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Electron paramagnetic resonance, optical absorption and IR spectroscopic studies of the sulphate mineral apjohnite

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Abstract

Apjohnite, a naturally occurring Mn-bearing pseudo-alum from Terlano, Bolzano, Italy has been characterized by EPR, optical, IR and Raman spectroscopy. The optical spectrum exhibits a number of electronic bands around 400 nm due to Mn(II) ion in apjohnite. From EPR studies the parameters derived, $g = 2.0$ and $A = 8.82$ mT confirm $\text{MnO}(\text{H}_2\text{O})_5$ distorted octahedra. The presence of iron impurity in the mineral is reflected by a broad band centered around 8400 cm^{-1} in the NIR spectrum. A complex band profile appears strongly both in IR and Raman spectra with four component bands around 1100 cm^{-1} due to the reduction of symmetry for sulphate ion in the mineral. A strong pair of IR bands at 1681 and 1619 cm^{-1} with variable intensity is a proof for the presence of water in two states in the structure of apjohnite.

Keywords: Apjohnite; Pseudo-alum; Optical absorption spectrum; EPR; Near-infrared spectroscopy; IR and Raman spectroscopy

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1. Introduction

Alums have the general formula $RM(SO_4)_2 \cdot 12H_2O$ or $R_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O$, where M = trivalent aluminum, iron, chromium, manganese, cobalt, gallium, rhodium or thallium and R = monovalent sodium, potassium, ammonia, lithium, or cesium. The alums form two groups namely kalinite or potash alum and the halotrichite mineral series. The halotrichite mineral series alums are pickeringite, halotrichite, bilinite, apjohnite, dietrichite and wupatkiite. Apjohnite belongs to pseudo-alums. Raman microscopy of apjohnite has been reported [1].

Apjohnite mineral used in the present study originates from Terlano, Bolzano, Italy. Chemical analysis was reported and yields the calculated crystallochemical formula $(Mn_{0.64} Mg_{0.28} Zn_{0.06} Fe_{0.02}) Al_2 (SO_4)_4 \cdot 22H_2O$ [2]. Its crystal structure is monoclinic with space group $P2_1/c$. The lattice constants are $a = 0.6198(2)$, $b = 2.4347(4)$, $c = 2.1266(4)$ nm, $\beta = 100.28(3)^\circ$ and $Z = 4$. In the crystal structure four crystallographically independent sulphate ions are present. One acts as a unidentate ligand to the M(II) ion, and the other three are involved in complex hydrogen bond arrays involving coordinated water molecules to both cations and to the lattice water molecules. The SO_4 tetrahedra, $Al(H_2O)_6$ octahedra, and $MnO(H_2O)_5$ octahedra are connected by a H bonding system; the only direct connection between polyhedra is by sharing of an O between S(4) and Mn [3-4]. The effect of cation and its symmetry on spectral properties can be explained by crystal field theory. Octahedral coordination of Mn(II) in apjohnite has five valence electrons occupying three in t_{2g} and two in e_g orbitals and ${}^6A_{1g}$ forms the ground state. The transitions of $MnO(H_2O)_5$ groups are spin forbidden. However visible spectrum shows sharp bands near 400 nm (25000 cm^{-1}) for all Mn-complexes [5,6].

IR spectra of alums based on one monovalent and one trivalent cation have been published [7]. Ross reported the interpretation of the infrared spectrum of potassium alum as ν_1 , 981 cm^{-1} ; ν_2 , 465 cm^{-1} ; ν_3 , $1200, 1105\text{ cm}^{-1}$; ν_4 , 618 and 600 cm^{-1} for $(SO_4)^{2-}$. Water stretching modes were reported at 3400 and 3000 cm^{-1} , bending modes at 1645 cm^{-1} , and librational modes at 930 and 700 cm^{-1} [8]. The Raman spectra of synthetic alums have been extensively studied [9,10]. However, little attention has been paid on the study of the spectra of naturally occurring, Mn bearing alum-apjohnite. So far for this mineral no studies of the optical absorption, electron paramagnetic resonance and IR studies have been reported. Therefore in this work we report the electron paramagnetic resonance, optical absorption, NIR and IR spectroscopy of apjohnite and review the Raman data reported on natural pseudo-alums [1].

2. Experimental Studies

A white sample of apjohnite from Terlano, Bolzano, Italy is used in the present work. EPR spectra of the powdered sample were recorded at room temperature (RT) on JEOL JES-TE100 ESR spectrometer operating at X-band frequencies ($\nu = 9.1\text{-}9.5$ GHz), having a 100 KHz field modulation to obtain a first derivative EPR spectrum. DPPH with a g value of 2.0036 is used for g factor calculations.

Varian Cary 3 UV-Visible spectrophotometer, equipped with Diffuse Reflectance Accessory (DRA) was employed to record the electronic spectrum of the sample in the region between 200 and 900 nm. The diffuse reflectance measurements were converted into absorption (arbitrary units) using the Kubelka-Munk function ($f(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$). Data manipulation was performed using Microsoft Excel. The details of experimental techniques were followed as reported [11]. Raman microprobe spectroscopy consists of Renishaw 1000 Raman microscope system in conjunction with monochromator, a filter system and a Charge Coupled Device (CCD) was employed. He-Ne laser was used to excite the sample. Small crystals of the apjohnite mineral were used to record the Raman spectrum in the range 4000 to 100 cm^{-1} . Other details of the experimental technique have already been reported [12,13].

Spectroscopic manipulations such as baseline adjustment, smoothing and normalization were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel "PEAKFIT" software package which enabled the type of fitting function to be selected and specific parameters to be fixed or varied accordingly. Band fitting was carried out using a Lorentz-Gauss cross product function with a minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.9975.

3. Results and analysis

3.1. Electron paramagnetic resonance analysis

If manganese is present in the mineral, electron paramagnetic resonance will show its presence by a six line pattern in the EPR spectrum. Fig.1 shows the EPR spectrum of polycrystalline apjohnite mineral observed at room temperature. It is well known that in the transition metal ion EPR studies, Mn(II) is easily observable at room temperature, even if present in minute levels, compared to other ions. Fig. 2 clearly indicates the presence of Mn(II) in the sample. It contains a strong sextet at the centre of the spectrum corresponding to the electron spin transition $+1/2 >$ to $-1/2 >$. Generally, in most of the cases, the powder spectrum is characterized by a sextet, corresponding to this transition. The other four transitions, corresponding to $\pm 5/2 > \leftrightarrow \pm 3/2 >$ and $\pm 3/2 > \leftrightarrow \pm 1/2 >$ are not seen due to their high anisotropy in D. The observed $g = 2.0$ and $D = 33$ mT. This value of D indicates a considerable amount of distortion around the central metal ion. From the powder spectrum of the mineral, the hyperfine splitting (HFS) constant A can be calculated from the position of the allowed HF line using the formula [14].

$$H_m = H_0 - Am - (35 - 4m^2) \left(\frac{A^2}{8H_0} \right).$$

Here H_m is the magnetic field corresponding to $m \leftrightarrow m$ in HF line

H_0 is the resonance magnetic field.

m is the nuclear spin magnetic quantum number.

The value of A at room temperature is found to be 8.82(1) mT. Further the strength of the HFS depends on the matrix and is mainly determined by the electro negativity of the anion neighbours. The magnitude of the HFS constant, A provides a qualitative measure of the ionic nature of bonding between the Mn(II) ion. Using the hyperfine-coupling constant obtained from the EPR spectrum and with Matumura's plot [15], the percentage of covalency of Mn-ligand bond has been calculated. This corresponds to an ionicity of 93%

The percentage of covalency of Mn-O bond is calculated with their electronegativities X_p and X_q [16]

$$C = \frac{1}{n} \left[1 - 0.16(X_p - X_q) - 0.035(X_p - X_q)^2 \right]$$

Here n is the number of ligands around Mn(II) ion. The percentage of covalency obtained is 8.5% assuming $X_p = X_{Mn} = 1.4$ and $X_q = X_S = 3.5$. Again the approximate value of hyperfine constant (A) is calculated by using covalency (C) using the equations [16,17]

$$A_{iso} = (2.04C - 104.5) 10^{-4} \text{ cm}^{-1}.$$

The value obtained is $87 \times 10^{-4} \text{ cm}^{-1}$. This calculated value agrees well with the observed hyperfine constant ($87 \times 10^{-4} \text{ cm}^{-1}$) indicating ionic character for Mn-O bond in the complex under study. Further the g value for the hyperfine splitting was indicative of the nature of bonding. If the g value shows negative shift with respect to free electron g value (2.0023), the bonding is ionic and conversely, if the shift is positive then the bonding is more covalent in nature [18]. In the present work, from the observed negative ($2.00 - 2.0023 = -0.0023$) shift in the g value, it is apparent that the Mn(II) is in an ionic environment.

3.2. Optical absorption spectral analysis

Optical absorption spectra of apjohnite in the range $50000 - 11110 \text{ cm}^{-1}$ (200-900 nm) and $8700 - 8000 \text{ cm}^{-1}$ are shown in Figs. 3a and b. The spectra discussed here have all the features that appear due to various electronic transitions involving manganese and iron. The observations are in tune with the chemical analysis. The spectra of the sample observed here have bands at 8482, 8288 (with a shoulder at 8116), 11975, 22730, 25640, 27780, 33900 and 45455 cm^{-1} . These bands are divided into two sets for easy analysis as 8482, 8288 (with a shoulder at 8116) and 11975 cm^{-1} (835 nm) as first set and 22730, 25640, 27780, 33900 and 45455 cm^{-1} (440, 390, 360, 295 and 220 nm) as second set in the sample. The bands in the second set correspond to the Mn(II) ion. The observed bands have been assigned to the d-d transitions of the d^5 ion having ground state ${}^6A_{1g}(S)$ following Tanabe-Sugano diagrams [19]. In a lower symmetry environment, the Mn(II) ion exhibits bands corresponding to the transitions from the ground state ${}^6A_{1g}(S)$ to ${}^4T_{1g}(G)$, ${}^4T_{2g}(G)$, ${}^4A_{1g}(G)$, ${}^4E_g(G)$, ${}^4T_{2g}(D)$, ${}^4E_g(D)$ and ${}^4T_{1g}(P)$ states respectively with increasing order of energy [20]. Assignment of each band to an appropriate electronic transition is difficult due to complexity of the transitions and multiplicity and distortions of the sites occupied by the transition metal ion. Therefore the energy matrices for d^5 configuration are solved for different Dq, B and C with Trees's correction term. The following values give best fit to the observed energies of the bands. $Dq = 600$, $B = 900$ and $C = 3290 \text{ cm}^{-1}$ and $\alpha = 90 \text{ cm}^{-1}$. Observed and calculated values energies of the transitions for Mn(II) in octahedral site in the sample are presented in Table 1.

The first set of bands are characteristic of Fe(III) and Fe(II) ions occupying octahedral environment in the mineral (see below). The only spin allowed transition, ${}^5T_{2g} \rightarrow {}^5E_g$ which shows a strong band for all ferrous ion complexes [21,22] in the region 11000-8000 cm^{-1} . The two observed bands (Fig. 3b) centered around 8400 cm^{-1} are broad and intense assigned as two components of the same transition ${}^5T_{2g} \rightarrow {}^5E_g$ and the average of these bands (8482 and 8288 cm^{-1}) i.e. 8385 cm^{-1} is taken as 10Dq. The splitting of 10Dq band (8482 – 8288 = 194 cm^{-1}) indicates that it is due to dynamic Jahn-Teller effect in the excited 5E_g state since the splitting value is an intermediate between 100 and 2000 cm^{-1} [23,24]. In many of the iron bearing silicates [25] and Mn-bearing zoisite [26] a broad band in the range 13000-11000 cm^{-1} has been observed and assigned to ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transition for ferric ion. A broad weak band observed in apjohnite mineral at 11975 cm^{-1} could be due to Fe(III) impurity in the mineral. Sharp strong bands in the optical spectrum around 400 nm provide valid evidence for the presence of Mn^{2+} ion in the mineral. This result is in harmony with the EPR results. The mineral is white which is unusual for a mineral containing Mn^{2+} .

3.3. Near-infrared and infrared spectroscopy

The Near-IR spectral regions may be conveniently divided into three regions (a) the high wavenumber region $> 7500 \text{ cm}^{-1}$. In this region electronic bands due to characteristic of Fe^{2+} and Fe^{3+} ions are observed. Bands in the spectrum shown in Fig.4a, the high wavenumber region between 7200 and 6300 cm^{-1} are attributed to the first overtone of the fundamental hydroxyl stretching mode. The 6000-4200 region spectrum shown in Fig.4b, where the bands in the range 6000- 5500 cm^{-1} are attributed to water combination modes of the hydroxyl fundamentals of water and the bands in the lower range 5500-4200 cm^{-1} are assigned to the combination of the stretching and deformation modes of the apjohnite. The mid-IR spectra as studied, may also be subdivided into four spectral regions: (a) 3700 to 2500 cm^{-1} region where OH fundamental vibrations are observed (Fig.5a); (b) 1800 to 1400 cm^{-1} range where the water bending modes are observed (Fig. 5b); (c) 1200 to 800 cm^{-1} region shows bands due S-O stretching vibrations (Fig. 5c) and (d) the low wavenumber region (700-645 cm^{-1}) displays a single mode for $(\text{SO}_4)^{2-}$ (Fig. 5d). As Raman spectroscopy of apjohnite has already been reported [1], the analysis are not discussed here. The results of the NIR spectra are given in Table 2 and the results of the mid-IR spectra in Table 3.

The 3700 to 2500 cm^{-1} spectral region

The OH stretching region of apjohnite is shown in Fig. 5a. The IR spectrum shows five bands at 3512, 3397, 3334, 3253 and 3112 cm^{-1} . The first two bands are assigned to OH stretching vibrations of water (ν_3) where as the bands at 3334, 3253 and 3112 cm^{-1} are identified as ν_1 mode of H_2O . In this region Raman spectrum (Fig. 6a) also displays almost similar band positions at 3496, 3406, 3337 and 3252 of which 3406 cm^{-1} band is most intense and sharp.

The 1800 to 1400 cm^{-1} spectral region

This region is significant for the observation of H₂O bending modes. The ν_2 water-bending modes are very weak in Raman but they more pronounced in the IR spectrum (Fig. 5b). A broad band profile centered at $\sim 1600\text{ cm}^{-1}$ from which four bands are resolved at 1681, 1639, 1619 and 1517 cm^{-1} . From this group of bands, two bands are sharp and strong at 1681 and 1619 cm^{-1} with a shoulder at 1639 cm^{-1} . The appearance of ν_2 mode on the higher wavenumber side at 1681 cm^{-1} is an indication of strongly hydrogen bonded water and the 1619 cm^{-1} mode to weakly hydrogen bonded water. This complexity of bands provides evidence for the existence of water in several states in the structure of apjohnite. The observation of four HOH bending modes is in harmony with the observation of four OH stretching modes in the Raman spectrum and five OH stretching vibrations in the infrared spectrum.

The 1200 to 600 cm⁻¹ spectral region

The infrared spectra for the fundamental vibrations of $(\text{SO}_4)^{2-}$ in the apjohnite mineral are shown in Figs. 5c and d. All the spectral features in this region are characteristic of sulphate groups. The free $(\text{SO}_4)^{2-}$ ion has ideal tetrahedral (T_d) symmetry and gives four fundamental vibrations at $981(\nu_1)$, $451(\nu_2)$, $1104(\nu_3)$, $613(\nu_4)\text{ cm}^{-1}$. Of these, ν_1 mode is non-degenerate, ν_2 mode is doubly degenerate and ν_3 and ν_4 modes are triply degenerate. In solid sulphate compounds the degeneracies are often removed by lowering of symmetry imposed by the molecular environment [27,28]. For ideal tetrahedral (T_d) symmetry all modes are Raman active while ν_1 and ν_2 are IR inactive. For pseudo-alums, the symmetry is lowered and all vibrations become active. In the present investigation, the most intense complex band around 1100 cm^{-1} resolved into a number of bands both in IR and Raman spectra (Figs. 5c and 6b) are assigned to the $\nu_3(\text{SO}_4)^{2-}$ antisymmetric stretching vibrations. The shoulder band at 982 cm^{-1} is attributed to the $\nu_1(\text{SO}_4)^{2-}$ symmetric stretching vibrations. A single broad band in IR at 667 cm^{-1} (Fig. 5d) is identified as the ν_4 mode. The $\nu_2(\text{SO}_4)^{2-}$ bending modes are not observed in IR as they occur below the cut-off point for the diamond ATR cell. However, this mode could be observed at 496 cm^{-1} in Raman (Fig. 6c). Bishop and Murad reported bands for both the synthetic and natural minerals at 663 and 630 cm^{-1} [29]. The analysis of IR and Raman spectra of apjohnite is presented in Table 3 along with the Raman data reported on Mn-bearing alum and also compared with that of Fe-bearing alums from three different origins. The OH region bands ($3500\text{--}3100\text{ cm}^{-1}$) observed both in IR and Raman agree closely with the Raman data already reported for apjohnite. One additional band observed in IR at 3122 cm^{-1} is assigned to OH stretch $\nu_1\text{ H}_2\text{O}$. In the case of Fe^{2+} alums bands in this region are observed but shifted to higher wavenumber side. Since OH region bands are so sensitive, Mn and Fe alums could readily be differentiated. Such distinction is important for the detection of pseudo-alums in sulphate efflorescent deposits as occurs in mineral slag deposits. From the study of IR spectra, sharp bands at $\sim 320\text{ cm}^{-1}$ have been reported for Mn^{2+} and Fe^{2+} in complexes with M-O_6 coordination [30]. The low energy Raman bands in the range $400\text{--}360\text{ cm}^{-1}$ observed for these alums are attributable to Mn-O/Fe-O vibrations.

4. Conclusions

1. Chemical analysis of the apjohnite mineral indicated that it contains manganese

- 0.64 and iron 0.06 wt% in the mineral as is verified by the spectroscopic analyses reported in this paper..
2. EPR results show that only Mn(II) is present in the mineral in distorted octahedral environment. The g and A values observed in the spectrum are 2.0 and 8.82 mT with D = 33 mT. The percentage of covalency obtained is 8.5%. The observed and calculated A values are in good agreement.
 3. The optical absorption indicates that Mn(II) ion in the sample is present in a distorted octahedral environment. The crystal field and Racah parameters evaluated are $Dq = 600$, $B = 900$ and $C = 3290 \text{ cm}^{-1}$ and $\alpha = 90 \text{ cm}^{-1}$. Further the spectrum indicating that iron is present in +2 state in the sample.
 4. The Infrared spectrum of apjohnite is assigned to fundamentals of water molecules and sulphate ions.
 5. The Raman spectrum of apjohnite is compared with published data and is almost identical.

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Table 1

Band headed data with the assignments for Mn(II) in apjohnite

 $Dq = 600$, $B = 900$ and $C = 3290 \text{ cm}^{-1}$ and $\alpha = 90 \text{ cm}^{-1}$

Wavelength (nm)	Wave number (cm^{-1})		Transition from ${}^6A_{1g}$
	Observed	Calculated	
835*	11975*		${}^4T_{1g}(G)^*$
440	22730	22689	${}^4T_{1g}(G)$
390	25640	26176	${}^4T_{2g}(G)$
360	27780	27250	${}^4A_{1g}(G), {}^4E_g(G)$
295	33900	32322	${}^4E_g(D)$
220	45455	44384	${}^4T_{1g}(P)$

* Due to Fe^{3+} ion

Table 2
 Analysis of the near-infrared bands in apjohnite

Band position (cm ⁻¹)	Assignment
8482*	Fe ²⁺ transition: ⁵ T _{2g} → ⁵ E _g
8288*	”
8116sh	”
6917	First fundamental overtone of OH stretch
6769c	”
6495c	”
5725	Water OH overtones
5610c	”
5150	”
5050c	”
4900c	”
4520	Combination of OH stretch and deformation

*average of the two bands represents Fe²⁺ transition
 Sh-shoulder; c-component band

Table 3

IR and Raman spectroscopic data (cm^{-1}) of Mn and Fe bearing pseudo-alums from different origins

Apjohnite Mn ²⁺ alum	Apjohnite Mn ²⁺ alum	Apjohnite Mn ²⁺ alum	Halotrichite Fe ²⁺ alum	Halotrichite Fe ²⁺ alum	Halotrichite Fe ²⁺ alum	Assignments [7,31]
(Italy)	(Italy)	(Italy)	(Italy)	(Spain)	(California)	
Present work	Present work	Reported [1]	Unpublished Data by Frost	Unpublished Data by Frost	Unpublished Data by Frost	
IR	Raman	Raman	Raman	Raman IR	IR	
3512	3496	3490	3452	3546 3538	3694	OH stretch ν_3 (B_g) H ₂ O
3397	3406	3394	3369	3425 3397	3573	OH stretch ν_3 (A_g) H ₂ O
3334	3337	3281	3255	3269 3228	3493	OH stretch ν_1 H ₂ O
3253	3252	3122	3166		3263	OH stretch ν_1 H ₂ O
3112					3031	OH stretch ν_1 H ₂ O
		2925	2944	2943	2873	Organic impurity
					2501	“
1681		1658		1662 1650	1654	ν_2 (B_g) H ₂ O
1639		1620			1604	ν_2 (A_g) H ₂ O
1619						ν_2 (A_g) H ₂ O
1517				1568		Combination band
					1453	Combination band
1197	1198	1148	1148	1147 1134	1145	ν_3 (A_g) SO ₄
1138	1143	1113	1112		1107	ν_3 (B_g) SO ₄
1105	1137	1088	1091	1084 1076	1075	ν_3 (B_g) SO ₄
1070	1117	1070	1070			ν_3 (B_g) SO ₄
		1051	1053		988	ν_3 (B_g) SO ₄

982		997	995			1048	$\nu_1(A_g) \text{ SO}_4$
		991		988			$\nu_1(A_g) \text{ SO}_4$
		975	975	984	949	1017 (send up)	
				983		992	$\nu_1(A_g) \text{ SO}_4$
				982		949	$\nu_1(A_g) \text{ SO}_4$
872						918	$\nu_L(A_g) \text{ H}_2\text{O}$
						709	$\nu_L(B_g) \text{ H}_2\text{O}$
					717	626	$\nu_4(B_g) \text{ SO}_4$
	673			624			$\nu_1(A_g) \text{ AlO} *$
667	623	617	622	605	587	580	$\nu_4(B_g) \text{ SO}_4$
						570	$\nu_4(A_u) \text{ SO}_4$ or $\nu_T(B_g) \text{ H}_2\text{O}$
	505	530	529				$\nu_2(A_g) \text{ SO}_4$
	496	466	468	467		495	$\nu_2(A_g) \text{ SO}_4$
		427	424	445			$\nu_2(A_g) \text{ SO}_4$
	417		390	422			$\nu_1(A_g) \text{ MnO}$ or $\text{FeO} *$
				380			$\nu_1(A_g) \text{ FeO} *$
		336	347	362			$\nu_1(A_g) \text{ MnO}$ or $\text{FeO} *$
		313	314			318	Lattice modes *
		264	267	245			“
				221			Lattice modes
				204			Lattice modes
				182			Lattice modes
				116			Lattice modes

* suggested assignment

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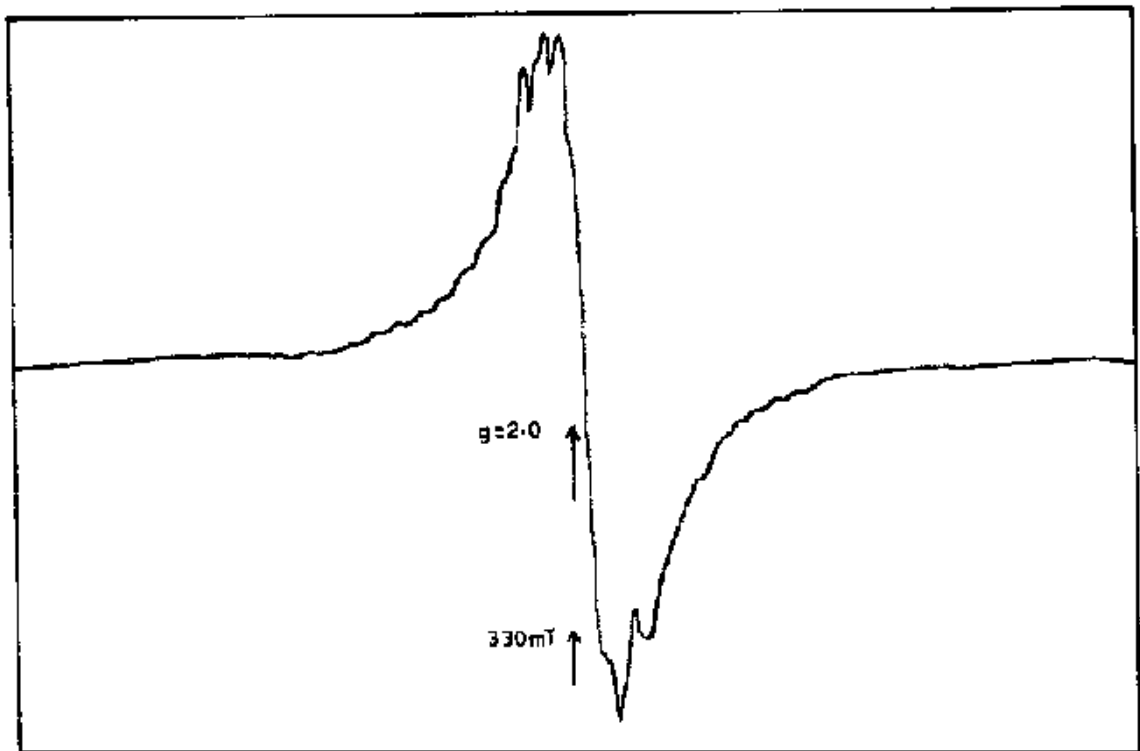


Fig.1 EPR spectrum of apjohnite mineral at RT ($\nu = 9.41236$ GHz) from 80 mT to 580 mT

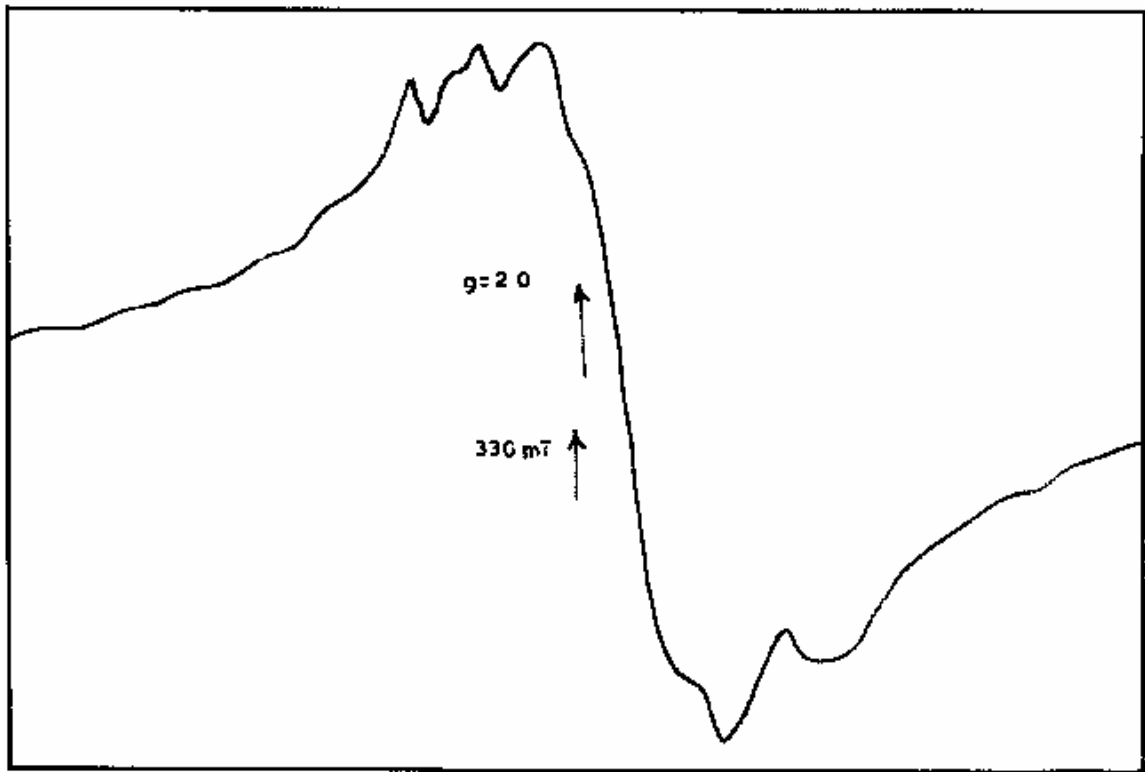


Fig.2 EPR spectrum of apjohnite mineral at RT ($\nu = 9.41236$ GHz) from 255 mT to 405 mT.

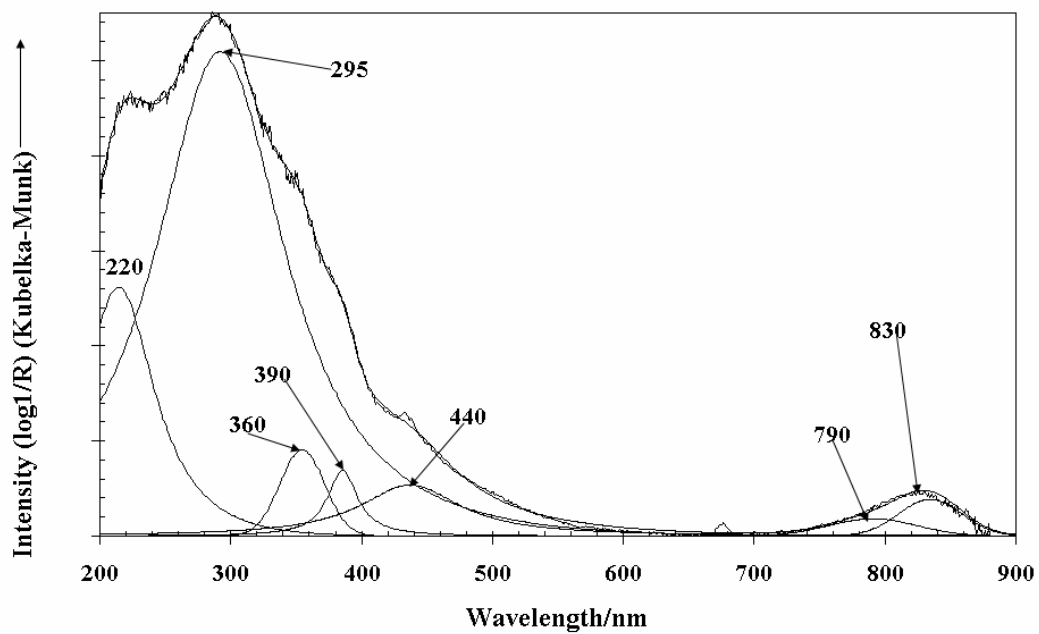


Fig. 3a.

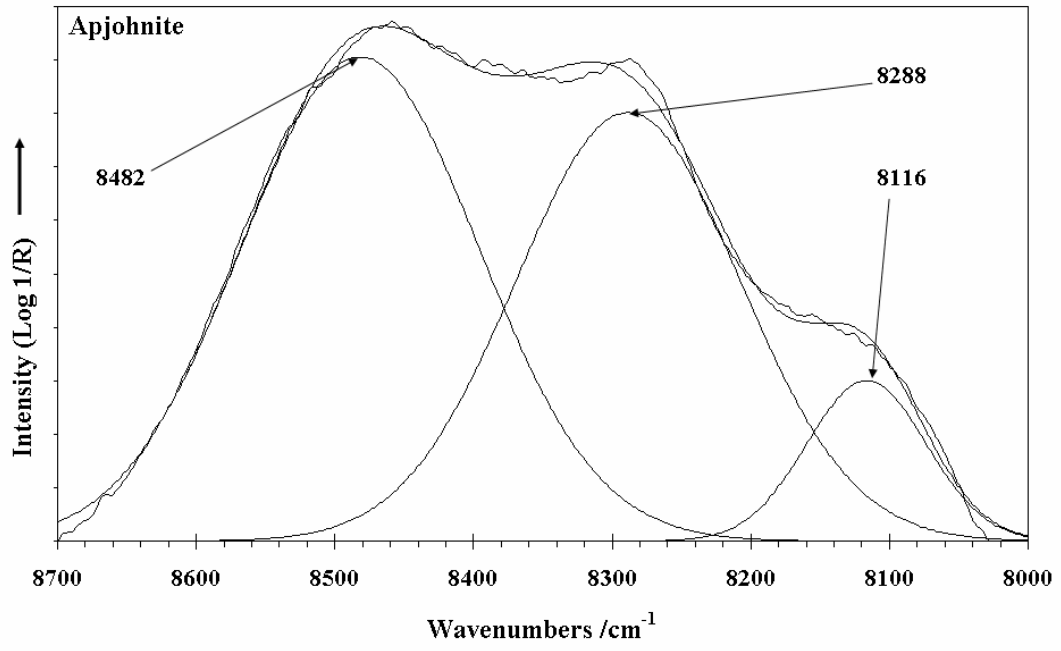


Fig. 3b.

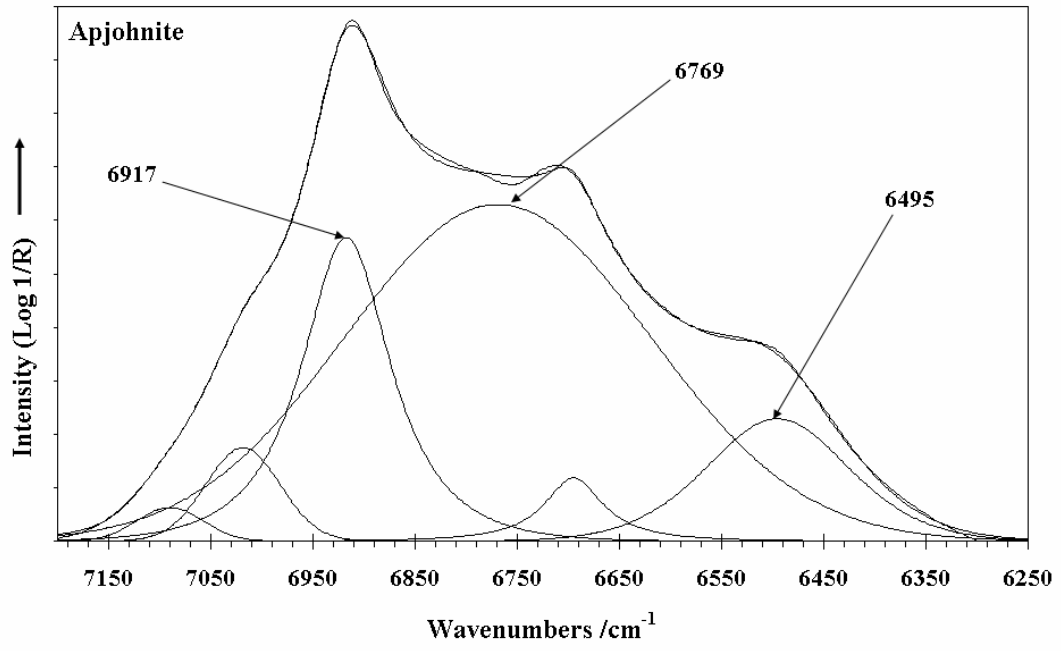


Fig. 4a

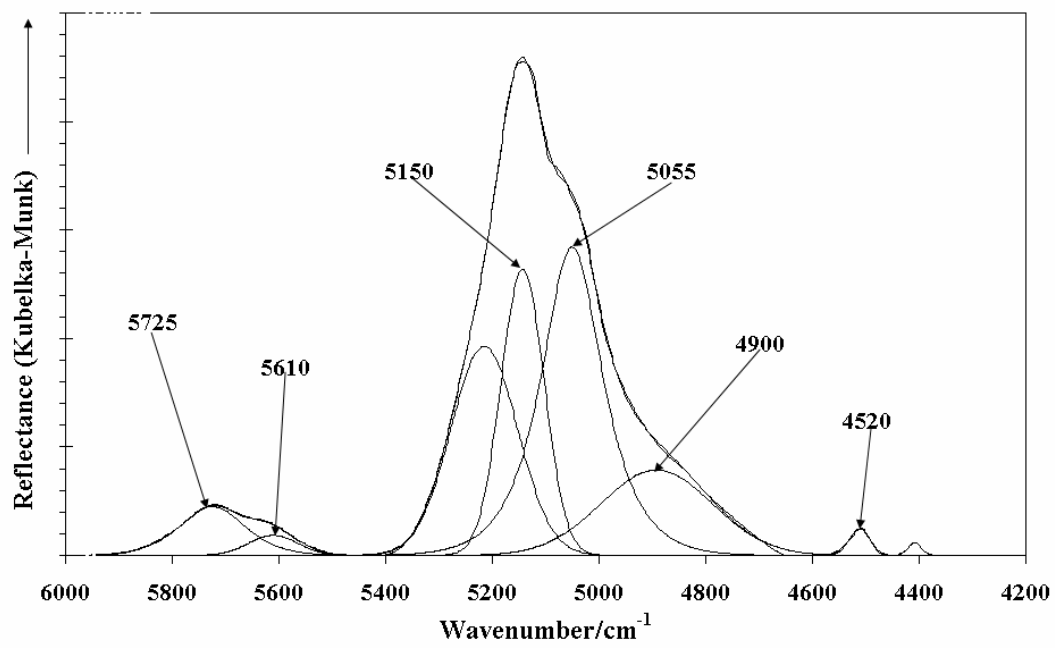


Fig. 4b

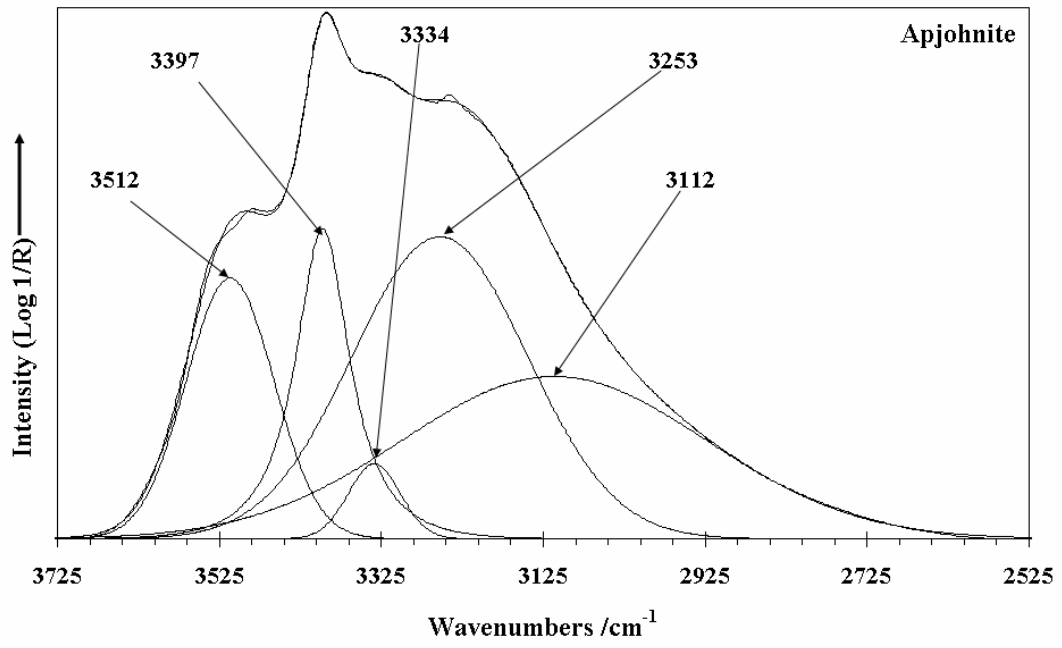


Fig. 5a.

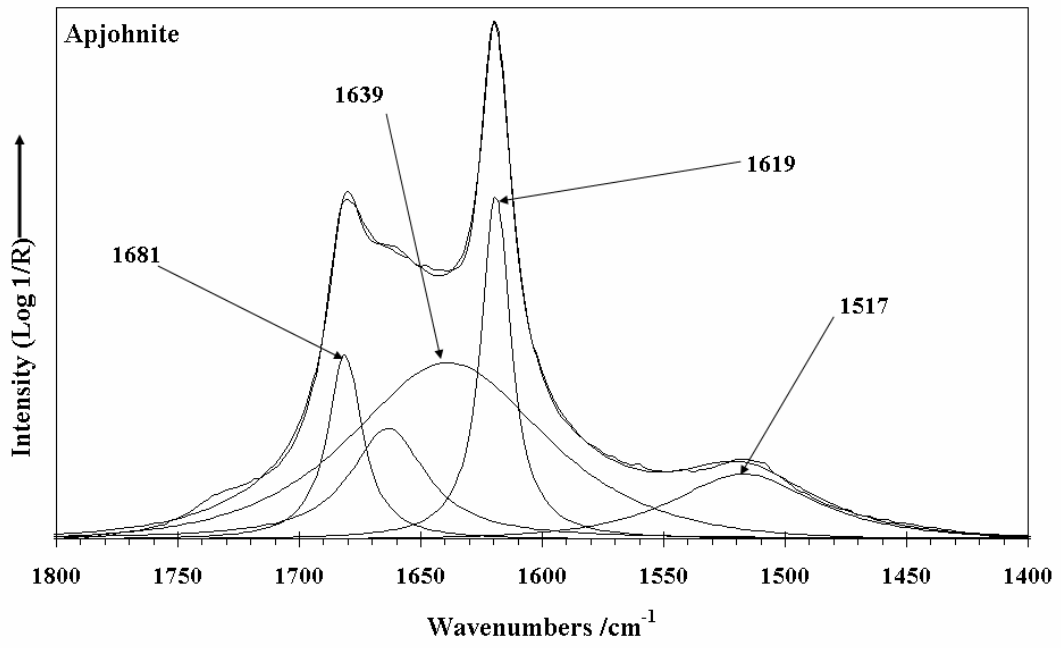


Fig.5b.

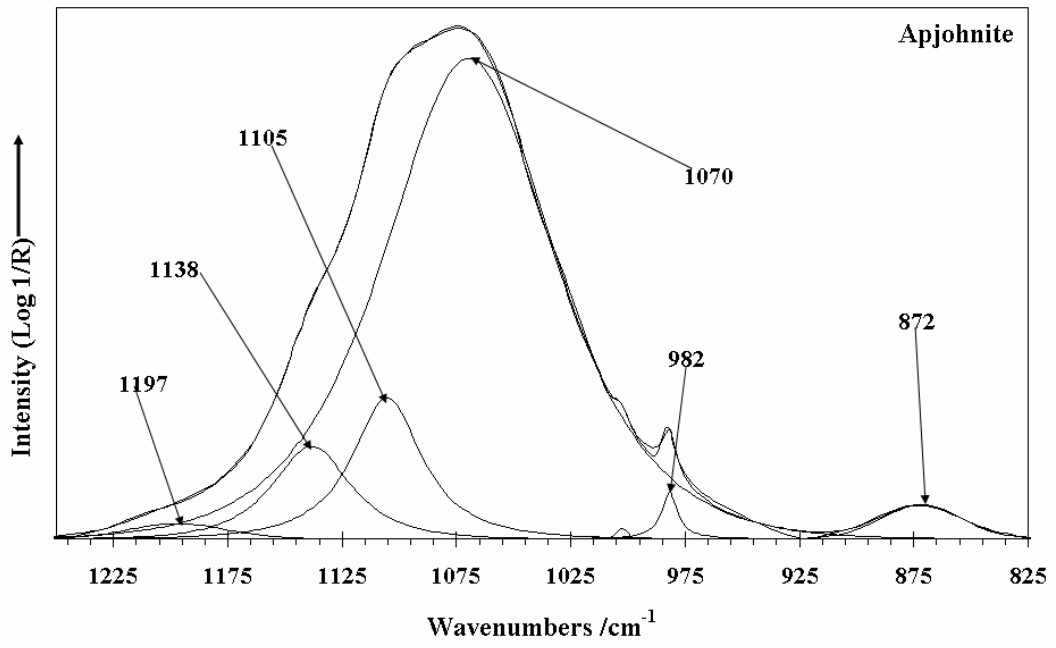


Fig. 5c.

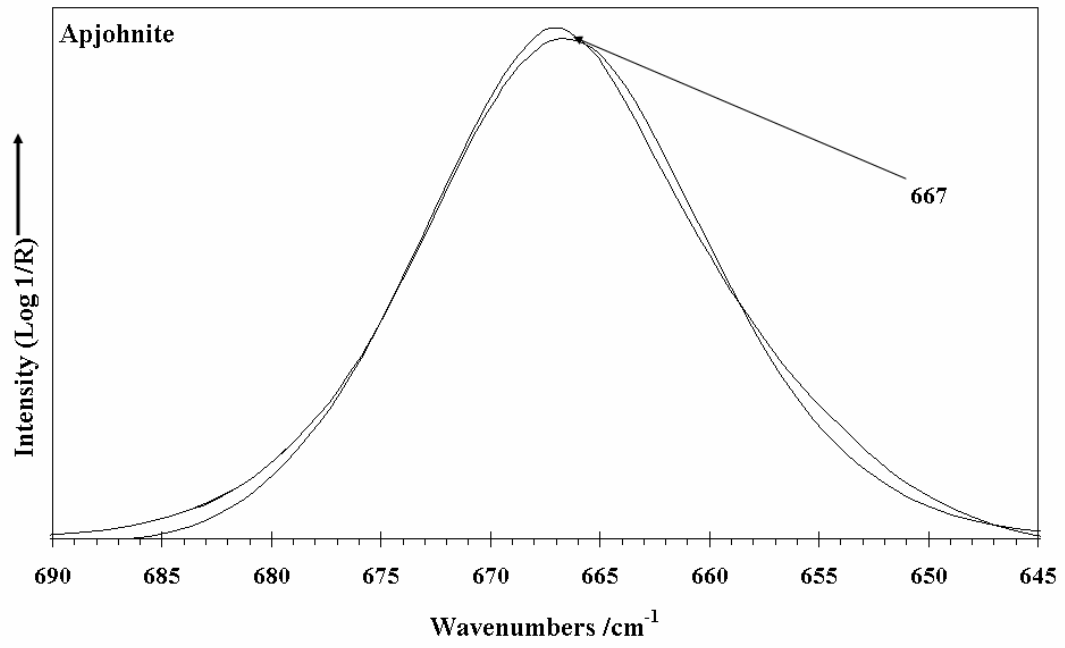


Fig. 5d

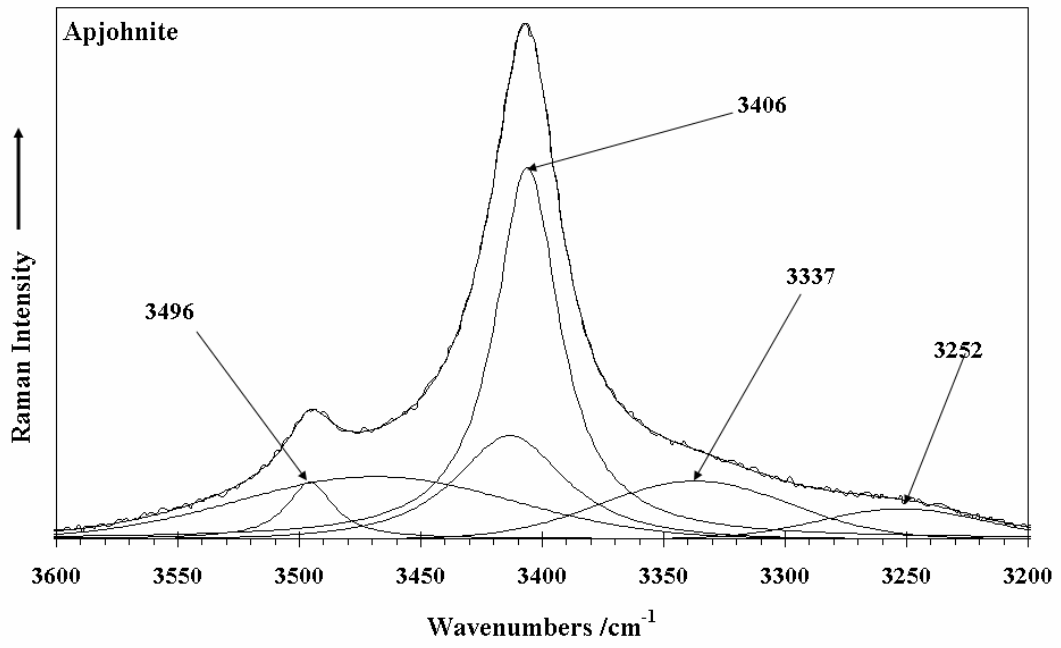


Fig. 6a.

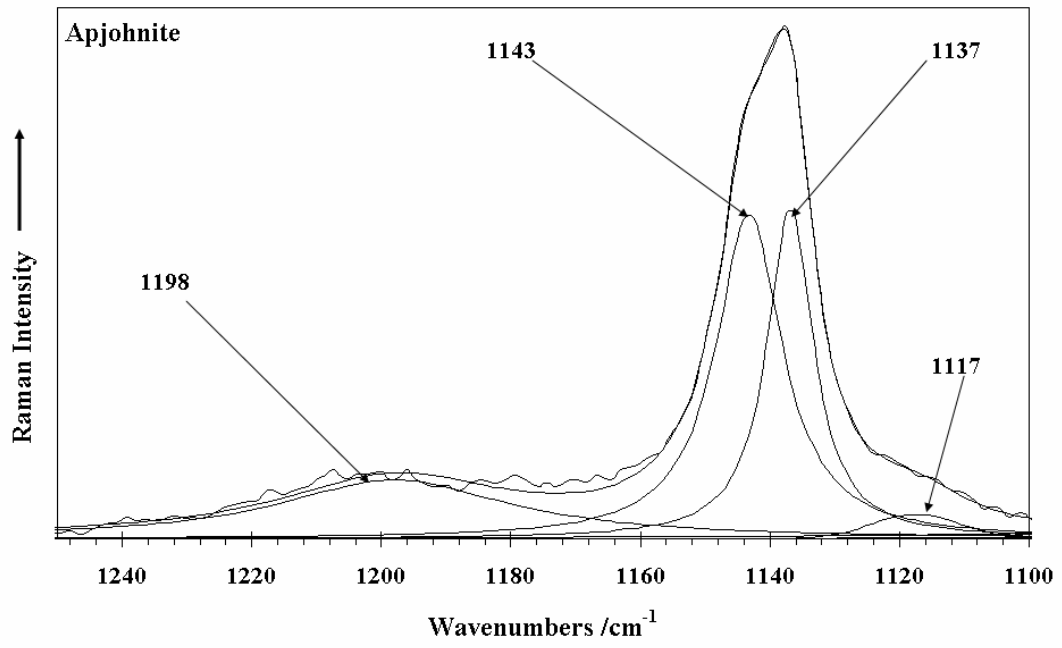


Fig. 6b

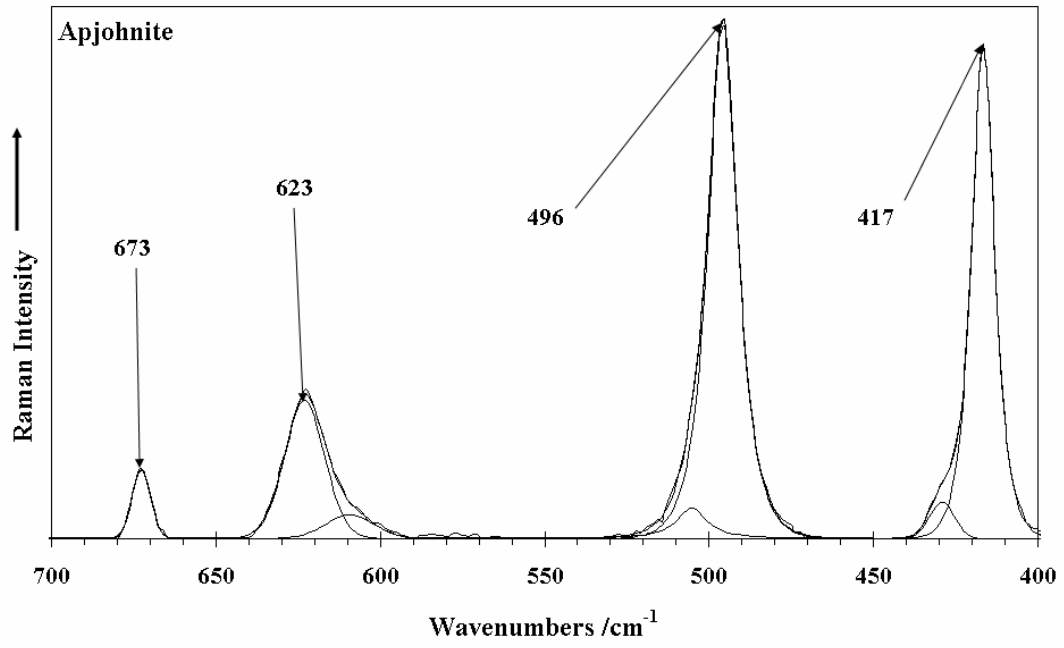


Fig. 6c.