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Frost, Ray L. and Keeffe, Eloise C. (2009) *Raman spectroscopic study of the metatellurate mineral : Xocomecatlite $Cu_3TeO_4(OH)_4$* . *Journal of Raman Spectroscopy*, 40. pp. 866-869.

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Raman spectroscopic study of the metatellurate mineral: Xocomecatlite



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The mineral xocomecatlite is a hydroxy metatellurate mineral with Te^{6+}O_4 units. Tellurates may be subdivided according to their formula into three types of tellurate minerals: type (a) $(\text{AB})_m(\text{TeO}_4)_p\text{Z}_q$, type (b) $(\text{AB})_m(\text{TeO}_6)_x\text{H}_2\text{O}$ and (c) compound tellurates in which a second anion including the tellurite anion, is involved. The mineral Xocomecatlite is an example of the first type. Raman bands for xocomecatlite at 710, 763 and 796 cm^{-1} and 600 and 680 cm^{-1} are attributed to the $\nu_1(\text{TeO}_4)^{2-}$ symmetric and ν_3 antisymmetric stretching mode. Raman bands observed at 2867 and 2926 cm^{-1} are assigned to TeOH stretching vibrations and enable estimation of the hydrogen bond distances of 2.622 Å (2867 cm^{-1}), 2.634 Å (2926 cm^{-1}) involving these OH units. The hydrogen bond distances are very short implying that they are necessary for the stability of the mineral.

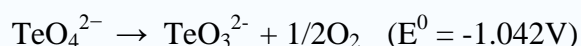
KEYWORDS: tellurate, tellurite, xocomecatlite, kurankhite, tlapallite, Raman spectroscopy

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INTRODUCTION

Tellurates are very rare minerals because the tellurate anion is very easily reduced to the tellurite anion. There are three types of tellurate minerals: type (a) $(AB)_m(\text{TeO}_4)_pZ_q$, type (b) $(AB)_m(\text{TeO}_6)_x \cdot x\text{H}_2\text{O}$ and type (c) compound tellurates in which a second anion is involved. An example of type (a) is the mineral xocomecatlite¹⁻³. Another tellurate mineral is mcalpineite, ideally $\text{Cu}_3\text{TeO}_6 \cdot \text{H}_2\text{O}$ ², a type (b) compound. Kuranakhite is also an example from this group. Xocomecatlite, $\text{Cu}_3\text{TeO}_4(\text{OH})_4$, is related to the mineral tlalocite, $\text{Cu}_{10}\text{Zn}_6(\text{TeO}_3)(\text{TeO}_4)_2\text{Cl}(\text{OH})_{25} \cdot 27\text{H}_2\text{O}$. Both originate from Moctezuma, Sonora, Mexico. Another related tellurate mineral is tlapallite $\text{H}_6(\text{Ca,Pb})_2(\text{Cu,Zn})_3\text{SO}_4(\text{TeO}_3)_4\text{TeO}_6$ which is a mixed anionic mineral containing both tellurate and tellurite anions. This mineral is an example of type (c). Williams determined the powder X-ray diffraction patterns of xocomecatlite and suggested, based upon powder X-ray diffraction, the mineral was orthorhombic³. Williams suggested that the mineral was a mixed tellurate-tellurite mineral but this proved to be incorrect and xocomecatlite is a metatellurate mineral of type (a) above³. The single crystal structure of xocomecatlite has not been achieved and the exact structure is unknown. As such, Raman spectroscopy has the potential to add fundamental knowledge of the xocomecatlite mineral structure.

It is important to understand the relationship between the tellurate and tellurite anions. In contrast to the extensive list of tellurites, there are very few tellurate minerals. The tellurate ion can be either TeO_4^{2-} or TeO_6^{6-} . Unlike sulphate, tellurate is a good oxidising agent; it can be reduced to tellurite or tellurium. The E^0 value is significant as it gives an indication of the strength of the tellurate ion as an oxidising agent.



Tellurate exists in two forms, metatellurate ion, TeO_4^{2-} , and orthotellurate ion, TeO_6^{6-} . Some compounds include both metatellurates and orthotellurates. Xocomecatlite is an example of a metatellurate. Metatellurates are analogous to sulphates; however, these minerals are rare. Orthotellurates are much more common and therefore form most of the chemistry of tellurates. In neutral conditions,

pentahydrogen orthotellurate ion, H_5TeO_6^- , is most common; in basic conditions, tetrahydrogen orthotellurate ion, $\text{H}_4\text{TeO}_6^{2-}$, is more common and in acid conditions, the orthotelluric acid, H_6TeO_6 , is more common. Siebert synthesised these types of compounds and published the results of their infrared spectra ⁴. The number of tellurate minerals is greatly overshadowed by the number of tellurite minerals, i.e. minerals containing TeO_3^{2-} units.

Raman spectroscopy has proven especially useful for the study of related minerals ⁵⁻⁹. Tellurates such as xocomecatlite may form relationships with minerals such as macalpite ² or its reduced products such as teineite ¹⁰. Raman spectroscopy is important in our understanding of diagenetically related minerals as often occurs with many tellurate and tellurite minerals ¹¹⁻²¹. The aim of this paper is to present Raman spectra of the natural selected tellurate mineral xocomecatlite and to relate them to the structure of the mineral. The research reported here, is part of systematic studies on the vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

EXPERIMENTAL

Minerals

The mineral xocomecatlite was sourced from the mine Mina Bambollita, Moctezuma, Sonora, Mexico. The compositions of this mineral has been reported by Anthony *et al.* (page 768) ²². The composition of the mineral was found to be TeO_3 39.0%, CuO 53.0% and H_2O 8.0%

Raman microprobe spectroscopy

The crystals of the mineral xocomecatlite 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). The excitation

source was 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.

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.

RESULTS AND DISCUSSION

Farmer²³ stated that very little research has been undertaken on the vibrational spectroscopy of tellurates. Thus, few papers on the spectroscopy of natural tellurate minerals have been forthcoming. The spectroscopy of a range of tellurite and tellurate compounds has been published²⁴⁻²⁷. Only a few minerals with the tellurate anion have been discovered¹⁻³. The metatellurate anion TeO_4^{2-} should have T_d symmetry and therefore, four internal modes, namely A_1 (ν_1), E (ν_2) and $2F_2$ (ν_3 and ν_4). The flattened tetrahedrons form a square outline and help produce (in many of these minerals) a tetragonal (four fold) C_{4v} symmetry, which is an uncommon symmetry in minerals. Farmer based upon the work of Siebert^{4,28} defines the spectrum of $(\text{TeO}_4)^{2-}$ as ν_1 (A_1) 758 cm^{-1} , ν_2 (A_1) 364 cm^{-1} , ν_3 (E) 703 cm^{-1} and ν_4 (E) 326 cm^{-1} ²³. The orthotellurate ion, TeO_6^{6-} will have octahedral symmetry but may be strongly distorted. Vibrational modes for the tellurate anion should occur in the 620 to 650 cm^{-1} region and in the 290 to 360 cm^{-1} region. If the symmetry of the orthotellurate anion is reduced through for example bonding to a cation as is presumed in the xocomecatlite structure, then the loss of degeneracy will occur, and additional bands

observed. Siebert⁴ reported the infrared spectra of selected synthetic tellurates and antimonates. The position of the bands for the TeO_6^{6-} anion was defined by Siebert as ν_1 650 cm^{-1} (A_{1g}), ν_3 630 cm^{-1} (E_g), ν_2 375 cm^{-1} (F_{2g}). For the compound H_6TeO_6 infrared bands were observed at 605, 650, 658, 675, 708 and 730 cm^{-1} and were assigned to TeO stretching vibrations. In addition an intense band at 411 cm^{-1} is assigned to a δTeO bending mode (presumably ν_4 vibration). For the compound $\text{Na}_2\text{H}_4\text{TeO}_6$ infrared bands were observed at 429, 536, 587, 675 and 780 cm^{-1} . More complexity was observed in the spectrum of $\text{K}_2\text{H}_4\text{TeO}_6 \cdot 3\text{H}_2\text{O}$. Siebert also provided data for the compound $(\text{H}_4\text{TeO}_4)_x$. For this polytellurous acid, infrared bands were found at 450 cm^{-1} (δTeO) and stretching modes at 600, 720, 800 cm^{-1} . According to Siebert the TeO_6^{6-} anion is octahedral but is distorted. Thus infrared forbidden bands become activated.

The Raman spectrum of xocomecatlite in the 100 to 900 cm^{-1} region is shown in Fig. 1. A broad spectral profile with Raman bands at 600, 680, 710, 763 and 796 cm^{-1} are observed. The latter three bands are assigned to the ν_1 (TeO_4)²⁻ symmetric stretching mode. The Raman bands at 600 and 680 cm^{-1} are attributed to the ν_3 (TeO_4)²⁻ antisymmetric stretching mode. Farmer based upon the work of Siebert^{4,28} defined the spectrum of (TeO_4)²⁻ as ν_1 (A_1) 758 cm^{-1} , and ν_3 (E) 703 cm^{-1} . The bands in Fig. 1 more closely follow the work of Siebert as reported by Farmer. The two Raman bands at 710 and 763 cm^{-1} compare well. It is possible that the other Raman bands shown in Fig. 1 are that of the tellurite ion; thus the two bands at 796 and 680 cm^{-1} may be assigned to the tellurite anion.

Raman bands are observed at 438, 460 and 509 cm^{-1} (Fig. 1). Farmer based upon the work of Siebert^{4,28} defines the bending modes of (TeO_4)²⁻ as ν_2 (A_1) 364 cm^{-1} and ν_4 (E) 326 cm^{-1} ²³. Although the band positions are high compared with that found by Siebert from the infrared spectrum of metatelluric acid the band at 438 cm^{-1} may be assigned to the ν_2 (A_1) bending mode and the band at 509 cm^{-1} to the ν_4 (E) mode. A comparison may be made with the band positions for that of orthotellurate anion. For the Raman spectrum of kuranakhite $\text{PbMn}^{4+}\text{Te}^{6+}\text{O}_6$ the intense band at 462 cm^{-1} is assigned to the Te^{6+}O_6 ν_4 bending mode (Fig. 2). A second overlapping band at 452 cm^{-1} may be assigned to the same vibrational mode. The observation of two ν_4 bending modes fits well with the concept of two non-equivalent Te^{6+}O_6 units in

the mineral structure. The band at 407 cm^{-1} may be assigned to the ν_2 bending mode. The position of this band appears high compared with the data of Siebert. The conclusion is reached that the band positions for the $(\text{TeO}_4)^{2-}$ anion is different from that of the Te^{6+}O_6 anion. A series of strong Raman bands are observed in Fig. 1 in the 150 to 300 cm^{-1} region. Prominent Raman bands are observed at 149 , 161 , 189 , 259 and 291 cm^{-1} . These bands may be related to CuO stretching and OCuO bending vibrations.

The Raman spectrum of xocomecatlite in the 1800 to 3200 cm^{-1} region is displayed in Fig. 3. The Raman bands observed in this region are of very low intensity. Bands are observed at 2867 and 2926 cm^{-1} . Other low intensity bands are also observed in this Fig. . Siebert found a broad band in the infrared spectrum of $(\text{H}_2\text{TeO}_4)_x$ at 2360 cm^{-1} ⁴. For the synthetic compound $\text{Na}_2\text{H}_4\text{TeO}_6$ Siebert observed bands at 2270 and 2475 cm^{-1} . He assigned these bands to the first fundamental overtone of TeOH deformation modes. A more likely assignment is to the stretching vibrations of very strongly hydrogen bonded TeOH units.

The bands listed above in this work are attributed to TeOH stretching vibrations formed by the interaction of the protons with the oxygen of the selenite units. Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O hydrogen bond distances. Libowitzky showed that a regression function can be employed relating the hydroxyl stretching frequencies with regression coefficients better than 0.96 using infrared spectroscopy²⁹. The function is described as: $\nu_1 = 3592 - 304 \times 10^9 \cdot e^{\frac{-d(O-O)}{0.1321}}\text{ cm}^{-1}$. Thus OH---O hydrogen bond distances may be calculated using the Libowitzky empirical function. The values for the OH stretching vibrations listed above provide hydrogen bond distances of 2.622 \AA (2867 cm^{-1}), 2.634 \AA (2926 cm^{-1}). Other bands observed in Fig. 2 provide the following information 2.515 \AA (1957 cm^{-1}), 2.548 \AA (2320 cm^{-1}) and 2.537 \AA (2206 cm^{-1}). These hydrogen bond distances are very short for this mineral compared with that of many secondary minerals. Normally large hydrogen bond distances which are present in minerals such as perhamite can also be seen in other mixed anion minerals such as peisleyite where the distances ranging between $3.052(5)$ and $2.683(6)\text{ \AA}$. Such hydrogen bond distances are typical of secondary minerals. A range of hydrogen bond distances are observed from reasonably strong to weak hydrogen bonding. This range

of hydrogen bonding contributes to the stability of the mineral. In the case of xocomecatlite, the proton-tellurate interactions contribute to the stability of this tellurate mineral.

The Raman spectrum of xocomecatlite in the 900 to 1800 cm^{-1} region is shown in Fig. 4. The band at 1602 cm^{-1} may be attributed to the bending mode of adsorbed water. For the synthetic compounds $\text{K}_2\text{H}_4\text{TeO}_6$ and H_4TeO_4 , Siebert observed bands at around this position. The band at 974 cm^{-1} may be attributed to a CuOH deformation mode. The exact structure of xocomecatlite is unknown but it is likely that the OH units are bonded to the Cu.

CONCLUSIONS

The hydroxylated tellurate mineral xocomecatlite has been studied using Raman spectroscopy. Observed bands were assigned to the stretching and bending vibrations of the tellurate anion, $(\text{TeO}_4)^{2-}$, hydroxyl and water units in the xocomecatlite structure. A comparison of the Raman spectrum of tlapallite and kuranakhite is made and also with the infrared spectra reported by Siebert of synthetic metatelluric acid⁴. It is concluded that the position of the Raman band of the $(\text{TeO}_4)^{2-}$ anion is different from that of the TeO_6 anion. The Raman band positions are shifted.

Farmer based upon the infrared work of Siebert^{4,28} defined the spectrum of $(\text{TeO}_4)^{2-}$ as $\nu_1 (A_1)$ 758 cm^{-1} , and $\nu_3 (E)$ 703 cm^{-1} . Raman bands at 680, 710, 763 and 796 cm^{-1} are observed for xocomecatlite. The latter three bands are assigned to the $\nu_1 (\text{TeO}_4)^{2-}$ symmetric stretching mode. The Raman bands at 600 and 680 cm^{-1} are attributed to the $\nu_3 (\text{TeO}_4)^{2-}$ antisymmetric stretching mode. Since the tellurate anion is a very powerful oxidising agent, it is possible that some of the tellurate anions have been reduced to tellurite anion and thus the spectral profile in the 600 to 800 cm^{-1} region is a set of bands belonging to both tellurate and tellurite anions.

Raman bands observed at 2867 and 2926 cm^{-1} are assigned to TeOH stretching vibrations. Siebert found bands in similar positions but assigned the bands differently. The values for the OH stretching vibrations listed above provide hydrogen bond distances of 2.622 Å (2867 cm^{-1}), 2.634 Å (2926 cm^{-1}). Other bands observed in Fig.

2 provide the following information 2.515 Å (1957 cm⁻¹), 2.548 Å (2320 cm⁻¹) and 2.537 Å (2206 cm⁻¹). These values indicate very strongly hydrogen bonded OH units in the xocomecatlite structure which contribute to the stability of the structure.

Acknowledgements

The financial and infra-structure support of the Queensland University of Technology Inorganic Materials Research Program of the School of Physical and Chemical Sciences is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

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Fig. 2 Raman spectrum of kuranakhite in the 100 to 900 cm^{-1} region

Fig. 3 Raman spectrum of xocomecatlite in the 1800 to 3200 cm^{-1} region

Fig. 4 Raman spectrum of xocomecatlite in the 900 to 1800 cm^{-1} region

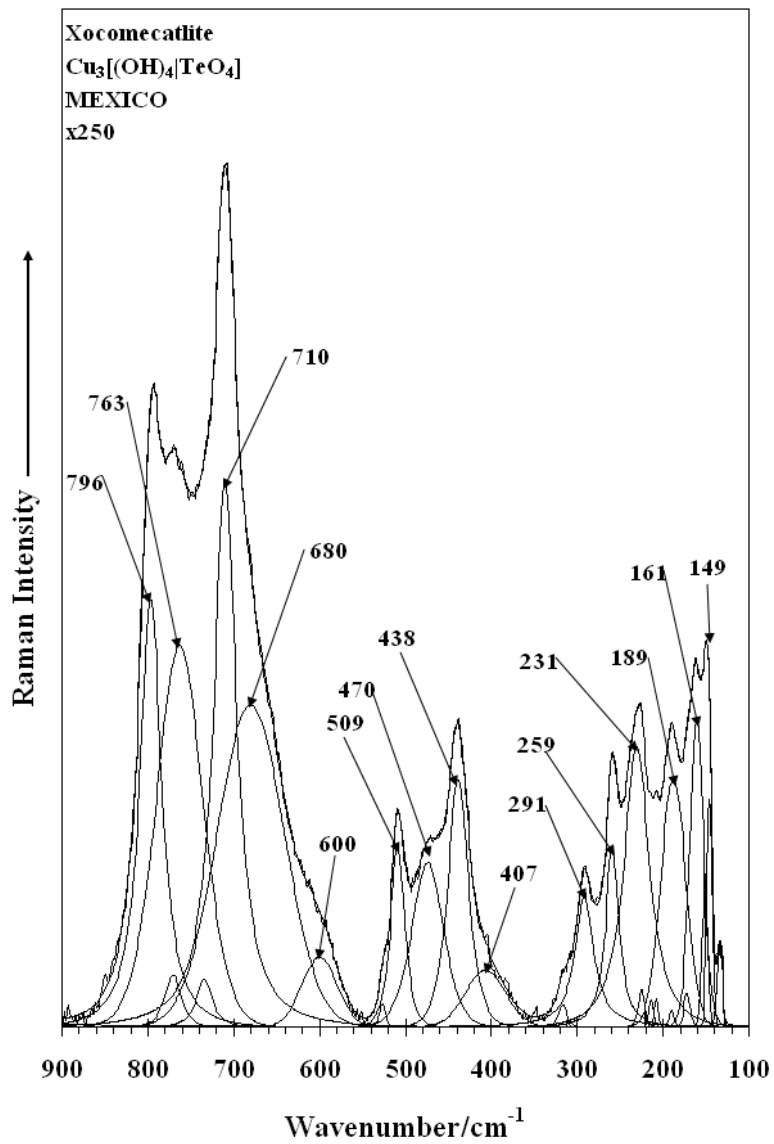


Fig. 1 xocomecatlite

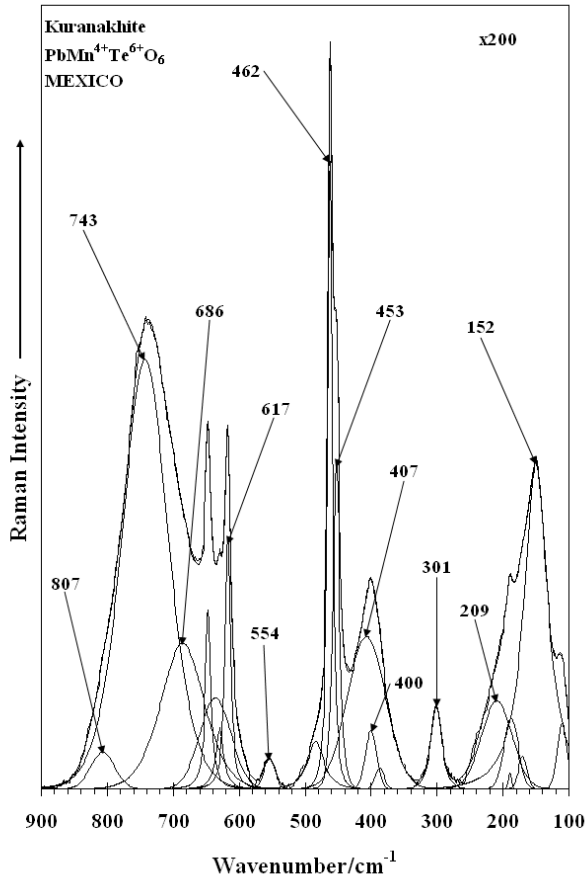


Fig. 2

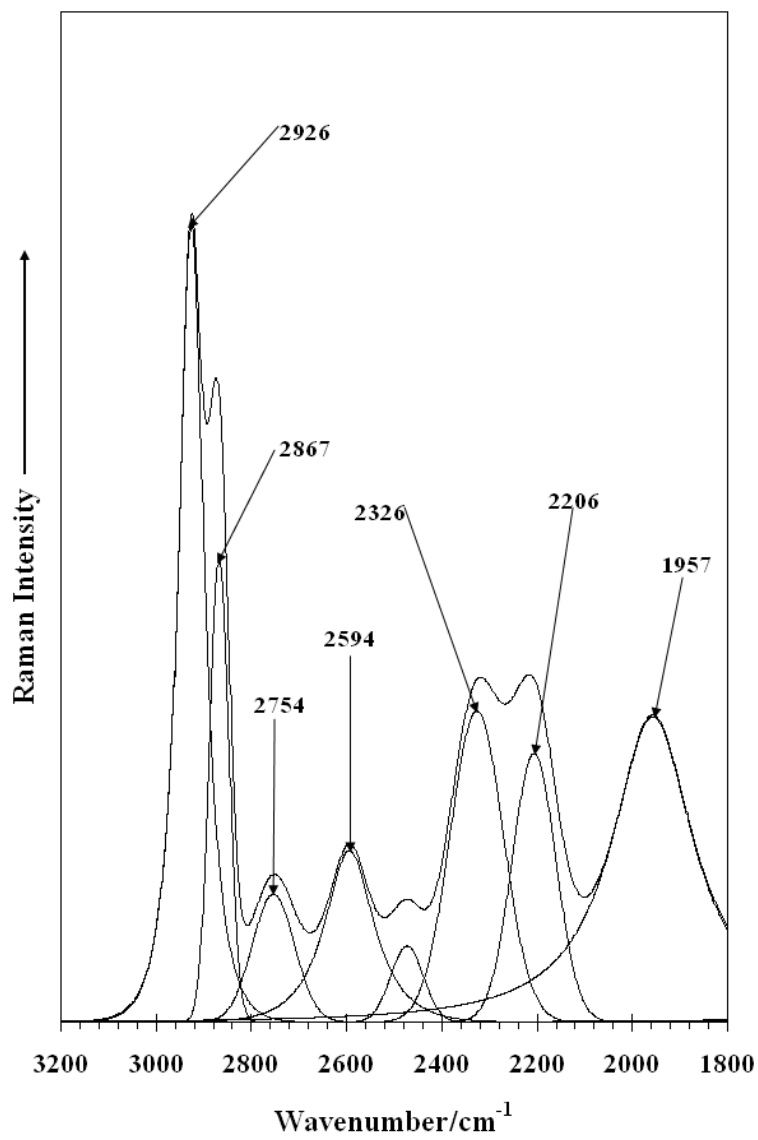


Fig. 2 xocomecatlite

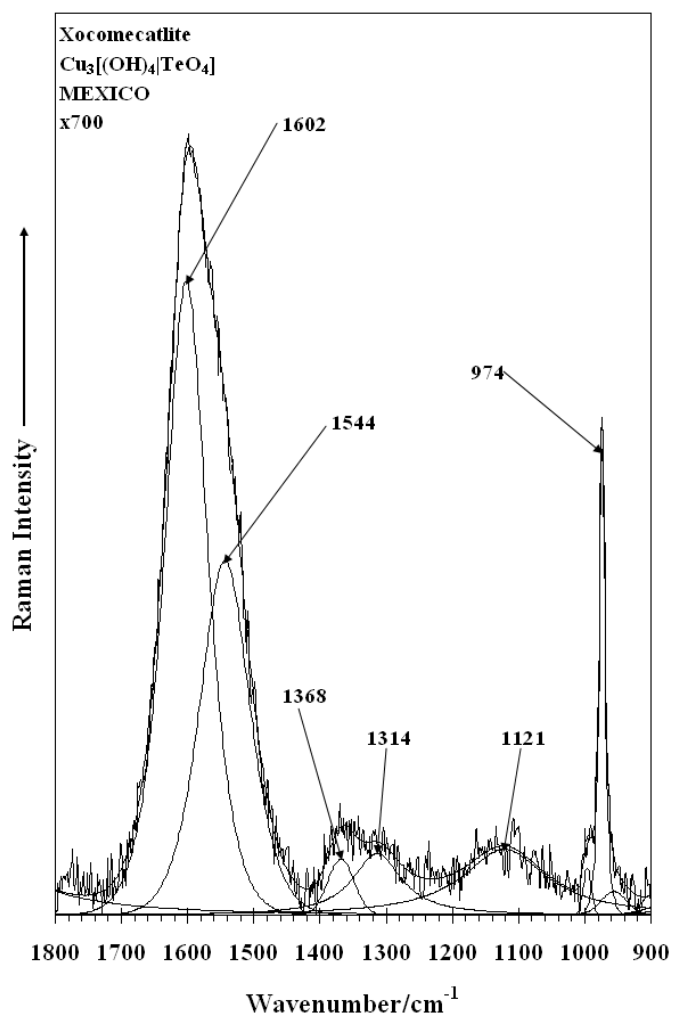


Fig. 3