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1 **Raman spectroscopic study kuranakhite**

2 **PbMn⁴⁺Te⁶⁺O₆—a rare tellurate mineral**

3
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9
10 **Tellurates are rare minerals as the tellurate anion is easily reduced to**
11 **the tellurite ion. An example of a tellurate containing mineral is**
12 **kuranakhite. Two bands at 617 and 686 cm⁻¹ are observed and assigned**
13 **to the Te⁶⁺O₆v₁ symmetric stretching mode. The observation of two**
14 **bands suggests the non-equivalence of the Te⁶⁺O₆ in the structure. The**
15 **broad band centred at 743 cm⁻¹ is attributed to the Te⁶⁺O₆v₃**
16 **antisymmetric stretching mode. Sharp intense bands at 452 and 462**
17 **cm⁻¹ are assigned to the Te⁶⁺O₆v₄ bending mode. A comparison of the**
18 **Raman spectra of kuranakhite with that of tellurate containing minerals**
19 **tlapallite and xocomecatlite is made.**

20
21 **KEYWORDS:** tellurate, kuranakhite, xocomecatlite, tlapallite, Raman spectroscopy,

22
23 **INTRODUCTION**

24
25 There exists in nature, a collection of minerals based upon the elements
26 selenium and tellurium. These minerals are the tellurates/selenates and the
27 tellurites/selenites. They minerals may be subdivided into groups according to
28 formula and structure¹. There are five groups based upon the formulae (a) A(XO₃),
29 (b) A(XO₃)_xH₂O, (c) A₂(XO₃)₃·xH₂O, (d) A₂(X₂O₅) and (e) A(X₃O₈). Of the
30 selenites, molybdomenite is an example of type (a); chalcomenite, clinochalcomenite,
31 cobaltomenite and ahlfeldite are examples of type (b) mandarinoite is an example of
32 type (c). There are no known examples of selenite minerals with formulae (d) and

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33 (e). The tellurite group, however, consists of minerals that can be categorised into
34 each of the five formula types.

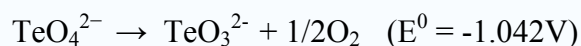
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36 Tellurates are very rare minerals because the tellurate anion is very easily
37 reduced to the tellurite anion. There are three types of tellurate minerals: type (a)
38 $(AB)_m(\text{TeO}_4)_p\text{Z}_q$, type (b) $(AB)_m(\text{TeO}_6)\cdot x\text{H}_2\text{O}$ and type (c), compound tellurates in
39 which a second anion is involved. An example of type (a) is the mineral
40 xocomecatlite²⁻⁴. Kuranakhite is also an example from this group. Xocomecatlite,
41 $\text{Cu}_3\text{TeO}_4(\text{OH})_4$, is related to the mineral tlalocite,
42 $\text{Cu}_{10}\text{Zn}_6(\text{TeO}_3)(\text{TeO}_4)_2\text{Cl}(\text{OH})_{25}\cdot 27\text{H}_2\text{O}$. Both originate from Moctezuma, Sonora,
43 Mexico. Another related tellurate mineral is tlalallite
44 $\text{H}_6(\text{Ca,Pb})_2(\text{Cu,Zn})_3\text{SO}_4(\text{TeO}_3)_4\text{TeO}_6$ which is a mixed anionic mineral containing
45 both tellurate and tellurite anions.

46

47 In contrast to the extensive list of tellurites, there are very few tellurate
48 minerals. The tellurate ion can be either TeO_4^{2-} or TeO_6^{6-} . Unlike sulphate, tellurate
49 is a good oxidizing agent; it can be reduced to tellurite or tellurium. The E^0 value is
50 significant as it gives an indication of the strength of the tellurate ion as an oxidising
51 agent.

52



53 Tellurate exists in two forms, metatellurate ion, TeO_4^{2-} , and orthotellurate ion,
54 TeO_6^{6-} . Compounds include both metatellurates and orthotellurates. Metatellurates
55 are analogous to sulfates, however, they are rare. Orthotellurates are much more
56 common and therefore forms most of the chemistry of tellurates. In neutral
57 conditions, pentahydrogen orthotellurate ion, H_5TeO_6^- , is most common; in basic
58 conditions, tetrahydrogen orthotellurate ion, $\text{H}_4\text{TeO}_6^{2-}$, is most common and in acid
59 conditions, the orthotelluric acid, H_6TeO_6 , is more common. The number of tellurate
60 minerals is greatly overshadowed by the number of tellurites minerals, minerals
61 containing TeO_3^{2-} units.

62

63 Raman spectroscopy has proven most useful for the study of minerals
64 especially where X-ray crystallographic data is uncertain or unknown.⁵⁻¹⁵
65 Diagenetically related minerals such as tellurates and tellurites may be studied using

66 Raman spectroscopy¹⁶⁻²¹. The tellurite ion is a strong oxidising agent and thus it is
67 rare to find a mineral with the tellurate ion and not have the tellurite or some other
68 anion present. The objective of this paper is to present the Raman spectrum of
69 kuranakhite and to relate the spectra to the molecular structure of the mineral.

70

71 **EXPERIMENTAL**

72

73 **Minerals**

74

75 The mineral kuranakhite was sourced from kuranakh deposite, Russia. This is the
76 „type“ mineral. The composition of the mineral, obtained from different sources, has
77 been reported by Anthony *et al.* (page 377)²². The analysis of the mineral was TeO₃
78 36.2%, MnO₂ 17.9% and PbO 46.0%. This provides a formula for the mineral as
79 Pb_{0.93}Mn_{0.81}TeO₆. The single crystal X-ray study of the mineral has not been
80 undertaken. Powder XRD indicates the mineral is orthorhombic.²³

81

82 **Raman microprobe spectroscopy**

83

84 Crystals of the kuranakhite were placed and orientated on the stage of an
85 Olympus BHSM microscope which was equipped with 10x and 50x objectives as part
86 of a Renishaw 1000 Raman microscope system. The system also includes a
87 monochromator, filter system and Charge Coupled Device (CCD). Raman spectra
88 were excited by a HeNe laser (633 nm) at a nominal resolution of 2 cm⁻¹ in the range
89 between 100 and 4000 cm⁻¹.

90

91 Spectroscopic manipulation such as baseline adjustment, smoothing and
92 normalisation were performed using the Spectralcalc software package GRAMS
93 (Galactic Industries Corporation, NH, USA). Band component analysis was
94 undertaken using the Jandel ‘Peakfit’ software package, which enabled the type of
95 fitting function to be selected and allows specific parameters to be fixed or varied
96 accordingly. Band fitting was done using a Gauss-Lorentz, cross-product function
97 with the minimum number of component bands used for the fitting process. The
98 Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was
99 undertaken until reproducible results were obtained with squared correlations (r^2)

100 greater than 0.995.

101

102

103 RESULTS AND DISCUSSION

104

105 Farmer²⁴ states that very little research has been undertaken on the vibrational
106 spectroscopy of tellurates. As such very few papers have been forthcoming. Only a
107 few minerals with the tellurate anion have been discovered²⁻⁴. The metatellurate
108 anion TeO_4^{2-} should have T_d symmetry and therefore four internal modes, namely A_1
109 (ν_1), E (ν_2) and $2F_2$ (ν_3 and ν_4). The orthotellurate ion, TeO_6^{6-} will have octahedral
110 symmetry but may be strongly distorted. Vibrational modes for the tellurate anion
111 should occur in the 620 to 650 cm^{-1} region and in the 290 to 360 cm^{-1} region. If the
112 symmetry of the tellurate anion is reduced through for example bonding to a cation as
113 in the kuranakhite structure then the loss of degeneracy will occur, and additional
114 bands observed. Siebert²⁵ reported the infrared spectra of selected synthetic
115 tellurates and antimonates. The position of the bands for the TeO_6^{6-} anion was
116 defined by Siebert as $\nu_1\ 650\text{ cm}^{-1}$ (A_{1g}), $\nu_3\ 630\text{ cm}^{-1}$ (E_g), $\nu_2\ 375\text{ cm}^{-1}$ (F_{2g}). For the
117 compound H_6TeO_6 infrared bands were observed at 605 , 650 , 658 , 675 , 708 and 730
118 cm^{-1} and were assigned to TeO stretching vibrations. In addition an intense band at
119 411 cm^{-1} is assigned to a δTeO bending mode (presumably ν_4 vibration). For the
120 compound $\text{Na}_2\text{H}_4\text{TeO}_6$ infrared bands were observed at 429 , 536 , 587 , 675 and 780
121 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
122 also provided data for the compound $(\text{H}_4\text{TeO}_4)_x$. For this polytellurous acid, infrared
123 bands were found at 450 cm^{-1} (δTeO) and stretching modes at 600 , 720 , 800 cm^{-1} .
124 According to Siebert the TeO_6^{6-} anion is octahedral but is distorted. Thus infrared
125 forbidden bands are activated.

126

127 The Raman spectrum of kuranakhite $\text{PbMn}^{4+}\text{Te}^{6+}\text{O}_6$ in the 100 to 900 cm^{-1}
128 region is displayed in Fig. 1. Two bands at 617 and 686 cm^{-1} are observed and
129 assigned to the $\text{Te}^{6+}\text{O}_6\ \nu_1$ symmetric stretching mode. The observation of two bands
130 suggests the non equivalence of the Te^{6+}O_6 in the structure. Such a concept would
131 need to be confirmed by X-ray diffraction. The broad band centred at 743 cm^{-1} is
132 attributed to the $\text{Te}^{6+}\text{O}_6\ \nu_3$ antisymmetric stretching mode. The width of this band may
133 indicate that it is composed of a number of overlapping bands. The assignment of the

134 Te^{6+}O_6 stretching bands is at variance to that proposed by Siebert.²⁵ The sharp
135 intense band at 462 cm^{-1} is assigned to the Te^{6+}O_6 ν_4 bending mode. A second
136 overlapping band at 452 cm^{-1} assigned to the same vibrational mode. The observation
137 of two ν_4 bending modes fits well with the concept of two non-equivalent Te^{6+}O_6 units
138 in the mineral structure. The band at 407 cm^{-1} may be assigned to the ν_2 bending
139 mode. The position of this band appears high compared with the data of Siebert.

141 A comparison may be made with the Raman spectra of other tellurate
142 minerals. In the Raman spectrum of xocomecatlite $\text{Cu}_3(\text{OH})_4\text{TeO}_4\cdot\text{H}_2\text{O}$ (Fig. 2) a
143 broad band that may be decomposed into component bands at 710, 763 and 796 cm^{-1} .
144 These bands are quite sharp. One possible assignment is the band at 796 cm^{-1} is
145 ascribed to the TeO_4 ν_1 symmetric stretching mode and the two bands at 710 and 763
146 cm^{-1} to the TeO_4 antisymmetric stretching mode. Another tellurate containing mineral
147 which may be useful for a comparison of the Raman spectra of kuranakhite is the
148 mixed anionic mineral tlallite $\text{H}_6(\text{Ca,Pb})_2(\text{Cu,Zn})_3\text{SO}_4(\text{TeO}_3)_4\text{TeO}_6$. This mineral
149 contains both the tellurite and tellurate anions in the structure. Raman bands are
150 observed for tlallite at 650, 708, 764 and 796 cm^{-1} (Fig. 3). It is difficult to
151 nominate a specific assignment for each of these bands, as the tellurate and tellurite
152 bands overlap. One probable assignment is as follows: the higher wavenumber bands
153 may be attributed to the tellurate ion $(\text{TeO}_6)^{2-}$ and the lower wavenumber bands to the
154 tellurite anion $(\text{TeO}_3)^{2-}$. Thus, the Raman band at 796 cm^{-1} is attributed to the ν_1
155 $(\text{TeO}_6)^{2-}$ antisymmetric stretching mode and the band at 764 cm^{-1} to the ν_1 $(\text{TeO}_3)^{2-}$
156 symmetric stretching mode. The band at 708 cm^{-1} may be attributed to the ν_1 $(\text{TeO}_6)^{2-}$
157 symmetric stretching mode and the band at 691 cm^{-1} to the ν_1 $(\text{TeO}_3)^{2-}$ antisymmetric
158 stretching mode. Importantly Raman bands are observed in similar positions for these
159 three tellurate containing minerals.

160

161 CONCLUSIONS

162

163 In nature, very few tellurate minerals exist. They may be subdivided according
164 to formula and structure. The tellurate ion is TeO_4^{2-} or TeO_6^{6-} . Unlike sulphate,
165 tellurate is a good oxidizing agent; it can be reduced to tellurite or even tellurium. As
166 a result of this, the number of tellurite minerals greatly out numbers that of tellurate
167 minerals. The ready reduction of the tellurate anion to the tellurite anion leads to

168 certain minerals such as tlapallite forming mixed anionic species in which both the
169 tellurate and tellurite ions exist. The mineral kuranakhite is one in which the tellurate
170 anion TeO_6^{6-} is retained. Raman spectroscopy has been used to characterise the
171 molecular structure of kuranakhite.

172

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174

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224 **List of Figs**

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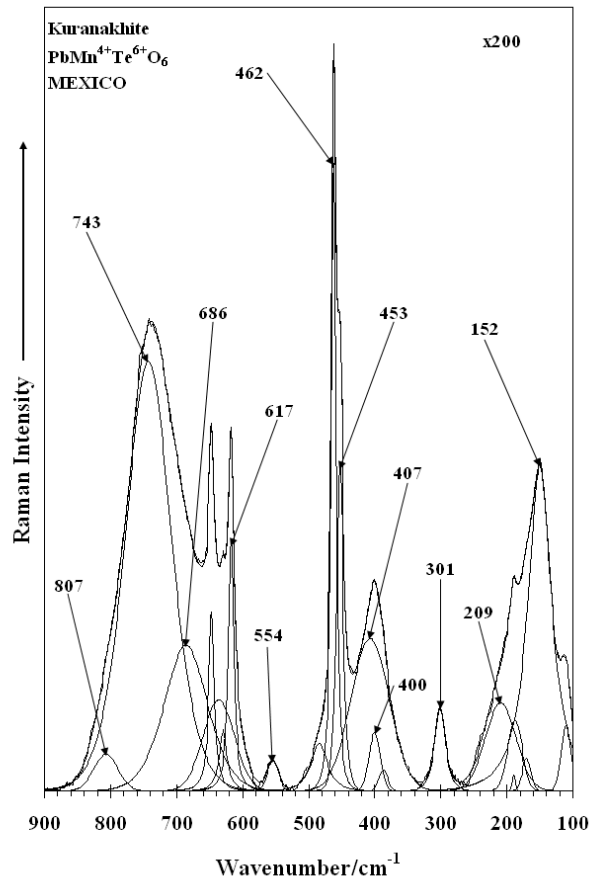
226 Fig. 1 Raman spectrum of kuranakhite in the 100 to 900 cm^{-1} region.

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228 Fig. 2 Raman spectrum of xocomecatlite in the 550 to 900 cm^{-1} region.

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230 Fig. 3 Raman spectrum of tlapallite in the 600 to 900 cm^{-1} region.

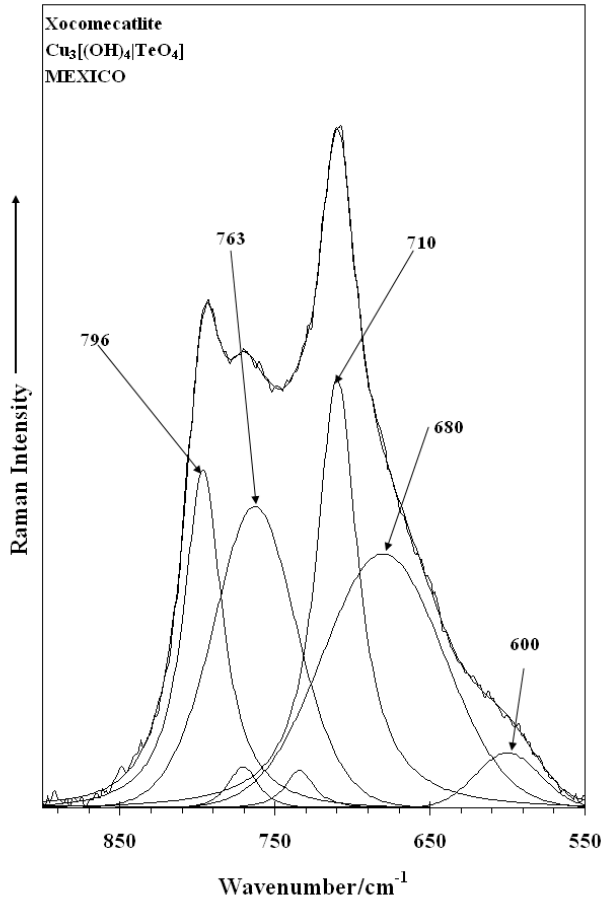


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233 **Fig. 1**

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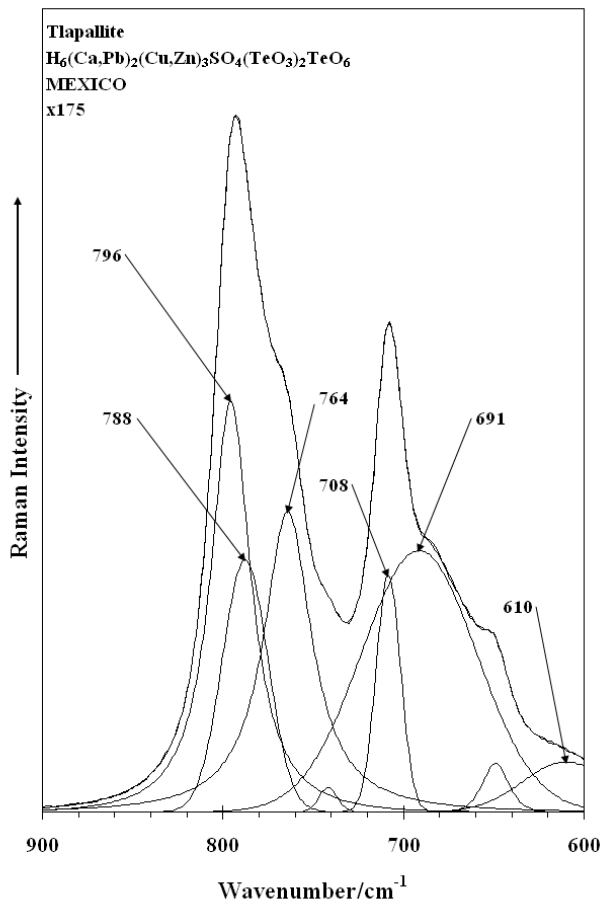
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237 **Fig. 2**

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241

242 **Fig. 3**

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