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Raman and infrared spectroscopic study of turquoise minerals

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18 **ABSTRACT**
19

20 Raman and infrared spectra of three well-defined turquoise samples,
21 $CuAl_6(PO_4)_4(OH)_8.4H_2O$, from Lavender Pit, Bisbee, Cochise county, Arizona; Kouroudaiko
22 mine, Faleme river, Senegal and Lynch Station, Virginia were studied, interpreted and
23 compared. Observed Raman and infrared bands were assigned to the stretching and bending
24 vibrations of phosphate tetrahedra, water molecules and hydroxyl ions. Approximate O-H···O
25 hydrogen bond lengths were inferred from the Raman and infrared spectra. No Raman and
26 infrared bands attributable to the stretching and bending vibrations of $(PO_3OH)^{2-}$ units were
27 observed.
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INTRODUCTION

The mineral turquoise is one of the oldest gem materials known. Its use in jewellery and for personal decoration can be traced back 70 centuries, to ancient Egypt [1,2]. Today, turquoise is popular in fine jewellery as well as in various cultures, most notably among Native Americans in the south-western United States [1,2]. The first orientation of turquoise studies allows archaeologists to investigate pre-Colombian turquoise trade structures in North America and identify or authenticate the natural sources of turquoise worldwide [3-7]. Various physico-chemical characteristics of turquoise were studied together with questions of turquoise provenance especially with regard to its wealth of colours (blue, green in various shades) and further properties important for its use in jewellery [8-15]. The sources of high-quality gem turquoise are limited and because this material (due to porosity characteristic for massive aggregates) easily accepts many treatments, the majority of gem turquoise are adulterated [2, 16,17]. Detection of the extent and character of these treatments, inclusive impregnation with polymers, is a very important job especially for use of non-destructive methods [18-21].

Turquoise was one of the first gem materials to be simulated by synthetics like glass, plastic, pressed turquoise powder bonded by resin, coloured gelmagnesite or howlite [22]. At the present time, synthetic turquoise is produced by the method of Gilson [23]. A set of analytical methods, such as PXRD and EDS analysis or ATR-IR, UV-VIS-NIR and Raman spectra are used for distinguishing these artificial replacements from natural turquoise [24]. Last, but not least, turquoise affected by extended exposure to sunlight and water weathered to chalky white minerals; this alteration processes are as yet, poorly understood [3-4].

Most of as yet published papers on turquoise (as mentioned above) are, however, usually, based only on one or several research methods; especially in the case of papers focused to infrared or Raman spectroscopy the data on chemical composition or values of unit-cell parameters of studied mineral phases are mostly missing. The main aim of this paper is to report the Raman and infrared spectra of three well-defined natural untreated turquoise samples from three different occurrences, and to relate the spectra to its molecular and crystal structure. Further aim of the paper is also to certify the possibility to use Raman data for the provenance of turquoise samples; this is the reason why three samples from various localities differing in morphology, colour and details in chemical composition were studied. The paper

2

66 follows the systematic research of the large group of oxyanions containing minerals [25-29],

67 and especially their molecular structure using IR and Raman spectroscopy [30-36].

68

69 **BACKGROUND INFORMATION**

70

71 Triclinic mineral turquoise belongs to a turquoise group; general formula for minerals

72 of this group may be written as $A_{0-1}B_6(PO_4)_4(OH)_8.4H_2O$. Most common substituents at the A

73 position are Cu^{2+}, Fe^{2+} Zn^{2+} or vacancy; at the B position then Al^{3+} or Fe^{3+} [4,37-39].

74

75 Turquoise usually occurs as apple-green, bluish green, sky-blue or greenish gray fine

76 granular, dense massive to cryptocrystalline aggregates, nodules, crusts or veinlets; small

77 short columnar crystals are rare [1,40]. It has dozens of occurrences but only few produce

78 commercial gem material or contain well-formed crystals [1,40]. Turquoise is uncommon

79 supergene mineral formed in the oxidized zone (mainly in arid climates) of phosphorus-rich

80 aluminous rocks (volcanic, phosphate-rich sediments, hydrothermal porphyry deposits etc.) in

81 the presence of Cu minerals [1,40].

82

83 The unit-cell parameters of turquoise were determined by Graham [41], the first

84 solution of its crystal structure was published by Cid-Dresdner [42]. Recently, the crystal

85 structure of turquoise refined by Kolitsch and Giester [43]. Turquoise contains in its crystal

86 structure $Cu\Phi_6$ octahedra, with $\Phi = 2 H_2O$ and $4 OH^-$, two $Al\Phi_6$ octahedra with $3 OH^-$, $1 H_2O$

87 and $2 O^{2-}$ and one $Al\Phi_6$ octahedron with $4 O^{2-}$ and $2 OH^-$, and two symmetrically distinct

88 $(PO_4)^{3-}$ tetrahedra [42,43]. No $(PO_3OH)^{2-}$ units were observed in its crystal structure [4,

89 42,43]. Only in the case of planerite, $Al_6(PO_4)_2(PO_3OH)_2.4H_2O$, the charge balance should be

90 maintained by the protonation, connected with Cu-site occupancy decrease [37]. However,

91 according to Kolitsch and Giester [43], the charge balance might be also achieved by

92 introducing additional Cu^{2+} or other cations in the partially occupied site at (1/2, 0, ½).

93

94 **EXPERIMENTAL**

95

96 **Minerals**

97

98   The studied samples of the mineral turquoise originated from three different
99 occurrences: Lavender Pit, Bisbee, Cochise county, Arizona (labelled as A) - little greenish
100 cryptocrystalline aggregates up to some cm in size (Fig. 1); Kouroudaiko mine, Faleme river,
101 Senegal (labelled as S) - light greenish blue globular aggregates up to 3 mm in size in
102 association with tiny transparent senegalite crystals (Fig. 2); Lynch Station, Virginia (labelled
103 as V) - rich groups of transparent dark sky-blue well-formed crystals up to 2 mm in size on
104 quartz gangue (Fig. 3).

105

106   Carefully hand-picked samples were used for X-ray powder diffraction experiments.
107 To minimize the complicated shape of background, the samples studied were placed on a flat
108 low-background silicon wafer. Powder XRD measurements were carried out with CuKα
109 radiation at a Bruker D8 Advance diffractometer (40 kV, 40 mA) in the range 4-70° 2θ in the
110 step-scan mode 0.01°/8 s. The position and intensities of reflections were calculated using the
111 Pearson VII profile shape function in the ZDS program package [44]. The measured patterns
112 were indexed using unit-cell parameters and space group proposed by Kolitsch and Giester
113 [43]. The unit-cell parameters refined from measured powder XRD using the program of
114 Burnham [45] are compared with published data in the Table 1.

115

116   All turquoise samples were quantitatively analysed by Cameca SX 100 electron
117 microprobe system in wavelength dispersion mode for chemical composition (Table 2).
118 Studied sample was mounted into the epoxide resin and polished. The polished surface was
119 coated with carbon layer 250 Å. An acceleration voltage of 15 kV, a specimen current of 10
120 nA, and a beam diameter of 5 μm were used. Well-defined natural and synthetic compounds
121 were used as standards. The raw intensities were converted to the concentrations using
122 automatic *PAP* matrix correction software package. On the basis of P+Si = 4 *apfu*, empirical
123 formula of turquoise from Arizona may be expressed as $(Cu_{0.90}Fe_{0.10}Zn_{0.01})_{\Sigma 1.01}Al_{6.08}$
124 $[(PO_4)_{3.99}(SiO_4)_{0.01}]_{\Sigma 4.00}(OH)_{8.24} \cdot 4H_2O$; from Senegal as $(Cu_{0.63}\square_{0.29}Fe_{0.05}Zn_{0.02}Ba_{0.01})_{\Sigma 1.00}$
125 $(Al_{5.99}Fe_{0.01})_{\Sigma 6.00}[(PO_4)_{3.71}(PO_3OH)_{0.29}]_{\Sigma 4.00}(OH)_{7.71} \cdot 4H_2O$ and from Virginia as
126 $(Cu_{1.03}Fe_{0.11}Ba_{0.02}Zn_{0.01}Ca_{0.01})_{\Sigma 1.18}(Al_{5.84}Fe_{0.16})_{\Sigma 6.00}(PO_4)_{4.00}(OH)_{8.36} \cdot 4H_2O$.

127

128

129 **Raman and infrared spectroscopy**

130

131   Fragments of aggregates and crystals of turquoise were placed on a polished metal
132   surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and
133   50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which
134   also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman
135   spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised
136   light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of $\pm$ 1 cm^{-1} in
137   the range between 200 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest
138   magnification (50x) were accumulated to improve the signal to noise ratio in the spectra.
139   Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the
140   authors provide more details of the experimental technique. Alignment of all samples in a
141   similar orientation has been attempted and achieved. However, differences in intensity may
142   be observed due to minor differences in the crystal orientation.
143
144   Infrared spectra was recorded by micro diffuse reflectance method (DRIFTS) on a
145   Nicolet Magna 760 FTIR spectrometer (range 4000-600 cm^{-1}, resolution 4 cm^{-1}, 128 scans, 2
146   level zero-filtering, Happ-Genzel apodization), equipped with Spectra Tech InspectIR micro
147   FTIR accessory. Sample of amount less than 0.050 mg was mixed without using pressure
148   with KBr. Samples were immediately recorded together with the same KBr as a reference.
149
150   Spectral manipulation such as baseline correction/adjustment and smoothing were
151   performed using the Spectracalc software package GRAMS (Galactic Industries Corporation,
152   NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software
153   package that enabled the type of fitting function to be selected and allows specific parameters
154   to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-
155   product function with the minimum number of component bands used for the fitting process.
156   The Lorentzian- Gaussian ratio was maintained at values greater than 0.7 and fitting was
157   undertaken until reproducible results were obtained with squared correlations of r^2 greater
158   than 0.995.
159

160   **RESULTS AND DISCUSSION**
161

162   **Crystal symmetry and vibrational spectra of turquoise**
163

164   Turquoise, $CuAl_6(PO_4)_4(OH)_8\cdot4H_2O$, is triclinic, space group $P\text{-}1 - C_i^1$, $Z = 1$. The

165 structure consists of distorted CuO_6 polyhedra, AlO_6 octahedra and PO_4 tetrahedra. By edge-

166 and corner-sharing of these polyhedra a fairly dense three-dimensional framework is formed

167 which is further strengthened by a system of hydrogen bonds [43].

168

169   In the crystal structure of turquoise there are one symmetrically distinct CuO_6

170 octahedron, three structurally distinct AlO_6 octahedra, two symmetrically distinct PO_4

171 tetrahedra, two structurally unequivalent water molecules and four structurally unequivalent

172 OH units [42,43]. Tentative interpretation of infrared and Raman spectra of turquoise studied

173 is based on factor group analysis of phosphates and water in turquoise published by Frost et

174 al.[13] and publications by Nakamoto [46], Čejka et al. [36], Keller [47-50], Pechkovskii et

175 al. [51], Goldsmith and Ross [52], Devamani and Alagar [53], Aguirre et al. [54], Frost et al.

176 [13, 55] and Reddy et al. [14].

177

178   According to Nakamoto [46], octahedral units XY_6 exhibit six normal vibrations,

179 from which ν_1 (A_{1g}) and ν_2 (E_g) stretching and ν_5 (F_{2g}) bending vibrations are Raman active,

180 while only ν_3 (F_{1u}) stretching and ν_4 (F_{1u}) bending vibrations are infrared active. Symmetry

181 lowering in the case of XY4Z2 may cause Raman and infrared activation of corresponding

182 vibrations and also splitting of degenerate vibrations. Free $(PO_4)^{3-}$ anion exhibits tetrahedral

183 T_d symmetry. In the case of a free ion of T_d symmetry, there are 9 normal vibrations

184 characterized by four distinguishable modes of vibrations: ν_1 (A_1) symmetric stretching

185 vibration, Raman active, ν_2 (δ) (E) doubly degenerate bending vibration, Raman active, ν_3

186 (F_2) triply degenerate antisymmetric stretching vibration, Raman and infrared active, ν_4 (δ)

187 (F_2) triply degenerate bending vibration, Raman and infrared active. T_d symmetry lowering

188 may cause infrared activation of the ν_1 and ν_2 vibrations and splitting of the doubly

189 degenerate ν_2 and triply degenerate ν_3 and ν_4 vibrations [36].

190

191 **Raman and infrared spectroscopy**

192

193   Full range Raman and infrared spectra of the studied minerals from Arizona (A),

194 Senegal (S) and Virginia (V) are given in Figs. 4a-f and their tentative assignments in Table

195 3. These spectra show the position of the bands and their relative intensities. It is obvious that

196 there are large parts of the spectra where little or no intensity is observed. Therefore, the

6

197 spectra are subdivided into sections according to the type of vibration is being investigated.

198 In this way the precise position of the bands can be detailed. Observed wavenumbers of the

199 Raman bands of the studied turquoise samples are close to the approximate wavenumbers

200 inferred from the Raman spectra of RRUFF's three turquois samples R50225, R50418 and

201 R50554.

202

203   Raman and infrared spectral regions of ν OH stretching vibrations are presented in

204 Figs. 5a-f. Raman bands et 3544, 3502, 3473 and 3450 cm^{-1} (A), 3527, 3506, 3471 and 3453

205 cm^{-1} (S) and 3499, 3473 and 3451 cm^{-1} (V) and infrared bands at 3509, 3465 and 3451 cm^{-1}

206 (A), 3607, 3506, 3464, 3450 and 3447 cm^{-1} (S) and 3505, 3465 and 3451 cm^{-1} (V) are

207 assigned to the ν OH stretching vibrations and assigned to the hydrogen bonded,

208 symmetrically distinct hydroxyls OH$^-$. Raman bands at 3397, 3279 and 3077 cm^{-1} (A), 3419,

209 3290 and 3092 cm^{-1} (S), 3410, 3273 and 3085 cm^{-1} (V), and infrared spectra at 3431, 3269,

210 3075 and 3067 cm^{-1} (A), 3276, 3072 and 3051 cm^{-1} (S) and 3417, 3288 and 3058 cm^{-1} (V) are

211 attributed to the ν OH stretching vibrations of symmetrically distinct hydrogen bonded water

212 molecules. Very weak Raman and infrared bands at 2932, 2920 and 2934 cm^{-1} are probably

213 connected with organic impurities.

214

215   Libowitzky's empirical relation [56] enables to infer from the wavenumbers of

216 Raman and infrared bands of minerals assigned to the ν OH stretching vibrations

217 approximate O-H$\cdots$O hydrogen bond lengths. In the case of studied turquoise samples

218 inferred hydrogen bond lengths vary from 2.98 to 2.67 Å. This agrees very well with X-ray

219 single crystal structure data 2.970-2.670 Å [42] and 3.020-2.685 Å [43].

220

221   Broad Raman bands at 1609 cm^{-1} (A), 1614 cm^{-1} (S) and 1632 cm^{-1} (V) and infrared

222 bands at 1646 and 1595 cm^{-1} (A), 1654 and 1587 cm^{-1} (S) and 1622 cm^{-1} (V) are attributed to

223 the ν_2 (δ) H_2O bending vibrations of the symmetrically distinct differently hydrogen bonded

224 water molecules (Figs. 6a-f). Observed infrared bands at 1474 cm^{-1} (A), 1467 cm^{-1} (S) and

225 1513 cm^{-1} (V) are assigned to overtones or combination bands.

226

227   The Raman spectra in the 800 to 1400 cm^{-1} spectral range and infrared spectra in the

228 500 to 1300 cm^{-1} spectral range are reported in Figs. 7a-f. Raman bands at 1173, 1160 and

229 1105 cm^{-1} (A), 1184, 1161 and 1104 cm^{-1} (S), and 1185, 1162 and 1105 cm^{-1} (V) and infrared

230   bands and shoulders at 1195, 1158, 1103 and 1084 cm^{-1} (A), 1194, 1143, 1104 and 1082 cm^{-1}

231   (S), and 1192, 1142, 1110 and 1092 cm^{-1} (V) are connected with split triply degenerate ν_3

232   $(PO_4)^{3-}$ antisymmetric stretching vibrations.

233   Very intense Raman bands at 1042 cm^{-1} (A), 1041 cm^{-1} (S), 1042 cm^{-1} (V) and

234   infrared bands at 1055 cm^{-1} (A), 1056 cm^{-1} (S), 1042 cm^{-1} (V) are assigned to the ν_1 $(PO_4)^{3-}$

235   symmetric stretching vibrations. Raman bands at 1065 cm^{-1} (A), 1064 cm^{-1} (S) and 1065 cm^{-1}

236   (V) are also related to the ν_1 $(PO_4)^{3-}$ vibrations. Some of the Raman bands and shoulders at

237   1004, 985 and 931 cm^{-1} (A), 1031, 991, 935 cm^{-1} (S), 1020, 985, 942, 889 cm^{-1} (V) and

238   infrared bands and shoulders 1034, 1011, 990, 964, 899 cm^{-1} (A), 1035, 1002, 948, 897 cm^{-1}

239   (S), 1008, 991, 956, 897 cm^{-1} (V) may also be related to these vibrations, however more

240   probably may be attributed to the δ Al-OH and δ Cu-OH bending vibrations together with the

241   Raman bands at 815 cm^{-1} (A), 836 and 815 cm^{-1} (S), 811 cm^{-1} (V) and infrared bands at 835

242   cm^{-1} (A), 835 cm^{-1} (S), 835 cm^{-1} (V), while the infrared bands at 785 and 727 cm^{-1} (A), 786

243   and 722 cm^{-1} (S), 784, 723 cm^{-1} (V) are assigned to the librational modes of water molecules.

244   Because the character of the Raman spectra of all three studied turquoise samples in

245   the region from 1200 to 900 cm^{-1} is practically identical, it is very improbable that in the

246   structure of the turquoise sample from Senegal could be present the $(PO_3OH)^{2-}$ units, as

247   expected from the mechanism of planerite substitution proposed by Foord and Taggart [37].

248   More distinctive is therefore the explanation of vacancy given by Kolitsch and Giester [43].

249

250   The Raman spectra of turquoise in the 300 to 800 cm^{-1} spectral range are displayed in

251   Figs. 8a-c. Raman bands and shoulders at 643, 593, 571 and 550 cm^{-1} (A), 642, 592, 571 and

252   548 cm^{-1} (S), 663, 644, 629, 611, 593, 571 and 551 cm^{-1} (V) are assigned to the split out-of-

253   plane triply degenerate ν_4 (δ) $(PO_4)^{3-}$ bending vibrations. Some of observed bands, however,

254   may be also connected with the Al(O,OH) bending vibrations and Cu-O stretching vibrations.

255   Coincidence (an overlap) of the mentioned vibrations is supposed. Raman bands and

256   shoulders at 506, 485, 471, 457, 438, 426, 417 and 387 cm^{-1} (A), 511, 483, 469, 460, 437,

257   423, 417 and 385 cm^{-1} (S), 511, 498, 486, 469, 449, 437, 425, 417, 409 and 385 cm^{-1} (V) are

258   related to the split doubly degenerate ν_2 (δ) $(PO_4)^{3-}$ bending vibrations. These bands may

259   partly overlap with bands of Cu-O stretching vibrations and bending vibrations.

260

261   Raman bands at 337, 321 and 303 cm^{-1} (A), 335, 320 and 301 cm^{-1} (S), 367, 339, 319

262   and 303 cm^{-1} (V).- these bands may probably be related to the stretching and bending

8

263   vibrations of Cu-(O,OH,H$_2$O) and Al-(O,OH,H$_2$O). Raman bands observed in the region from

264   300 to 100 cm^{-1} (Figs. 9a-c) may be assigned to OCuO bending vibrations, OAlO bending

265   vibrations and lattice vibrations.

266

267   **CONCLUSIONS**

268

269   1. Raman and infrared spectra of three well defined turquoise samples were recorded.

270

271   2. Observed Raman and infrared bands are tentatively interpreted and assigned to the

272   stretching and bending vibrations of (PO$_4$)$^{3-}$ tetrahedra and of vibrations of hydrogen bonded

273   water molecules and hydroxyl ions. No Raman and infrared bands which could be

274   unambiguously attributed to the stretching and bending vibrations (PO$_3$OH)$^{2-}$ were observed.

275

276   3. Approximate O-H···O hydrogen bond lengths are inferred from observed Raman and

277   infrared bands connected with the ν OH stretching vibrations of water molecules and

278   hydroxyl ions.

279

280   4. Observed Raman and infrared spectra of studied turquoise samples are very similar and

281   comparable. From the results may be inferred that Raman spectroscopy may be very well

282   used to distinguish natural turquoise samples from possible imitations including

283   impregnations of natural material. Vibrational spectra of natural turquoise samples from

284   various localities possessing different morphology, colours etc. are very close. Vibrational

285   spectroscopy cannot be therefore offer reliable data for the provenance determination of

286   natural turquoise.

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TABLES

438

439 Table 1 Unit-cell parameters of turqouise samples (for triclinic space group *P*-1)

440

	Virginia	Senegal	Arizona	[43]	[39]
a [Å]	7.411 (3)	7.411 (5)	7.410 (5)	7.410(1)	7.426(8)
b [Å]	7.632 (3)	7.635 (6)	7.635 (6)	7.633(1)	7.634(8)
c [Å]	9.905 (4)	9.904 (7)	9.901 (7)	9.904(1)	9.91(1)
α [°]	68.43 (3)	68.46 (5)	68.43 (5)	68.42(1)	68.67(8)
β [°]	69.65 (2)	69.64 (5)	69.63 (5)	69.65(1)	69.70(8)
γ [°]	65.05 (3)	65.03 (5)	65.05 (5)	65.01(1)	65.01(8)
V [Å^3]	459.9 (3)	460.0 (7)	459.7 (6)	460.3(1)	461.5(9)

441

442

443 Table 2 Chemical composition of studied turquoise samples (wt. %)

444

	Virginia	Senegal	Arizona	Ideal
CaO	0.04	0.00	0.00	
FeO*	0.92	0.42	0.83	
BaO	0.37	0.21	0.00	
CuO	9.76	6.17	8.61	9.78
ZnO	0.12	0.24	0.13	
Al_2O_3	35.37	37.92	37.33	37.60
Fe_2O_3*	1.56	0.12	0.00	
SiO_2	0.00	0.00	0.09	
P_2O_5	33.75	35.27	34.09	34.90
H_2O**	17.52	17.90	17.62	17.72
total	99.41	98.25	98.69	100.00
Ca^{2+}	0.006	0.000	0.000	
Fe^{2+}	0.108	0.047	0.095	
Ba^{2+}	0.020	0.011	0.000	
Cu^{2+}	1.032	0.625	0.898	
Zn^{2+}	0.013	0.023	0.013	
Σ Me^{2+}	1.178	0.706	1.006	
□	0.000	0.294	0.000	
Al^{3+}	5.835	5.987	6.078	
Fe^{3+}	0.165	0.013	0.000	

Σ Me^{3+}	6.000	6.000	6.078
(SiO$_4$)	0.000	0.000	0.012
(PO$_4$)	4.000	3.706	3.988
(PO$_3$OH)	0.000	0.294	0.000
Σ T	4.000	4.000	4.000
OH	8.356	7.706	8.236
H$_2$O	4.00	4.00	4.00

445

446 FeO* and Fe$_2$O$_3$* contents were calculated on the basis of Me^{2+}/Me^{3+} cations; H$_2$O** content

447 was calculated on the basis of charge balance and ideal content of 4 H$_2$O molecules.

448

449 Table 3 Tentative assignment of turquoise spectra

Raman			Infrared			Tentative assignment
A	S	V	A	S	V	
3544	3527			3607		
3502	3506	3499	3509	3506	3505	
3473	3471	3473	3465	3464	3465	ν OH stretch of $(OH)^-$
3450	3453	3451	3451	3450	3451	
				3447		
3397	3419	3410	3431		3417	
3279	3290	3273	3269	3276	3288	
3077	3092	3085	3075	3072	3058	ν OH stretch of water molecules
			3067	3051		
		1632	1646	1654	1622	
1609	1614		1595	1587		δ H_2O bend
			1474	1467	1513	overtones of combination bands
1173	1184	1185	1195	1194	1192	
1160	1161	1162	1158	1143	1142	
1105	1104	1105	1103	1104	1110	ν_3 $(PO_4)^{3-}$ antisymmetric stretch
			1084	1082	1092	
1065	1064	1065	1055	1056		
1042	1041	1042			1042	ν_1 $(PO_4)^{3-}$ symmetric stretch
	1031	1020	1034	1035		
1004			1011	1002	1008	
985	991	985	990		991	
931	935	942	964	948	956	δ Al-OH and/or δ Cu-OH
	836	889	899	897	897	
815	815	811	835	835	835	
			785	786	784	
			727	722	723	libration modes od H_2O
		663				
643	642	644				
		629				ν_4 $(PO_4)^{3-}$ bend and/or
		611				Al-(O,OH) bend and/or
593	592	593				Cu-O stretch
571	571	571				
550	548	551				
506	511	511				
		498				ν_2 $(PO_4)^{3-}$ bend and/or
485	483	486				Cu-O stretch and bend

18

471	469	469	
457	460	449	
438	437	437	
426	423	425	
417	417	417	
		408	
387	385	385	
		367	
337	335	339	Cu-(O,OH,H$_2$O) and Al-(O,OH,H$_2$O) stretch and bend
321	320	319	vibrations (?)
303	301	303	
276	277		
260	259	259	
		252	
245	244	246	lattice vibrations and/or
233	231	233	O-Cu-O bend and/or
219	218	218	O-Al-O bend
211	210	212	
200	196	202	
176	175	177	
155	152	156	

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