



## 30 1. Introduction

31

32 Magnesium based hydrotalcite is also known as iowaite. Iowaite is a hydrous  
33 magnesium-ferric oxychloride mineral. It occurs as bluish-green close-green crystals in  
34 calcite-brucite veins and cavities in magnesian slates and altered dolostones. . The usual  
35 formula is  $Mg_6Fe_2^{3+}(OH)_{16}Cl_2 \cdot 4H_2O$ . Oxidation of iowaite results in the formation of  $Mg_4FeO$   
36  $(Cl,CO_3)(OH)_8 \cdot 4H_2O$ . On exposure to the atmosphere it turns whitish green with a rusty  
37 overtone, owing to loss of zeolitic water. Iowaite belongs to R $\bar{3}m$  space group. The  
38 hexagonal unit cell parameters are  $a = 0.3116$  nm,  $c = 2.4113$  nm.[1-4]. Its structure  
39 consisting of three brucite like layers and three disordered inter layers. The water molecules  
40 are migrating within the inter layers [4]. The mineral iowaite does not show any marked  
41 variation in composition. Iowaite from the Korshunovskoe, Siberia contain  $MgO = 39.80$ ,  
42  $Fe_2O_3 = 24.71$  and  $Cl = 5.41$  wt%. Further ESR studies on it indicate that the presence of  
43 Fe(III) in the crystal structure and Mn(II) as an impurity[1]. Also Raman and IR spectra were  
44 reported on this compound [2]. Hydrotalcites has many applications such as nano-  
45 composites, in the removal of environmental hazards in acid mine drainage, anion  
46 exchangers, disposal of radio-active wastes, heavy metal removal from contaminated water  
47 etc., [2,5-7]. Research into the use of these hydrotalcites results from their potential  
48 application as catalysts, adsorbents and anion exchangers [5]. In this study, the authors made  
49 an attempt to determine the valence state of iron and the site symmetry using electron  
50 paramagnetic resonance (EPR), optical absorption, Raman and infrared spectroscopic  
51 features of natural iowaite from Australia.

52

## 53 2. Experimental

54

55 A light green coloured iowaite originating from Australia is used in the present work.  
56 EPR spectra of the sample in powder form are recorded at room temperature (RT) and liquid  
57 nitrogen temperature (77 K) on a JEOL JES-TE100 ESR spectrometer operating at X-band  
58 frequencies ( $\nu = 9.41095$  GHz), having a 100 KHz field modulation to obtain a first  
59 derivative EPR spectrum.

60

61 Optical absorption spectrum of the sample was recorded at room temperature in the  
62 region 200- 2500 nm on a Varian Cary 5E UV-Vis- NIR spectrophotometer. The spectra

63 were transformed according to the Kubelka-Munk algorithm. NIR spectrum of the sample  
64 was recorded on a Nicolet Nexus FT-IR spectrometer with a Nicolet near IR fibreport  
65 accessory. A white light source was employed with a quartz beam splitter and TECNIR.

66

67 The powdered mineral sample was placed and oriented on the stage of an Olympus  
68 BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000  
69 Raman microscope system. Raman spectra were excited by He-Ne laser (633nm) at a  
70 resolution of  $2\text{ cm}^{-1}$  in the range between 100 and  $4000\text{ cm}^{-1}$ . Other details of the  
71 experimental technique have already been reported [8,9]

72

### 73 **3. Results and Analysis**

74

#### 75 **3.1 EPR Results**

76

77 EPR studies are carried out at room temperature (RT) on a JEOLJE TES 100 ESR  
78 spectrometer operating at X band frequencies ( $\nu = 9.41095\text{ GHz}$ ) having a 100 kHz field  
79 modulation and a phase sensitive detection to obtain a first derivative EPR signal. The EPR  
80 spectrum of powdered iowaite is shown in Fig.1. The spectrum can be divided into two parts.  
81 First part, having resonances at low field region, centered around 170 mT and another part,  
82 consisting of a broad line situated around 350 mT. The low field resonances have g values of  
83 4.279 and 3.911. These lines can be ascribed to Fe(III) resonances in the mineral sample  
84 [10], based on previous observations. Fe(III) is having five unpaired electrons and hence  $S =$   
85  $5/2$ . The spin states in the absence of an external magnetic field are  $|\pm 1/2\rangle, |\pm 3/2\rangle$   
86 and  $|\pm 5/2\rangle$ . These three Kramer's doublets are separated by 2D and 4D respectively.  
87 Application of external magnetic field, splits these Kramer's doublets into six levels labelled  
88 as  $|-5/2\rangle, |-3/2\rangle, |-1/2\rangle, |1/2\rangle, |3/2\rangle$  and  $|5/2\rangle$  respectively. EPR transitions between  
89 these levels will give rise to five resonances, known as fine structure lines. However, in case  
90 of Fe(III), the resonances are ranging in the whole magnetic field range of X-band EPR  
91 spectrometer, i.e., g values range very largely. This type of observation has been explained,  
92 by considering that the three Kramers doublets are populated at temperature of measurement.  
93 As mentioned in the literature [10], the observed g values range from  $30/7$  to  $2/7$ , 2 to 6 and  
94  $2/7$  to 6 depending upon the population of a particular Kramers doublet. However, in case of  
95 a powder spectrum, the resonances at  $30/7$  and 2 are generally observed, due to large

96 anisotropy in g values. In the present case, we have observed resonances at  $g = 4.279$  and  
97  $3.911$ . In addition, the broad line at  $g \approx 2$  also arises from Fe(III) impurity. The literature  
98 survey indicates that the observation of  $g=30/7$  resonances confirms that the Fe(III) impurity  
99 is under the influence of a strong tetragonal distortion [10]. A close look at high field  
100 resonances indicates a sextet, in addition to the broad bond, already discussed earlier. The g  
101 value of this sextet is  $2.007$  and the hyperfine coupling constant is  $9.04$  mT. These spin  
102 Hamiltonian parameters confirm that the impurity responsible for these resonances is Mn(II).  
103 The low intensity of the sextet indicates a very low concentration of impurity. The other  
104 resonances can be thought of arising from Mn(II) lines, due to non-zero value of D.  
105 However, due to their low intensity, the value of D cannot be estimated.

106  
107 The molecular formula indicates the presence of Fe(III), as observed by EPR. The  
108 small amount of Mn(II) impurity might have entered the lattice in place of Mg(II),  
109 considering the ionic radii and charge of these two ions.

### 110 111 **3.2 Optical absorption Results**

112  
113 Ferric iron, Fe(III), has the electronic configuration Ar ( $3d^5$ ) with a half filled d-shell  
114 having one unpaired electron in each of the orbital. Hence, ground state configuration is  
115  $t_{2g}^3 e_g^2$  and has only spin forbidden d-d transitions. These occur from the ground state  ${}^6A_{1g}(S)$   
116 to the excited states  ${}^4T_{1g}(G)$ ,  ${}^4T_{2g}(G)$ ,  ${}^4A_{1g}(G)$ ,  ${}^4E(G)$ ,  ${}^2T_{1g}(D)$ ,  ${}^4E_g(D)$  and  ${}^4T_{1g}(P)$  states in  
117 regular octahedron sites. The degeneracy of E and T states being lifted with lower symmetry.

118  
119 Optical absorption spectrum of iowaite recorded in the mull form at RT is shown in  
120 Fig.2. The spectrum shows energies at  $12660$ ,  $13070$ ,  $13425$ ,  $16130$   $\text{cm}^{-1}$  in the UV-Vis  
121 region. The very sharp band observed at  $13070$   $\text{cm}^{-1}$  with split component on either side (at  
122  $12660$  and  $13425$   $\text{cm}^{-1}$  with average of  $13043$   $\text{cm}^{-1}$ ) is assigned to the transition  ${}^6A_{1g}(S) \rightarrow$   
123  ${}^4T_{1g}(G)$ . Similar assignment is also made in carbonate mineral (dolomite) [11] whereas the  
124 band at  $16130$   $\text{cm}^{-1}$  is assigned to  ${}^4T_{2g}(G)$  transition. The band visible around  $21000$   $\text{cm}^{-1}$  due  
125 to the transition of  ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$ ,  ${}^4E_g(G)$  transition is not seen. This may be due to low  
126 concentration of iron in the mineral. These bands are characteristic of Fe(III) ion in  
127 octahedral symmetry in the mineral. This is also further supported by EPR studies. Using the  
128 Tree's polarization term [12] the energy matrices of the  $d^5$  configuration are solved for

129 various B,C and Dq values. A comparison is also made between the calculated and  
 130 observed energies of the bands and these are presented in Table 1.

131

132

**Table 1**

133 Band headed data with assignments for Fe(III) in natural iowaite.

134

$$Dq = 900, B = 600 \text{ and } C = 2595 \text{ cm}^{-1} \quad \alpha = 90 \text{ cm}^{-1}$$

Wave length (nm)	Wave number (cm <sup>-1</sup> )		Transition from <sup>6</sup> A <sub>1g</sub>
	Observed	Calculated	
790	12660		<sup>4</sup> T <sub>1g</sub> (G)
765	13070	13087	
745	13425		
620	16130	16852	<sup>4</sup> T <sub>2g</sub> (G)
--	--	20739	<sup>4</sup> E(G) <sup>4</sup> A <sub>1g</sub> (G)

135

136

### 137 **3.3. NIR and infrared spectroscopy**

138

139 Water has three fundamental modes. They are symmetric OH stretch ( $\nu_1$ ), H-O-H  
 140 bending mode ( $\nu_2$ ) and asymmetric OH stretch ( $\nu_3$ ). In solid these will appear at 3220 ( $\nu_3$ ),  
 141 1620( $\nu_2$ ) and 3400 ( $\nu_1$ ) cm<sup>-1</sup> [13]. The shifting of  $\nu_1$  and  $\nu_3$  towards lower frequency side and  
 142  $\nu_2$  towards higher frequency is due to hydrogen bonding [14] The carbonate ion has six  
 143 normal modes of vibration, the symmetric stretching mode  $\nu_1$ , which is infrared active, the  
 144 out of plane bending mode  $\nu_2$ , the asymmetric stretching mode  $\nu_3$  and in-plane bending mode  
 145  $\nu_4$ .  $\nu_3$  and  $\nu_4$  are doubly degenerate. The fundamental frequencies of CO<sub>3</sub><sup>2-</sup> ion are  $\nu_1 = 1063$ ,  
 146  $\nu_2 = 879$ ,  $\nu_3 = 1415$  and  $\nu_4 = 680$  cm<sup>-1</sup> [15,16]

147

148

149

150

151 ***The 10000 to 6500 cm<sup>-1</sup> spectral region***

152

153 Fig. 3 shows near infrared spectrum of natural iowaite mineral from 10000 – 6500 cm<sup>-1</sup>  
154 region. In this region the two bands observed at 9678 and 8661 cm<sup>-1</sup> are broad and intense  
155 and is assigned to the two components of the transition  ${}^5T_{2g} \rightarrow {}^5E_g$  which is clearly due to  
156 trace of Fe(II) present in the sample. The average of these bands 9170 cm<sup>-1</sup> is taken as 10Dq.  
157 The group of bands at 7174 with maximum intensity are assigned to  $2\nu_3$  the asymmetric OH  
158 stretch in the mineral. Hydroxyl exists as part of the structure and the stretching mode  
159 appears whenever water is present in any form. The  $\nu_{OH}$  overtone gives rise to a band in the  
160 NIR spectrum [14]. Accordingly the bands observed at 7681 and 6986 cm<sup>-1</sup> are assigned to  
161 the first overtone of OH.

162

163 ***The 6000 to 4000 cm<sup>-1</sup> spectral region***

164

165 The spectral region from 6000 to 4000 cm<sup>-1</sup> is made up of two parts the 4000 – 4600  
166 cm<sup>-1</sup> region in which OH combination bands are to be found and 4600 – 5600 cm<sup>-1</sup> in which  
167 water combination bands are observed. Fig.4 shows profile of bands around 4300 cm<sup>-1</sup> with  
168 large intensity (4401,4347, 4294, 4129 cm<sup>-1</sup>) and are assigned to the water OH combination.  
169 Where as the intense band observed at 5080 cm<sup>-1</sup> is attributed to the water OH overtone. The  
170 band observed at 5554 cm<sup>-1</sup> with weak intensity is attributed to the first fundamental overtone  
171 OH stretching mode [15].

172

173 The IR spectra as studied also be subdivided into three spectral regions: (a) 3700 to  
174 2900 cm<sup>-1</sup> region where OH fundamental vibrations are observed (Fig.5); (b) 1750 to 1250  
175 cm<sup>-1</sup> range where the water bending modes are observed (Fig. 6); (c) 1125 to 525 cm<sup>-1</sup> region  
176 shows bands due carbonate stretching vibrations (Fig. 7). As Raman spectroscopy of iowaite  
177 has already been reported [1], the analysis is not discussed here.

178

179 ***The 3700 to 2900 cm<sup>-1</sup> spectral region***

180

181 The OH stretching region of iowaite is shown in Fig.5. The IR spectrum shows several  
182 bands at 3685, 3662, 3647, 3633,3572,3433,3269 and 3051 cm<sup>-1</sup>. The very sharp bands at  
183 3685, 3662 and 3633 cm<sup>-1</sup> with component at 3647 cm<sup>-1</sup> are assigned to Mg<sub>3</sub>OH, Mg<sub>2</sub>FeOH

184 and Fe<sub>3</sub>OH bands. Similar assignments were already reported in the literature [2]. This  
185 assignment is due to OH stretching vibrations of water ( $\nu_3$ ). Whereas other two broad and  
186 intense bands at 3572 and 3433 cm<sup>-1</sup> and two weak bands at 3269 and 3051 cm<sup>-1</sup> are assigned  
187 to the stretching vibrations of inter layer water.

188

### 189 ***The 1750 to 1250 cm<sup>-1</sup> spectral region***

190

191 This region is significant for the observation of H<sub>2</sub>O bending modes. The  $\nu_2$  water-bending  
192 modes are more pronounced in the IR spectrum. Fig.6 shows a broad and sharp band at 1639  
193 cm<sup>-1</sup> is noticed in spectrum. The appearance of  $\nu_2$  mode on the lower wave number side is an  
194 indication of weakly hydrogen bonded water. This complexity of bands provides evidence for  
195 the existence of water in several states in the structure of iowaite. Broad and intense profile  
196 centered at 1468 cm<sup>-1</sup> with maximum half width is identified as due to  $\nu_3$  CO<sub>3</sub><sup>2-</sup> anti-  
197 symmetric stretching vibrations.

198

### 199 ***The 1125 to 525 cm<sup>-1</sup> spectral region***

200

201 The infrared spectra for the fundamental vibrations of carbonate in the iowaite mineral  
202 are shown in Fig. 7. All the spectral features in this region are characteristic of carbonate  
203 groups. The band at 1016 cm<sup>-1</sup> in the spectrum is attributed to CO symmetric stretching  
204 mode. The intense band at 1065 cm<sup>-1</sup> with component at 1088 cm<sup>-1</sup> is identified as  $\nu_1$  the  
205 symmetric stretching mode of carbonate.[15]. Another group of bands observed around 600  
206 cm<sup>-1</sup> to 640 cm<sup>-1</sup> are identified as due to  $\nu_4$  of carbonate ion.

207

### 208 ***Raman spectroscopy***

209

210 The low energy Raman bands in the range 3740-3600 cm<sup>-1</sup> observed for this compound are  
211 shown in Fig 8. The bands in this region are often attributable to water fundamentals and Mg-  
212 O/Fe-O lattice vibrations. The observed Raman energies of the bands are similar to the  
213 reported bands [2].

214

### 215 **Conclusions**

216

- 217 1. Natural iowaite crystal structure is similar to synthetic iowaite and is compared with  
218 already reported data which is similar.  
219
- 220 2. EPR results are indicating that Fe(III) and Mn(II) are present in the mineral in distorted  
221 octahedral environment. The  $g = 4.279, 3.911$  and  $2.0$  are ascribed to Fe(III) and  $g$  and  $A$   
222 value observed in the spectrum are  $2.007$  and  $9.04$  mT are due to Mn(II) in the mineral.  
223 This results are supporting the molecular formula that the sample contains Fe(III) and  
224 Mn(II) impurity might have entered the lattice in place of Mg(II).  
225
- 226 3. The optical absorption studies are indicating that only Fe(III) ion in mineral is present in  
227 distorted octahedral environment.  
228
- 229 4. Near infrared spectrum is due to overtones and combinations of water molecules and  
230 carbonate ions. Further IR studies are due to water and carbonate ions in the mineral.  
231
- 232 5. Raman spectrum is compared with already reported data and is identical.  
233

#### 234 **Acknowledgements**

235 Authors wish to express their sincere thanks Prof. P.S.Rao, Dept of Chemistry,  
236 Pondicherry University, Pondicherry, India for providing EPR instrumental facility.  
237  
238



239 **References**

240

- 241 1. M.P. Mazurov, T.A. Korneva, L.M.Zhitova, V.E. Istomin, N.A. Stopipovskaya,  
242 A.T. Titov, Zapiski Vserossiiskogo, Mineralogicheskogo Obshchestva, **129** (2000) 8  
243 (Russian).
- 244 2. R.L.Frost and Adebajo, Moses and Erickson, Spect. Chim Act A **61** (2005) 613
- 245 3. R.S.W. Braithwaite, P.J.Dunn, R.G.Pritchard, W.H.Pear, Miner.Mag. **58** (1994) 79.
- 246 4. Atlmann, Rudolf, Donnay, Joseph D.H., Am. Miner. **54** (1969) 296.
- 247 5. R. L. Frost, J. M. Bouzaid, A. W. Musumeci, J. T. Kloprogge and W. N. Martens, J.  
248 Therm. Anal.  
249 Calorim. **86** (2006) 437.
- 250 6 R. L. Frost and K. L. Erickson, Spectrochim. Acta, Part A **60** (2004) 3001.
- 251 7. R. L. Frost and K. L. Erickson, J. Therm. Anal. Calorim. **78** (2004) 367.
- 252 8. R.L. Frost and R.L. Weier, Raman Spectroscopy, **34** (2003b) 776.
- 253 9 R.L. Frost and R.L. Weier, Thermo Chim.Acta **409** (2004) 79.
- 254 10. P. Sambasiva Rao and S. Subramanian, Mol. Phys., **54** (1985)415.
- 255 11. S. Lakshmi Reddy, R.L.Frost, G.Sowjanya, N.C.G.Reddy, G.Siva Reddy and B.J.Reddy  
256 Advances in Condensed Matter Physics Vol. 2008 , 8 pages, IDNo: 175862 (2008)
- 257 12. W.Low and G. Losengasten, J. Mol. Spectroscopy, **12** (1964) 319.
- 258 13. K.Nakamoto “ Infrared Spectra of Inorganic and Coordination Compounds”,  
259 Wiley, New York (1970)
- 260 14. G.R. Hunt and J.W. Saliesbury, Mod. Geol, **1** (1970) 283..
- 261 15. G.R.Hunt and J.W. Salisbury, Modern Geology **2** (1971) 23.
- 262 16. G.Herzberg, In: Infrared and Raman spectra of Polyatomic Molecules, Vol.II  
263 (Lancaster USA) 178 (1966)

264

265

266

267 *List of Figures*

268

269 **Fig.1. ESR spectrum of natural iowaite at room temperature ( $\nu = 9.41095$  GHz)**

270

271 **Fig.2 Optical absorption spectrum of natural iowaite at room temperature**

272

273 **Fig. 3. NIR spectrum of natural iowaite at room temperature from  $10000\text{ cm}^{-1}$  to  $6500$**   
274  **$\text{cm}^{-1}$ .**

275 **Fig. 4. NIR spectrum of natural iowaite in the range  $6000$  to  $4000\text{ cm}^{-1}$**

276

277 **Fig. 5. IR spectrum of iowaite from  $3700\text{ cm}^{-1}$  to  $2900\text{ cm}^{-1}$ .**

278

279 **Fig. 6. IR spectrum of iowaite from  $1750\text{ cm}^{-1}$  to  $1250\text{ cm}^{-1}$ .**

280

281 **Fig. 7 IR Spectrum of iowaite at room temperature from  $1125$  to  $525\text{ cm}^{-1}$**

282

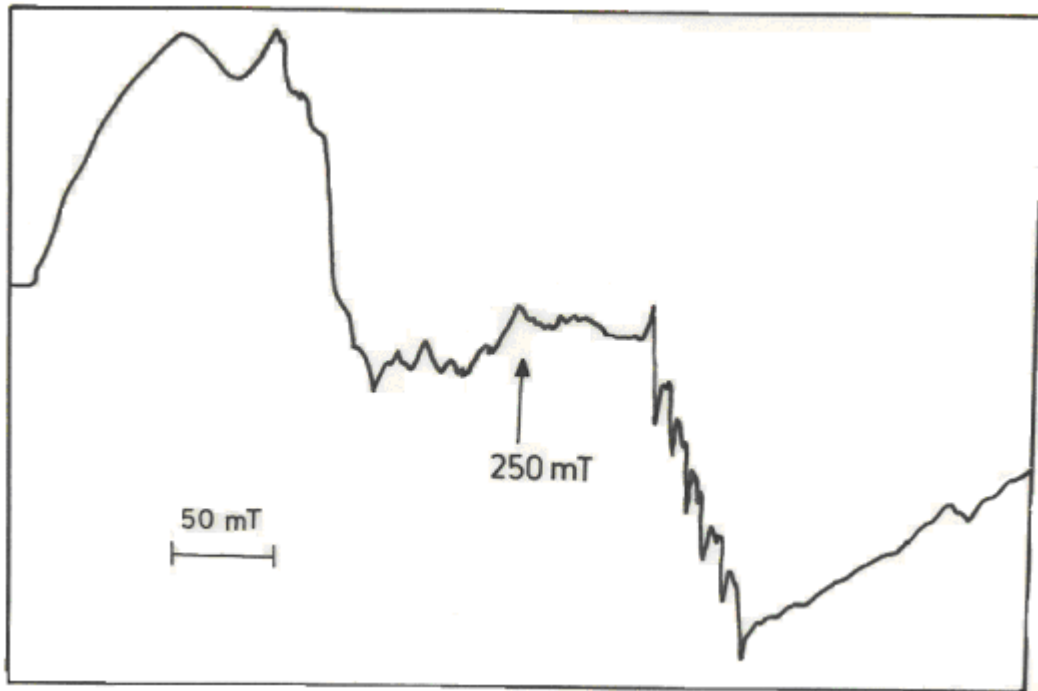
283 **Fig. 8 Raman spectrum of natural iowaite at room temperature**

284

285

286

287



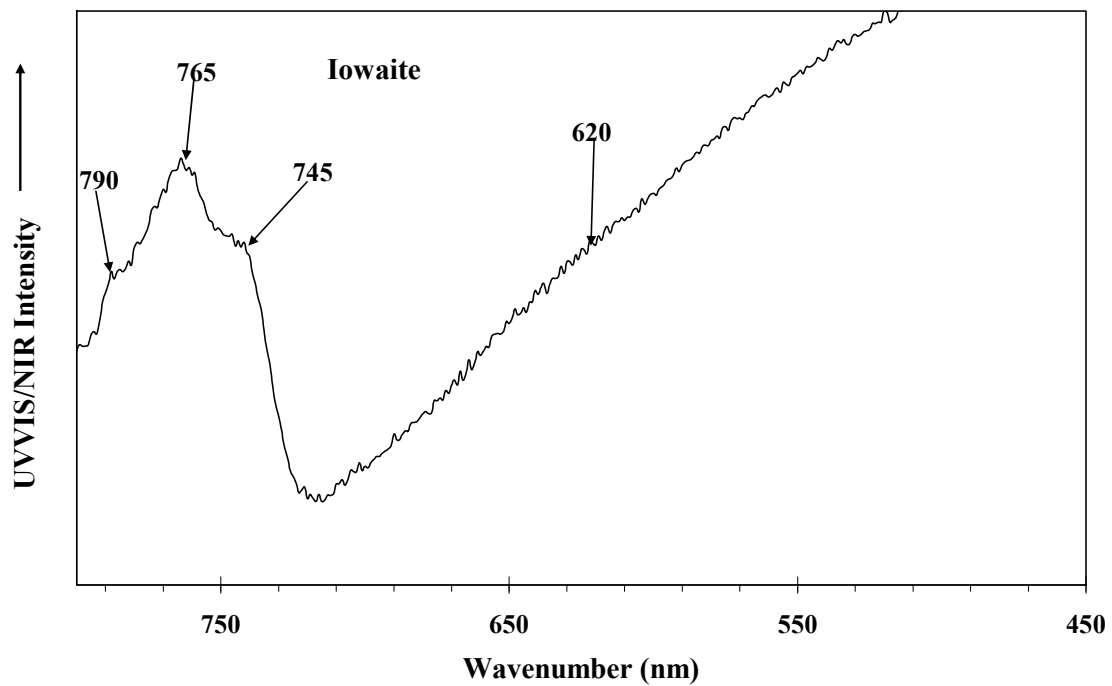
288

289 **Fig.1. ESR spectrum of natural iowaite at room temperature ( $\nu = 9.41095$  GHz)**

290

291

292



293

294

**Fig.2 Optical absorption spectrum of natural iowaite at room temperature**

295

296

297

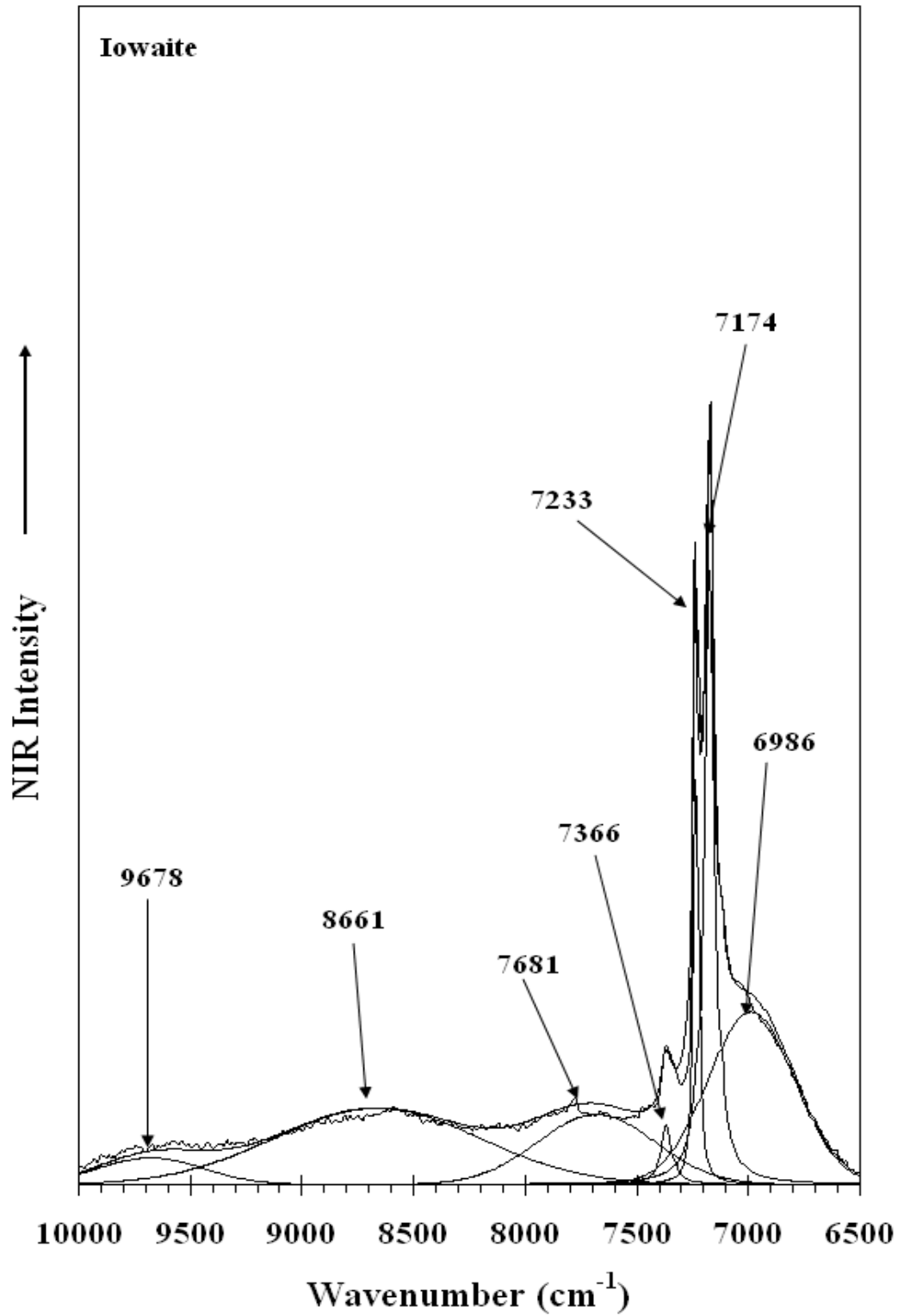
298

299

300

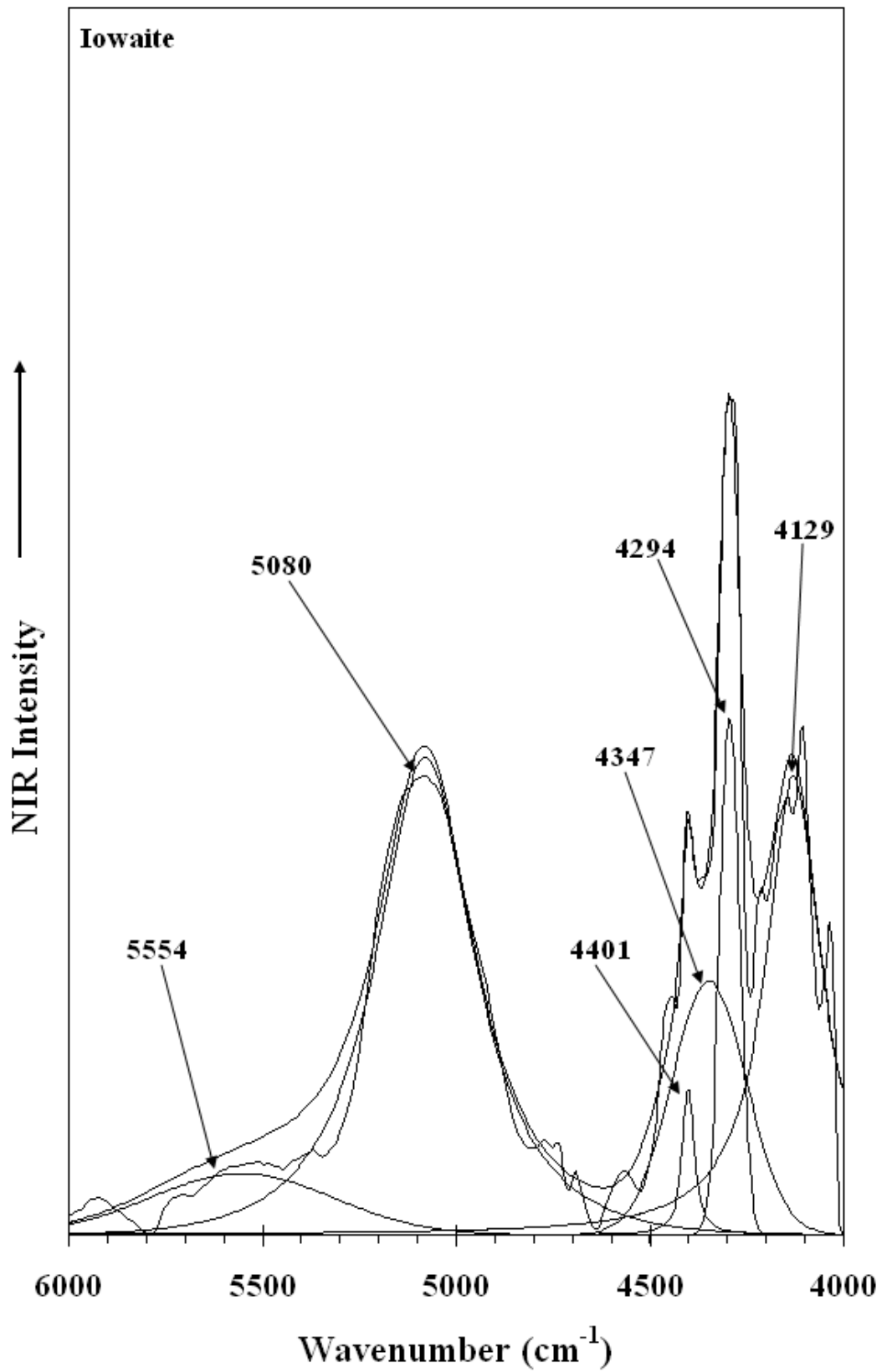
301

302



303  
 304  
 305  
 306

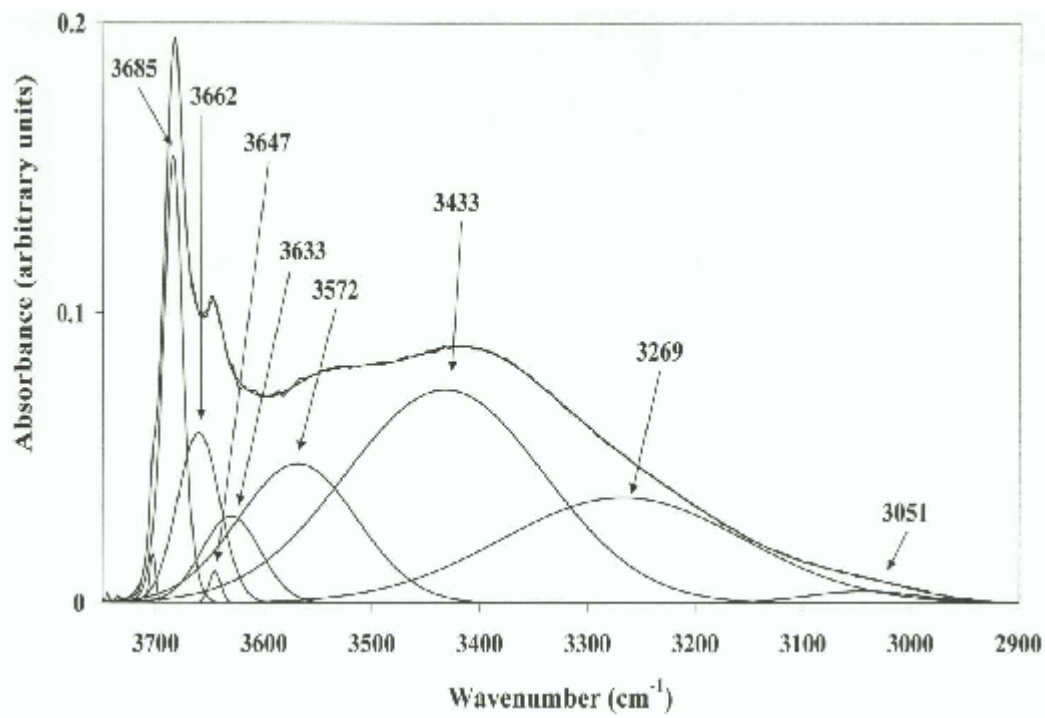
Fig. 3. NIR spectrum of natural iowaite at room temperature from 10000 cm<sup>-1</sup> to 6500 cm<sup>-1</sup>.



307

308

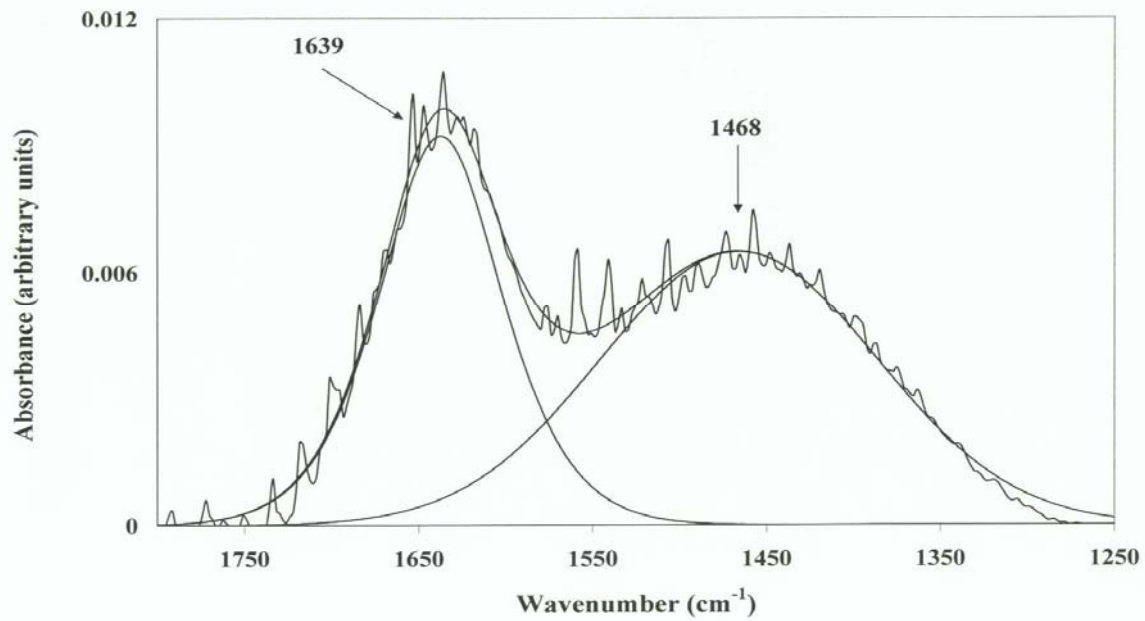
Fig. 4. NIR spectrum of natural iowaite in the range 6000 to 4000 cm<sup>-1</sup>



309  
310  
311

**Fig. 5. IR spectrum of iowaite from 3700  $\text{cm}^{-1}$  to 2900  $\text{cm}^{-1}$ .**

312



313

314

**Fig. 6. IR spectrum of iowaite from 1750 cm<sup>-1</sup> to 1250 cm<sup>-1</sup>.**

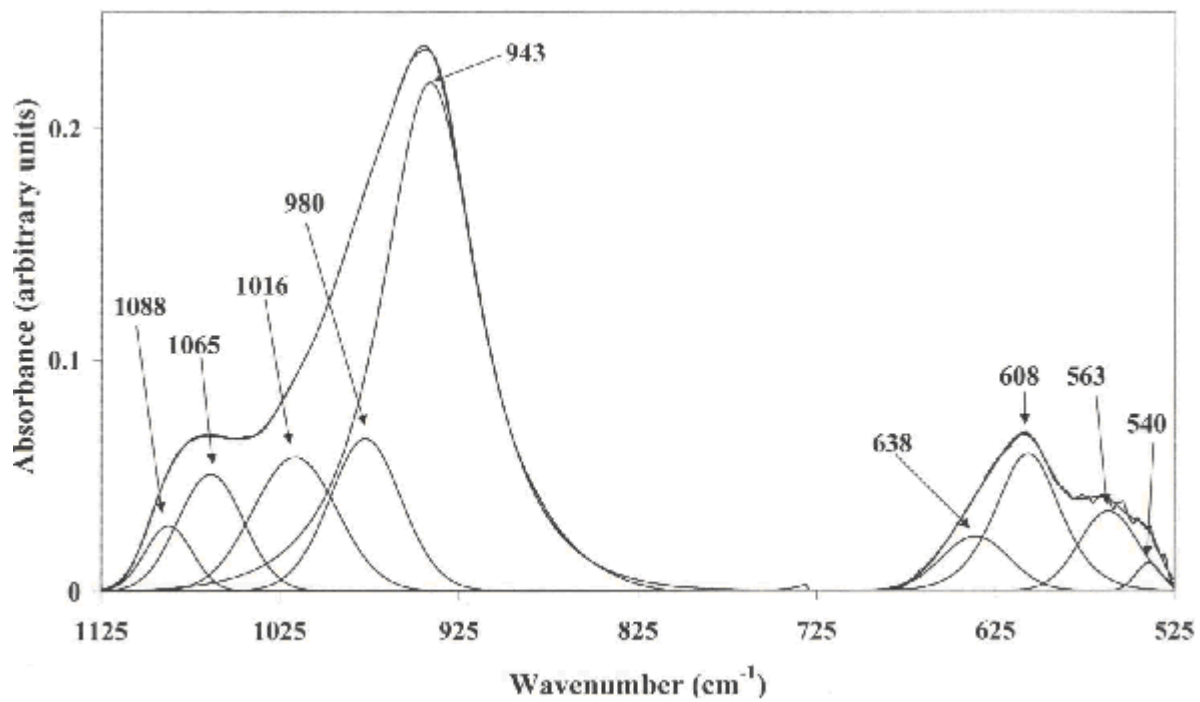
315

316

317



318



319

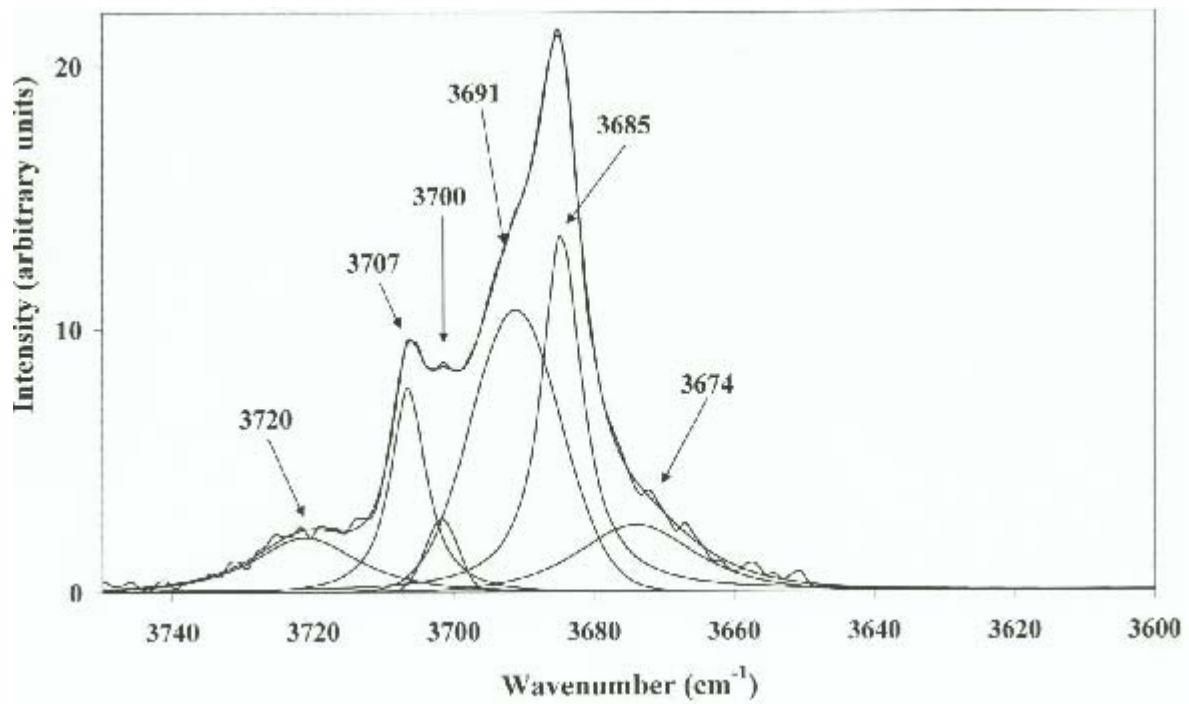
320

321 **Fig. 7 IR Spectrum of iowaite at room temperature from 1125 to 525 cm<sup>-1</sup>**

322

323

324



325

326

**Fig. 8 Raman spectrum of natural iowaite at room temperature**