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1 **Raman spectroscopic study of the mixed anion mineral**

2 **Yecoraite $\text{Bi}_5\text{Fe}_3\text{O}_9(\text{Te}^{4+}\text{O}_3)(\text{Te}^{6+}\text{O}_4)_2 \cdot 9\text{H}_2\text{O}$**

3
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9
10
11 **Abstract**

12
13 **Tellurates are rare minerals as the tellurate anion is readily reduced to**
14 **the tellurite ion. Often minerals with both tellurate and tellurite anions**
15 **in the mineral are found. An example of such a mineral containing**
16 **tellurate and tellurite is yecoraite. Raman spectroscopy has been used**
17 **to study this mineral, the exact structure of which is unknown. Two**
18 **Raman bands at 796 and 808 cm^{-1} are assigned to the $\nu_1(\text{TeO}_4)^{2-}$**
19 **symmetric and $\nu_3(\text{TeO}_3)^{2-}$ antisymmetric stretching modes and Raman**
20 **bands at 699 cm^{-1} are attributed to the $\nu_3(\text{TeO}_4)^{2-}$ antisymmetric**
21 **stretching mode and the band at 690 cm^{-1} to the $\nu_1(\text{TeO}_3)^{2-}$ symmetric**
22 **stretching mode. The intense band at 465 cm^{-1} with a shoulder at 470**
23 **cm^{-1} is assigned the $(\text{TeO}_4)^{2-}$ and $(\text{TeO}_3)^{2-}$ bending modes. Prominent**
24 **Raman bands are observed at 2878, 2936, 3180 and 3400 cm^{-1} . The**
25 **band at 3936 cm^{-1} appears quite distinct and the observation of multiple**
26 **bands indicates the water molecules in the yecoraite structure are not**
27 **equivalent. The values for the OH stretching vibrations listed provide**
28 **hydrogen bond distances of 2.625 Å (2878 cm^{-1}), 2.636 Å (2936 cm^{-1}),**
29 **2.697 Å (3180 cm^{-1}) and 2.798 Å (3400 cm^{-1}). This range of hydrogen**
30 **bonding contributes to the stability of the mineral. A comparison of the**
31 **Raman spectra of yecoraite with that of tellurate containing minerals**
32 **kuranakhite, tlapallite and xocomecatlite is made.**

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36 **Keywords:** tellurate, tellurite, yecoraite, xocomecatlite, Raman spectroscopy
37

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38

39 **Introduction**

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41

42

43 Tellurates are very rare minerals because the tellurate anion is very easily
44 reduced to the tellurite anion. There are three types of tellurate minerals: type (a)
45 $(AB)_m(\text{TeO}_4)_pZ_q$, type (b) $(AB)_m(\text{TeO}_6) \cdot x\text{H}_2\text{O}$ and type (c), compound tellurates in
46 which a second anion is involved. Yecoraite $\text{Bi}_5\text{Fe}_3\text{O}_9(\text{Te}^{4+}\text{O}_3)(\text{Te}^{6+}\text{O}_4)_2 \cdot 9\text{H}_2\text{O}$
47 is an example of type (c) ¹. Yecoraite is a mixed anion mineral with both tellurite
48 and metatellurate anions in the structure. The mineral is diagenetically related to the
49 mineral montanite $\text{Bi}_2\text{Te}^{6+}\text{O}_6 \cdot 2\text{H}_2\text{O}$, an orthotellurate mineral ². An example of type
50 (a) is the mineral xocomecatlite ³⁻⁵. One likely scenario is that the orthotellurate anion
51 or the metatellurate anion has been reduced, thus forming the tellurite anion. Thus the
52 mineral ends up as a mixed anion mineral.

52

53 Another tellurate mineral is mcalpineite, ideally $\text{Cu}_3\text{TeO}_6 \cdot \text{H}_2\text{O}$ ⁴, a type (b)

54 compound. Kuranakhite is an example from this group. Xocomecatlite,

55 $\text{Cu}_3\text{TeO}_4(\text{OH})_4$, is related to the mineral tlalocite,

56 $\text{Cu}_{10}\text{Zn}_6(\text{TeO}_3)(\text{TeO}_4)_2\text{Cl}(\text{OH})_{25} \cdot 27\text{H}_2\text{O}$. Both originate from Moctezuma, Sonora,

57 Mexico. Another related tellurate mineral is tlalallite

58 $\text{H}_6(\text{Ca},\text{Pb})_2(\text{Cu},\text{Zn})_3\text{SO}_4(\text{TeO}_3)_4\text{TeO}_6$ which is a mixed anionic mineral containing

59 both tellurate and tellurite anions. This mineral is an example of type (c). Williams

60 determined the powder X-ray diffraction patterns of yecoraite and suggested, based

61 upon powder X-ray diffraction, the mineral was orthorhombic ¹. Williams showed

62 that the yecoraite was a mixed tellurate-tellurite mineral. The single crystal structure

63 of yecoraite has not been achieved and the exact structure is strictly unknown. As

64 such Raman spectroscopy has the potential to add fundamental knowledge to the

65 yecoraite mineral structure.

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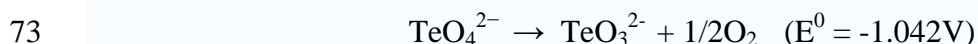
67 It is important to understand the relationship between the tellurate and tellurite

68 anions. In contrast to the extensive list of tellurites, there are very few tellurate

69 minerals. The tellurate ion can be either TeO_4^{2-} or TeO_6^{6-} . Unlike sulphate, tellurate

70 is a good oxidizing agent; it can be reduced to tellurite or even tellurium. The E^0

71 value is significant as it gives an indication of the strength of the tellurate ion as an
72 oxidising agent.



74 Tellurate exists in two forms, metatellurate ion, TeO_4^{2-} , and the orthotellurate ion,
75 TeO_6^{6-} . Compounds include both metatellurates and orthotellurates. Xocomecatlite
76 is an example of a metatellurate. Metatellurates are analogous to sulfates; however,
77 these minerals are rare. Orthotellurates are much more common and therefore form
78 most of the chemistry of tellurates. In neutral conditions, pentahydrogen
79 orthotellurate ion, H_5TeO_6^- , is common; in basic conditions, tetrahydrogen
80 orthotellurate ion, $\text{H}_4\text{TeO}_6^{2-}$, is more common and in acid conditions, the orthotelluric
81 acid, H_6TeO_6 , is more common. Siebert synthesised these types of synthetic
82 compounds and published the results of their infrared spectra ⁶. The number of
83 tellurate minerals is greatly overshadowed by the number of tellurite minerals, i.e.
84 minerals containing TeO_3^{2-} units. Yecoraite $\text{Bi}_5\text{Fe}^{3+}_3(\text{TeO}_3)(\text{TeO}_4)_2 \cdot 9(\text{H}_2\text{O})$ is named
85 after its discovery locality, San Martin de Porres Mine, west of Yecora, Sonora,
86 Mexico and is defined as a compound tellurite.

87
88

89 Raman spectroscopy has proven especially useful for the study of related
90 minerals ⁷⁻¹¹. Tellurates such as yecoraite may form relationships with other minerals
91 such as montanite ⁴ or its reduced products. Raman spectroscopy is important in our
92 understanding of diagenetically related minerals as often occurs with many tellurate
93 and tellurite minerals ¹²⁻²². The aim of this paper is to present Raman of the natural
94 selected tellurate mineral yecoraite and to relate the spectra to the structure of the
95 mineral, the structure of which is unknown. This research reported here, is part of
96 systematic studies on the vibrational spectra of minerals of secondary origin in the
97 oxide supergene zone and their synthetic analogs.

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99

100 **EXPERIMENTAL**

101 ***Minerals***

102

102 The mineral yecoraite was sourced from Marie Elena Mine, Yecora, Sonora, Mexico
103 and supplied by the Mineralogical Research Company. The compositions of this
104 mineral has been reported by Anthony *et al.* (page 771) ²³.

105

106 *Raman microprobe spectroscopy*

107

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

116

117 Spectroscopic manipulation such as baseline adjustment, smoothing and
118 normalisation were performed using the Spectracalc software package GRAMS
119 (Galactic Industries Corporation, NH, USA). Band component analysis was
120 undertaken using the Jandel 'Peakfit' software package, which enabled the type of
121 fitting function to be selected and allows specific parameters to be fixed or varied
122 accordingly. Band fitting was done using a Gauss-Lorentz cross-product function
123 with the minimum number of component bands used for the fitting process. The
124 Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was
125 undertaken until reproducible results were obtained with squared correlations of r^2
126 greater than 0.995.

127

128

129 **Results and discussion**

130

131 Farmer²⁴ stated that very little research has been undertaken on the vibrational
132 spectroscopy of tellurates. As such very few papers have been forthcoming. Only a
133 few minerals with the tellurate anion have been discovered³⁻⁵. The metatellurate
134 anion TeO_4^{2-} should have T_d symmetry and therefore four internal modes, namely A_1
135 (ν_1), E (ν_2) and $2F_2$ (ν_3 and ν_4). The flattened tetrahedrons form a square outline and
136 help produce (in many of these minerals) a tetragonal (four fold) symmetry, which is
137 an uncommon symmetry in minerals. Farmer based upon the work of Siebert^{6,25}
138 defines the spectrum of $(\text{TeO}_4)^{2-}$ as $\nu_1 (A_1) 758\text{ cm}^{-1}$, $\nu_2 (A_1) 364\text{ cm}^{-1}$, $\nu_3 (E) 703\text{ cm}^{-1}$
139 and $\nu_4 (E) 326\text{ cm}^{-1}$ ²⁴. The orthotellurate ion, TeO_6^{6-} will have octahedral symmetry

140 but may be strongly distorted. Vibrational modes for the tellurate anion should occur
141 in the 620 to 650 cm^{-1} region and in the 290 to 360 cm^{-1} region. If the symmetry of the
142 tellurate anion is reduced through for example bonding to a cation as is presumed in
143 the yecoraite structure, then the loss of degeneracy will occur, and additional bands
144 observed. Siebert⁶ reported the infrared spectra of selected synthetic tellurates and
145 antimonates. The position of the bands for the TeO_6^{6-} anion was defined by Siebert as
146 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
147 infrared bands were observed at 605, 650, 658, 675, 708 and 730 cm^{-1} and were
148 assigned to TeO stretching vibrations. In addition an intense band at 411 cm^{-1} is
149 assigned to a δTeO bending mode (presumably ν_4 vibration). For the compound
150 $\text{Na}_2\text{H}_4\text{TeO}_6$ infrared bands were observed at 429, 536, 587, 675 and 780 cm^{-1} . More
151 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
152 data for the compound $(\text{H}_4\text{TeO}_4)_x$. For this polytellurous acid, infrared bands were
153 found at 450 cm^{-1} (δTeO) and stretching modes at 600, 720, 800 cm^{-1} . According to
154 Siebert the TeO_6^{6-} anion is octahedral but is distorted. Thus infrared forbidden bands
155 become activated. The tellurite ion should show a maximum of six bands. The free
156 ion will have C_{3v} symmetry and four modes, $2A_1$ and $2E$. Farmer based upon the
157 work of Siebert^{6,25} defines the spectrum of $(\text{TeO}_3)^{2-}$ as ν_1 (A_1) 758 cm^{-1} , ν_2 (A_1) 364
158 cm^{-1} , ν_3 (E) 703 cm^{-1} and ν_4 (E) 326 cm^{-1} ²⁴. In this research we apply this
159 spectroscopy to the mineral yecoraite.

160
161 The Raman spectrum of yecoraite in the 600 to 1000 cm^{-1} region is shown in
162 Figure 1. A broad spectral profile with Raman bands centred at 700 cm^{-1} with
163 component bands at 640, 690 and 699 cm^{-1} are found. In addition two bands are
164 observed at 796 and 808 cm^{-1} . The assignment of Raman bands for this mineral is
165 difficult because of the overlap of the vibrations from the $(\text{TeO}_4)^{2-}$ and $(\text{TeO}_3)^{2-}$ units.
166 For tellurates the $(\text{TeO}_4)^{2-}$ ν_3 antisymmetric stretching mode occurs at wavenumbers
167 higher than the ν_1 symmetric stretching mode. In comparison, for tellurites the
168 $(\text{TeO}_3)^{2-}$ ν_3 antisymmetric stretching mode occurs at wavenumbers lower than the ν_1
169 symmetric stretching mode. Thus the two bands at 796 and 808 cm^{-1} are assigned to
170 the ν_1 $(\text{TeO}_4)^{2-}$ symmetric and ν_3 $(\text{TeO}_3)^{2-}$ antisymmetric stretching modes
171 respectively. The Raman bands at 699 cm^{-1} are attributed to the ν_3 $(\text{TeO}_4)^{2-}$
172 antisymmetric stretching mode and the band at 690 cm^{-1} to the ν_1 $(\text{TeO}_3)^{2-}$ symmetric
173 stretching mode.

174

175

176 The low wavenumber region of yecoraite in the 100 to 600 cm^{-1} region is
177 shown in Figure 2. This spectral region displays those bands which are attributable to
178 the $(\text{TeO}_4)^{2-}$ and $(\text{TeO}_3)^{2-}$ bending modes and water librational modes. The intense
179 band at 465 cm^{-1} with a shoulder at 470 cm^{-1} is assigned to these bending modes. In
180 the Raman spectrum of yecoraite there is a band at 578 cm^{-1} which may be ascribed to
181 the water librational mode. Farmer based upon the work of Siebert^{6,25} defined the
182 bending modes of $(\text{TeO}_4)^{2-}$ as $\nu_2 (A_1)$ 364 cm^{-1} $\nu_4 (E)$ 326 cm^{-1} ²⁴. Although the band
183 positions are high compared with that found by Siebert from the infrared spectrum of
184 metatelluric acid the band at 438 cm^{-1} may be assigned to the $\nu_2 (A_1)$ bending mode
185 and the band at 509 cm^{-1} to the $\nu_4 (E)$ mode. A comparison may be made with the
186 band positions for that of orthotellurate anion. The two bands for yecoraite at 301 and
187 355 cm^{-1} are assigned to the $(\text{TeO}_3)^{2-}$ $\nu_2 (A_1)$ bending mode and the two bands at 390
188 and 396 cm^{-1} may be ascribed to the $(\text{TeO}_3)^{2-}$ $\nu_4 (E)$ bending mode. The Raman
189 band at 235 cm^{-1} may be attributed to FeO stretching vibrations.

190

191 A comparison may be made with the Raman spectra of other tellurate
192 minerals. In the Raman spectrum of xocomecatlite $\text{Cu}_3(\text{OH})_4\text{TeO}_4 \cdot \text{H}_2\text{O}$ a broad band
193 that may be decomposed into component bands at 710, 763 and 796 cm^{-1} . These bands
194 are quite sharp. One possible assignment is the band at 796 cm^{-1} is ascribed to the
195 TeO_4 ν_1 symmetric stretching mode and the two bands at 710 and 763 cm^{-1} to the
196 TeO_4 antisymmetric stretching mode. Another tellurate containing mineral which
197 may be useful for a comparison of the Raman spectra of kuranakhite is the mixed
198 anionic mineral tlappallite $\text{H}_6(\text{Ca,Pb})_2(\text{Cu,Zn})_3\text{SO}_4(\text{TeO}_3)_4\text{TeO}_6$. This mineral
199 contains both the tellurite and tellurate anions in the structure. Raman bands are
200 observed for tlappallite at 650, 708, 764 and 796 cm^{-1} . It is difficult to nominate a
201 specific assignment for each of these bands, as the tellurate and tellurite bands
202 overlap. One probable assignment is as follows: the higher wavenumber bands may
203 be attributed to the tellurate ion $(\text{TeO}_6)^{2-}$ and the lower wavenumber bands to the
204 tellurite anion $(\text{TeO}_3)^{2-}$. Thus, the Raman band at 796 cm^{-1} is attributed to the ν_1
205 $(\text{TeO}_6)^{2-}$ antisymmetric stretching mode and the band at 764 cm^{-1} to the $\nu_1 (\text{TeO}_3)^{2-}$
206 symmetric stretching mode. The band at 708 cm^{-1} may be attributed to the $\nu_1 (\text{TeO}_6)^{2-}$
207 symmetric stretching mode and the band at 691 cm^{-1} to the $\nu_1 (\text{TeO}_3)^{2-}$ antisymmetric

208 stretching mode. Importantly Raman bands are observed in similar positions for these
209 three tellurate containing minerals.

210

211 The Raman spectrum of yecoraite in the 2100 to 3700 cm^{-1} region is displayed
212 in Figure 3. Prominent bands are observed at 2878, 2936, 3180 and 3400 cm^{-1} .

213 The band at 3936 cm^{-1} appears quite distinct and the observation of multiple bands
214 indicates the water molecules in the yecoraite structure are not equivalent.

215 These bands listed above are attributed to OH stretching vibrations formed by the
216 interaction of the protons with the oxygen of the tellurate and tellurite units. Studies
217 have shown a strong correlation between OH stretching frequencies and both O \cdots O
218 bond distances and H \cdots O hydrogen bond distances. Libowitzky showed that a
219 regression function can be employed relating the hydroxyl stretching frequencies with
220 regression coefficients better than 0.96 using infrared spectroscopy²⁶. The function is

221 described as: $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}} \text{ cm}^{-1}$. Thus OH \cdots O hydrogen bond
222 distances may be calculated using the Libowitzky empirical function.

223 The values for the OH stretching vibrations listed above provide hydrogen bond
224 distances of 2.625 Å (2878 cm^{-1}), 2.636 Å (2936 cm^{-1}), 2.697 Å (3180 cm^{-1}) and
225 2.798 Å (3400 cm^{-1}). The hydrogen bond distances in this mineral are very short
226 compared with that of many secondary minerals. Normally large hydrogen bond
227 distances which are present in minerals such as perhamite can also be seen in other
228 mixed anion minerals such as peisleyite where the distances ranging between 3.052(5)
229 and 2.683(6) Å. Such hydrogen bond distances are typical of secondary minerals. A
230 range of hydrogen bond distances are observed from reasonably strong to weak
231 hydrogen bonding. This range of hydrogen bonding contributes to the stability of the
232 mineral

233

234 CONCLUSIONS

235

236 The Raman spectrum of the hydrated tellurate-tellurite mineral yecoraite,
237 $\text{Bi}_5\text{Fe}^{3+}_3(\text{TeO}_3)(\text{TeO}_4)_2 \cdot 9(\text{H}_2\text{O})$, has been studied. Observed bands were assigned to
238 the stretching and bending vibrations of the metatellurate anion, $(\text{TeO}_4)^{2-}$ and tellurite
239 anion, $(\text{TeO}_3)^{2-}$, and water units in the yecoraite structure. It is apparent that bands
240 attributable to the tellurate anion $(\text{TeO}_4)^{2-}$ and tellurite anion $(\text{TeO}_3)^{2-}$ overlap, making

241 the actual assignation of the bands for this mineral quite difficult. A comparison of the
242 Raman spectrum of other tellurate and tellurite minerals including kuranakhite and
243 tlapallite, a mixed anion mineral, with the Raman spectra of other tellurate minerals
244 has been made.

245

246 **DFT calculations**

247

248 DFT type calculations were attempted for this mineral in order to determine
249 the precise calculated position of bands attributable to the tellurate and tellurite
250 anions. Given that the exact structure is unknown, this makes the calculations
251 difficult. Further the presence of protons in the structure results in calculations which
252 are not possible. The calculations cannot reach a minimum. The energy well is very
253 broad and very shallow resulting in continuous reiterations with no results

254

255

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257

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265 **References**

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312

List of Figures

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315 **Figure 1 Raman spectrum of yecoraite in the 600 to 1000 cm⁻¹ region**

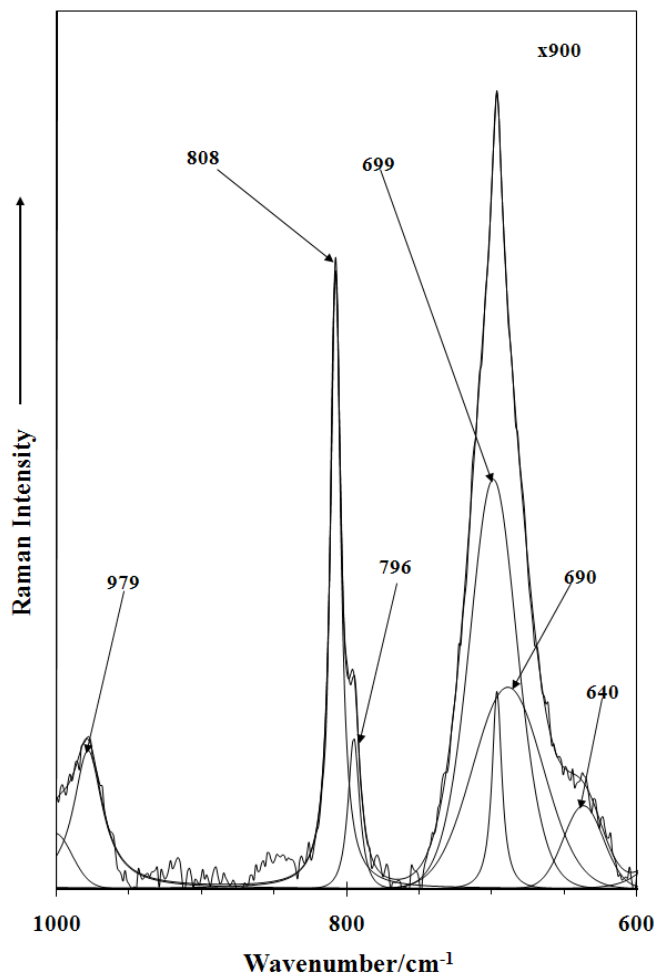
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317 **Figure 2 Raman spectrum of yecoraite in the 100 to 600 cm⁻¹ region**

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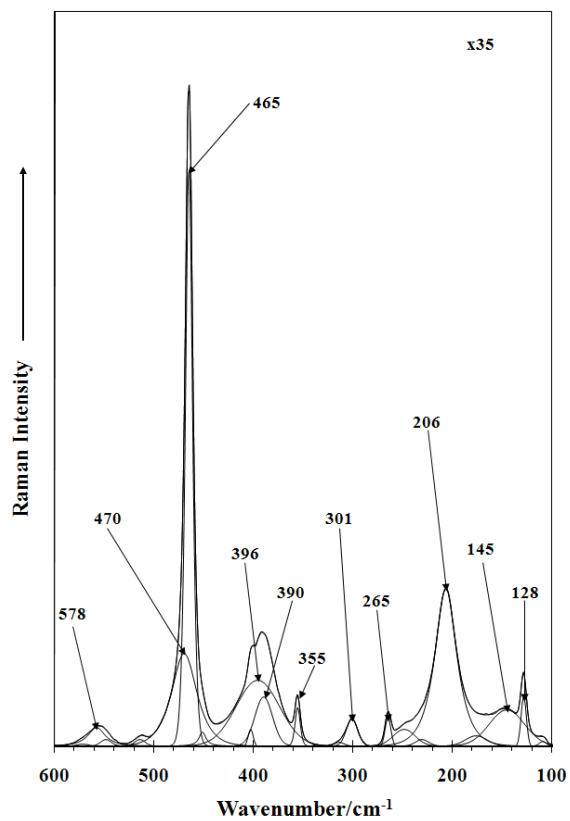
319 **Figure 3 Raman spectrum of yecoraite in the 2800 to 3600 cm⁻¹ region**

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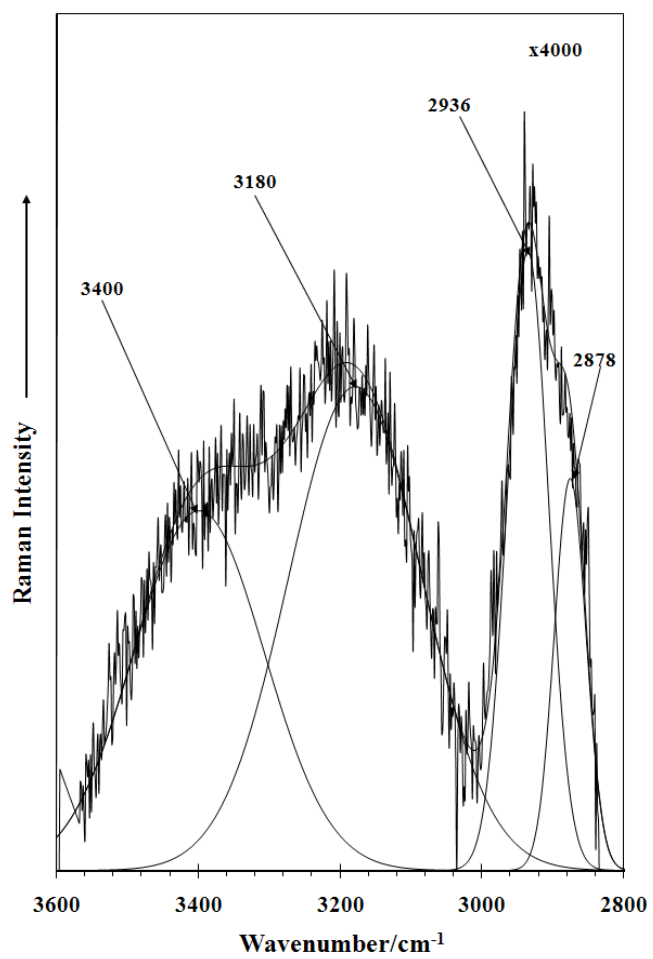
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Figure 1 yecoraite



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Figure 2



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Figure 3