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Raman spectroscopic study of the tellurite minerals: rajite and denningite

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Abstract

Tellurites may be subdivided according to formula and structure. There are five groups based upon the formulae (a) $A(XO_3)$, (b) $A(XO_3).xH_2O$, (c) $A_2(XO_3)_3.xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Raman spectroscopy has been used to study rajite and denningite are examples of group (d). Minerals of the tellurite group are porous zeolite-like materials.

Raman bands for rajite observed at 740, and 676 and 667 cm^{-1} are attributed to the ν_1 $(Te_2O_5)^{2-}$ symmetric stretching mode and the ν_3 $(TeO_3)^{2-}$ antisymmetric stretching modes respectively. A second rajite mineral sample provided a more complex raman spectrum with Raman bands at 754 and 731 cm^{-1} assigned to the ν_1 $(Te_2O_5)^{2-}$ symmetric stretching modes and two bands at 652 and 603 cm^{-1} are accounted for by the ν_3 $(Te_2O_5)^{2-}$ antisymmetric stretching mode. The Raman spectrum of dennigite displays an intense band at 734 cm^{-1} attributed to the ν_1 $(Te_2O_5)^{2-}$ symmetric stretching mode with a second Raman band at 674 cm^{-1} assigned to the ν_3 $(Te_2O_5)^{2-}$ antisymmetric stretching mode. Raman bands for rajite, observed at (346, 370) and 438 cm^{-1} are assigned to the $(Te_2O_5)^{2-}$ ν_2 (A_1) bending mode and ν_4 (E) bending modes.

Keywords: tellurite, tellurate, Raman spectroscopy, rajite, denningite

1. Introduction

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

33 Selenites and tellurites may be subdivided according to formula and structure
34 [1]. There are five groups based upon the formulae (a) $A(XO_3)$, (b) $A(XO_3) \cdot xH_2O$, (c)
35 $A_2(XO_3)_3 \cdot xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Of the selenites molybdomenite is an
36 example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite
37 are minerals of type (b) mandarino is an example of type (c). There are no known
38 examples of selenite minerals with formula (d) and (e). Tellurite minerals which
39 belong to type (a) are fairbankite, balyakinite, plumbotellurite, mocktezumite,
40 magnolite and smirnite and tellurite minerals which are type (b) include graemite,
41 teineite and chaloalite. Zemmanite and emmonsite are examples of group (c). Rajite
42 and denningite are examples of tellurite minerals of type (d). Tellurite minerals such
43 as spiroffite, winstanleyite, carlfreisite and pingguite are examples of type (e).
44 Further information may be obtained by consulting the web site
45 <http://www.mindat.org/dana.php?a=34>.

46
47 The mineral denningite $(Ca, Mn^{2+})[Mn^{2+}Zn^{2+}](Te_2O_5)_2$ is a zeolite-like
48 tellurite with a negatively charged framework of $[Zn_2(TeO_3)_3]$ [2, 3]. It has large open
49 channels of 8.28 Å parallel to [0001] [4]. The mineral, and related compounds, have
50 been synthesised [5-7]. Substitution of Zn by other cations such as Mn^{2+} can occur
51 [8, 9]. A related mineral is spiroffite $(Zn, Mn^{2+})(Te_3O_8)$ [10]. Rajite $Cu^{2+}(Te_2O_5)_2$, is
52 found in the tellurium rich deposits of Mexico [2, 11, 12]. The other pyrotellurite
53 related mineral is mackayite $Fe^{3+}(Te^{4+})_2O_5(OH)$ [13-16]. According to Anthony et al.
54 [17] some uncertainty exists as to the formula of this mineral. The importance of
55 these tellurium bearing minerals is their open framework structures with negatively
56 charged surfaces and zeolitic pores [18]. The minerals fit into the Dana
57 Classification, 8th edition as $A_2(XO_3)_3 \cdot xH_2O$ [web site
58 <http://www.mindat.org/dana.php?a=34&b=3>]. Other related tellurite minerals are
59 cliffordite $UTe_3^{4+}O_9$ [19, 20] and keystoneite $Mg_{0.5}[Ni^{2+}Fe^{3+}(TeO_3)_3]_4 \cdot 5H_2O$ [21, 22].

60
61
62 Raman spectroscopy has proven very useful for the study of minerals [23-33].
63 Indeed, Raman spectroscopy has proven most useful for the study of diagenetically
64 related minerals as often occurs with many minerals [34-41]. Some previous studies
65 have been undertaken by the authors, using Raman spectroscopy to study complex
66 secondary minerals formed by crystallisation from concentrated sulphate solutions.

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

71

72 **2. Experimental**

73

74 *Minerals*

75

76 The mineral rajite originated from the Lone Pine Mine, Catron County, New
77 Mexico, USA. The mineral denningite originated from Moctezuma mine, New
78 Mexico. The second denningite sample originated from the Bambolla mine,
79 Moctezuma, Sonora, Mexico. The minerals were supplied by The Mineralogical
80 Research Company. The compositions have been reported by Anthony et al. [42].

81

82

83 *Raman microprobe spectroscopy*

84

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

93

94 ***Infrared spectroscopy***

95 Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer
96 with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525
97 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1}
98 and a mirror velocity of 0.6329 cm/s . Spectra were co-added to improve the signal to
99 noise ratio.

100

101 Spectroscopic manipulation such as baseline adjustment, smoothing and
102 normalisation were performed using the Spectracalc software package GRAMS
103 (Galactic Industries Corporation, NH, USA). Band component analysis was
104 undertaken using the Jandel ‘Peakfit’ software package, which enabled the type of
105 fitting function to be selected and allows specific parameters to be fixed or varied
106 accordingly. Band fitting was done using a Gauss-Lorentz cross-product function
107 with the minimum number of component bands used for the fitting process. The
108 Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was
109 undertaken until reproducible results were obtained with squared correlations of r^2
110 greater than 0.995. Further details on the manipulation of the data has been published
111 [24, 26, 30, 31, 34, 36, 37, 41, 43, 44] .

112

113

114 **3. Results and discussion**

115

116 Farmer [45] states that very little research has been undertaken on
117 selenates/selenites or tellurates/tellurites. No minerals with the selenate ion SeO_4^{2-}
118 have been discovered and reported [46]. The tellurite ion should show a maximum of
119 six bands. The free ion will have C_{3v} symmetry and four modes, $2A_1$ and $2E$. Farmer
120 based upon the work of Siebert [47, 48] defines the spectrum of $(\text{TeO}_4)^{2-}$ as $\nu_1 (A_1)$
121 758 cm^{-1} , $\nu_2 (A_1)$ 364 cm^{-1} , $\nu_3 (E)$ 703 cm^{-1} and $\nu_4 (E)$ 326 cm^{-1} [45]. A comparison
122 may be made with the spectroscopy of the selenite anion. The selenite ion should
123 show a maximum of six bands. The free ion will have C_{3v} symmetry and four modes,
124 $2A_1$ and $2E$. Nakamoto [49] gives these as $807, 432 \text{ cm}^{-1} (A_1)$ and $737, 374 \text{ cm}^{-1} (E)$.

125

126

127 The comment may be made, that there is very little published on the vibrational
128 spectroscopy of tellurite and/or tellurate minerals, especially the Raman spectroscopy
129 of these minerals.

130

131 The Raman spectrum of rajite in the 500 to 900 cm^{-1} region is displayed in
132 Figure 1. The spectroscopy of tellurites/selenites is interesting in that, like many
133 mineral arsenates, the symmetric stretching mode is observed at higher wavenumbers
134 than the antisymmetric stretching mode [50]. Two Raman bands for rajite observed at
135 754 and 731 cm^{-1} are assigned to the $\nu_1 (\text{Te}_2\text{O}_5)^{2-}$ symmetric stretching modes. The
136 two bands at 652 and 603 cm^{-1} are accounted for by the $\nu_3 (\text{Te}_2\text{O}_5)^{2-}$ antisymmetric
137 stretching mode. Two Raman bands of a second rajite mineral samples are observed
138 in Figure 2 at 740, and 676 and 667 cm^{-1} and are attributed to the $\nu_1 (\text{Te}_2\text{O}_5)^{2-}$
139 symmetric stretching mode and the $\nu_3 (\text{TeO}_3)^{2-}$ antisymmetric stretching modes
140 respectively. The Raman spectrum of dennigite is shown in Figure 3. An intense
141 band is observed at 734 cm^{-1} and is attributed to the $\nu_1 (\text{Te}_2\text{O}_5)^{2-}$ symmetric stretching
142 mode. A small shoulder is observed at 766 cm^{-1} which may be due to a second
143 tellurite phase. The Raman band of dennigite at 674 cm^{-1} is assigned to the ν_3
144 $(\text{Te}_2\text{O}_5)^{2-}$ antisymmetric stretching mode. A comparison may be made with the band
145 positions of selenite minerals. An intense band at 813 cm^{-1} for chalcomenite and 811
146 cm^{-1} for clinochalcomenite are assigned to the symmetric stretching $(\text{SeO}_3)^{2-}$ units.
147 The values of ν_1 based upon infrared spectra for sodium, calcium and copper
148 selenites are 788, 784 and 774 cm^{-1} . Vlaev has shown that the band positions in the
149 infrared spectra of cobalt selenites depends upon the degree of hydration [51, 52].

150

151 Vibrational spectroscopic data on tellurites is scarce. However some data on
152 selenite minerals is available for comparison. The values of ν_1 for sodium, calcium
153 and copper selenites are at 788, 784 and 774 cm^{-1} . In contrast, the values for the ν_3
154 antisymmetric stretching mode occur at 740, 713 and 714 cm^{-1} . The value for ν_2 bands
155 occurs between 449 and 461 cm^{-1} and ν_4 bands between 387 and 427 cm^{-1} [50].
156 Bäumer et al. proved that in the case of infrared spectra of M^{2+} selenite monohydrates,
157 the stretching vibrations of selenite units are located in the regions $760 \leq \nu_1 \text{SeO}_3 \leq$
158 855 cm^{-1} and $680 \leq \nu_3 \text{SeO}_3 \leq 775 \text{ cm}^{-1}$ [53]. Khandelwal and Verma and Verma
159 attributed the Raman (infrared) bands in the spectra of UO_2SeO_3 at 381 and 389 (390)
160 cm^{-1} to the $\nu_4 (\text{SeO}_3)^{2-}$, at 497 (500) cm^{-1} to the $\nu_2 (\text{SeO}_3)^{2-}$, as 724 and 731 (700) cm^{-1}

161 to the ν_3 (SeO_3)²⁻, 829 (820-840) cm^{-1} to the ν_1 (SeO_3)²⁻, and bands at 878 (875 sh)
162 and 884 (920-940) cm^{-1} to the ν_1 and ν_3 (UO_2)²⁺, respectively [54, 55]. The same
163 authors assigned observed Raman and infrared bands for $(\text{NH}_4)_2(\text{UO}_2)_2(\text{SeO}_3)_3 \cdot 6\text{H}_2\text{O}$
164 at 384, 390 (395), 475 (498), 731 and 829 (700 and 830), and 800 (808) cm^{-1} to the ν_4 ,
165 ν_2 , ν_3 and ν_1 modes, respectively, and those at 879 and 883 (872), and (900) cm^{-1} to
166 the ν_1 and ν_3 (UO_2)²⁺ modes, respectively. Similar spectra were observed and
167 interpreted for $\text{K}_2(\text{UO}_2)_2(\text{SeO}_3)_3 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2(\text{UO}_2)(\text{SeO}_3)_2$, and
168 $\text{K}_2(\text{UO}_2)(\text{SeO}_3)_2 \cdot 3\text{H}_2\text{O}$.

169

170 Raman bands for rajite, observed at (346, 370) and 438 cm^{-1} are assigned to
171 the $(\text{Te}_2\text{O}_5)^{2-}$ ν_2 (A_1) bending mode and ν_4 (E) bending modes respectively (Figure 2).
172 The very weak Raman bands of denningite at 450 and 479 cm^{-1} is assigned to the
173 $(\text{Te}_2\text{O}_5)^{2-}$ ν_4 (E) bending modes and the bands at 349 and 381 cm^{-1} are ascribed to the
174 $(\text{Te}_2\text{O}_5)^{2-}$ ν_2 (A_1) bending modes. The two Raman bands at 155 and 237 cm^{-1} for
175 denningite are probably related to MnO stretching vibrations. The Raman spectrum of
176 the rajite mineral from New Mexico in the 100 to 500 cm^{-1} region is shown in Figure
177 4. Greater complexity is observed in this spectrum. The two bands at 362 and 393
178 cm^{-1} are assigned to the $(\text{Te}_2\text{O}_5)^{2-}$ ν_2 (A_1) bending modes; and the two bands at 430
179 and 459 cm^{-1} are ascribed to the $(\text{Te}_2\text{O}_5)^{2-}$ ν_4 (E) bending modes. Two strong Raman
180 bands are observed for rajite at 299 and 318 cm^{-1} and are assigned to CuOTe
181 stretching vibrations. The sharp bands at 127, 146 and 162 cm^{-1} are probably related
182 to the CuOTe bending vibrations. The observation of multiple bands in each of the
183 spectral regions supports the concept of the non-equivalence of the $(\text{Te}_2\text{O}_5)^{2-}$ units in
184 the rajite structure.

185

186 In the infrared spectrum of rajite as shown in Figure 5, a complex spectral
187 pattern with multiple overlapping bands is observed. It is probable that the band at
188 766 cm^{-1} is due to the ν_1 $(\text{Te}_2\text{O}_5)^{2-}$ symmetric stretching mode. If the $(\text{Te}_2\text{O}_5)^{2-}$ ion
189 was perfectly symmetric, this band should not be observed. However because of the
190 distortion of the anion the infrared forbidden band becomes active. The three bands at
191 665, 701 and 728 cm^{-1} may be assigned to the ν_3 $(\text{Te}_2\text{O}_5)^{2-}$ antisymmetric stretching
192 modes.

193

194

195 **4. Conclusions**

196

197

198 Raman spectroscopy has been used to study the tellurite minerals rajite and
199 denningite, which are minerals of formula type $A_2(X_2O_5)$ where A is Cu^{2+} for the
200 mineral rajite and is Mn^{2+} for the mineral denningite. Substitution of Mn^{2+} by Zn or
201 Ca occurs for denningite resulting in a more complex formula $(Ca, Mn^{2+})[Mn^{2+}$
202 $Zn^{2+}](Te_2O_5)_2$. Raman spectroscopy enables bands to be assigned to the internal
203 vibrations which are characteristic of the $(Te_2O_5)^{2-}$ anion. A comparison is made with
204 the band positions of selected selenite minerals.

205

206

207

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209

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214

215

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- 303
- 304

305 **List of Figures**

306

307 Figure 1 Raman spectrum of rajite from New Mexico in the 500 to 900 cm^{-1} range

308

309 Figure 2 Raman spectrum of rajite from New Mexico in the 150 to 950 cm^{-1} range

310

311 Figure 3 Raman spectrum of denningite from Mexico in the 100 to 950 cm^{-1} range

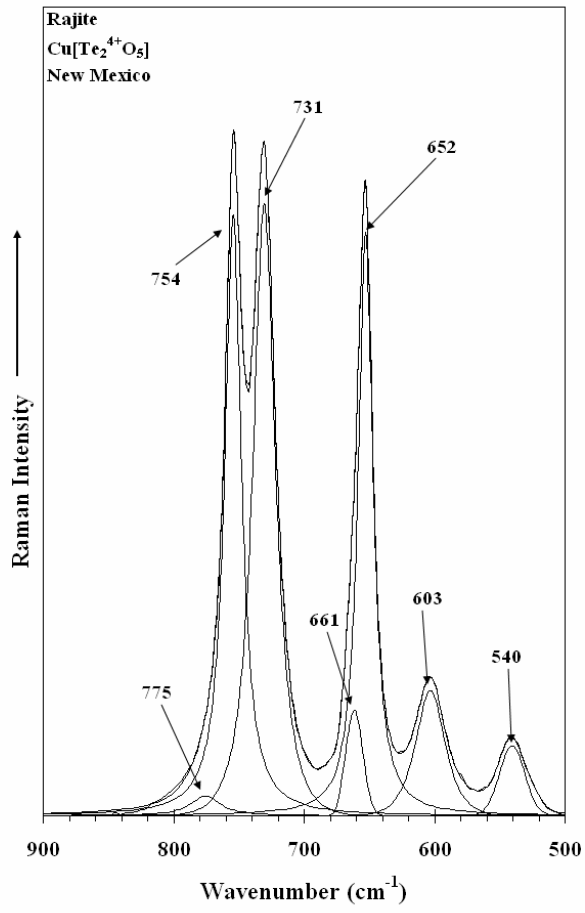
312

313 Figure 4 Raman spectrum of rajite from New Mexico in the 100 to 500 cm^{-1} range

314

315 Figure 5 Infrared spectrum of rajite from New Mexico in the 550 to 850 cm^{-1} range

316

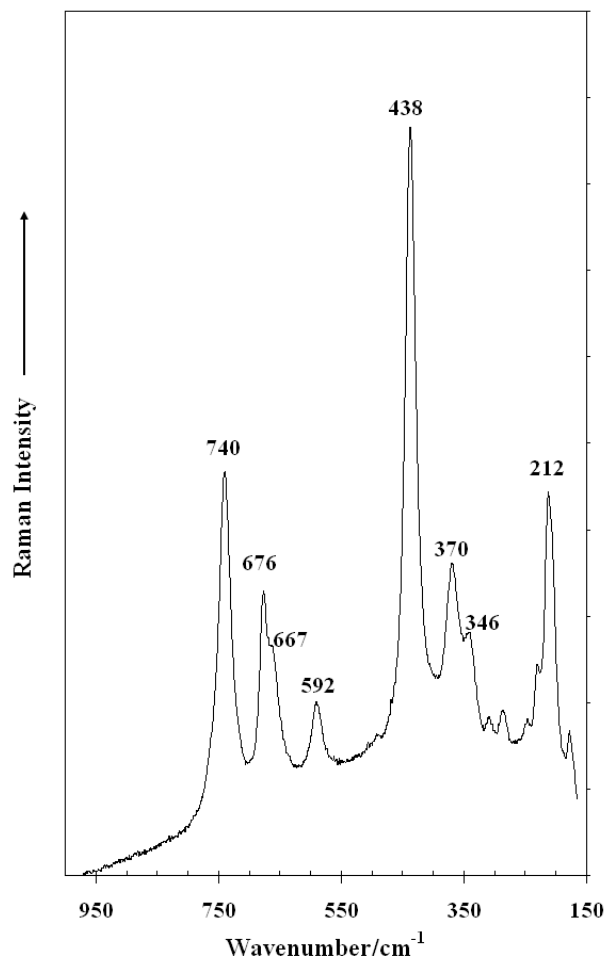


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318

319 **Figure 1**

320



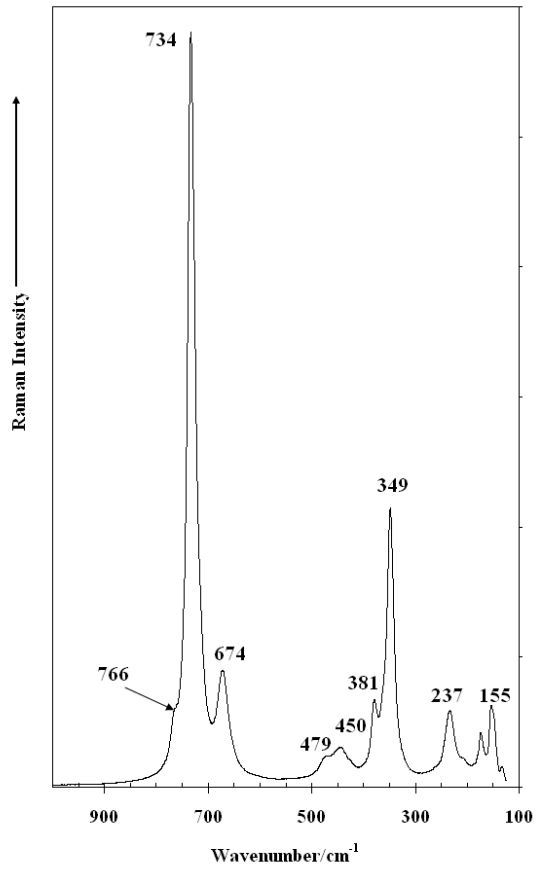
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322

323 **Figure 2**

RS-rajite

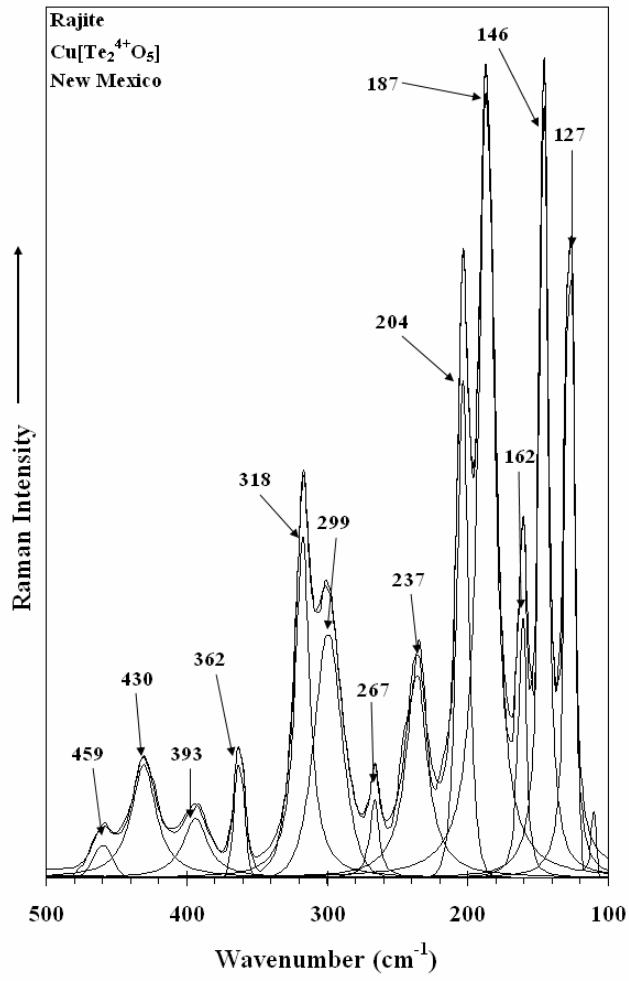
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326

327 **Figure 3** **RS denningite**

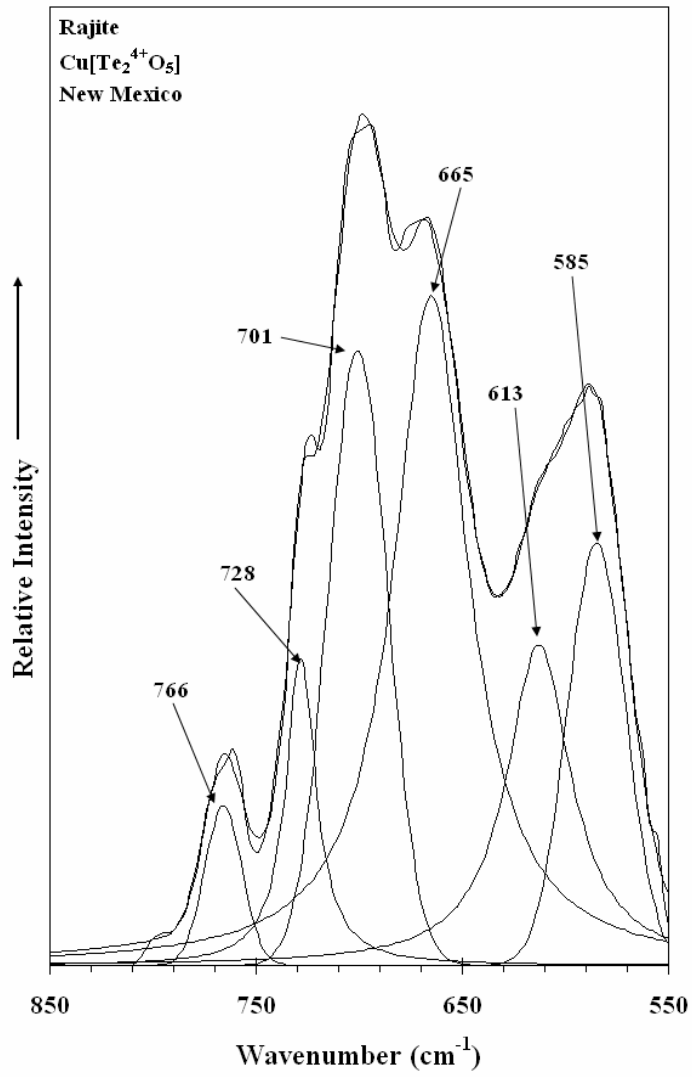


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329

330 **Figure 4**

331



332

333

334 **Figure 5**

335