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Infrared spectroscopic study of halloysite-potassium acetate intercalation complex

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ABSTRACT

Mid-infrared (MIR) and near-infrared (NIR) spectroscopy have been used to study the molecular structure of halloysite and potassium acetate intercalated halloysite and to determine the structural changes of halloysite through intercalation. The MIR spectra show all fundamental vibrations including the hydroxyl units, basic aluminosilicate framework and water molecules in the structure of halloysite and its intercalation complex. Comparison between halloysite and halloysite-potassium acetate intercalation complex shows almost all bands observed for halloysite are also observed for halloysite-potassium acetate intercalation complex apart from bands observed in the 1700-1300 cm^{-1} region, but with differences in band intensity. However, NIR, based on MIR spectra, provide sufficient evidence to analyze the structural changes of halloysite through intercalation. There are obvious differences between halloysite and halloysite-potassium acetate intercalation complex in the all spectral ranges. Therefore, the reproducibility of measurement and richness of qualitative information should be simultaneously considered for proper selection of a spectroscopic method for molecular structural analysis.

KEYWORDS Halloysite; Potassium acetate; Intercalation complex; Near-infrared spectroscopy; Mid-infrared spectroscopy

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1. Introduction

Halloysite is a kind of aluminosilicate clay with hollow nanotubular structure mined from natural deposits [1]. It is a polytype of kaolinite ($\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$) and differs mainly in the morphology of the crystals, which are curved or rolled [2]. Halloysite hollow microtubules have typical nanoscale dimensions. The structure and chemical composition of halloysite are similar to those of kaolinite but halloysite can intercalate a monolayer of water molecules giving a basal spacing near 10 Å [3]. Halloysite occurs mainly in two different polymorphs, the hydrated form (basal distance around 10 Å) with the minimal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, and the dehydrated form (basal distance around 7 Å) with the minimal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, being identical to kaolinite.

Intercalation of inorganic and organic species in the interlayer spaces of halloysite, such as formamide [3, 4], dimethylsulfoxide [5], urea [6], potassium acetate [2], aniline [7] and hydrazine [8], has already been known for decades and has recently began to gain increasing importance, mainly due to the possibility of using this class of complexes to obtain nanocomposites for potential industrial applications [6]. These studies have been carried out either for differentiating halloysite from kaolinite or gaining the insight into the reactivity of halloysite to organic complexes [9]. Further studies of halloysite and potassium acetate intercalated halloysite are required to increase our fundamental knowledge.

Vibrational spectroscopic methods such as near-infrared (NIR) and mid-infrared (MIR) spectroscopy have been considered as an alternative analytical method because they are fast and non-destructive [10]. NIR has been widely applied to study clay mineral such as organoclays and montmorillonites [11-13]. To date there have been few reports of using NIR spectroscopy in the kaolinite and halloysite intercalates. However, NIR spectroscopy is such a powerful technique and is seriously underutilized in this regard. In the present work, MIR and NIR spectroscopy of intercalated halloysite have been compared and analysed for structural modification of halloysite. The obvious differences between halloysite and its intercalation complex in the all range of spectra are elucidated. The purpose is not only to demonstrate that the NIR region provides information comparable with that obtained by MIR, but also to reveal higher sensitivity of this spectral region to structural change of clay

30 mineral.

31

32 **2. Experimental methods**

33 ***2.1. Materials***

34 The sample used in this study was the natural halloysite from Guizhou province of China. Its
35 chemical composition in wt% is SiO₂ 40.47, Al₂O₃ 39.95, Fe₂O₃ 0.43, MgO 0.03, CaO 0.76, Na₂O 0.05,
36 K₂O 0.12, TiO₂ 0.05, P₂O₅ 0.15, MnO 0.06, loss on ignition 17.93. The potassium acetate (A. R) was
37 purchased from Beijing Chemical Reagents Company, China.

38

39 ***2.2. The intercalation composite preparation***

40 The potassium acetate (KAc) intercalate was prepared by immersing 10 g of halloysite in 20 ml of
41 KAc solution at a mass percentage concentration of 30%. The sample was stirred for 10 minutes at
42 room temperature. The complex was allowed to dry at room temperature before the MIR and NIR
43 spectroscopy analysis.

44

45 ***2.3. Mid-infrared spectroscopy***

46 Mid-Infrared spectra were obtained in reflectance mode using a Nicolet Nexus 870 Fourier
47 transform infrared spectroscopy (FT-IR) spectrometer with a smart endurance single bounce diamond
48 ATR cell. Spectra over the 4000-600 cm⁻¹ range were obtained by the co-addition of 64 scans with a
49 resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal
50 to noise ratio. No sample preparation was involved.

51

52 ***2.4. Near-infrared spectroscopy***

53 Near-infrared spectra were collected in reflectance mode using a Nicolet Nexus FT-IR
54 spectrometer with a Nicolet Near-IR Fibreport accessory (Nicolet Nexus, Madison, Wisconsin, USA).
55 A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were
56 obtained from 12000 to 4000 cm⁻¹ (909-2500 nm) by the co-addition of 64 scans at a resolution of 8
57 cm⁻¹. A mirror velocity of 1.2659 m/s was used.

58 The spectral manipulations of baseline adjustment, smoothing and normalization were performed
59 using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band
60 component analysis was carried out using Peakfit software (Jandel Scientific, Postfach 4107, D-40688
61 Erkrath, Germany). Lorentz-Gauss cross product functions were used through out and peakfit analysis
62 undertaken until squared correlation coefficients with $r^2 > 0.998$ were obtained.

63 **3. Results and discussion**

64 **3.1. Mid-Infrared (MIR) Spectroscopy**

65 Halloysite is a polytype of kaolinite and has inner and inner surface hydroxyls, the same as
66 kaolinite. The difference between these two polytypes is due to the different morphologies and
67 interlayer water in halloysite [2]. Kaolinite is normally planar and halloysite has curved surfaces. The
68 MIR spectra of halloysite and halloysite-KAc intercalation complex are shown in Fig. 1 and 2. Some
69 variations in both the band positions and intensities of the OH, Si-O and Al-O group vibrational modes
70 between halloysite and halloysite-KAc intercalation complex are observed. For convenience, the MIR
71 spectra of these two samples are divided into two sections; they are (a) the 3850-2850 cm^{-1} region
72 attributed to OH stretching vibration modes (Fig.1) and (b) the 1750-650 cm^{-1} region due to the basic
73 aluminosilicate framework and water molecule in the structure of these two samples (Fig.2).

74

75 **3.1.1. 3850-2850 cm^{-1} region**

76 The MIR spectra of halloysite and halloysite-KAc intercalation complex in the 3850-2850 cm^{-1}
77 region are shown in Fig.1. Farmer [14] and Frost [15, 16] pointed that, with an exact threefold axis,
78 coupling between these three hydroxyl group would give rise to one symmetrical in-phase vibration,
79 with a dipole oscillation along the threefold axis-that is, perpendicular to the sheets-and two mutually
80 degenerate, out-of-phase, vibrations with dipole oscillations in the plane of the sheets. In this region, it
81 is also concluded that there are four kinds of hydroxyl groups in halloysite, i.e. outer surface hydroxyl,
82 inner surface hydroxyl, inner hydroxyl and absorbed water hydroxyl [17]. Therefore, bands are
83 observed in this region at 3693, 3681, 3652, 3625, 3561, 3442, 3266 and 3168 cm^{-1} , which are
84 attributed to symmetrical in-phase vibration of surface hydroxyl, the out-of-phase vibration of surface
85 hydroxyl, inner hydroxyl and absorbed water hydroxyl [18]. After intercalation with KAc, the
86 spectrum shows small shift in these bands. Moreover, two new bands are observed at 3604 and 3002

87 cm^{-1} which are assigned to the stretching band of hydrogen-bonded OH [19] and CH_3 stretching of the
88 acetate intercalated halloysite. It is pointed out that KAc molecule possessing both proton-donor and
89 proton-acceptor group is easily intercalated. The acetate ion has only proton-acceptor capability and
90 can form hydrogen bonds with the gibbsitic sheet, only. Ledoux and White [25] concluded that the
91 new band may result from the formation of a weak hydrogen bond between the inner surface
92 hydroxyls and the acetate ion. Meanwhile, the potassium ion fits into the ditrigonal cavity and
93 influences both the position and the intensity of the hydroxyl vibration modes.

94

95 **3.1.2. 1750-650 cm^{-1} region**

96 Fig. 2 shows the MIR spectra of halloysite and halloysite-KAc intercalation complex in 1750-650
97 cm^{-1} region. Between 1250 and 650 cm^{-1} characteristic bands of silicate can be observed, mainly those
98 corresponding to Si-O bonds in the tetrahedral sheet, and also to M-O stretching vibrational bands. This
99 interval of wavenumber is complex because the lattice modes and the intercalation molecule also have
100 some influence in this region of the spectrum [20]. Therefore, it is important to note that the spectra in
101 this region not only provide the information about the nature of the octahedral sheet, but also display
102 the characteristic bands of OH deformation. The intercalation of the halloysite with KAc caused
103 significant differences in the intensities of the bands at 1124 and 1083 cm^{-1} . At the same time, these two
104 bands shift to 1116 and 1095 cm^{-1} after intercalation. Two strong bands at 998 and 1031 cm^{-1} are
105 assigned to the Si-O-Si in-plane vibrations. The shift of the two Al-OH deformation bands of 906 and
106 939 cm^{-1} to 898 and 914 cm^{-1} is an indication of KAc molecule intercalation into the interlayer of
107 halloysite. The spectrum in this region presents two bands at 752 and 794 cm^{-1} , which are typical of the
108 OH translational vibrations. After intercalation, these two bands shift to 754 and 790 cm^{-1} .

109

110 In the study of the intercalation of halloysite with KAc, not only is it necessary to study the
111 hydroxyl bands and basic structure bands but the acetate bands should also be analysed. When
112 halloysite is intercalated with KAc significant changes occurred in the region 1250-1750 cm^{-1} of
113 vibration spectrum. The intercalation reaction destroys the inherent hydrogen bond of halloysite and
114 presents some new bonds [9]. The symmetric deformation band of the CH_3 group is observed in the
115 spectrum at 1346 cm^{-1} for halloysite-KAc intercalation complex. It is proposed that the CH_3 group of
116 the acetate is interacting with the silica sheet [19]. The symmetric stretching band of the O-C-O unit

117 shifted to 1415 cm^{-1} as a result of hydrogen-bonding with inner surface OH groups in the complex. The
118 bands are observed at 1567 cm^{-1} , which are due to the antisymmetric $\nu(\text{COO})$ stretching vibrations.
119 These results also provide evidence that KAc has entered the interlayer of halloysite and is not
120 adsorbed on the external surfaces of the halloysite.

121

122 **3.2. Near-Infrared Spectroscopy**

123 The near-infrared (NIR) technique mainly measures overtones and combination bands of the
124 fundamental vibration of O-H, N-H and C-H bands in the mid-infrared region [21, 22]. For
125 convenience, the NIR spectra of halloysite and halloysite-KAc intercalation complex are divided into
126 three sections, they are (a) the $4700\text{-}4000\text{ cm}^{-1}$ region (Fig.3); (b) the $6200\text{-}4700\text{ cm}^{-1}$ region attributed
127 to combination of OH, Si-OH and CH vibrational modes (Fig.4) and (c) the $8000\text{-}6000\text{ cm}^{-1}$ region is
128 the high wavenumber region (Fig.5).

129

130 **3.2.1. $4700\text{-}4000\text{ cm}^{-1}$ region**

131 The NIR spectra in the $4700\text{-}4000\text{ cm}^{-1}$ region for halloysite and halloysite-KAc intercalation
132 complex are shown in Fig. 3. Here combination bands are observed. The intense band at 4531 cm^{-1}
133 appears in the spectrum of halloysite and corresponds to $(\nu+\delta)_{\text{AlOH}}$ combination modes [11]. The
134 halloysite and montmorillonite clay are usually characterised by this band [12]. After intercalation, the
135 corresponding band is located at 4504 cm^{-1} , showing red shifts of 27 cm^{-1} . Moreover, the intensity of
136 this band becomes lower than halloysite. At the same time, four bands at $4624, 4566, 4451$ and 4416
137 cm^{-1} are similar in position but not in intensity. This variability may be attributed to intercalate with
138 KAc. Three bands of $4331, 4261$ and 4200 cm^{-1} become 4362 and 4315 cm^{-1} when halloysite
139 intercalated with KAc. These bands are assigned to the combination for “inner surface hydroxyls” and
140 “inner hydroxyls” whose coupled stretching and bending modes gave rise to bands at $3695\text{-}3620\text{ cm}^{-1}$
141 and near 912 cm^{-1} [23]. Intercalation reaction is initiated with a reorientation of the interlayer hydroxyl
142 groups and/or proton migration under the influence of the KAc molecules adsorbed at the external
143 surfaces of the particles. These results provide another evidence to conclude that KAc has entered the
144 structure of halloysite and influenced the near-infrared spectrum.

145

3.2.2. 6200-4700 cm⁻¹ region

The 6200-4700 cm⁻¹ NIR spectral region shows broad bands (Fig.4), these bands are attributed to interlayer water and intercalation KAc molecules. There are differences in intensity and position in this region between halloysite and halloysite-KAc intercalation complex. Three broad bands are observed at 5025, 5164 and 5241 cm⁻¹ for halloysite and assigned to the combination of (ν)_{OH} and (δ)_{HOH} vibration modes [24]. These bands are very strong in intensity to be interpreted as interlayer water vibration modes. These bands provide evidence that the water exists in the layers of halloysite. However, these bands for halloysite-KAc intercalation complex shift to 5098, 5187 and 5257 cm⁻¹ and two new bands at 4844 and 4987 cm⁻¹ in this region are observed. It is reported that the halloysite-KAc intercalation complex was formed from the expansion of halloysite with both KAc and molecular water [2]. Therefore, these shift and appearance are attributed to that the water coordinated to KAc is intercalated into the interlayer of halloysite. The NIR spectrum in the 5500-6000 cm⁻¹ region is the spectra region for the first fundamental overtones of acetate ion. The relatively low intensity bands are observed at 5623, 5723, 5795, 5935 and 5982 cm⁻¹ in the spectrum of halloysite-KAc intercalation complex and are not observed in this spectrum region of halloysite. The band at 5982 and 5935 cm⁻¹ result from the overtone of ν (CH₃) and 2 ν (COO) stretching vibrations. It is noted that the bands of 5795 and 5623 cm⁻¹ are almost the same in intensity. These two bands are assigned to the overtone of the CH₃ stretching bands observed at 3002 and twice the wavenumber of the symmetric deformation band of the CH₃ (1346 cm⁻¹) in the MIR spectrum.

3.2.3. 8000-6000 cm⁻¹ region

The NIR spectral region between 6000 and 8000 cm⁻¹ is the region where the fundamental overtone of the OH stretching bands (Fig. 5). The bands are observed for halloysite at 6580, 6923, 7081, 7216 and 7671 cm⁻¹ and are assigned to the first fundamental overtone of the OH stretching vibrations at 3266, 3442, 3561, 3625 and 3693 cm⁻¹. These bands are attributed to inner hydroxyl units on the Al in the halloysite [12]. The NIR spectrum of halloysite-KAc intercalation complex does not vary very significantly in this region. The band observed in this region for halloysite shift to lower position at 7390, 7174, 7050, 6884, 6550 cm⁻¹ and with low intensity. This is due to the inner surface hydroxyl of halloysite hydrogen bonding with the acetate ion. As reported by Frost [2], if the halloysite is intercalated with a salt of a short-chain aliphatic acid such as potassium acetate, then a concomitant

176 decrease in the intensity of some hydroxyl bands is observed. This result is in good agreement with the
177 result of MIR spectra.

178

179 **4. Conclusions**

180 The combination of the MIR and NIR spectroscopic investigations has proven to be very
181 informative in the determination of the intercalation of KAc into the interlayer of halloysite. MIR
182 spectra provide greater spectral features and better spectral resolution, and can be effectively used to
183 analyze the OH stretching vibration and the basic structural vibration in halloysite and halloysite-KAc
184 intercalation complex. Such differences, however, are too subtle to be useful in studying the structural
185 changes. This is because the interlayer of halloysite and halloysite-KAc contain water molecules; it
186 makes study on the change on structure using MIR rather difficult.

187

188 Based on analysis of the features and assignment for bands of MIR spectra, the NIR spectra
189 provide the significant differences and the obvious structural change between halloysite and
190 halloysite-KAc intercalation complex. Therefore, to better know the change on the structure after
191 intercalation, the full spectra range including MIR and NIR will provide the best results rather than
192 only the specific spectral regions.

193

194 **Acknowledgment**

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232
233

234 **LIST OF FIGURES**

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236 **intercalation complex**

237

238 **Fig.2 The 1750-650 cm⁻¹ region of MIR spectra of (a) halloysite and (b) halloysite-KAc**
239 **intercalation complex**

240

241 **Fig.3 The 4700-4000 cm⁻¹ region of NIR spectra of (a) halloysite and (b) halloysite-KAc**
242 **intercalation complex**

243

244 **Fig.4 The 6200-4700 cm⁻¹ region of NIR spectra of (a) halloysite and (b) halloysite-KAc**
245 **intercalation complex**

246

247 **Fig.5 The 8000-6000 cm⁻¹ region of NIR spectra of (a) halloysite and (b) halloysite-KAc**
248 **intercalation complex**

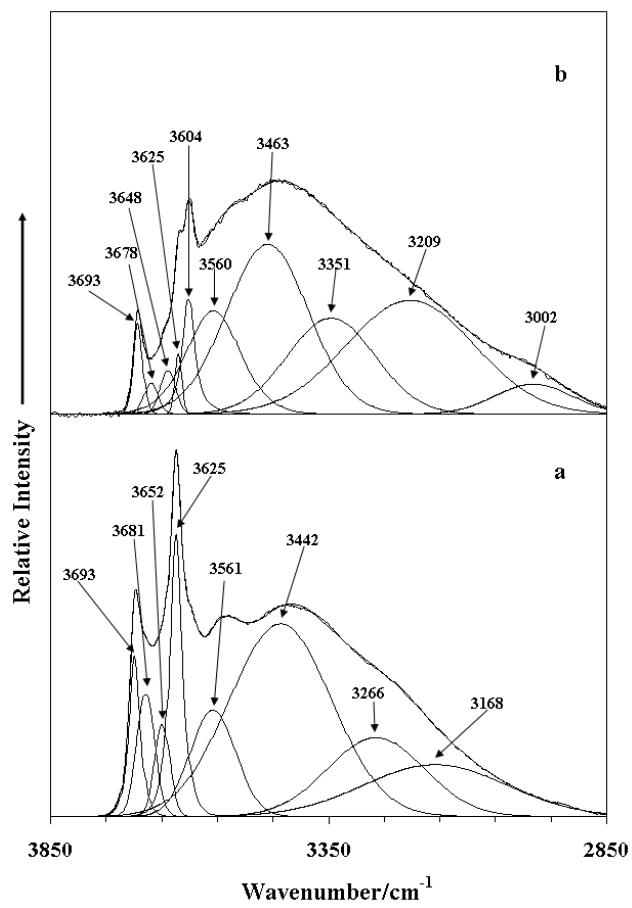


Fig.1

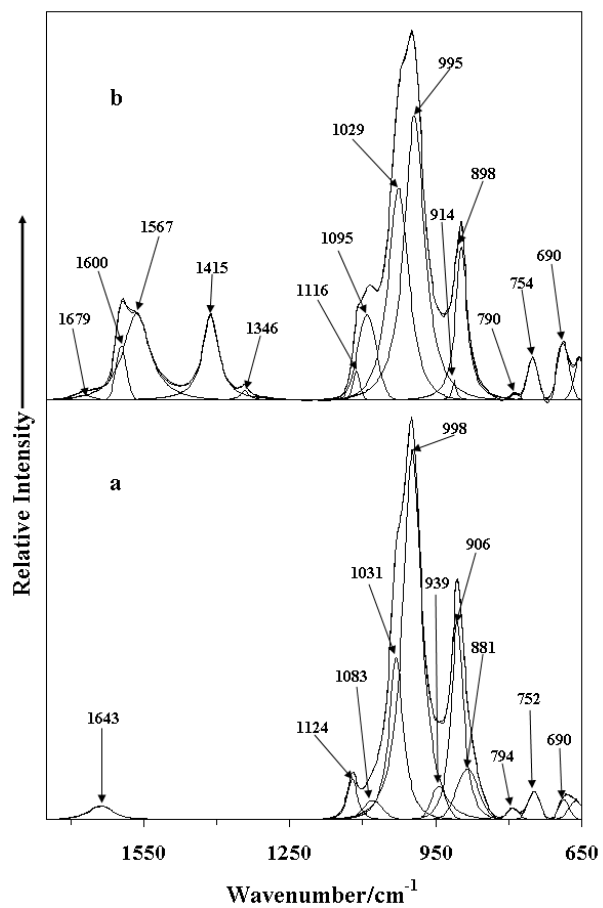


Fig.2

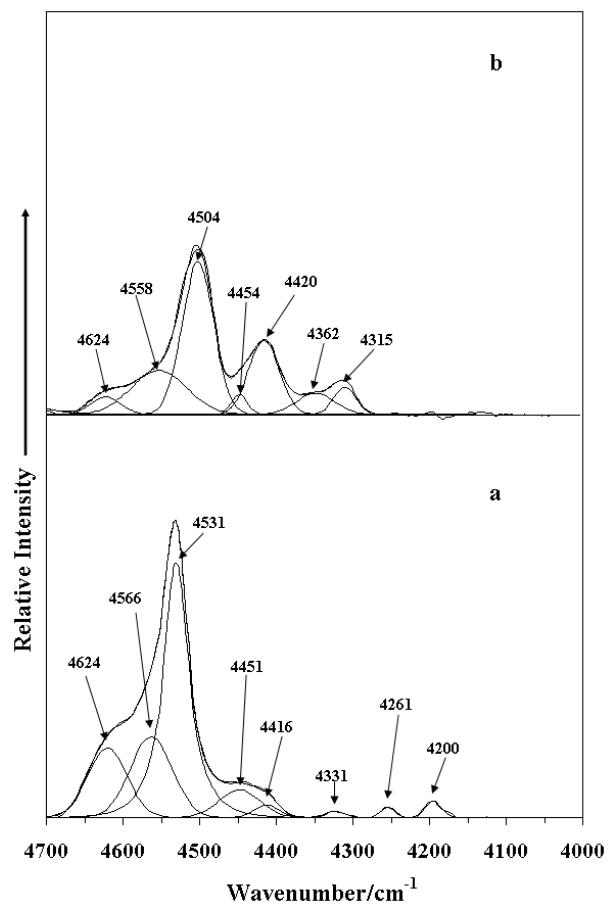


Fig. 3

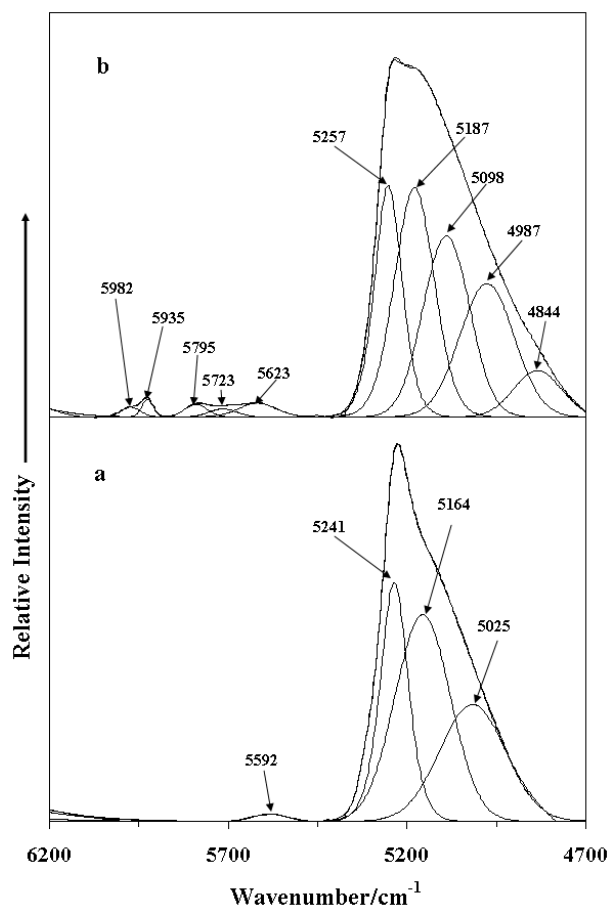


Fig. 4

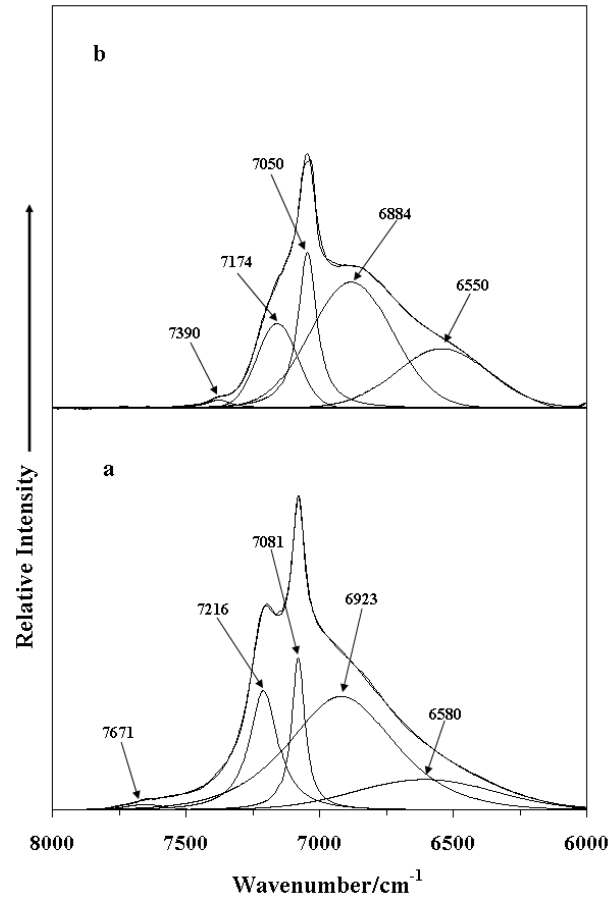


Fig. 5