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# Raman spectroscopic study of the tellurite minerals: carlfriesite and spiroffite

Ray L. Frost, • Marilla J. Dickfos and Eloise C. Keefe

Inorganic Materials Research Program, School of Physical and Chemical Sciences,  
Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001,  
Australia.

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## Abstract

Raman spectroscopy has been used to study the tellurite minerals spiroffite and carlfriesite, which are minerals of formula type  $A_2(X_3O_8)$  where A is  $Ca^{2+}$  for the mineral carlfriesite and is  $Zn^{2+}$  and  $Mn^{2+}$  for the mineral spiroffite. Raman bands for spiroffite observed at  $721$  and  $743\text{ cm}^{-1}$ , and  $650\text{ cm}^{-1}$  are attributed to the  $\nu_1$   $(Te_3O_8)^{2-}$  symmetric stretching mode and the  $\nu_3$   $(Te_3O_8)^{2-}$  antisymmetric stretching modes respectively. A second spiroffite mineral sample provided a Raman spectrum with bands at  $727\text{ cm}^{-1}$  assigned to the  $\nu_1$   $(Te_3O_8)^{2-}$  symmetric stretching modes and the band at  $640\text{ cm}^{-1}$  accounted for by the  $\nu_3$   $(Te_3O_8)^{2-}$  antisymmetric stretching mode. The Raman spectrum of carlfriesite showed an intense band at  $721\text{ cm}^{-1}$ . Raman bands for spiroffite, observed at  $(346, 394)$  and  $466\text{ cm}^{-1}$  are assigned to the  $(Te_3O_8)^{2-}$   $\nu_2$  ( $A_1$ ) bending mode and  $\nu_4$  ( $E$ ) bending modes. The Raman spectroscopy of the minerals carlfriesite and spiroffite are difficult because of the presence of impurities and other diagenetically related tellurite minerals.

*Keywords:* tellurite, tellurate, Raman spectroscopy, spiroffite, carlfriesite, rajite, denningite, zemannite, emmonsite

## 1. Introduction

Selenites and tellurites may be subdivided according to formula and structure [1]. There are five groups based upon the formulae (a)  $A(XO_3)$ , (b)  $A(XO_3) \cdot xH_2O$ , (c)

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• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

$A_2(XO_3)_3 \cdot xH_2O$ , (d)  $A_2(X_2O_5)$  and (e)  $A(X_3O_8)$ . Of the selenites molybdomenite is an example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite are minerals of type (b) mandarino is an example of type (c). There are no known examples of selenite minerals with formula (d) and (e).

Tellurite minerals which belong to type (a) are fairbankite, balyakinite, plumbotellurite, mocktezumite, magnolite and smirnite and tellurite minerals which are type (b) include graemite, teineite and chaloalite. Zemmanite and emmonsite are examples of group (c). Rajite and denningite are examples of tellurite minerals of type (d). Tellurite minerals such as spiroffite, winstanleyite, carlfreisite and pingguite are examples of type (e). Further information may be obtained by consulting the web site <http://www.mindat.org/dana.php?a=34>.

The mineral carlfriesite ( $CaTe_3O_8$ ) is a zeolite-like tellurite with a negatively charged framework of  $(Te_3O_8)^{2-}$  units [2-4]. It has large open channels of 8.28 Å parallel to [0001] [5]. The mineral, and related compounds, have been synthesised [6-8]. Substitution of ca by other cations such as  $Mn^{2+}$  can occur [9, 10]. A related mineral is spiroffite  $(Zn, Mn^{2+})(Te_3O_8)$  [11].

Spiroffite  $(Zn, Mn^{2+})(Te_3O_8)$ , is found in the tellurium rich deposits of Mexico [12-14]. The other pyrotellurite related mineral is mackayite  $Fe^{3+}(Te^{4+})_2O_5(OH)$  [15-18]. According to Anthony et al. [19] some uncertainty exists as to the formula of some of these minerals. The importance of these tellurium bearing minerals is their open framework structures with negatively charged surfaces and zeolitic pores [20]. The minerals fit into the Dana Classification, 8th edition as  $A_2(XO_3)_3 \cdot xH_2O$  [web site <http://www.mindat.org/dana.php?a=34&b=3>]. Other related tellurite minerals are cliffordite  $UTe_3^{4+}O_9$  [21, 22] and keystoneite  $Mg_{0.5}[Ni^{2+}Fe^{3+}(TeO_3)_3]_4 \cdot 5H_2O$  [23, 24].

Raman spectroscopy has proven very useful for the study of minerals [25-35]. Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with many minerals [36-43]. Some previous studies have been undertaken by the authors, using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions.

The aim of this paper is to present Raman and infrared spectra of natural selected selenites and to discuss the spectra from a structural point of view. It is part of systematic studies on the vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

## **2. Experimental**

### ***Minerals***

The minerals spiroffite and carlfriesite originated from the Moctezuma mine, New Mexico, USA. The compositions have been reported by Anthony et al. (page 117 and 661) [44].

### ***Raman microprobe spectroscopy***

The crystals of spiroffite or carlfriesite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives as part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of  $2\text{ cm}^{-1}$  in the range between 100 and  $4000\text{ cm}^{-1}$ . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the  $520.5\text{ cm}^{-1}$  line of a silicon wafer.

### ***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  $4000\text{--}525\text{ cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of  $4\text{ cm}^{-1}$  and a mirror velocity of  $0.6329\text{ cm/s}$ . Spectra were co-added to improve the signal to noise ratio.

Spectroscopic manipulation such as baseline adjustment, smoothing and

normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which 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 Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz 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. Further details on the manipulation of the data has been published [26, 28, 32, 33, 36, 38, 39, 43, 45, 46] .

### 3. Results and discussion

Farmer [47] states that very little research has been undertaken on selenates/selenites or tellurates/tellurites. No minerals with the selenate ion  $\text{SeO}_4^{2-}$  have been discovered and reported [48]. The tellurite ion should show a maximum of six bands. The free ion will have  $C_{3v}$  symmetry and four modes,  $2A_1$  and  $2E$ . Farmer based upon the work of Siebert [49, 50] defines the spectrum of  $(\text{TeO}_4)^{2-}$  as  $\nu_1 (A_1)$   $758 \text{ cm}^{-1}$ ,  $\nu_2 (A_1)$   $364 \text{ cm}^{-1}$ ,  $\nu_3 (E)$   $703 \text{ cm}^{-1}$  and  $\nu_4 (E)$   $326 \text{ cm}^{-1}$  [47]. The comment may be made, that there is very little published on the vibrational spectroscopy of tellurite and/or tellurate minerals, especially the Raman spectroscopy of these minerals.

The Raman spectra of spiroffite and carlfriesite in the  $500$  to  $900 \text{ cm}^{-1}$  region are displayed in Figure 1. Two Raman bands for spiroffite observed at  $743$  and  $721 \text{ cm}^{-1}$  are assigned to the  $\nu_1 (\text{Te}_3\text{O}_8)^{2-}$  symmetric stretching modes. The band at  $650 \text{ cm}^{-1}$  is accounted for by the  $\nu_3 (\text{Te}_3\text{O}_8)^{2-}$  antisymmetric stretching mode. The Raman spectrum of a second spiroffite mineral samples is reported in Figure 2. The spectrum is dominated by the intense peak at  $727 \text{ cm}^{-1}$  attributed to the  $\nu_1 (\text{Te}_2\text{O}_5)^{2-}$  symmetric stretching mode. Two shoulder peaks are also noted at  $754$  and  $767 \text{ cm}^{-1}$ . The band at  $640 \text{ cm}^{-1}$  is assigned to the  $\nu_3 (\text{Te}_3\text{O}_8)^{2-}$  antisymmetric stretching mode. The Raman spectrum of carlfriesite is dominated by an intense band at  $1085 \text{ cm}^{-1}$  which can not be assigned to any  $(\text{Te}_3\text{O}_8)^{2-}$  vibrations and is more likely due to the presence of

carbonate. The band at  $712\text{ cm}^{-1}$  may be due to a  $\nu_1 (\text{Te}_3\text{O}_8)^{2-}$  symmetric stretching mode. However this assignment seems unlikely as the band position is less than that for most tellurite minerals.

Raman bands for spiroffite, observed at (346, 394) and  $466\text{ cm}^{-1}$  are assigned to the  $(\text{Te}_3\text{O}_8)^{2-} \nu_2 (A_1)$  bending mode and  $\nu_4 (E)$  bending modes respectively (Figure 1). In comparison the very weak Raman bands of denningite at  $450$  and  $479\text{ cm}^{-1}$  are assigned to the  $(\text{Te}_3\text{O}_8)^{2-} \nu_4 (E)$  bending modes and the bands at  $349$  and  $381\text{ cm}^{-1}$  are ascribed to the  $(\text{Te}_3\text{O}_8)^{2-} \nu_2 (A_1)$  bending modes. The two Raman bands at  $148$  and  $226\text{ cm}^{-1}$  of spiroffite are probably related to MnO or ZnO stretching vibrations. The two bands at  $524$  and  $575\text{ cm}^{-1}$  in Figure 2 appear to be not related to  $(\text{Te}_3\text{O}_8)^{2-}$  vibrations and may also be the result of impurity. The Raman band at  $465\text{ cm}^{-1}$  is assigned to the  $\nu_4 (E)$  bending mode, whilst the two bands at  $309$  and  $346\text{ cm}^{-1}$  are assigned to the  $\nu_2 (A_1)$  bending modes.

In the infrared spectrum of spiroffite and carlfriesite as shown in Figure 3, a complex spectral pattern with multiple overlapping bands is observed for both. It is probable that the bands at  $777$  and  $798\text{ cm}^{-1}$  for spiroffite is due to the  $\nu_1 (\text{Te}_3\text{O}_8)^{2-}$  symmetric stretching mode. If the  $(\text{Te}_3\text{O}_8)^{2-}$  ion was perfectly symmetric, this band should not be observed. However because of the distortion of the anion the infrared forbidden band becomes active. The band at  $694\text{ cm}^{-1}$  for spiroffite may be assigned to the  $\nu_3 (\text{Te}_3\text{O}_8)^{2-}$  antisymmetric stretching modes. The two infrared bands of carlfriesite at  $712\text{ cm}^{-1}$  may be related to the  $\nu_1 (\text{Te}_3\text{O}_8)^{2-}$  symmetric stretching mode. All other bands above this wavenumber is attributed to impurities probably carbonates. Equally well the bands above  $800\text{ cm}^{-1}$  for spiroffite are also ascribed to impurities.

#### 4. Conclusions

Raman spectroscopy has been used to study the tellurite minerals spiroffite and carlfriesite, which are minerals of formula type  $A_2(X_3O_8)$  where A is  $\text{Ca}^{2+}$  for the

mineral carlfriesite and is  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  for the mineral spiroffite. Substitution of  $\text{Mn}^{2+}$  by Zn or Ca may occur for spiroffite resulting in a more complex formula. Raman spectroscopy enables bands to be assigned to the internal vibrations which are characteristic of the  $(\text{Te}_3\text{O}_8)^{2-}$  anion.

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Figure 1 Raman spectrum of carlfriesite and spiroffite in the 100 to 1700  $\text{cm}^{-1}$  range

Figure 2 Raman spectrum of spiroffite in the 100 to 1000  $\text{cm}^{-1}$  range

Figure 3 Infrared spectrum of carlfriesite and spiroffite in the 550 to 1550  $\text{cm}^{-1}$  range

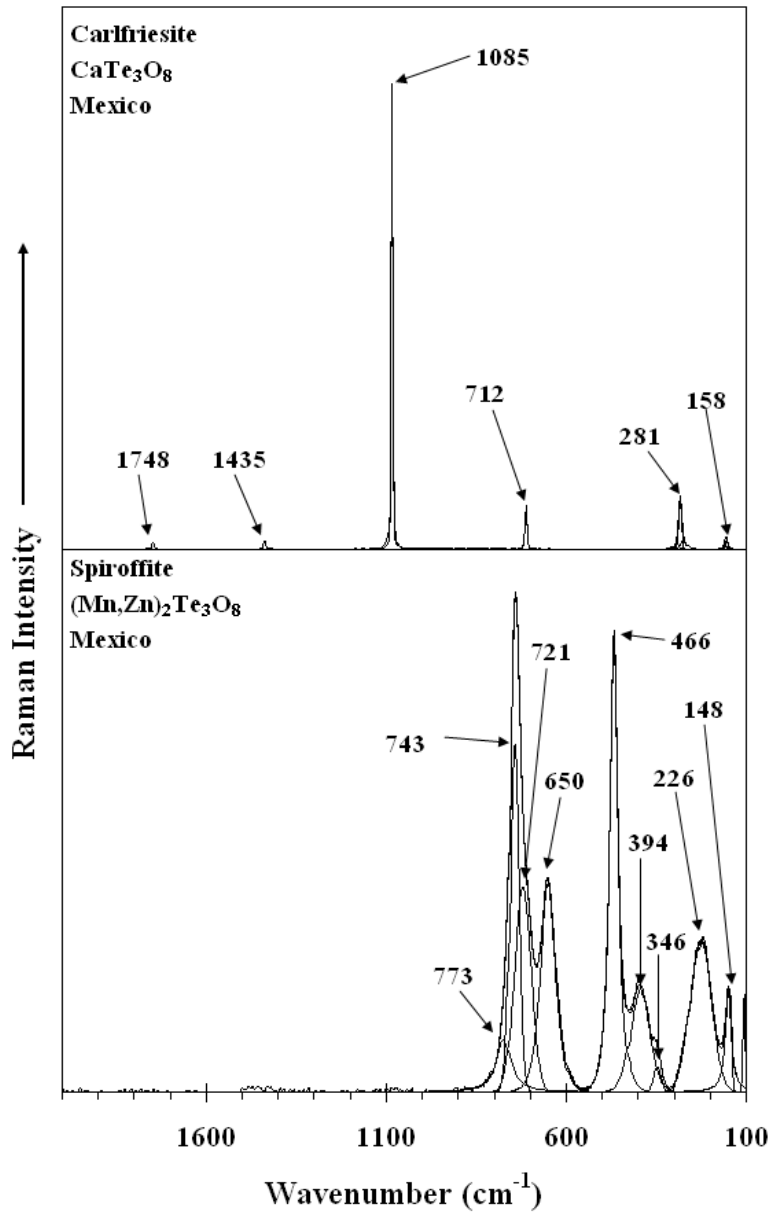
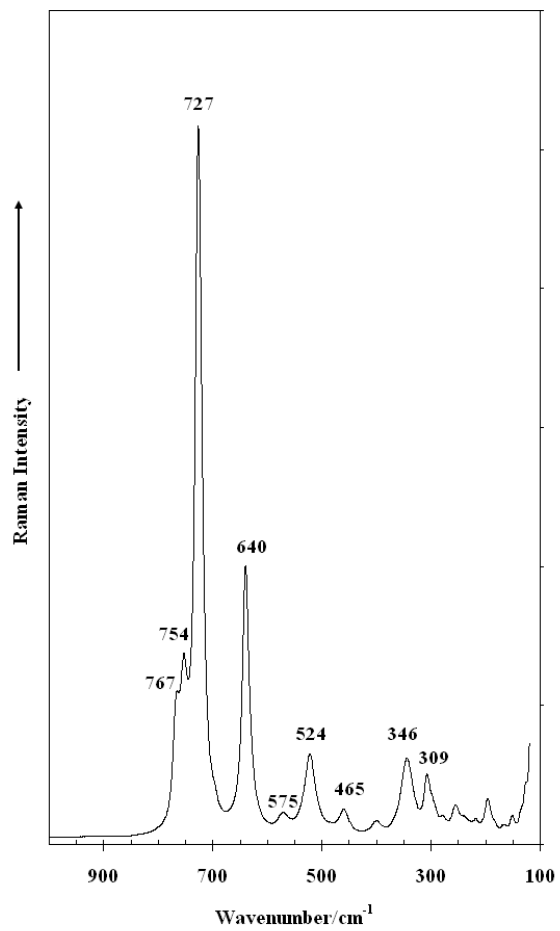
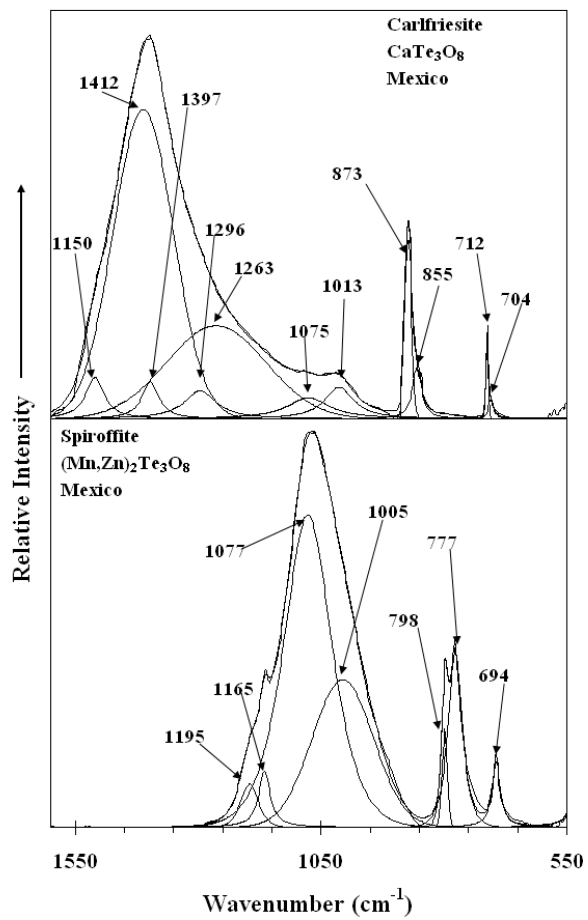


Figure 1



**Figure 2**



**Figure 3**