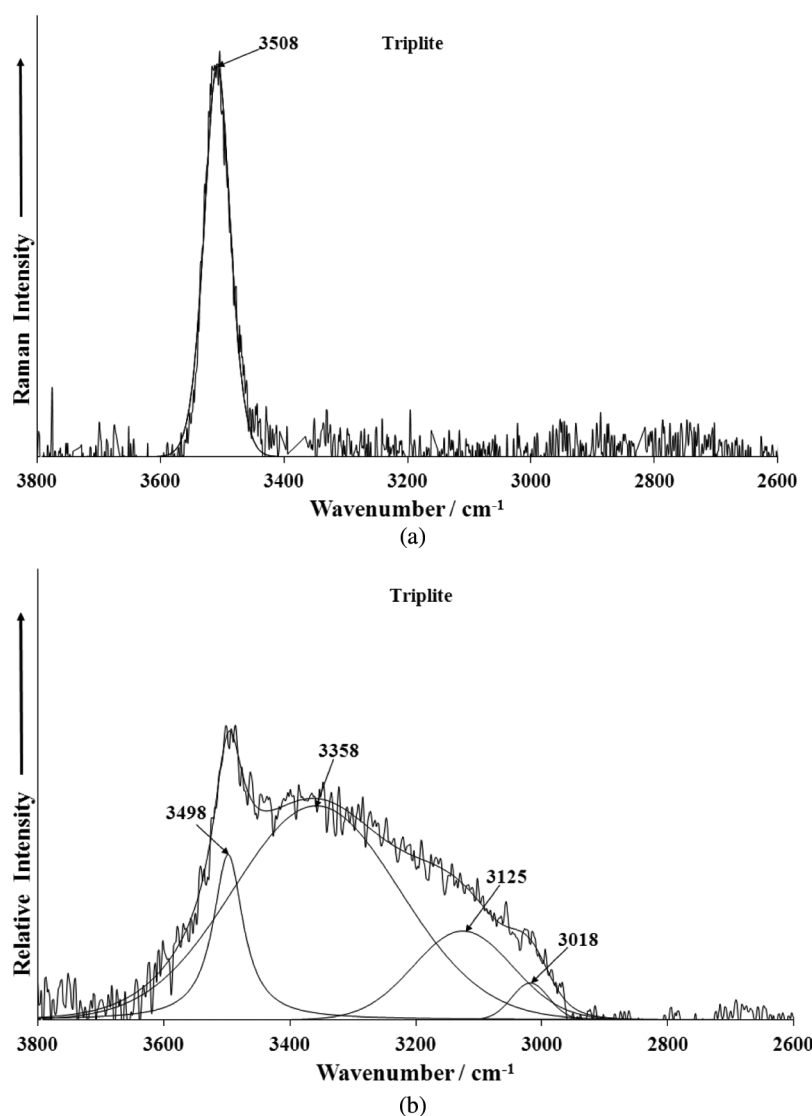


**FIGURE 4** (a) Raman spectrum of Tr-Zw (upper spectrum) in the  $300\text{--}800\text{ cm}^{-1}$  spectral range. (b) Raman spectrum of Tr-Zw (lower spectrum) in the  $100\text{--}300\text{ cm}^{-1}$  spectral range.

7.VII on page 392). The determined formula of the studied mineral is  $(\text{Fe}_{1.00}, \text{Mn}_{0.85}, \text{Ca}_{0.08}, \text{Mg}_{0.06})_{\Sigma 2.00}(\text{PO}_4)_{1.00}(\text{F}_{0.80}, \text{OH}_{0.20})_{\Sigma 1.00}$ . The triplite-zwieselite mineral is fundamentally a phosphate of Fe and Mn. The position of the phosphate symmetric stretching mode is a function of the cationic composition and therefore will vary with the Fe/Mn ratio. There have been almost no studies of the Raman spectra of triplite or zwieselite and their solid solutions.<sup>[13]</sup> Some spectra have been reported but no band assignments were forthcoming. The Raman spectrum in Fig. 3a displays a series of low-intensity bands at 1012, 1036, 1071, 1087, and 1127  $\text{cm}^{-1}$ . These bands are assigned to the  $\text{PO}_4^{3-} \nu_3$  antisymmetric stretching modes. The observation of multiple

bands supports the concept of a reduction of symmetry of the phosphate unit in the triplite-zwieselite structure.

The infrared spectrum of triplite-zwieselite over the 1300–500  $\text{cm}^{-1}$  spectral range is illustrated in Fig. 3b. A complex spectral profile is observed with a number of overlapping bands that may be resolved. The shoulder band centered at 955  $\text{cm}^{-1}$  may be assigned to the  $\text{PO}_4^{3-} \nu_1$  symmetric stretching mode; however, as the spectral profile is broad, this assignment is uncertain. The series of resolved bands at 1019, 1067, and 1114  $\text{cm}^{-1}$  are attributed to the  $\text{PO}_4^{3-} \nu_3$  antisymmetric stretching mode of triplite-zwieselite. As for the Raman spectrum, there have been almost no studies reporting the infrared spectra of the



**FIGURE 5** (a) Raman spectrum of Tr-Zw (upper spectrum) in the 2600–3800  $\text{cm}^{-1}$  spectral range. (b) Infrared spectrum of Tr-Zw (lower spectrum) in the 2600–3800  $\text{cm}^{-1}$  spectral range.

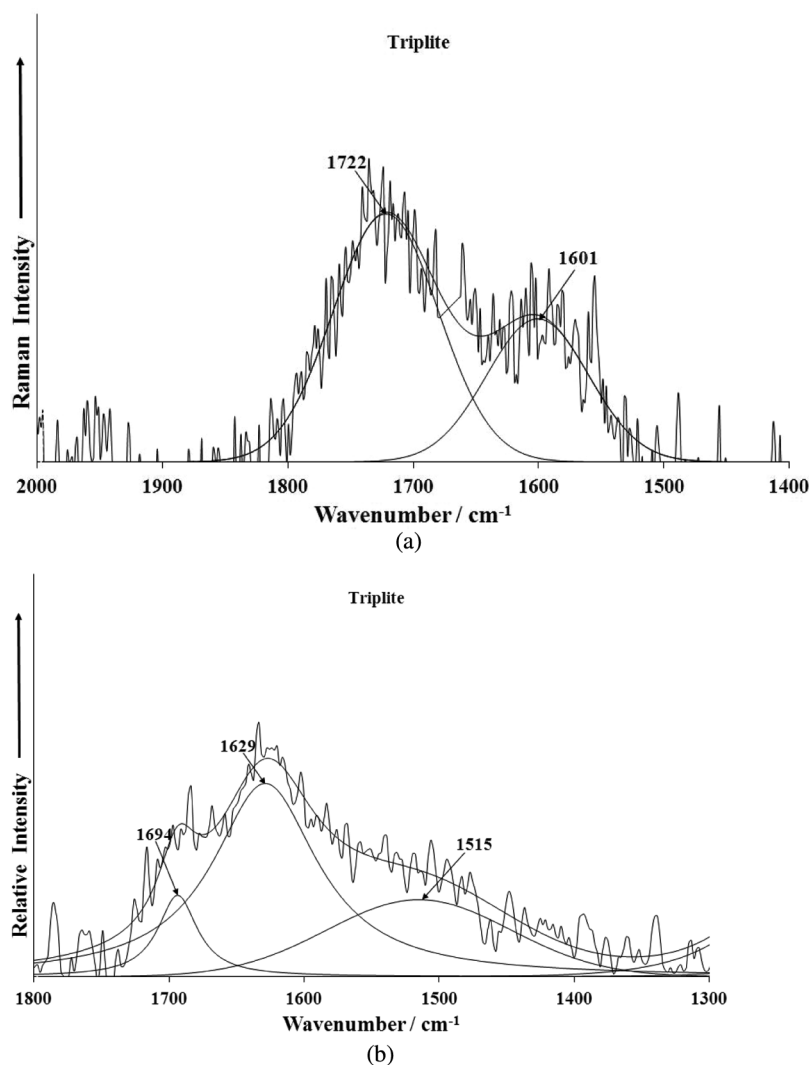
triplite-zwieselite series.<sup>[14]</sup> Certainly no attempts at band assignments have been made.

The Raman spectrum of triplite-zwieselite in the 800–300  $\text{cm}^{-1}$  spectral range is reported in Fig. 4a. The Raman spectrum over the 300–100  $\text{cm}^{-1}$  spectral region is reported in Fig. 4b. The first spectral region is where the phosphate bending modes are to be found. A series of Raman bands at 572, 604, 639, and 684  $\text{cm}^{-1}$  are observed and attributed to the  $\text{PO}_4^{3-}$   $\nu_4$  out-of-plane bending modes. A comparison may be made with other phosphate-containing minerals. A set of three bands for hopeite are observed at 634, 596, and 569  $\text{cm}^{-1}$  and are attributed to the  $\nu_4$  bending modes. Pawlig et al. reported bands at 637, 598, and 565  $\text{cm}^{-1}$ .<sup>[15]</sup> The two sets of results are in excellent agreement. Two bands

observed at 427 and 453  $\text{cm}^{-1}$  are assigned to the  $\text{PO}_4^{3-}$   $\nu_2$  bending modes. The band at 319  $\text{cm}^{-1}$  is thought to be a metal-oxygen stretching vibration. Raman bands in the far low wavenumber region are simply described as due to lattice vibrations.

The Raman spectrum of triplite-zwieselite in the 3800–2600  $\text{cm}^{-1}$  spectral range is reported in Fig. 5a. A single intense band is found at 3508  $\text{cm}^{-1}$  and is assigned to the stretching vibration of OH units. This band is observed at 3498  $\text{cm}^{-1}$  in the infrared spectrum (Fig. 5b). This band is superimposed on a broad spectral profile. Additional bands are observed at 3018, 3125, and 3358  $\text{cm}^{-1}$ . These bands may be attributed to water stretching vibrations.

The Raman spectrum of triplite-zwieselite in the 1400–2000  $\text{cm}^{-1}$  spectral range is reported in Fig. 6a.



**FIGURE 6** (a) Raman spectrum of Tr-Zw (upper spectrum) in the 1400–2000  $\text{cm}^{-1}$  spectral range. (b) infrared spectrum of Tr-Zw (lower spectrum) in the 1300–1800  $\text{cm}^{-1}$  spectral range.



The Raman spectrum suffers from a lack of signal; nevertheless, two Raman bands are observed at 1601 and 1722  $\text{cm}^{-1}$ . The infrared spectrum also lacks signal. Two broad bands are found at 1629 and 1694  $\text{cm}^{-1}$ . The Raman peak at 1601  $\text{cm}^{-1}$  and the infrared peak at 1629  $\text{cm}^{-1}$  are ascribed to water bending modes.

## CONCLUSIONS

We have studied the mineral series triplite-zwieselite with theoretical formula  $(\text{Mn}^{2+})_2(\text{PO}_4)(\text{F})-(\text{Fe}^{2+})_2(\text{PO}_4)(\text{F})$  from the El Criolo granitic pegmatite using electron microprobe, thermogravimetry, and Raman and infrared spectroscopy.

The chemical formula of the studied sample was found to be  $(\text{Fe}_{1.00}, \text{Mn}_{0.85}, \text{Ca}_{0.08}, \text{Mg}_{0.06})_{\Sigma 2.00}(\text{PO}_4)_{1.00}(\text{F}_{0.80}, \text{OH}_{0.20})_{\Sigma 1.00}$ . Thermogravimetry showed a mass loss of around 2.36% on heating to 1000°C.

Vibrational spectroscopy enables an assessment of the molecular structure of the triplite-zwieselite intermediate mineral sample. Two symmetric stretching modes are observed, implying that the phosphate units in the triplite-zwieselite intermediate structure are not equivalent.

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