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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

# Raman spectroscopic study of the tellurite mineral: Rodalquilarite $H_3Fe_2^{3+}(Te^{4+}O_3)_4Cl$

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## ARTICLE INFO

## ABSTRACT

Tellurites may be subdivided according to formula and structure. There are five groups based upon the formulae (a) A(XO₃); (b) A(XO₃)·xH₂O; (c) A₂(XO₃)₃·xH₂O; (d) A₂(X₂O₅) and (e) A(X₃O₈). Rodalquilarite, a tellurite mineral of type (a) has been studied using Raman spectroscopy. Observed from the spectra was the presence of protons, an essential stabilising element for the minerals structure and stability. The tellurite ion should show a maximum of six bands. The free tellurite ion shows $C_{3v}$ symmetry and has four modes, $2A_1$ and $2E$. Three Raman bands at 726, 755 and 780 cm⁻¹ are assigned to the $\nu_1$ $(TeO_3)^{2-}$ symmetric stretching mode and the two bands at 610 and 642 cm⁻¹ are attributed to the $\nu_3$ $(TeO_3)^{2-}$ antisymmetric stretching mode. The two bands at 321 and 345 cm⁻¹ and the two bands at 449 and 473 cm⁻¹ are assigned to the $(TeO_3)^{2-}$ $\nu_2$ $(A_1)$ bending mode and $(TeO_3)^{2-}$ $\nu_4$ $(E)$ bending mode. Raman bands observed at 2341, 2796 and 2870 cm⁻¹ are attributed to OH stretching vibrations caused by interaction between the protons and the oxygen of the tellurite units. The values for these OH stretching vibrations provide hydrogen bond distances of 2.550 (6) Å (2341 cm⁻¹), 2.610 (3) Å (2796 cm⁻¹) and 2.623 (2) Å (2870 cm⁻¹) which are comparatively short for secondary minerals.

## 1. Introduction

Selenites and tellurites may be subdivided according to formula and structure [1]. There are five groups based upon the formulae (a) A(XO₃); (b) A(XO₃)·xH₂O; (c) A₂(XO₃)₃·xH₂O; (d) A₂(X₂O₅) and (e) A(X₃O₈). Of the selenites, molybdomenite is an example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite are examples of type (b) mandarinoite is an example of type (c). There are no known examples of selenite minerals with the formula (d) and (e). The tellurite group, however, consists of minerals that can be categorised into each of the five formula types. Fairbankite, balyakinite, plumbotellurite, mocktezumite, magnolite and smirnite are examples of type (a); graemite, teineite and chaloalite are examples of type (b); zemmanite and emmonsite are examples of type (c); rajite and denningite are examples of type (d) and spiroffite, winstanleyite, carlfreisite and pingguite are examples of type (e). A further group, of alternate formula and structure, is one in which the minerals contain water and/or OH units. Of this group are the minerals sonoraite, cesbronite, guilleminite, marthozite, demesmaekerite and haynesite.

Rodalquilarite is a mineral which fits into the group known as selenites, tellurites and antimonites. The mineral is one which has a proton as one of its cations in the mineral structure. Rodalquilarite [2–6] H₃Fe₂³⁺(Te⁴⁺O₃)₄Cl is a zeolite-like tellurite mineral with a negatively charged framework of [Fe(TeO₃)]. It has large open channels of 8.28 Å parallel to [0 0 0 1] [7]. The structure of rodalquilarite is based on layers consisting of edge-sharing FeO₆ octahedra that are interconnected by TeO₃ pyramids on which a terminal H atom is present. In addition, a second set of TeO₃ pyramids, bonded to the FeO₆ octahedra, are linked across the layers by a shared H atom. These layers are held together only through the O–H–O interactions as well as additional, weak Te–Cl interactions [2]. Rodalquilarite is related to many other tellurite minerals including emmonsite, mackayite, sonoraite. These minerals are often found together in tellurite mineral deposits in paragentic relationships [8].

Rodalquilarite, as well as some related compounds have been synthesised [9–11]. Related minerals kinichilite, Mg₀.₅[Mn²⁺ Fe³⁺(TeO₃)₃]·4.5H₂O [12], and emmonsite, Fe₂³⁺Te₃⁴⁺O₉·2H₂O, are found in the tellurium rich deposits of Mexico [13]. The importance of these tellurium bearing minerals is their open framework structures with negatively charged surfaces and zeolitic pores [14]. Other tellurite minerals are cliffordite, UTe₃⁴⁺O₉ [15,16], and keystoneite, Mg₀.₅[Ni²⁺Fe³⁺(TeO₃)₃]·4.5H₂O [17,18].

Raman spectroscopy has proven very useful for the study of minerals [19–23]. Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals, as many tellurite minerals often are. The importance of rodalquilarite is that it is a type mineral; in other words it is used as a reference mineral

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for structural analysis. Some previous studies, using Raman spectroscopy, have been undertaken by the authors to study complex secondary minerals [24–35]. The objective of this research is to present Raman of the natural tellurite mineral rodalquilarite and to discuss the spectra from a molecular structural point of view. This research is part of systematic studies on the vibrational spectra of minerals of secondary origin in the oxide supergene zone.

## 2. Experimental

### 2.1. Minerals

The first rodalquilarite mineral sample originated from the Joe and Grand Central Mines, Tombstone, Cochise Co., Arizona, USA (sample 1). This is a type mineral. A type mineral is one which is used as a standard reference for that type of structure. Mineral samples were also obtained from Rodaquilar, Spain (sample 2) and from Wendy open pit, Tambo mine, El Indio deposit, Elqui Province, Coquimbo Region, Chile The Raman spectra of all three minerals was obtained. The composition of rodalquilarite has been reported by Anthony et al. [36, page 593].

### 2.2. Raman microprobe spectroscopy

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

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 ($r^2$) greater than 0.995.

## 3. Results and discussion

Farmer [37] stated that very little research has been undertaken on the vibrational spectroscopy of selenates/selenites or tellurates/tellurites. This statement is true to the present time. No minerals with the selenate ion $SeO_4^{2-}$ have been discovered and reported [38]. The tellurite ion should show a maximum of six bands. The free ion will have $C_{3v}$ symmetry and four modes, $2A_1$ and $2E$. These bands are all active in both the Raman and infrared spectra. Farmer, based upon the work of Siebert [39,40], defines the spectrum of $(TeO_3)^{2-}$ as $\nu_1$ ($A_1$) $758\,cm^{-1}$, $\nu_2$ ($A_1$) $364\,cm^{-1}$, $\nu_3$ ($E$) $703\,cm^{-1}$ and $\nu_4$ ($E$) $326\,cm^{-1}$ [37].

The Raman spectrum of rodalquilarite in the $500–900\,cm^{-1}$ region is shown in Fig. 1. The Raman spectrum of the second rodalquilarite mineral sample is shown in Fig. 2. A broad spectral profile caused by Raman bands at 725, 756 and $781\,cm^{-1}$ is assigned to the $\nu_1$ $(TeO_3)^{2-}$ symmetric stretching mode. These values may
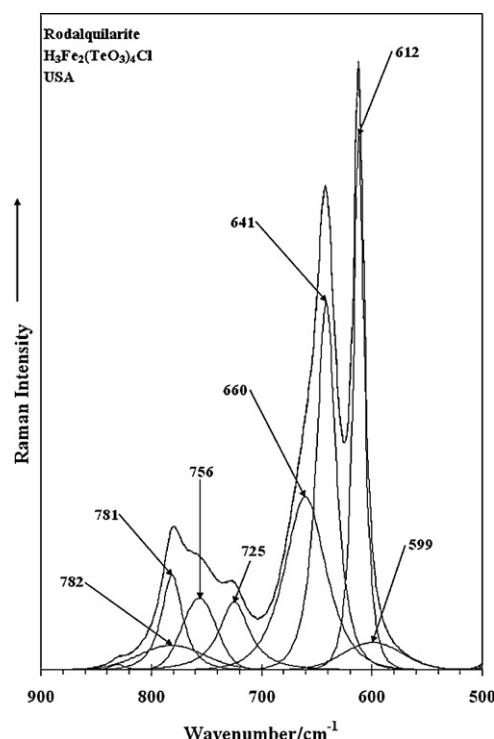


**Fig. 1.** Raman spectrum of rodalquilarite in the $500–900\,cm^{-1}$ region from Joe and Grand Central Mines, Tombstone, Cochise Co., Arizona, USA.

be compared with the published data of Farmer [37] who reported the $\nu_1$ ($A_1$) band at $758\,cm^{-1}$. Bands at 612 and $641\,cm^{-1}$, with a shoulder at $660\,cm^{-1}$, are attributed to the $\nu_3$ $(TeO_3)^{2-}$ antisymmetric stretching mode. Farmer [37] gave a value of $703\,cm^{-1}$ for the $\nu_3$ ($E$) mode. The Raman spectra of the two minerals are very similar. The three bands at 726, 755 and $780\,cm^{-1}$ are assigned to
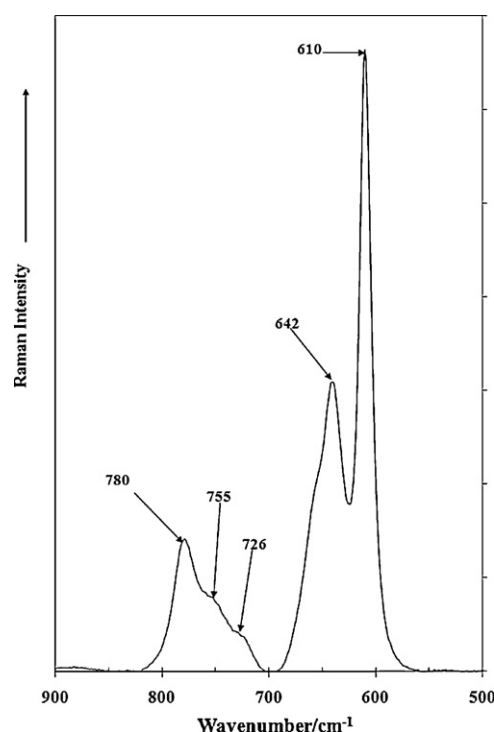


**Fig. 2.** Raman spectrum of rodalquilarite in the $500–900\,cm^{-1}$ region from the Moctezuma mine, New Mexico.