

A vibrational spectroscopic study of the silicate mineral inesite



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ABSTRACT

We have studied the hydrated hydroxyl silicate mineral inesite of formula $\text{Ca}_2(\text{Mn,Fe})_7\text{Si}_{10}\text{O}_{28}(\text{OH})\cdot 5\text{H}_2\text{O}$ using a combination of scanning electron microscopy with EDX and Raman and infrared spectroscopy. SEM analysis shows the mineral to be a pure monomineral with no impurities. Semiquantitative analysis shows a homogeneous phase, composed by Ca, Mn²⁺, Si and P, with minor amounts of Mg and Fe. Raman spectrum shows well resolved component bands at 997, 1031, 1051, and 1067 cm⁻¹ attributed to a range of SiO symmetric stretching vibrations of [Si₁₀O₂₈] units. Infrared bands found at 896, 928, 959 and 985 cm⁻¹ are attributed to the OSiO antisymmetric stretching vibrations. An intense broad band at 653 cm⁻¹ with shoulder bands at 608, 631 and 684 cm⁻¹ are associated with the bending modes of the OSiO units of the 6- and 8-membered rings of the [Si₁₀O₂₈] units. The sharp band at 3642 cm⁻¹ with shoulder bands at 3612 and 3662 cm⁻¹ are assigned to the OH stretching vibrations of the hydroxyl units. The broad Raman band at 3420 cm⁻¹ with shoulder bands at 3362 and 3496 cm⁻¹ are assigned to the water stretching vibrations. The application of vibrational spectroscopy has enabled an assessment of the molecular structure of inesite to be undertaken.

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34 **Keywords:** inesite, silicate, N'chwaning mine, Raman spectroscopy, infrared spectroscopy

35

36 **Introduction**

37 Inesite [1] is a hydrated calcium manganese silicate hydroxide of formula
38 $\text{Ca}_2(\text{Mn,Fe})_7\text{Si}_{10}\text{O}_{28}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. The mineral is triclinic and its habit includes prismatic
39 crystals with chisel-like terminations and tabular and fibrous and in radiating aggregates and
40 spherules. The mineral was named after the Greek for “fibers,” *ines*, in reference to its
41 common crystal habit. The mineral has outstanding colours from pink to orange or flesh-red to
42 rose. The mineral was first discovered in 1887 at the manganese mines at Nanzenbach,
43 northeast of Dillenburg, Germany [2] and is known from quite a number of sites worldwide
44 [3-6].

45
46 The structure of inesite has been solved by Otroshchenko et al. [7], who state that the crystals
47 of inesite are triclinic, space group $P\bar{1}$, with $a = 8.956$, $b = 9.257$, $c = 11.995$ Å, $\alpha = 91^\circ 54'$,
48 $\beta = 47^\circ 30'$, $\gamma = 85^\circ 50'$, and $Z = 1$. Inesite structure is composed of Mn octahedra, Ca
49 polyhedra, and Si tetrahedra [7]. The $[\text{Si}_{10}\text{O}_{28}]$ infinite ribbons lie parallel to layers composed
50 of Mn octahedra and Ca polyhedra. There are four different Mn octahedra (composed of Mn
51 + O, Mn + O + OH, Mn + O + H₂O, and Mn + O + OH + 1/2 H₂O) and five Si-O tetrahedra
52 (differing in interatomic distances) in the inesite structure [8]. Wan and Ghose stated that the
53 crystal structure of inesite provides the first example of double silicate chains with a
54 periodicity of five tetrahedra [9]. In their study of the structure, Wan and Ghose [8] chose
55 different orientation of crystallographic elements for mineral inesite, where $a = 8.889(2)$, $b =$
56 $9.247(2)$, $c = 11.975(3)$ Å, $\alpha = 88.15(2)^\circ$, $\beta = 132.07(2)^\circ$, $\gamma = 96.64(2)^\circ$. The crystal structure
57 of inesite is composed of two components: (1) single silicate chains with a five-tetrahedral-
58 repeat period, polymerized into double chains with alternating 6- and 8-membered rings and
59 (2) polyhedral bands, whose building blocks are a distorted pentagonal bipyramid around Ca
60 and octahedra around four crystallographic different Mn atoms. These two components are
61 linked into a three-dimensional framework by sharing corners, in addition to two edges of the
62 Ca polyhedron, which are shared by two silicate tetrahedra. The bridging Si-O bonds are
63 significantly longer (av. 1.64 Å) than the nonbridging Si-O bonds (av. 1.60 Å) [10]. The three
64 crystallographically independent water molecules serve as apical ligands to the Ca and Mn
65 atoms. The site of one of the water molecules is statistically occupied half the time,
66 accounting for five water molecules in the unit cell [8]. All seven hydrogen atoms are
67 involved in hydrogen bonding. The recipient of a hydrogen bond is either a water molecule or
68 a bridging oxygen atom bonded to two silicon only [8].

69 Raman spectroscopy has proven very useful for the study of silicate minerals [11-14].
70 Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related
71 minerals where isomorphic substitution may occur as with wardite, cyrilovite and inesite, as
72 often occurs with minerals containing phosphate groups. This paper is a part of systematic
73 studies of vibrational spectra of minerals of secondary origin. The objective of this research is
74 to report the Raman and infrared spectra of inesite and to relate the spectra to the molecular
75 structure of the mineral.

76 **Experimental**

77 *Samples description and preparation*

78 Inesite from N'chwaning mine in the Kalahari manganese field occurs in the vein- and vug-
79 hosted mineral associations in Wessels-type ore [15], which is oxide-rich, carbonate-poor
80 high-grade manganese ore formed by hydrothermal alteration of Mamatwan-type (braunite
81 lutite) ore [16]. Among four textural types of vein- and vug-hosted mineralization in
82 Wessels-type ore, inesite occurs in large isolated vugs or "pockets" [17]. In most vugs of this
83 type a crude concentric mineralogical zonation is observable. The wallrock is usually
84 composed of massive hematite or jacobsite, and inner lining along the wallrock contact is
85 composed of a fine crystalline, massive mixture of densely intergrown andradite, tephroite,
86 jacobsite, clinochlore, datolite and caryopilite. This fine crystalline assemblage is overgrown
87 by a more coarse grained mineral association containing euhedral crystals of a multitude of
88 mineral species ranging from andradite and hausmannite to xonotlite, tobermorite, datolite,
89 inesite and many more [18].

90

91 The sample was incorporated to the collection of the Geology Department of the Federal
92 University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-195. The sample was
93 gently crushed and the associated minerals were removed under a stereomicroscope Leica
94 MZ4. Scanning electron microscopy (SEM) in the EDS mode was applied to support the
95 mineral characterization.

96 .

97

98 *Scanning electron microscopy (SEM)*

99 Experiments and analyses involving electron microscopy were performed in the Center of
100 Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais,

101 Brazil (<http://www.microscopia.ufmg.br>). The results are given in the supplementary
102 information.

103

104 Inesite single crystal up to 1 mm was coated with a 5 nm layer of evaporated carbon.

105 Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-
106 6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode
107 were performed with a ThermoNORAN spectrometer model Quest and was applied to
108 support the mineral characterization.

109

110 **Raman spectroscopy**

111 Crystals of inesite were placed on a polished metal surface on the stage of an Olympus
112 BSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is
113 part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a
114 filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a
115 Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and
116 collected at a nominal resolution of 2 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between
117 200 and 4000 cm^{-1} . Some of these mineral fluoresced badly at 633 nm; as a consequence
118 other laser excitation wavelengths were used especially the 785 nm laser. Repeated
119 acquisitions on the crystals using the highest magnification (50x) were accumulated to
120 improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm^{-1}
121 line of a silicon wafer. Previous studies by the authors provide more details of the
122 experimental technique. Alignment of all crystals in a similar orientation has been attempted
123 and achieved. However, differences in intensity may be observed due to minor differences in
124 the crystal orientation.

125

126 A Raman spectrum of inesite is recorded on the RRUFF data base
127 [<http://rruff.info/inesite/display=default/R090030>]. This spectrum has been downloaded and
128 is included in the supplementary information.

129

130 **Infrared spectroscopy**

131 Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart
132 endurance single bounce diamond ATR cell. Spectra over the $4000\text{--}525\text{ cm}^{-1}$ range were

133 obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of
134 0.6329 cm/s . Spectra were co-added to improve the signal to noise ratio.

135

136 Spectral manipulation such as baseline correction/adjustment and smoothing were performed
137 using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH,
138 USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package
139 that enabled the type of fitting function to be selected and allows specific parameters to be
140 fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product
141 function with the minimum number of component bands used for the fitting process. The
142 Gaussian-Lorentzian ratio was maintained at values greater than 0.7 and fitting was
143 undertaken until reproducible results were obtained with squared correlations of r^2 greater
144 than 0.995.

145

146 **Results and Discussion**

147

148 *Chemical characterization*

149 The SEM image of inesite sample studied in this work is shown in Figure S1. Inesite crystals
150 show a prismatic habitus. Qualitative chemical composition shows a homogeneous phase,
151 composed by Ca, Mn and Si, with minor amounts of Al (Figure S2).

152

153 **Vibrational spectroscopy**

154 The Raman spectrum of inesite in the $100\text{ to }4000\text{ cm}^{-1}$ spectral range is illustrated in Figure
155 1a. This Raman spectrum shows the position of the Raman bands and their relative
156 intensities. It is obvious that there are large parts of the spectrum where little or no intensity is
157 observed. Therefore, the spectrum is subdivided into sections according to the type of
158 vibration being investigated. In this way, the precise position of the bands can be detailed.
159 The infrared spectrum of inesite in the $500\text{ to }4000\text{ cm}^{-1}$ spectral range is shown in Figure 1b.
160 The reflectance spectrum starts at $\sim 500\text{ cm}^{-1}$ because the ATR cell absorbs all infrared
161 radiation below this wavenumber. As for the Raman spectrum, the infrared spectrum is
162 subdivided into sections depending upon the type of vibration being examined. The complete
163 infrared spectrum displays the position of the infrared bands and their relative intensity. It is
164 noted that there is significant intensity in the hydroxyl stretching region in both the Raman
165 and infrared spectra.

166

167 The Raman spectrum of inesite over the 850 to 1400 cm^{-1} spectral range is shown in Figure
168 2a. The Raman spectrum is dominated by a series of intense overlapping Raman bands with
169 resolved component bands at 997, 1031, 1051, and 1067 cm^{-1} . These bands are attributed to a
170 range of SiO symmetric stretching vibrations. The structure consists of infinite ribbons of
171 $[\text{Si}_{10}\text{O}_{28}]$ units and with silicate double chains with alternate 6- and 8-membered rings. Thus,
172 it is not unexpected that there are differing SiO stretching vibrations. In the Raman spectrum
173 of inesite from the RRUFF data base, Raman bands are identified at 1013, 1025 and 1067
174 cm^{-1} . The position of these bands is in harmony with the Raman bands shown in Figure 4a.
175 Dowty showed that the $-\text{SiO}_3$ units had a unique band position of 980 cm^{-1} [19] (see Figures 2
176 and 4 of this reference). Dowty also showed that Si_2O_5 units had a Raman peak at around
177 1100 cm^{-1} .

178

179 The infrared spectrum of inesite over the 700 to 1200 cm^{-1} spectral range is provided in
180 Figure 2b. The infrared spectrum is complex with multiple overlapping bands. The Raman
181 bands in the 1000 to 1100 cm^{-1} spectral range are also observed in the infrared spectrum with
182 infrared bands at 1021, 1042, 1057, 1083 and 1101 cm^{-1} . Infrared bands are found at 896,
183 928, 959 and 985 cm^{-1} . These bands are attributed to the OSiO antisymmetric stretching
184 vibrations. These bands were not observed or were of very low intensity in the Raman
185 spectrum. It is likely that the infrared bands at 720, 743, 771 are due to water librational
186 modes or hydroxyl deformation modes.

187

188 The Raman spectrum of inesite over the 550 to 800 cm^{-1} spectral range and the 100 to 550
189 cm^{-1} spectral range is shown in Figure 3. The Raman spectrum (Figure 3a) is dominated by
190 an intense broad band at 653 cm^{-1} with shoulder bands at 608, 631 and 684 cm^{-1} . These
191 bands are associated with the bending modes of the OSiO units of the 6- and 8-membered
192 rings of the $[\text{Si}_{10}\text{O}_{28}]$ units. The Raman spectrum from the RRUFF data base shows a very
193 intense Raman band at 651 cm^{-1} with shoulder bands at 606, 687 and 710 cm^{-1} . The position
194 of the bands from the RRUFF data base is in good agreement with the bands shown in Figure
195 3a.

196

197 The Raman spectrum (Figure 3) may be divided into sections (a) Raman bands in the 350 to
198 467 cm^{-1} spectral range and (b) bands between 100 to 301 cm^{-1} region. The first group of
199 bands are attributed to CaO and MnO stretching and bending vibrations. The Raman bands

200 below 300 cm^{-1} may simply be described as external vibrations or lattice modes. In the
201 RRUFF spectrum, Raman bands are detailed at 337, 348, 421, 445 and 489 cm^{-1} .

202

203 The Raman spectrum of inesite in the hydroxyl stretching region is reported in Figure 4a.
204 There are two features in this spectrum (a) the sharp band at 3642 cm^{-1} and (b) the broad band
205 centred upon 3420 cm^{-1} . The first band with its shoulders at 3612 and 3662 cm^{-1} are assigned
206 to the OH stretching vibrations of the hydroxyl units. The observation of multiple OH
207 stretching bands supports the concept of non-equivalent hydroxyl units in the inesite
208 structure. The broad Raman band at 3420 cm^{-1} with shoulder bands at 3362 and 3496 cm^{-1} are
209 assigned to the water OH stretching vibrations.

210

211 The infrared spectrum of inesite in the 2700 to 3800 cm^{-1} spectral range is shown in Figure
212 4b. The infrared spectrum is broad with multiple overlapping bands. The sharp bands at
213 3609 and 3638 cm^{-1} are attributed to the OH stretching vibrations of the OH units. The series
214 of resolved component bands at 2944 , 3108 , 3261 , 3379 and 3429 cm^{-1} are ascribed to water
215 stretching vibrations. The observation of multiple water OH stretching vibrations supports the
216 concept of non-equivalent water molecules in the inesite structure. This means that water
217 exists in the inesite structure in different molecular environments.

218

219 The Raman spectrum of inesite over the 1500 to 1900 cm^{-1} spectral range is shown in Figure
220 5a. The infrared spectrum of inesite over the 1200 to 1800 cm^{-1} spectral range is provided in
221 Figure 5b. The Raman bands at 1608 , 1653 and 1671 cm^{-1} are assigned to water bending
222 vibrational modes. The observation of three bands supports the concept of water molecules in
223 different molecular environments with different hydrogen bond strengths. This concept is
224 reinforced by the series of bands in the infrared spectrum at 1607 , 1638 and 1670 cm^{-1}
225 assigned to water bending modes. The infrared spectrum also displays two bands at 1417 and
226 1470 cm^{-1} .

227

228 CONCLUSIONS

229 Inesite is a hydrated hydroxyl silicate mineral of formula $\text{Ca}_2(\text{Mn,Fe})_7\text{Si}_{10}\text{O}_{28}(\text{OH})\cdot$
230 $5\text{H}_2\text{O}$ Raman spectroscopy complimented with infrared spectroscopy has been used to
231 study aspects of the molecular structure of this silicate mineral inesite. The structure of

232 inesite is triclinic. As a consequence multiple silicate vibrational modes are observed.
233 Raman and infrared bands are observed and attributed to silicate, hydroxyl and water
234 vibrational stretching and bending modes. As a consequence at the molecular level non-
235 equivalent silicate units exist in the structure of inesite. As a consequence multiple
236 silicate vibrational modes are observed.

237

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251 **References**

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253 [1] W.E. Richmond, *Amer. Min.* 27 (1942) 563-569.

254 [2] S.G. Gordon, *. Science*, 56 (1922) 50.

255 [3] A. Schneider, *Jahrb. Preuss. Geol. Reichsans*, (1888) 472.

256 [4] A. Hamberg, *Geol. For. Forh.*, 16 (1894) 304.

257 [5] O.C. Farrington, *N. Jahrb. f. Mineral.*, (1901) 364-367.

258 [6] G. Flink, *Z. Krist.* 58 (1923) 356-385.

259 [7] L.P. Otroshchenko, V.I. Simonov, N.V. Belov, *Doklady Akademii Nauk SSSR*, 238

260 (1978) 1344-1347.

261 [8] C. Wan, S. Ghose, *Amer. Min.* 63 (1978) 563-571.

262 [9] W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Volume IV. Arsenates,

263 Phosphates, Vanadates, Mineral Data Publishing, Tucson, 2000.

264 [10] C. Wan, S. Ghose, *Naturwissenschaften*, 62 (1975) 96.

265 [11] R.L. Frost, Y. Xi, *Radiat. Eff. Defects Solids*, 168 (2013) 72-79.

266 [12] R.L. Frost, Y. Xi, *Vib. Spectrosc.*, 64 (2013) 33-38.

267 [13] R.L. Frost, Y. Xi, R. Scholz, L.F.C. Horta, *Spectrochim. Acta*, A109 (2013) 138-145.

268 [14] R.L. Frost, Y. Xi, R. Scholz, A. Lopez, F.M. Belotti, *J. Mol. Struct.*, 1042 (2013) 1-7.

269 [15] J. Gutzmer, N.J. Beukes, *Ore Geol. Rev.* 11 (1996) 405-428.

270 [16] N.J. Beukes, A.M. Burger, J. Gutzmer, *J. Geol.* 98 (1995) 430-451.

271 [17] J. Gutzmer, N.J. Beukes, *Econ. Geol.* 90 (1995) 823-844.

272 [18] J. Gutzmer, B. Cairncross, *Min. Rec.* 24 (1993) 365-368.

273 [19] E. Dowty, *Phys. Chem. Min.* 14 (1987) 80-93.

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275

276

277 **List of Figures**

278

279

280 **Figure 1 (a) Raman spectrum of inesite over the 100 to 4000 cm⁻¹ spectral range (b)**
281 **infrared spectra of inesite over the 500 to 4000 cm⁻¹ spectral range**

282

283 **Figure 2 (a) Raman spectrum of inesite over the 800 to 1400 cm⁻¹ range (b) Infrared**
284 **spectrum of inesite over the 500 to 1300 cm⁻¹ range.**

285

286 **Figure 3 (a) Raman spectrum of inesite over the 300 to 800 cm⁻¹ range (b) Raman**
287 **spectrum of inesite over the 100 to 300 cm⁻¹ range.**

288

289 **Figure 4 (a) Raman spectrum of inesite over the 2600 to 3800 cm⁻¹ spectral range (b)**
290 **Infrared spectrum of inesite over the 2400 to 3800 cm⁻¹ range.**

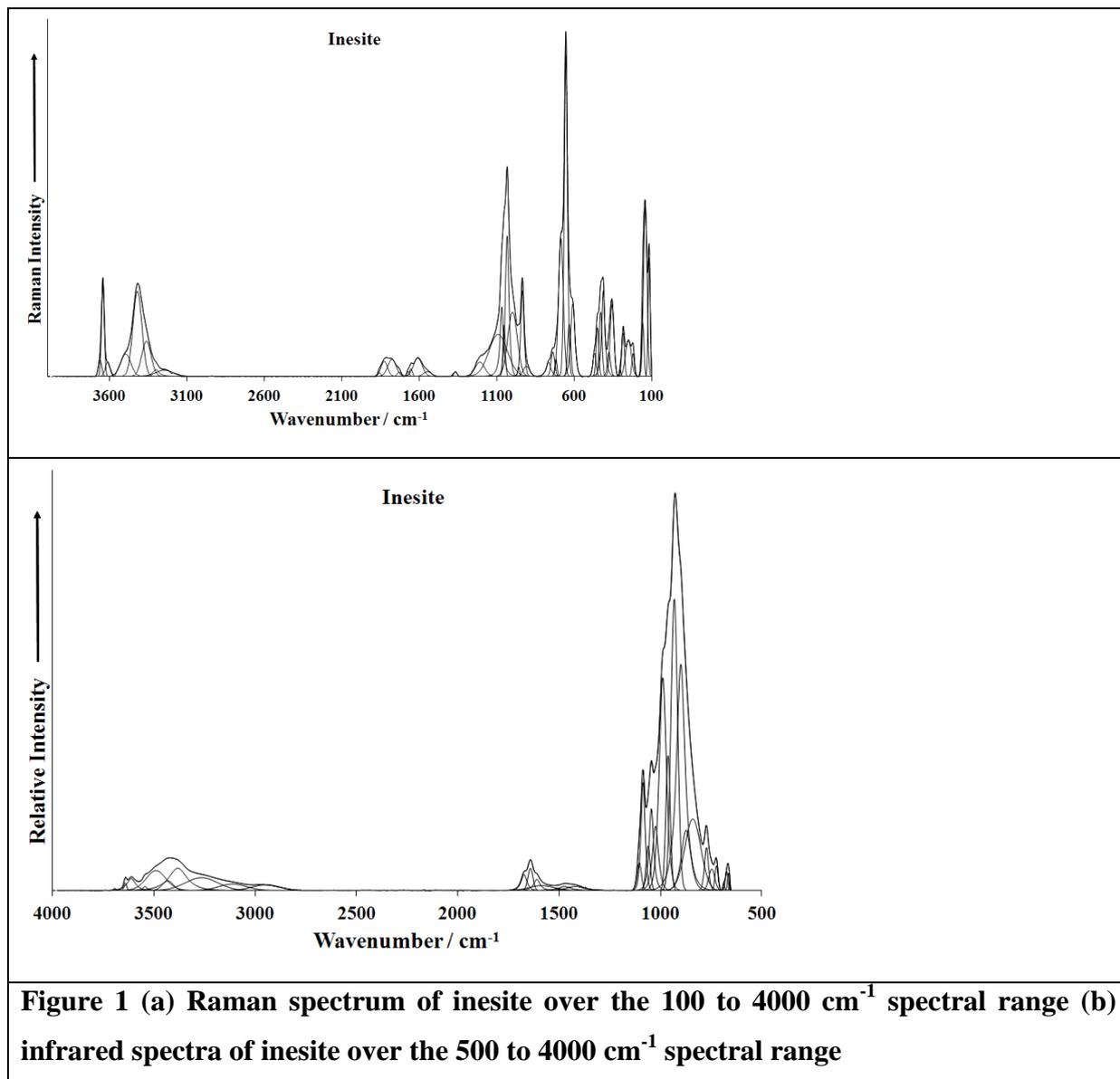
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292 **Figure 5 (a) Raman spectrum of inesite over the 1400 to 1800 cm⁻¹ spectral range (b)**
293 **Infrared spectrum of inesite over the 1300 to 1900 cm⁻¹ range.**

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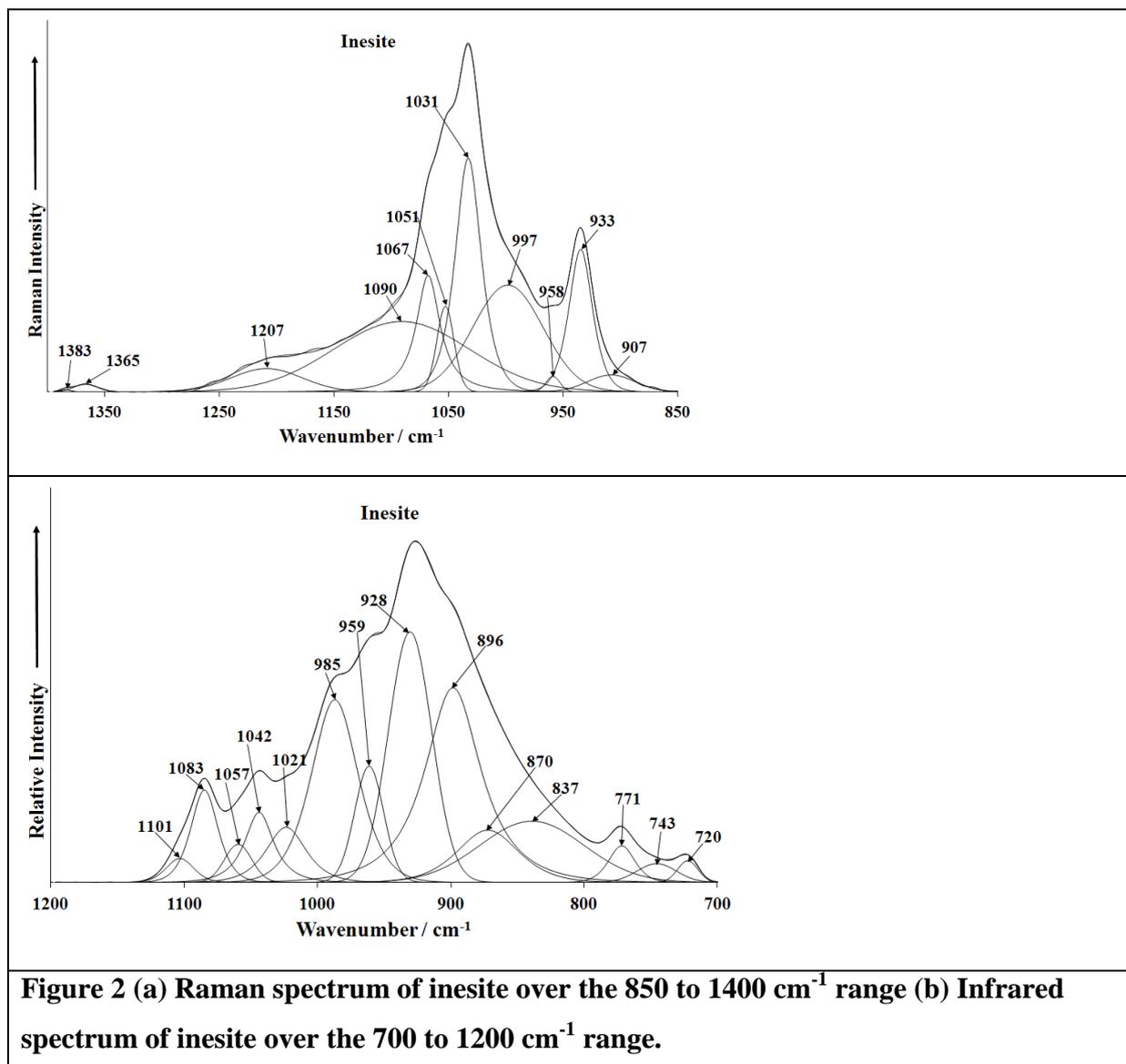
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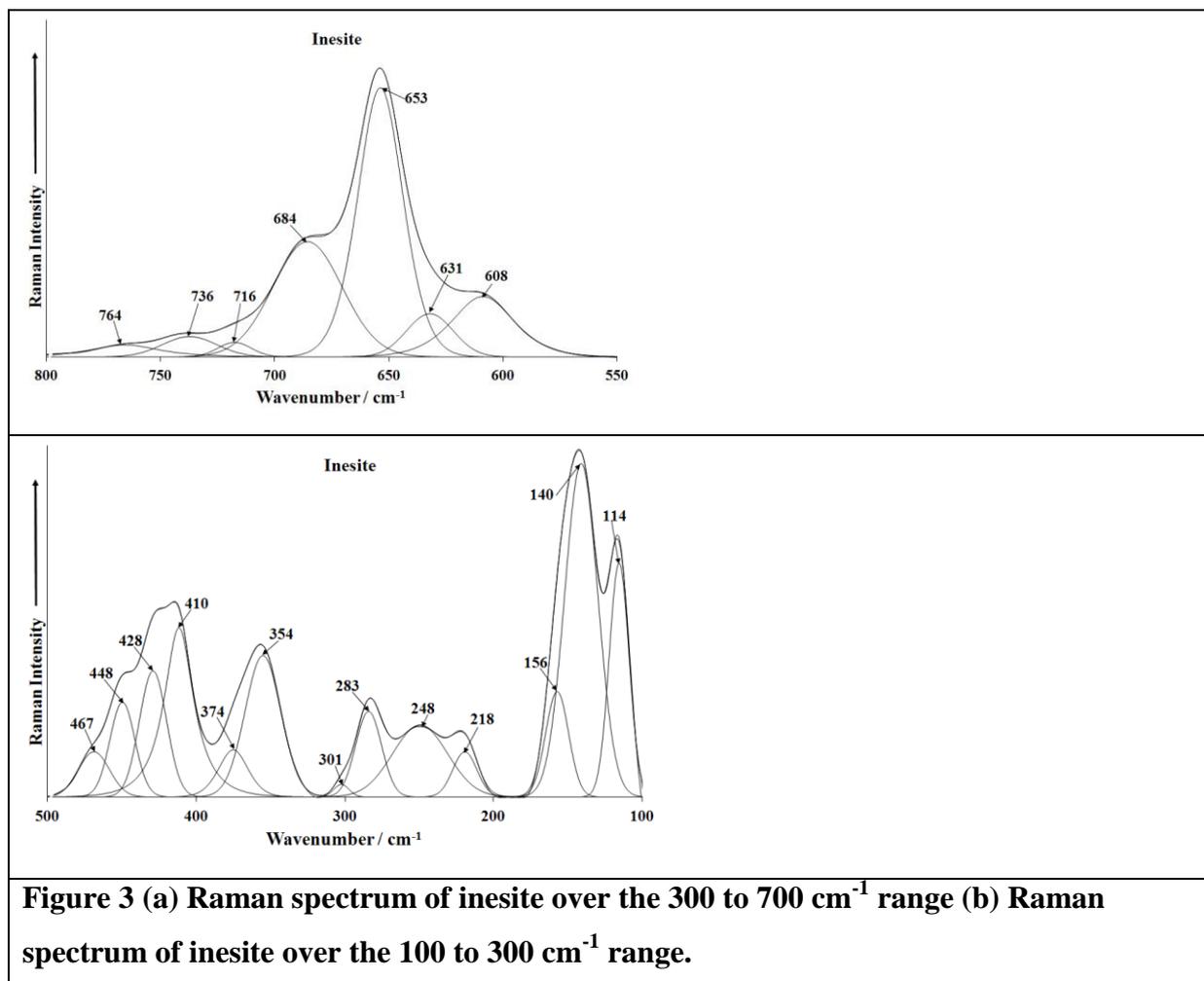
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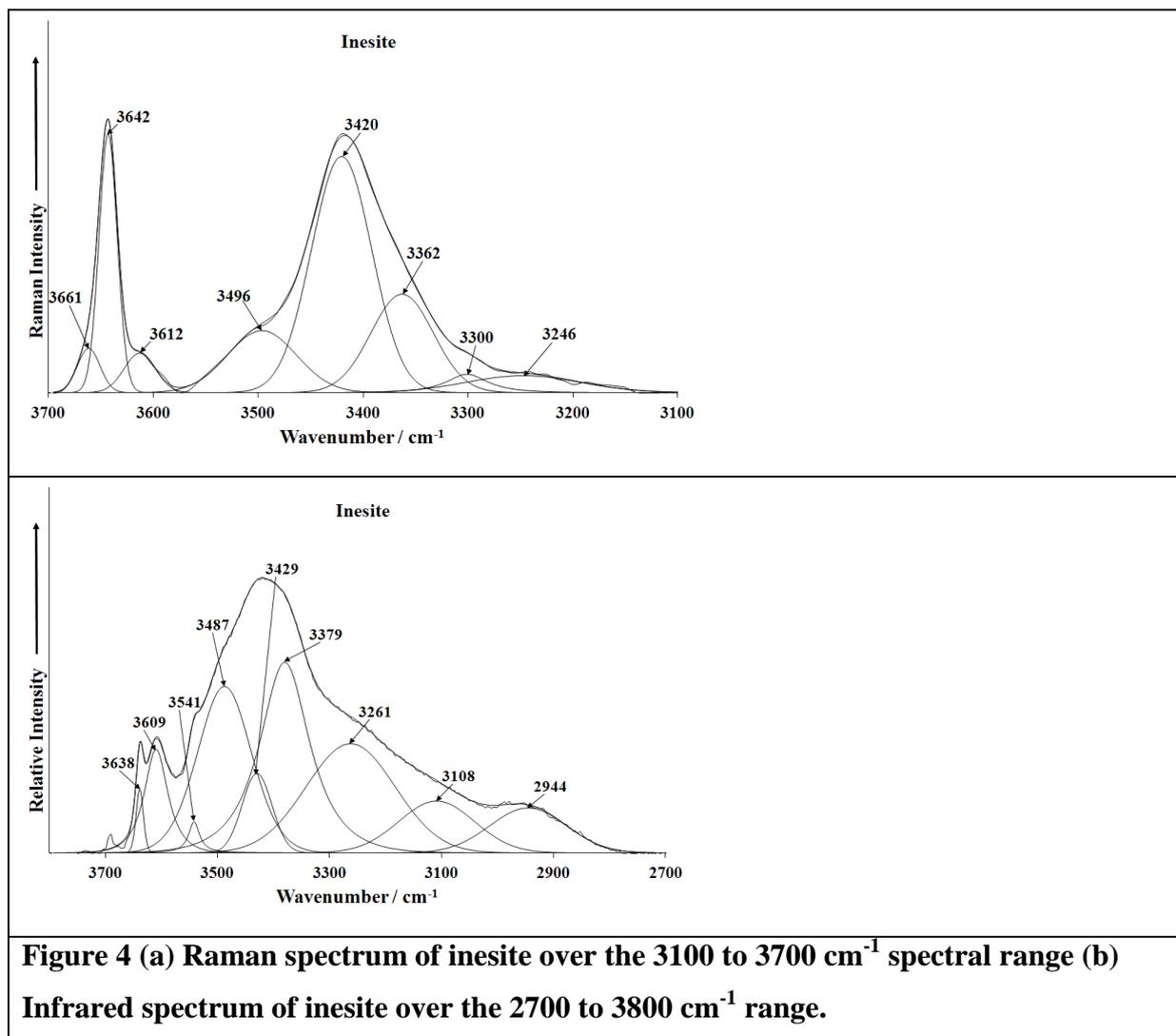
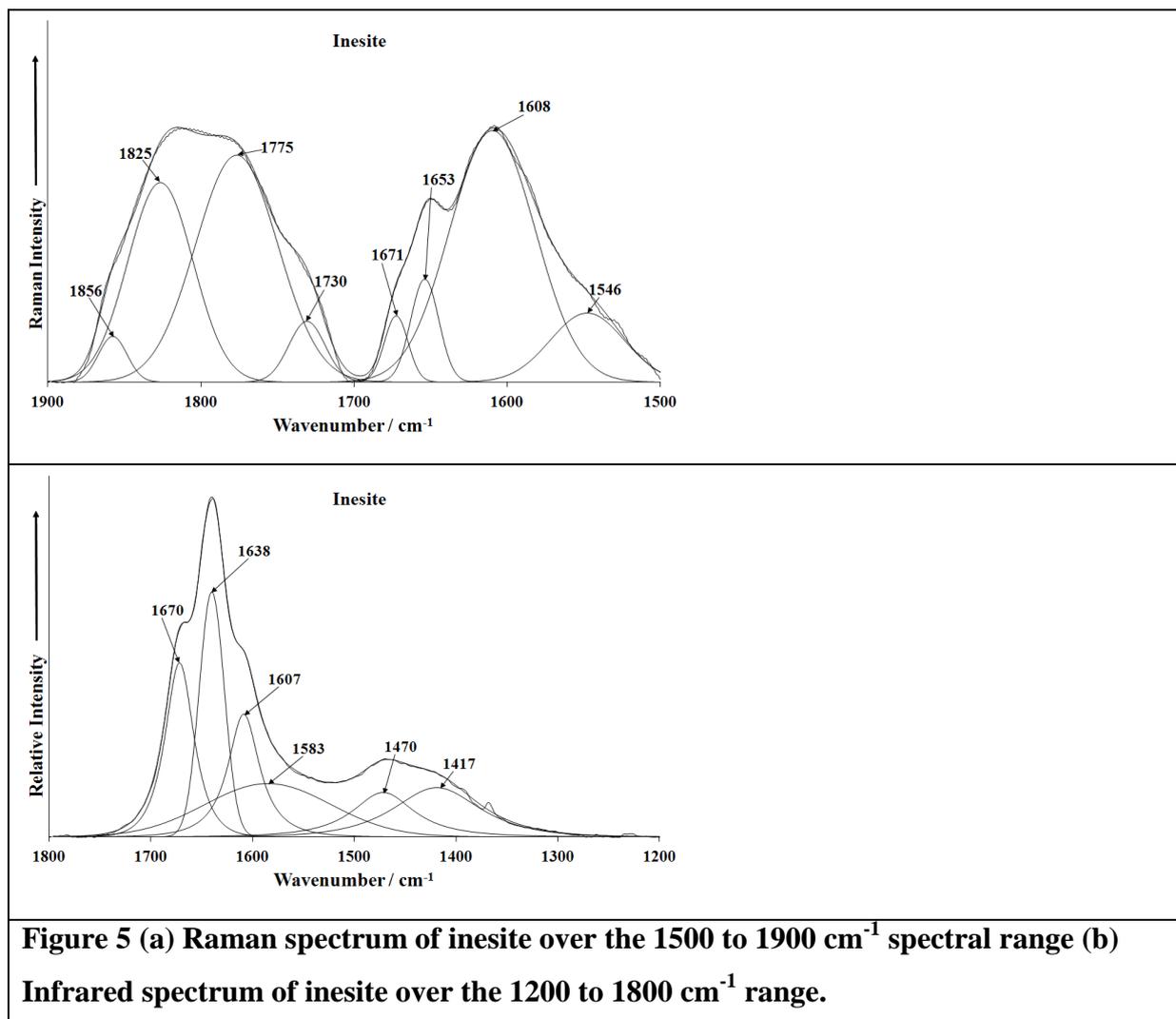


Figure 4 (a) Raman spectrum of inesite over the 3100 to 3700 cm^{-1} spectral range (b) Infrared spectrum of inesite over the 2700 to 3800 cm^{-1} range.



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