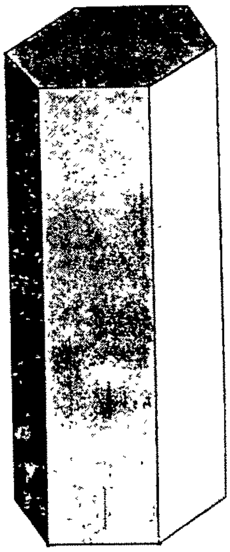


Chapter - 5

Vibrational Spectroscopic Studies

5 - VIBRATIONAL SPECTROCOPIC STUDIES

There is no detailed account on Indian beryls especially with reference to studies on its volatile constituents, but for some brief work by Babu et al. (1994) and Panjikar (1995). An attempt has therefore, been made by the author to characterise the channel constituents and volatile species in the Indian beryls with special reference to those from Orissa using vibrational spectroscopy (IR and Raman) technique. Deciphering the channel constituents would indicate the parent fluid (basic or acidic) from which the beryl crystals have crystallised. An attempt is also made to categorise beryls according to the classification given by Aurisichhio et al. (1988) using Fourier transform infrared (FT-IR) spectroscopy in the structural vibration region (1200 - 400 cm^{-1}) and also to observe the behaviour of hydrous species at elevated temperatures. Before directly venturing on to the experimental results, a brief account on vibrational spectroscopy (IR and Raman) is discussed below.

Water molecules, hydroxyl ions and fluid inclusions are more or less unavoidable components of a mineral Both H_2O and OH^- are ubiquitous in minerals, and can be present either as a major component required by the mineral stochiometry or accidental trace components (Aines 1984; Aines and Rossman, 1984a). These trace hydrous species are of interest to earth scientist because incorporation of even small amount of hydrogen affects the rheological properties (Aines and Rossman, 1985, Rossman, 1988) and the stability field of the phase of a mineral, and lowers its melting temperatures (Hofmeister, 1995). They also affect physical, chemical, electronic and optical properties of the mineral.

5.1 VIBRATIONAL SPECTROSCOPY (INFRARED AND RAMAN)

In minerals, hydrogen is most commonly bonded to oxygen and this OH group absorbs infrared photons efficiently. Atoms bonded in molecular systems vibrate at frequency between 10^{12} and 10^{14} Hz. The exact frequency of vibration between bonded atoms depend on the interatomic forces. Atoms and molecular groups have a number of fundamental vibrational frequencies or modes, with which they vibrate and these correspond to specific energy states of the molecules. Vibrational energies of molecules and crystals lie in approximate energy range of 4500-100 cm^{-1} This corresponds to the energy of light in the infrared region of electromagnetic spectrum. Hence transitions between vibrational energy levels of a molecule can be induced by incident infrared radiation, which is absorbed when the frequency corresponds to the vibrational modes of the sample. Vibrational modes can also be studied by a light scattering experiment in which an incident light beam has its energy changed by an inelastic collision with the vibrating molecular groups (*Raman scattering*).

Individual peaks in the IR spectra may be associated with the presence of particular structural groups within the sample Vibrational spectroscopy is also an alternative tool to analysis by normal chemical or diffraction methods, since vibrational spectra can be easily obtained for crystalline or amorphous solids, liquids or gases and also can be applied for systems with low atomic weight.

In infrared spectroscopy, infrared radiation is passed through a sample and the intensity of the transmitting light is measured as a function of its wavelength. *Fourier transform infrared* (FT-IR) *spectrometer* is an improved version of the conventional IR spectrometer, wherein light intensity is measured in the time domain, then converted via a

Fourier transform (using computer software) to intensity versus energy (Griffith and Haseth, 1986, Rossman, 1988). FT-IR spectrometer used by the author housed at Regional Sophisticated Instrumentation centre (RSIC), IIT, Mumbai is shown in *Plate 5.1a* In a Raman scattering experiment, visible light (laser beam) is passed through the sample Most of the light exits from the sample with no change, but a small fraction (around 10^{-13}) is scattered by the atoms. Small portion of this scattered light (10^{-6} of the incident light) interacts with the sample to induce a vibrational mode When this occurs, the energy of the scattered light is reduced by an amount corresponding to the energy of the vibrational transition. Such non-elastic scattering is known as *Raman scattering*, while elastic light scattering with no change in energy is known as *Raleigh scattering*. Raman spectrometer at RSIC, IIT, Mumbai, used by the author for the present study is depicted in *Plate 5.1b*.

Different vibrational modes have variable relative intensities in infrared and Raman spectra Some modes are active in one region but not in the other, and sometimes some modes are not observed at all (Hofmeister, 1995). In an infrared spectroscopic experiment, the light interacts directly with an oscillating molecular dipole. So for a mode to be *IR active*, it must be associated with a changing dipole moment Generally asymmetric vibrations tend to give stronger IR absorption than symmetric mode as they are associated with larger dipole moment changes In Raman scattering, the incident light is responsible for inducing an instantaneous dipole moment by deforming the electron cloud around the molecule If the displacement of the electron cloud corresponds to that of a vibrational modem it is said to be *Raman active* (MacMillan and Hofmeister, 1988). Magnitude of the induced dipole moment is related to the ease with which the electron cloud may be deformed, a property that can be

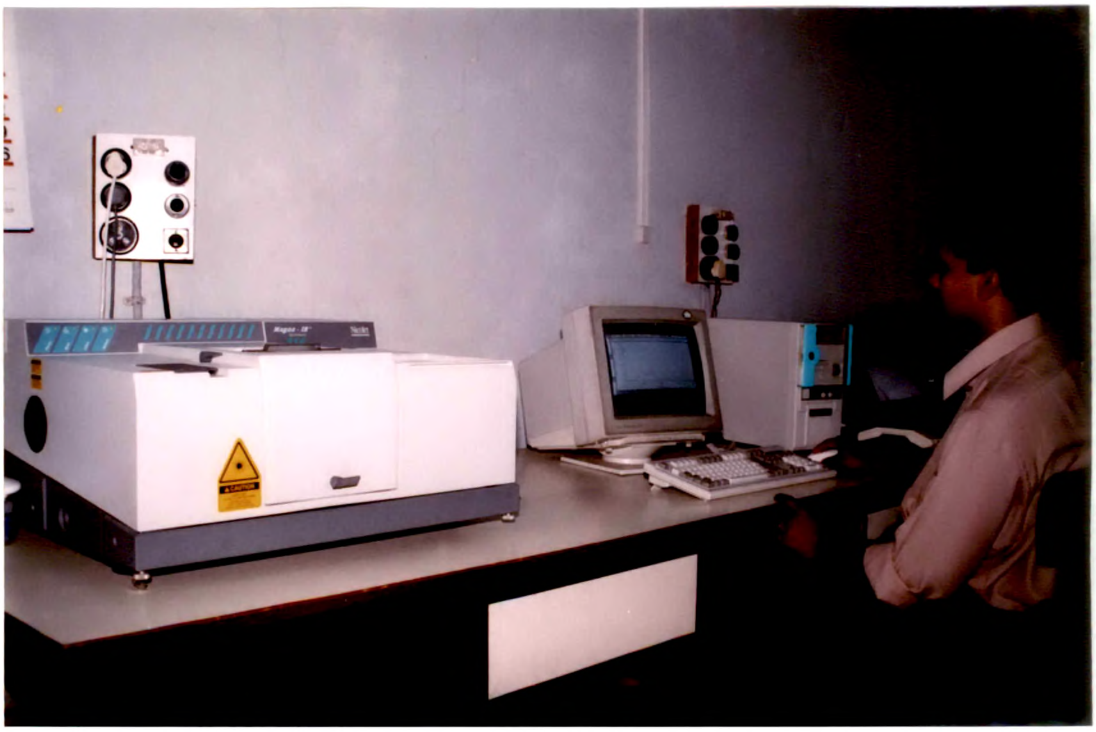


Plate 5.1a : Fourier Transform Infrared Spectroscope at RSIC, IIT, Mumbai

Plate 5.1b : Raman Spectroscope at RSIC, IIT, Mumbai

measured by polarizability In contrast to IR spectra, the symmetric modes tend to give the strongest Raman signals due to large changes in polarizability. The normal vibrational modes of a H_2O molecule is shown in *Figure* (*5.1*). In general a molecule containing 'n' atoms will have 3n-6 vibrational modes (3n-5 for a linear molecule such as OH).

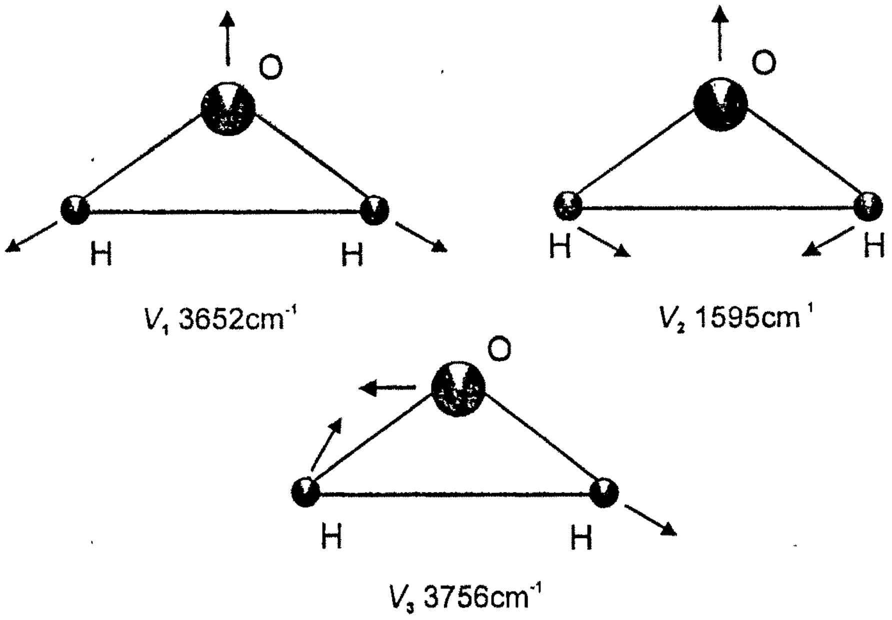


Figure 5.1 **: Representation of the three normal vibrational modes of a water molecule. V_1 - indicates symmetric stretching vibration, V_2 - indicates bending vibration and V_3 - indicates asymmetric vibration mode.**

In mineralogy, vibrational spectroscopy is commonly used to identify specific molecular groups such as hydroxyl, water molecule and oxyanions such as CO_3, SO_4 and NO_3. The OH stretching motion vibration for *free ions* occur at around 3735 cm^{-1}, but in mineral structure the exact frequency depends on the strength of hydrogen bonding to other surrounding oxygen ions The spectral region below 4000 cm^{-1} is referred to as the 'infrared' (IR) For H_2O molecule, the symmetric stretching mode(V_1) and asymmetric stretching (V_3) mode vibration occur in the 3800 - 3600 cm^{-1} region and its presence is the first indication that a mineral contains hydrogen. Whereas the bending mode (V_2) vibration occurs around 1600 cm^{-1} (Aines 1984; Aines and Rossman, 1984a). The presence or absence of bending mode related vibration (V_2) absorption provides the primary distinction between two major hydrous species, H_2O and OH^- (Aines and Rossman, 1984a). In liquid water, these absorptions are broad because of the continuum of hydrogen bonding interactions which occur in bulk water The existence of water is further confirmed by the combination modes at 5200 cm^{-1} (1900nm) which involve bending motions (Rossman 1988) The general positions of water and OH vibrational bands in minerals are shown in the *Table 5.1*.

Table 5.1 **: General positions of water and OH vibrational bands in minerals**

Wavenumber (cm^{-1})	Wavelength (μm)	Species and motions
1630	6.1	H_2O bend
3500	2 9	OH stretch
3400	2.8	OH stretch
4200	2.5	*m-OH motions
5200	1.9	H_2O combination mode (bend + stretch)
7100	1.4	1st OH overtone

*metal

EXPERIMENTAL DETAILS

Infrared absorption spectra were obtained at room temperature from doubly polished thin slices of Orissan beryls (colourless, blue, green and yellow) and beryls from Tamil Nadu (Karur - Kangayam), Kerala (melankode) and Bihar (Hazirbagh), orienting either parallel or normal to *c*-axis. FT-IR spectra in the frequency range 4000 - 2000 cm^{-1} for single crystal and 4000 - 400 cm^{-1} for powder samples were recorded using *NICOLET Magna IR 550 FT-IR spectrometer*. Spectral resolution was set at 4 cm^{-1}. Background effects due to atmospheric H_2O and CO_2 were subtracted. In case of slice cut parallel to *c*-axis, IR spectra were taken for both polarisation using a grid polarizer deposited on a substrate of KRS-5, enclosed in a stainless steel ring. Samples were prepared as compressed discs of powdered beryl and KBr (2 to 5 wt%) to minimise polarisation effects. Discs were prepared taking same amount of mechanically ground powder and compacted under 10^{10} Pa pressure. Raman spectroscopy were carried out using *Rammor HG2S, Jobin Yuon Argon laser.*

5. 2 FT-IR SPECTROSCOPY

5.2.1 EXPERIMENTAL RESULTS AND DISCUSSION

As explained earlier (section 3.1), the six cornered linked tetrahedral SiO_4 rings in the beryl structure lie one above the other along the C_6 axis in such a way to form intercommunicating channels of quite large dimension (*Figures 5.2a & b*) These channels do not have a uniform diameter, but instead consists of cavities with a diameter of ≈5Å separated by 'bottle necks' with a diameter of about 2 8Å. Although beryl is nominally anhydrous mineral, it is known from chemical studies that considerable amounts of water (upto 2 5 to 2.9

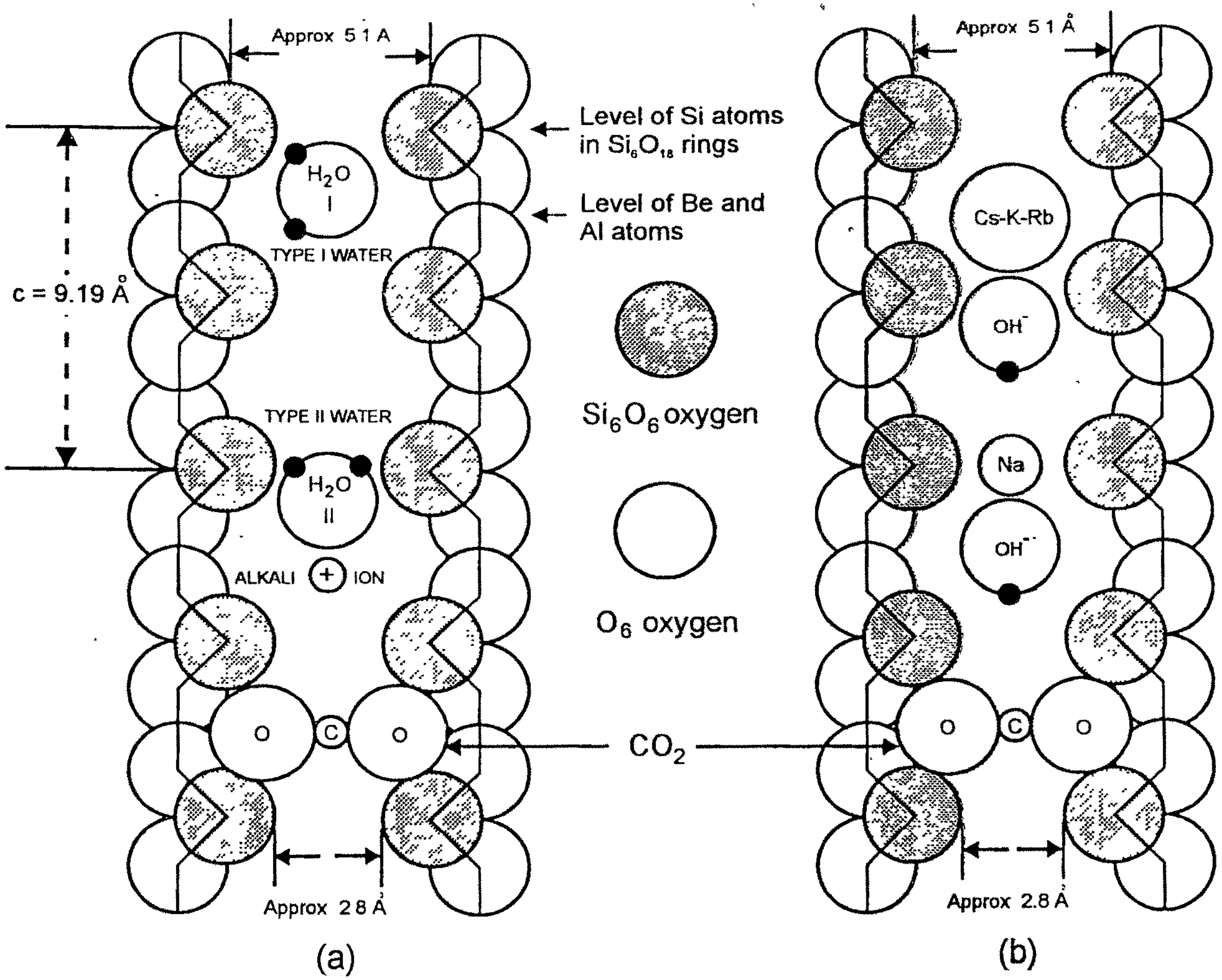


Figure 5.2 : Schematic drawing of the structure of beryl projected parallel to *c*-axis. a) indicating presence of two types of water molecules and b) indicating presence of OH^- molecules assciated with larger alkali ions (modified after Wood and Nassau, 1968).

by wt%· Feklichev, 1963; Bakakin and Belov, 1962)) may occur in these channels and still do not modify the crystal structure. Apart from water molecules, the other contents of the channels are CO_2, alkali cations e.g. Li, Na, K, Ca, Rb, Cs (Wood and Nassau, 1967; Cohen et al., 1977, Hawthorne and Cerny, 1977; Zimmerman, 1981; Aurisichhio et al., 1988, Manier - Glavinaz et al, 1989; and Mathew et al., 1997) and He and Ar (Danon and Kupl, 1958).

Wood and Nassau (1967) inferred that hydrogen speciation in beryl is in the form H_2O and it occupied two distinct sites; designated as *Type - I* and *Type - II* (*Figure 5.2a*). The *type - I* H_2O has its two - fold axis parallel to basal plane of beryl, i.e. normal to the plane of the rings and undergoes (hindered)rotation about an axis normal to the H-O-H plane, the rotation quantum being 170 cm^{-1} (Wood and Nassau, 1967). These water molecules apparently form weak ($\Delta \approx 80$ cm^{-1}) hydrogen bonds with oxygens of silicate rings. The *type - II* water molecule has its two-fold axis parallel to six-fold axis i.e. parallel to the plane of the rings and apparently forms weak hydrogen bonds with two oxygens on either side of the same ring. The concentration of *type - II* water molecules is related to the alkali content, as the disposition of *type - II* water is on account of rotation of H_2O molecule due to the dipole moment of adjacent alkali ion (Wood and Nassau, 1967; Manier - Galvinaz et al., 1989; Aines and Rossman, 1984b) (*Figure 5.2a*). This is supported by much higher rotational frequency ($V'_r = 314$ cm^{-1}· Wood and Nassau, 1967), implying stronger bonding between H_2O and host structure The author's polarisation studies on Indian beryls (from Orissa, Bihar, TN and Kerala) also confirm the existence of these two types of water molecules (*Figure 5.3*).

Figures 5.4a & b, represents polarised spectra of two synthetic beryls analysed by Wood and Nassau (1967). It can be seen in these figures that a flux grown synthetic crystal showing total absence of hydrous species *(Figure 5.4a)*, while, a hydrothermally grown beryl

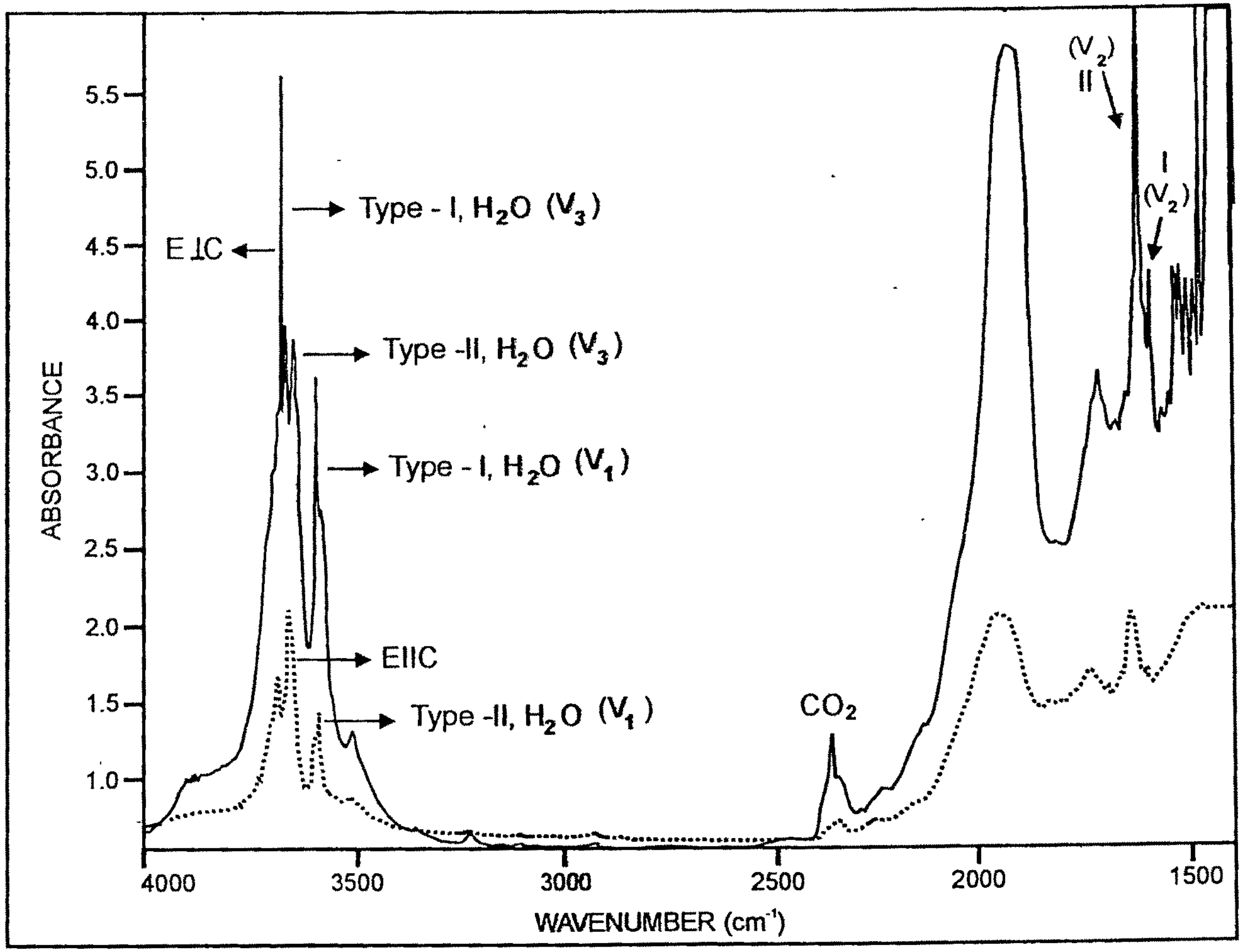


Figure 5.3 : Polarised FT - IR spectra of beryl **in two directions** (E‖c) and (E⊥ c) indicating presence of two types of water molecules. (V_2 indicate bending mode H_2O)

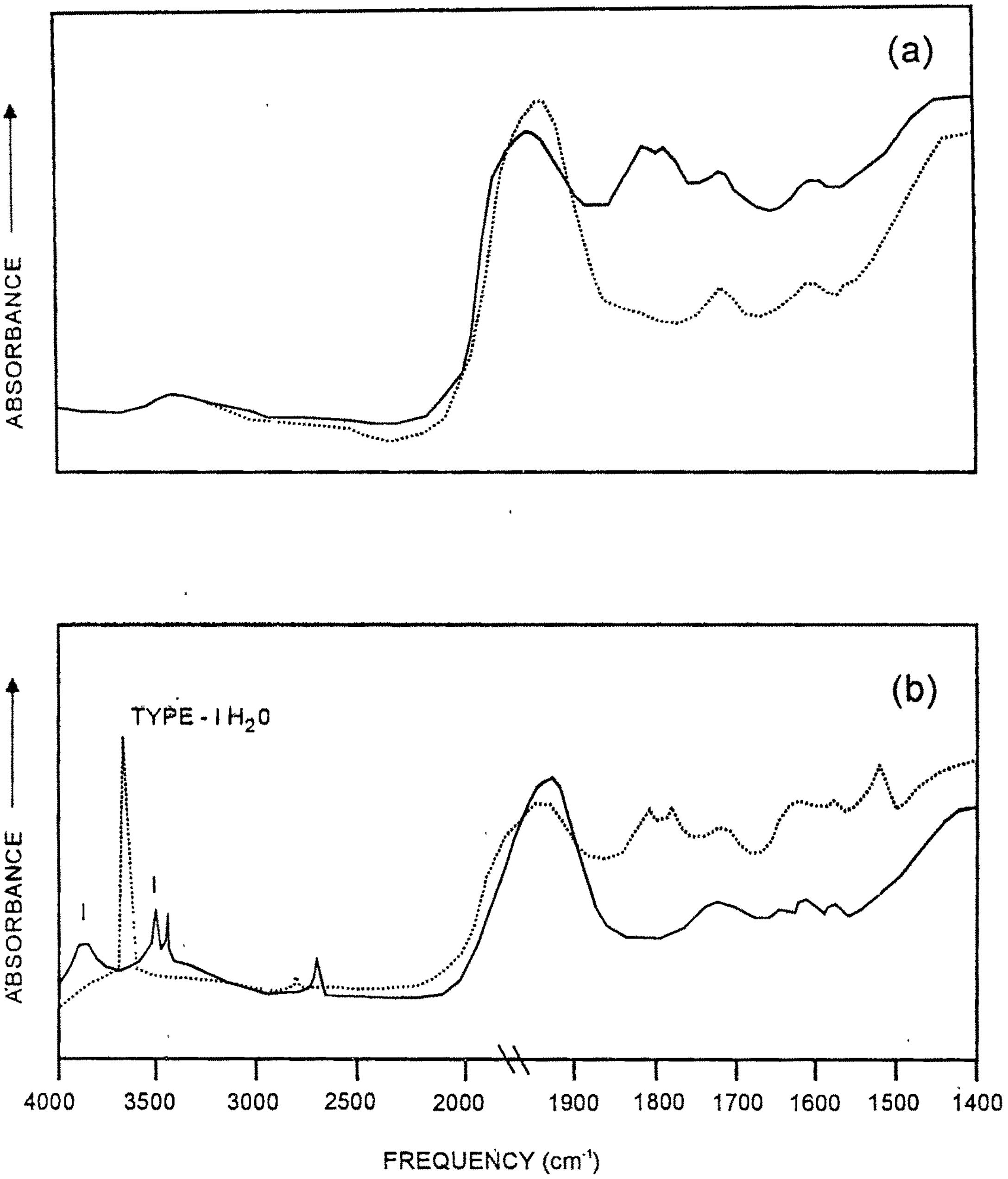


Figure 5.4 · Infrared Absorption Spectra of. (a) Flux grown beryl and (b) Hydrothermal beryl (Spectra of Wood and Nassau, 1967)

crystal in alkali free medium shows a number of peaks related to H_2O (Type -I) (*Figure 5.4b*). Thus it is clear that beryls grown in hydrous (hydrothermal) environment absorb considerable amount of water. *Figures 5.5 a to d,* represents unpolarised FT-IR spectrum of natural Orissan beryls and *Figures 5.6 a to c*, represent FT-IR spectrum of beryl crystals from Tamil Nadu and Kerala. The natural beryl crystals show a set of lines not present in the crystals grown hydrothermally in alkali free medium. Such lines in natural crystals are attributed to *type - II* H_2O molecules related to the presence of alkalis (Wood and Nassau, 1967) Manier - Glavinaz at al.(1989) observed that, on leaching alkalis in an hydrothermal medium using HCl acid solutions (600°C, 1.5kbar), there is increase in *type - I* H_2O intensity and decrease in *type - II* H_2O intensity with progressive leaching.

Infrared spectra were obtained; (i) in the 3600 cm^{-1} region where stretching modes of water vibrates, (ii) in the 1600 cm^{-1} where the bending mode occurs and (iii) in the 2300 cm^{-1} region where CO_2 shows absorption. Wood and Nassau (1967), assigned 3800 - 3400 cm^{-1} (OH stretching mode) frequency range absorption bands to two types of H_2O molecules in beryl IR spectra in the region of 4000 - 2000 cm^{-1} were collected from 1.0mm size doubly polished crystals of beryls, cut normal to *c* - axis.

Following observations were made on Orissan beryls :

a) *Goshenite* (colourless) (*Figure 5.5a*), the fundamental symmetric stretching motion (V_1) of type - I H_2O is observed at 3555 cm^{-1} and asymmetrical stretching motion (V_3) is observed at 3699 cm^{-1}. The type - II water molecule shows V_1-mode at 3606 cm^{-1} and V_3-mode at 3662 cm^{-1}

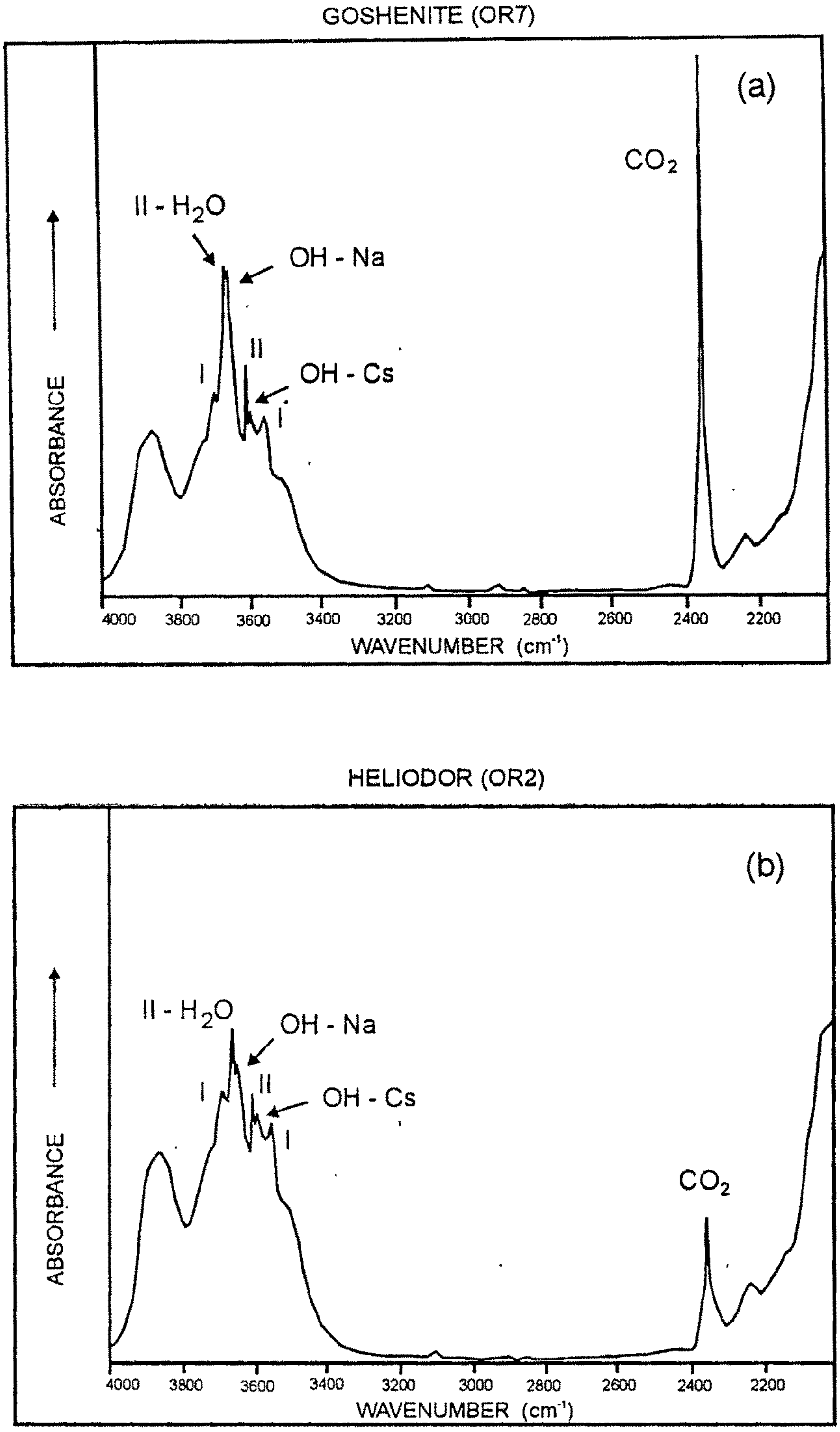


Figure 5.5 : Single crystal FT-IR spectra of (a) colourless and (b) yellow beryl depicting presence of hydrous species and CO_2 molecule in the channel site.

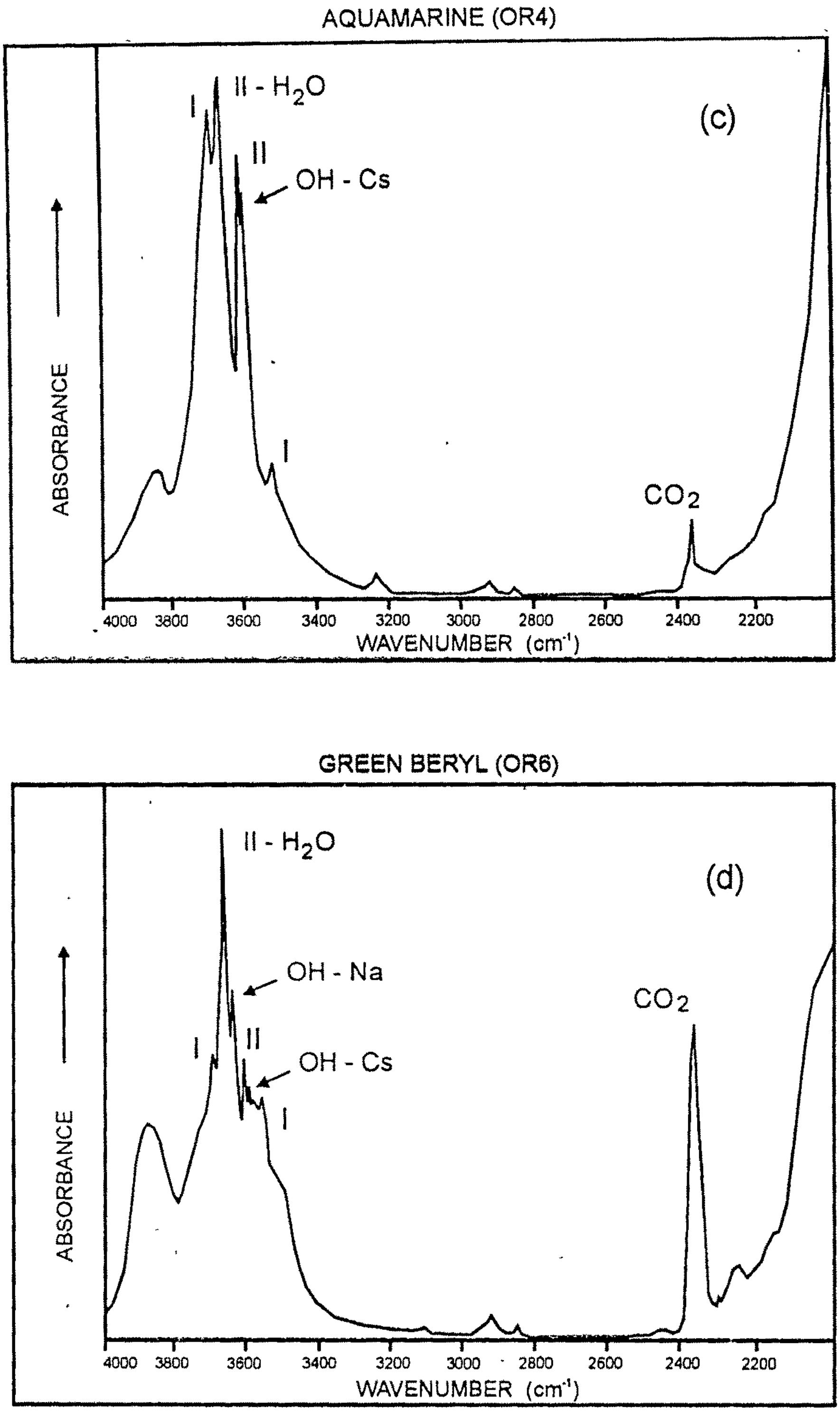
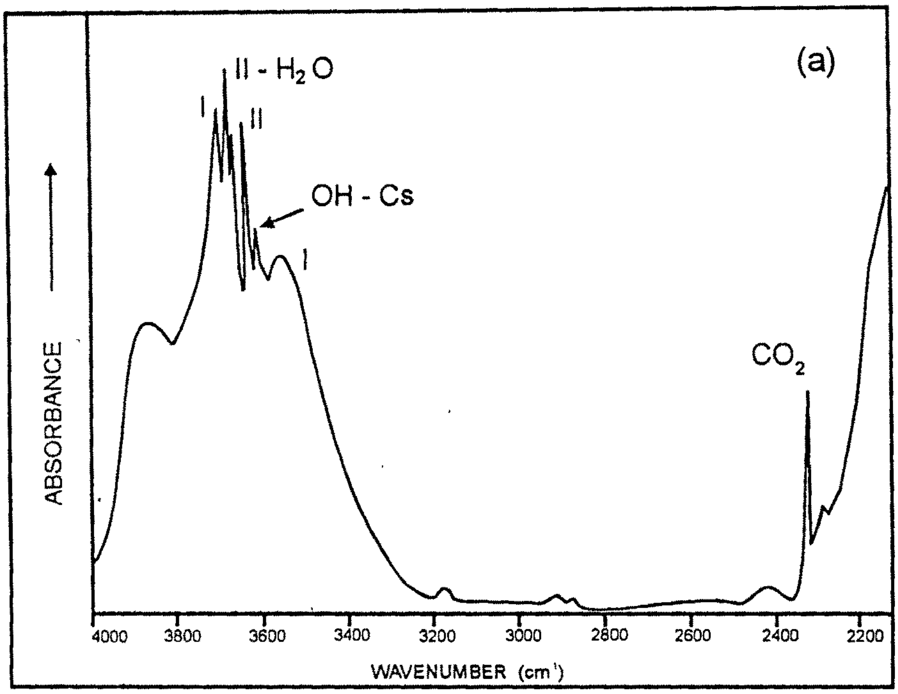


Figure 5.5 : Single crystal FT-IR spectra of (c) blue and (d) green beryl depicting presence of various hydrous species and CO_2 molecules in the channel site. Green beryl shows predominance of type-II H_2O molecule compared to other coloured beryls

KARUR AQUAMARINE (TN1)



KERALA GREEN BERYL (K1)

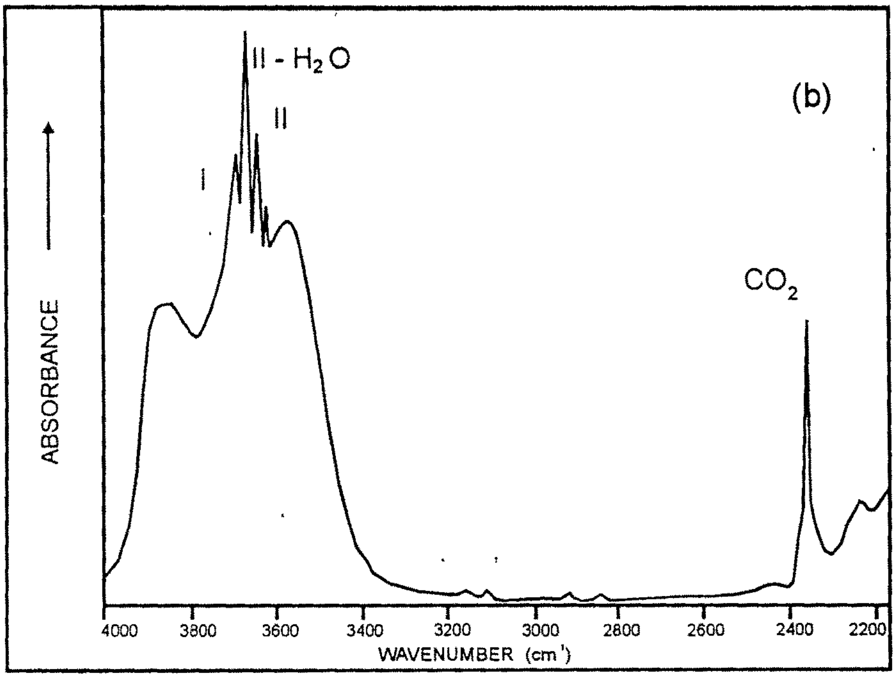


Figure 5.6 : Single crystal FT-IR spectra of (a)Tamil Nadu (Karur) and (b) Kerala green beryl indicating more of type-II water molecules in green beryl compared to blue beryl.

b) *Heliodor* (yellow) (*Figure 5.5b*) shows V_1-mode of type - I at 3560 cm^{-1} and V_3-mode at 3698 cm^{-1}. For type - II H_2O, V_1-mode is observed at 3607 cm^{-1} and V_3-mode at 3661 cm^{-1}.

c) *Aquamarine* (sky blue) (*Figure 5.5c*), the V_1-mode of type - I water molecules is observed at 3552 cm^{-1} while the V_3-mode is discerned at 3698 cm^{-1}. For type - II water, V_1-mode is seen at 3606 cm^{-1} and V_3-mode at 3660 cm^{-1}.

d) *Green beryl* (Fe bearing without significant Cr) (*Figure 5.5d*), shows type - I, V_1-mode at 3555 cm^{-1} and V_3-mode at 3699 cm^{-1} For type - II water molecule, V_1-mode is observed at 3606 cm^{-1} and V_3-mode at 3660 cm^{-1}. The IR absorbance observed above 3850 cm^{-1} bands commonly arises from linear combination and multiple overtones.

The IR spectral details of molecular species in beryls from Orissa are summarised in *Table 5.2*

Table 5.2 **: Vibrational bands of Molecular species from single crystal and KBr pellets experiments**

Molecular Species	Vibrational mode	Goshenite OR7	Aqua marine OR4	Heliodor OR2	Green beryl OR6	KBr pellets	Wood & Nasssau (1967)
H_2O Type - I	ν_1	3555	3552	3555	3555	3555	3555
	ν_2	1600	1596	1603	1602	1560	1595
	ν_3	3699	3690	3698	3699	3698	3694
H_2O Type - II	ν_1	3606	3606	3607	3606	3598	3592
	ν_2	1632	1633	1633	1633	1630	1628
	ν_3	3662	3660	3661	3660	3660	3655
OH - Na		3654	----	3653	3654	3654	----
OH - Cs		3595	3594	3595	3595	----	----
CO_2		2360	2360	2360	2360	2362	2360

As discussed earlier the bending mode vibration of H_2O is commonly observed in the region of 1400 - 1600 cm^{-1} (Wood and Nassau, 1967). However, in our study on single crystal (1 0mm thick) no such lines were observed, probably due to lack of transmittance in the region above 2000 cm^{-1} According to Aines and Rossman (1984b) absence of these higher vibration modes indicates the molecular species to be OH. This fact is significant if the bending mode vibrations expected around 1600 cm^{-1} is absent, due to the interference from silicate absorption when thick samples are used, as in the present study described above These lines were able to be observed when the samples were further thinned to 100 μm (*Figure 5.3*) As observed in *Figure 5.3*, the *type - II* vibration frequency is slightly greater, since the adjacent alkali ions rotate the water molecules in the channel. This tighter bonding with charged alkali ions results in higher rotational combination frequency of the *type - II* spectrum, which inturn causes higher deformation frequency and symmetric bending.

In all the four FT-IR spectra of Orissan beryls (colourless, blue, green and yellow), it is observed that the *type - II* H_2O is dominant. A similar observation has also been made by Panjikar (1995) on beryls from Orissa. This indicates that in these beryls there is increased substitutions in octahedral Al and tetrahedral Be sites, coupled with incorporation of alkalis into channels. Therefore, *type - II* H_2O is directly related to the incorporation of alkalis into channel (Wood and Nassau, 1967; Sherrif and Grundy, 1988; Manier-Glavinaz et al., 1989). This substitution results in *type - II* H_2O becoming dominant due to the dipole effect of H_2O Oxygens of these water molecules are attracted by alkali ions and turn their two fold axis parallel to the 6-fold axis of beryl crystal

The significant observations made by the author in the above four spectra of Orissan beryls are the presence of variable amount of *type - II* water in different coloured beryls, although collected from same locality (Badmal pegmatite province). As explained earlier, the *type - II* water molecule is dominant in all the four beryls, however, among the four coloured beryls, the IR spectrum shows predominance of *type - II* water molecules in green beryl (*Figure 5.5 d*) as compared to other coloured beryls. Whereas the IR spectrum (*Figure 5.5c*) of blue beryl shows predominance of *type - I* water molecule in comparison with other coloured beryls According to the above observation, among the four Orissan coloured beryls, the natural green beryl is richer in alkalis. A similar type of observation were also made by Blak *et al.* (1982) on beryls from Brazil. However, as shown in *Table 5.3*, the alkali content irrespective of colour is same in almost all crystals. This suggests that a major amount of alkalis in blue and in minor amount in colourless and yellow beryl are situated in interstitial sites between Be^{2+} and Al^{3+} or in substitutional sites, while in green beryls the alkalis are in the structural channel. *The effect of alkalis on colouration in beryls have been completely ruled out by many authors (Wood and Nassau, 1968; Samolovich et al., 1971; Goldman et al., 1977).*

In addition to the common *type - I* and *type - II* water molecules, a small amount of water molecules is also observed around 3120 cm^{-1} in both polarisation directions (*Figures 5.5a to d*), without any bending vibration counterpart. The above inference is in contrast to the observation of Charoy *et al* (1996) that such lines are oriented only parallel to the *c*-axis. The bands at 2820 and 2925 cm^{-1} are from surface absorbance, which on heating above 120 °C disappears

Table 5.3 : **Electron Probe chemical analysis of four coloured Orissan beryls**

Wt%	Green beryl (OR6)	Yellow beryl (OR2)	Blue beryl (OR4)	Colourless beryl (OR7)
SiO_2	64.240	67.038	63.187	65.544
Al_2O_3	17.442	18.091	17.134	16.686
FeO^t	0.744	0.543	0.519	0.537
MnO	0.012	0.006	---	0.037
MgO	0.081	0.001	0.099	0.083
CaO	0.014	0.013	0.032	0.025
K_2O	0.031	0.010	0.002	---
Na_2O	0 275	0.220	0.234	0.206
F	0.057	0.146	0.164	0.203
Cr_2O_3	0.031	---	0.040	0.047
TiO_2	---	0.003	---	---
V_2O_3	0 012	---	0.050	----
NiO	0.016	0 033	0.040	0.033
CoO	0 056	0.025	---	0.025
BeO	n d	n d	n.d	n d
Li,Cs,Rb	n.d	n d	n.d	n d
H_2O	n d	n d	n.d	n.d
Total	83.011	86.129	81 461	84.447

n d - not determined

All the Orissan samples studied show strong and sharp peak polarised only along $E\perp c$ around 2360 cm^{-1} (*Figures 5.5 a to d*). This peak corresponds to the asymmetric stretching mode of CO_2 vibration, since except V_1-mode, all other vibration modes (V_3 and V_2) are IR active, whereas V_1 is Raman active (Farmer, 1974, Macmillan and Hofmeister, 1988). Such bands of CO_2 are found to be absent in synthetic beryls (*Figures 5.4 a & b*). In all the IR spectra (*Figures 5.5 a to d*) the base of the peak is slightly enlarged and asymmetrical. Two bands at 2450 and 2250 cm^{-1} observed on either side of the CO_2 peak is attributed to the combination bands of both stretching and coupled hindered motion of CO_2 (Aines and Rossman, 1984). The asymmetric vibration of CO_2 at 2360 cm^{-1} is 20 cm^{-1} higher than the free CO_2 vibration (2340 cm^{-1}), implying strong interaction with the host crystal as it is tightly wedged in the structural channel (*Figure 5.2 a & b*). This close fitting is due to the length of CO_2 molecule which is equal to 4.96Å and the diameter of the cavity being 5.1Å.

Aurisichhio *et al* (1994) observed that the type - II band at 3663 cm^{-1} is a combination of two bands, when observed at 77 °K. One due to *type - II* H_2O at 3663 cm^{-1} and other at 3658 cm^{-1} due to OH - Na association. In the present FT-IR study by the author at room temperature, the 3658 cm^{-1} band is seen at 3654 cm^{-1} (*Figures 5.5 a to d*) as a separate low peak apart form 3663 cm^{-1} *type - II* H_2O. This indicates that the 3654 cm^{-1} band is not associated with H_2O, but a separate hydrous species, possibly $(OH)^-$ group. This is in accordance with the expectations of Aurisichhio *et al.* (1994) Several authors (Wood and Nassau, 1967; Wickershiem and Buchanan, 1959, 1965; Manier - Glavinaz et al., 1989; Schmetzer and Kiefert, 1990) had also advocated the possible presence of OH^- group in the beryl lattice However, its definite assignment in the beryl structure is still debatable. In accordance with Aurisichhio *et al.*(1994), the author favours its presence in the channel site, since $(OH)^-$ group can also be attracted to the alkali cation as the dipolar H_2O (*Figure 5.2b*).

The incorporation of Li, Na and Cs was first proposed by Belov (1958) which was later on accepted by several workers (Hawthorne and Cenry, 1977; Aurisichhio *et al.* 1988; Artiloi et al., 1994). Belov envisaged substitution of Li^+ for Be^{2+}, coupled with introduction of Na^+ and Cs^+ in the channel to compensate for the charge deficiency created. Hawthorne and Cerny, 1977 also agreed to above hypothesis, but he further proposed that part of the Li may also be present in the channel. Aurisichhio *et al.* (1994) suggested that, if both Na and Cs are present, the absorption band is close to 3595 - 3597 cm^{-1}. Thus the 3600 cm^{-1} band becomes a combination of three absorption frequencies; *type - II* H_2O, OH-Na, and OH-Cs. In the present study, although the Cs content (*Table 5.3*) is not analysed, in the IR spectra a low weak absorbance at 3595 cm^{-1} (*Figures 5.5a to d*) is seen close to the 3606 cm^{-1} (V_1, *type - II* band) This peak, the author presumes, is of OH - Cs as suggested by Aurisichhio *et al.* (1994).

As shown in *Figure 5.7a & b*, the powder FT-IR spectra of yellow and colourless beryl respectively indicate a dominant *type - I* (V_3-mode) water molecule as compared to *type - II* (V_3-mode) when observed in single crystal spectra (*Figure 5.5a & b*). The above behaviour of water molecule is also observed in other coloured beryls. An increase in V_3 *type - I* H_2O intensity in powder spectra indicates an increase in proportion of *type - I* water molecule at the expense of V_3 *type - II* water molecule The above observation discerns that, on crushing there is probable release or movement of alkali ions from their original position; and thereby causing the *type - II* H_2O to rotate back to *type - I* H_2O. This, however, is a tentative explanation by the author and a detailed work is warranted to explain the above phenomenon

As explained before transition elements like Fe^{3+} and Fe^{2+}, alkali cations and rare gases like He and Ar (Danon and Kupl, 1958) occupy channel site as a result of interstitial solid solution and further existence of two important kinds of substitution in beryl gives rise to two distinct substitutional solid solution i.e. octahedral and tetrahedral substitutions (Auroschhio et al ,1988) '*Octahedral beryl*' in which dominant substitution is Fe^{2+} and Mg^{2+} for Al^{3+} on octahedral site and '*tetrahedral beryl*' in which dominant substitution is Li^+ for Be^{2+} in the distorted tetrahedral site. Such substitutions modify the cell parameters because of the difference on ionic radii of Al^{3+}/Be^{2+} and the replacing ions. Based on c/a ratio, Auroschhio et al (1988) classified beryls into three groups , 1) *octahedral beryl*, c/a value from 0.994 to 0 996Å, ii) *tetrahedral beryl*, c/a value from 0.999 to 1.003Å and iii) *normal beryl*, c/a value

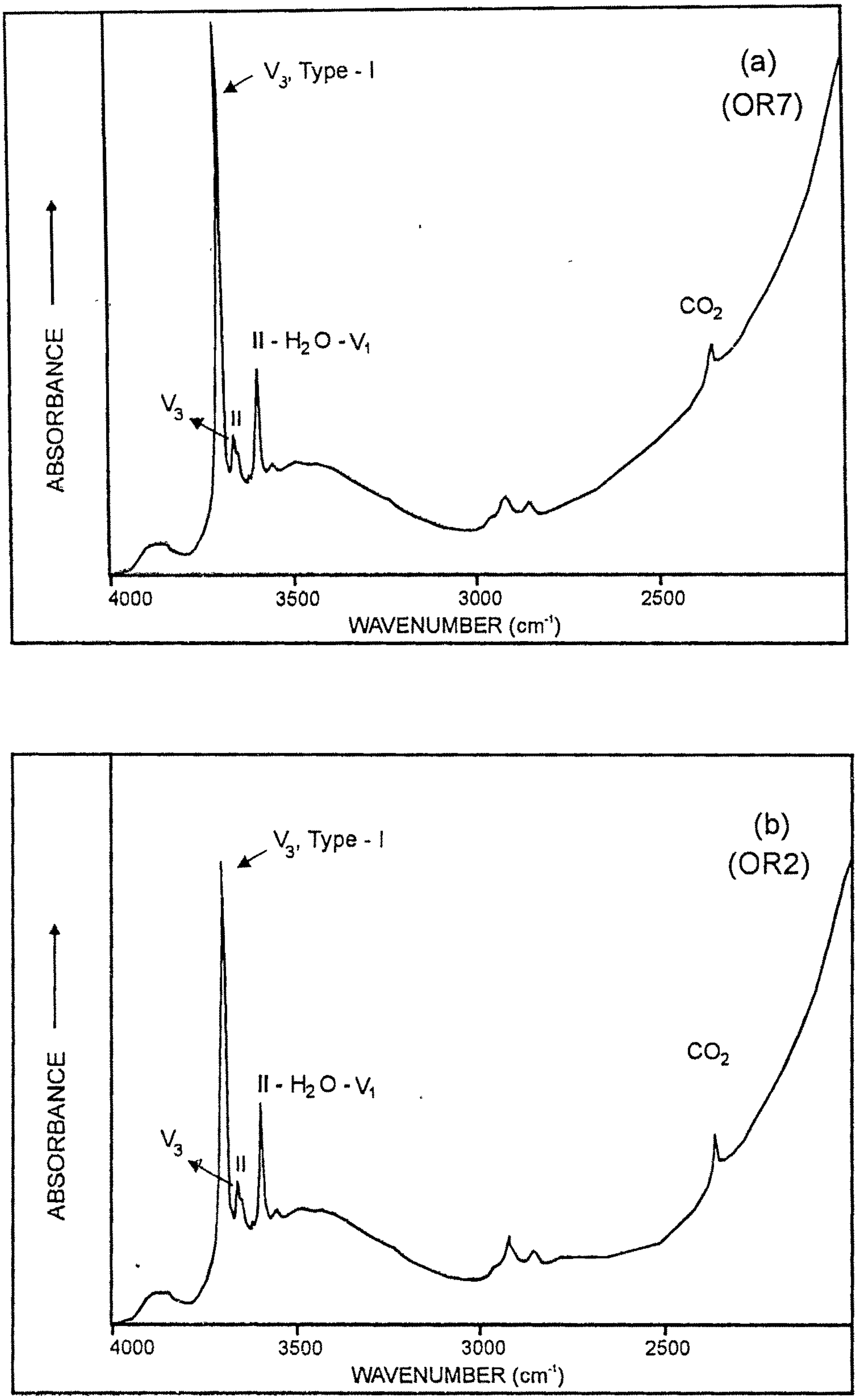


Figure 5 7 . Powder FT-IR spectra of (a) colourless and (b) yellow beryl indicating increase in intensity of assymetrical mode (V_3)of type-I water molecule on powdering from 0 997 to 0.998Å Normal beryl includes those where substitution occurs in both octahedral and tetrahedral sites. With this aspect in mind the author has studied cell parameters of various beryls using both single and powder X-ray diffraction analysis.

Table 5.4 : **Cell parameters of the beryls studied**

Colour/ Sample No.	Cell Parameters (Å) c	a	c/a	Volume (Å)^3	Type
*Colourless (OR7)	9.204	9.199	0.9994	674.87	Tetrahedral
*Green (OR6)	9.176	9.208	0.9964	673.77	Octahedral
*yellow (OR2)	9.176	9.227	0.9950	676.55	Octahedral
*Blue (OR4)	9.207	9.238	0.9944	680.46	Octahedral
TN blue (TN1)	9 209	9 239	0.9966	680.53	Oct-Normal
Kerala green (K1)	9.175	9.227	0.9943	676 48	Octahedral
Bihar Blue-green	9.172	9.192	0.9978	671 14	Normal
Siberian yellow (SB1)	9.206	9.227	0.9966	678.77	Oct-Normal
Brazilian colourless (BR1)	9.207	9.227	0 9978	678.84	Normal

*Orissan sample

5.2.2 STRUCTURAL VIBRATION (1200 - 400 cm^{-1})

Structural vibrations in the region of 1200 - 400 cm^{-1}, were studied using powdered samples of beryl (*Figure 5.8*). Octahedral and tetrahedral replacements have been reflected adequately on the IR spectra. By and large this region can be divided into three zones; (i)

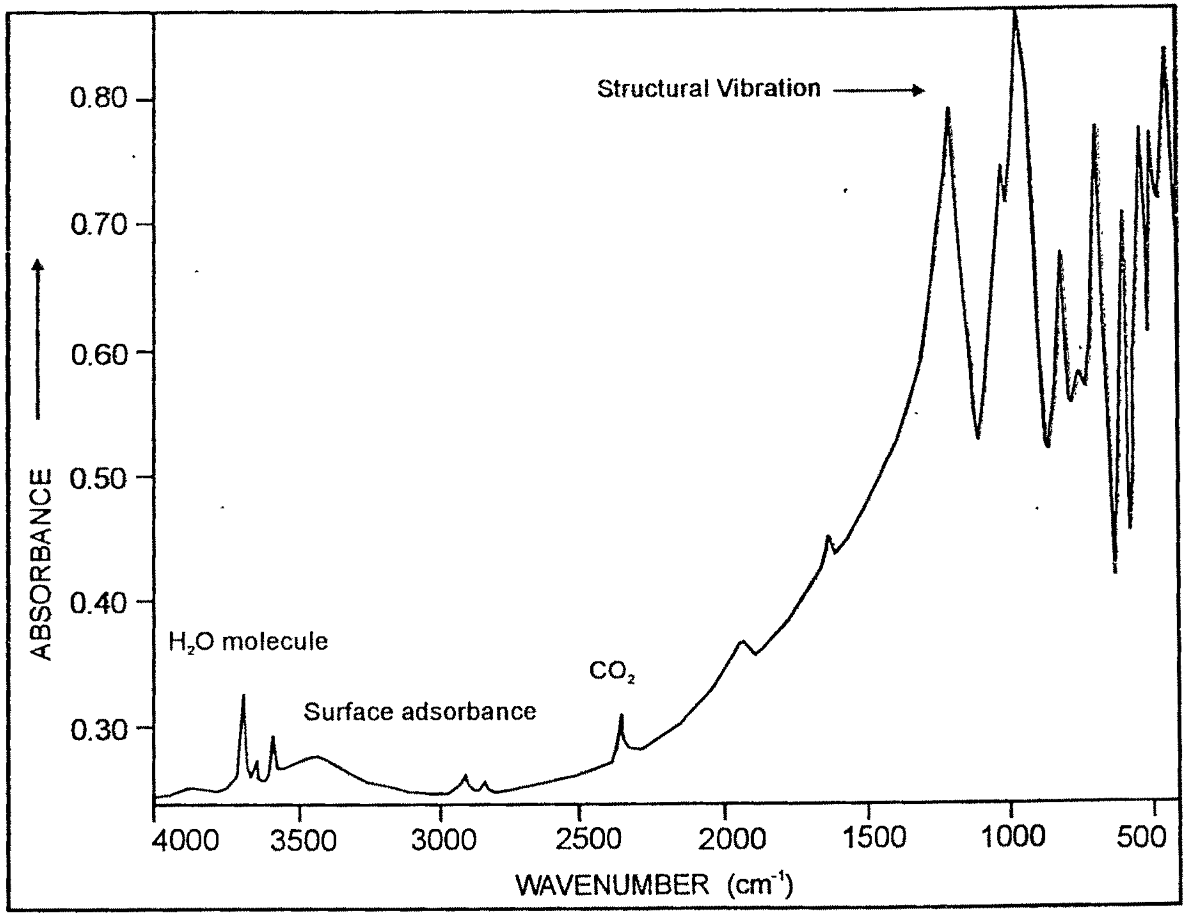


Figure 5.8 : Powder FT-IR spectra of beryl in the range 4000 - 400cm^{-1}

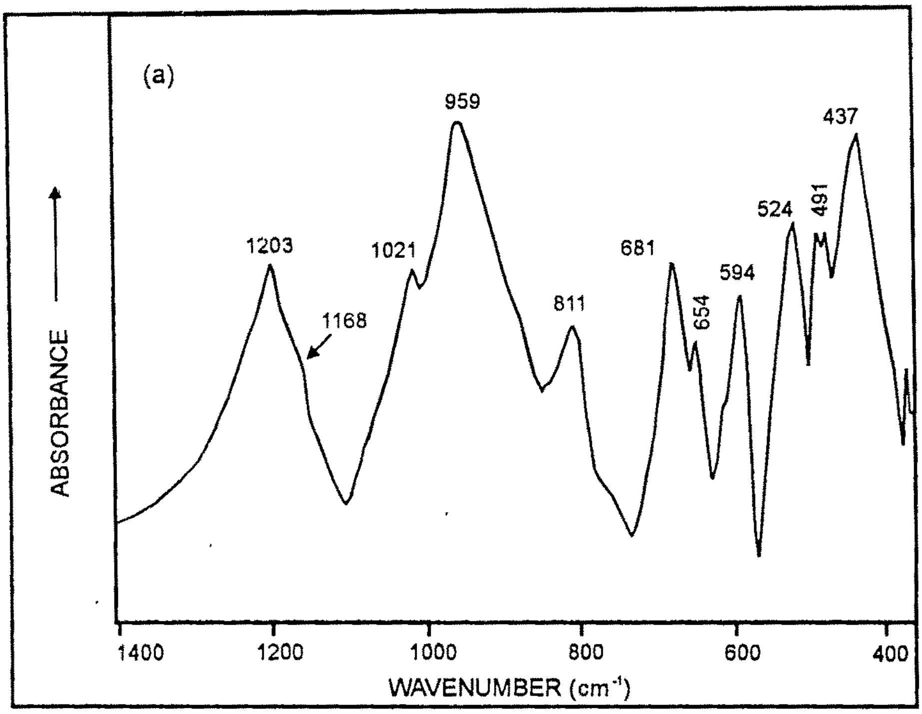
1200 - 900 cm^{-1} belonging to the Si-O-Si; (ii) 850 - 650 cm^{-1} to Be-O and (iii) 600 - 400 cm^{-1} to Al-O and Si-O

Zone(i)

The spectral region between 1200 - 900 cm^{-1} corresponds to the internal Si-O vibrations (Gervais et al., 1973). Several authors (Bakakin et al., 1970; Adams and Gardner, 1974; Hofmeister, 1988) have assigned 1200 cm^{-1} to Si-O-Si ring vibration. Later Aurisichhio *et al* (1994) confirmed this by correlating with c/a ratio, bond lengths and site occupancies. The IR spectra of all the four Orissan beryls (*Figure. 5.9a to 5.12a*) show the 1201 cm^{-1} vibration Absence of peaks at 1170 cm^{-1} and 1050 cm^{-1} and presence of band at 1200 cm^{-1} indicates that these beryls are alkali poor (Plyusnina, 1964; Manier-Glavinaz et al.,1989). Aurisichhio *et al.*(1994) attributed such vibrational bands to '*normal type*' beryl.

In the 1200 - 900 cm^{-1} region, the 1201 cm^{-1} band of normal beryl shifts to 1195 - 1150 cm^{-1} region in both tetrahedral and octahedral beryls as a result of broadening of the 1133 cm^{-1} band (Bakakin et al., 1970). With an increase in tetrahedral replacement, the relatively weak 1090 cm^{-1} band in normal beryls increase in intensity and shifts to 1060 - 1070 cm^{-1} and at the same time, the intensity of 1020 cm^{-1} band decreases (Bakakin et al., 1970; Aurisichhio et al., 1994) Increased substitution for Al and Be, coupled with the incorporation of alkalis may result in shift towards higher frequency and broadening of this band due to slight changes in the silicon tetrahedron geometry due to the replacement of Be by Li (Manier - Glavinaz et al., 1989)

COLOURLESS BERYL (OR7)



FSD TRACE

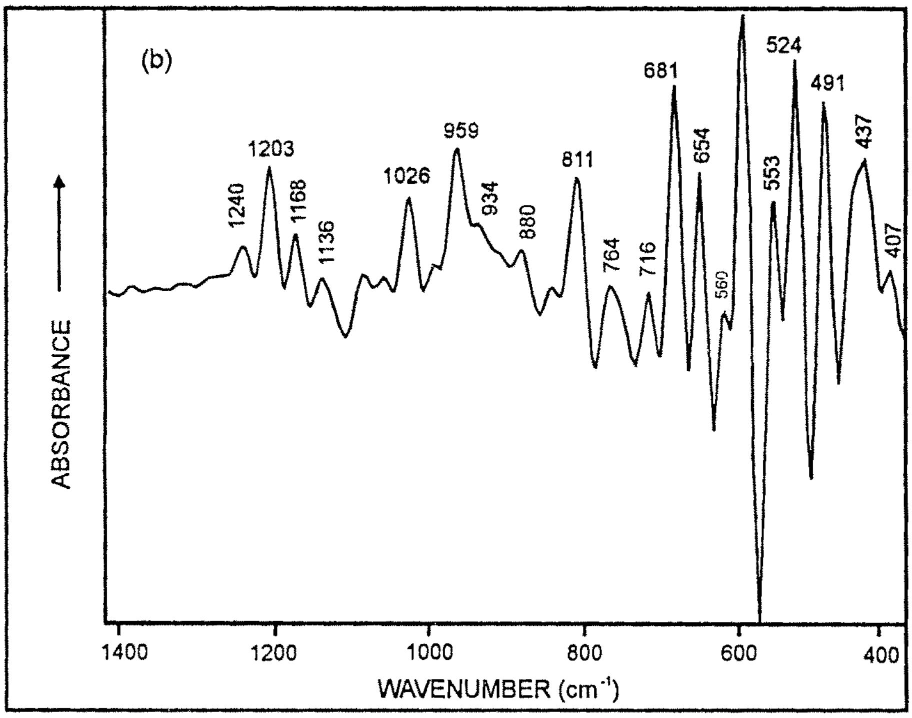
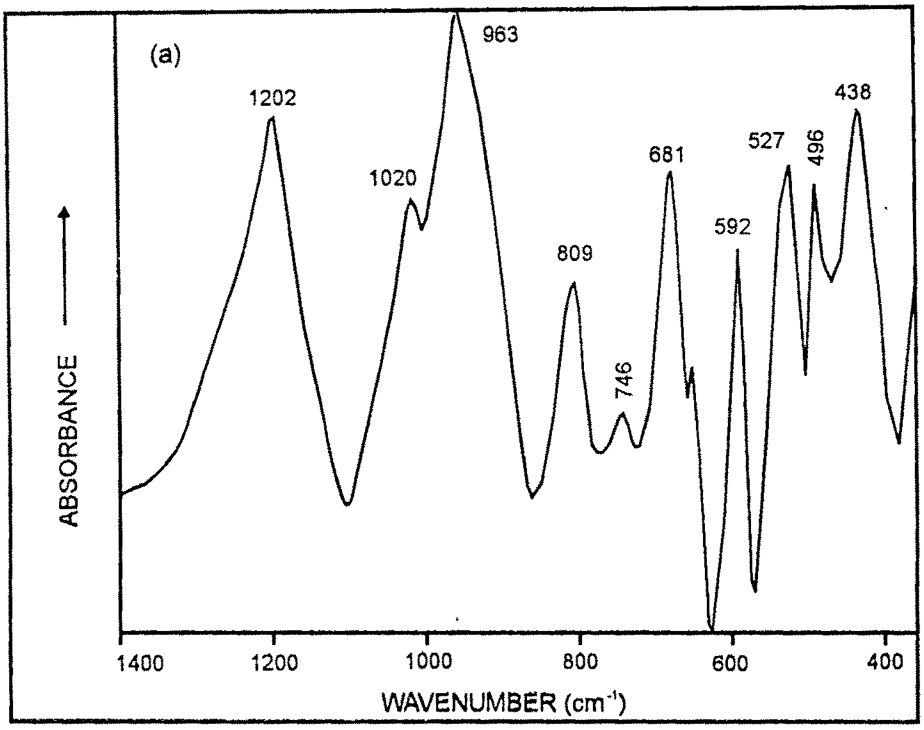


Figure 5 9 FT-IR spectra of colourless beryl a) normal FT-IR spectra and b) FSD trace of it.

YELLOW BERYL (OR2)



FSD TRACE

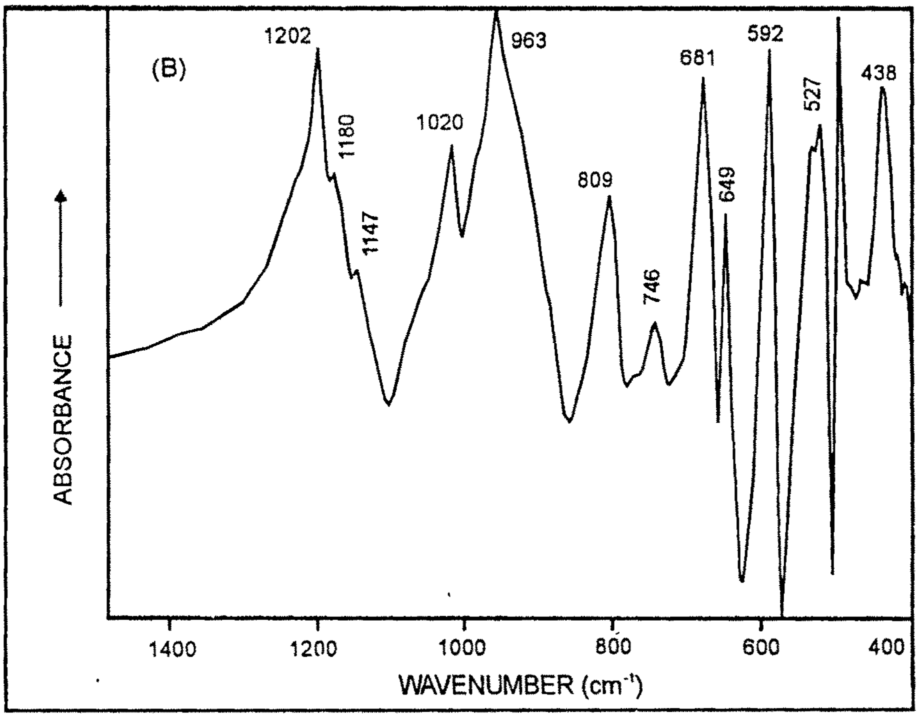
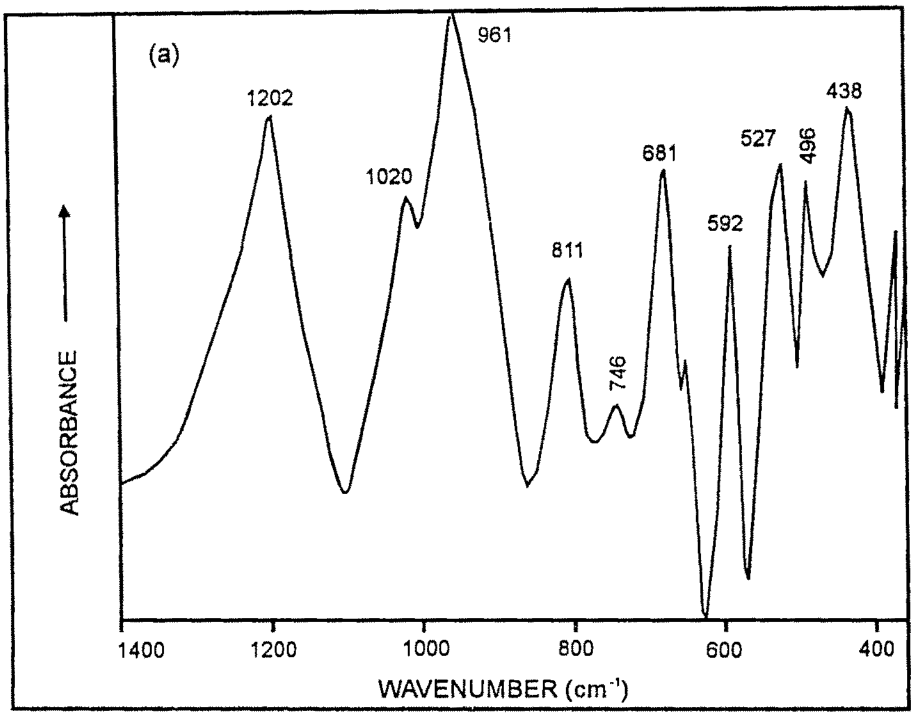


Figure 5.10 · FT-IR spectra of yellow beryl (heliodor). a) normal FT-IR spectra and b) FSD trace of it.

BLUE BERYL (OR4)



FSD TRACE

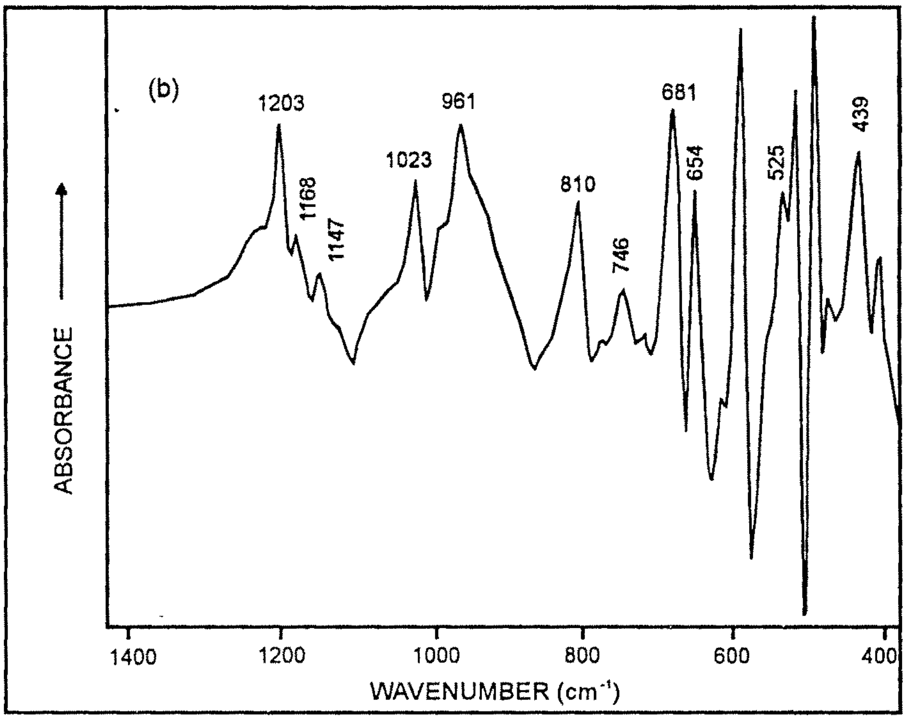


Figure 5.11 : FT-IR spectra of blue beryls. a) normal FT-IR spectra and b) FSD trace of blue beryl.

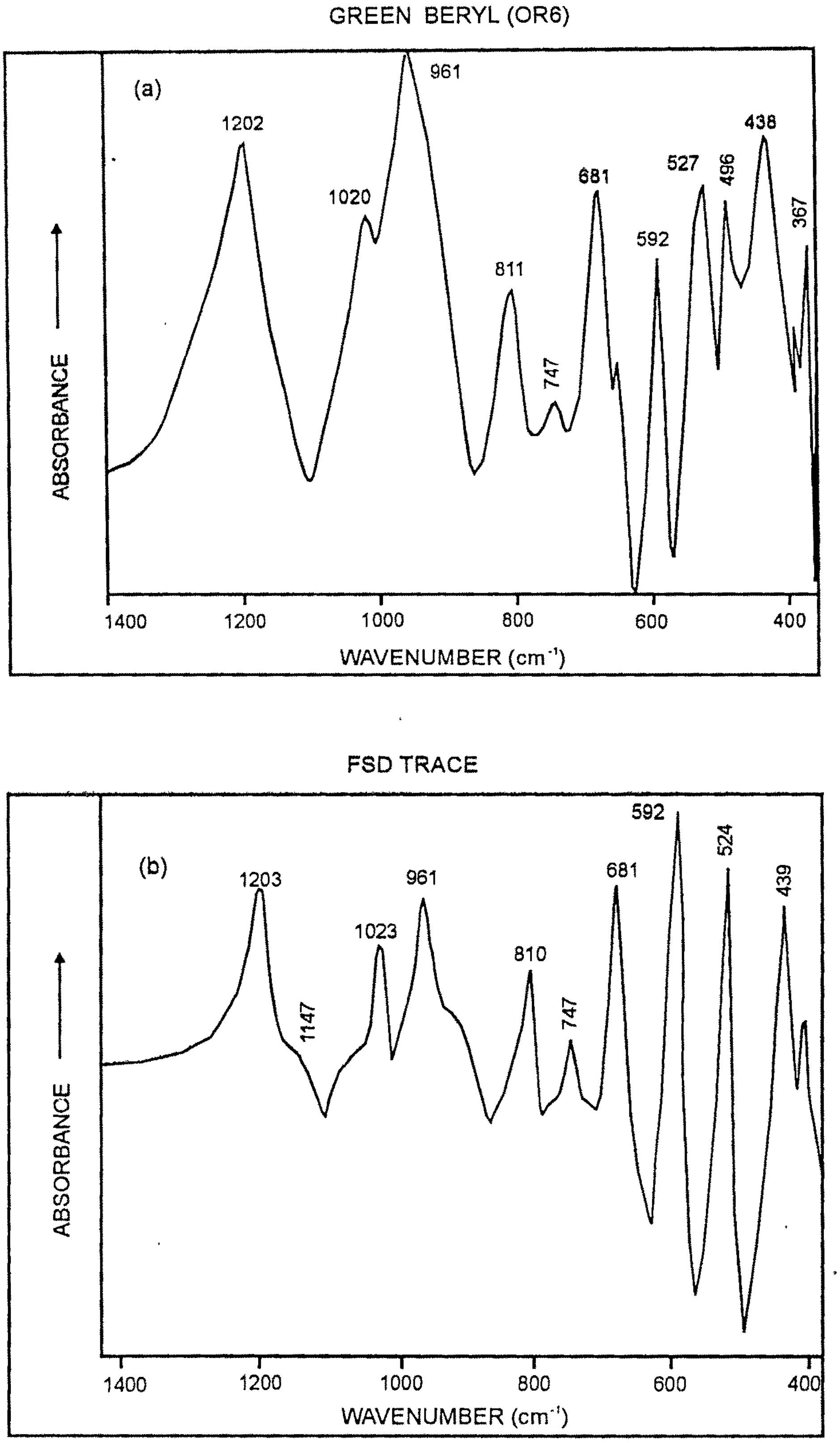


Figure 5.12 : FT-IR spectra of green beryl. a) normal FT-IR spectra
b) FSD trace of green beryl

As shown in *Figures 5.9a to 5.12a*, a low absorbance peak is seen at 1026 cm^{-1} and also small shoulder at 1070 cm^{-1}. These peaks indicate that the Orissan beryls are octahderally (1026 cm^{-1}) as well as partially tetrahedrally (1070 cm^{-1}) substituted. According to Aurisichhio et al (1994), 1070 cm^{-1} band appears when the extent of substitution in tetrahedral site attains 0 19 atoms per formula According to Plyusnina (1964), even a small amount of lithium in beryl introduces changes into the structure of the major band. He observed growth of bands at different regions with increasing proportion of LiO_2:

(i) 1136 cm^{-1} band appears when the Li_20 content is 0.06%;

(ii) at 0 25%, the 1060 - 1070 cm^{-1} band begins to show and

(iii) additional peak in the 800 cm^{-1} band becomes sharp when the Li_20 content is 0.428%.

Plyusnina (1964) considered the above bands to be associated with variation in the length of the external bonds, Si-O-Al and Si-O-Be respectively. Based on Plyusnina (1964) observation it can be interpreted that the Orissan beryls to be more of octahedral type with minor tetrahedral substitutions

As shown in *Figures 5.9b - 5.12b*, on carrying out Fourier Self Deconvolution (FSD), the 1070 cm^{-1} band which is seen as shoulders in a normal FT-IR spectrum (*Figures 5.9a to 5.12a*) is clearly resolved as small absorbance peak. Similarly FSD spectrum indicates that the 1021, 960 and 745 cm^{-1} bands are not single bands, but denote combination of bands.

Zone (ii)

The absorption band at 809 - 811 cm^{-1} is attributed to Be-O vibration (Hofmeister, 1988, Plyusnina, 1964) The 745 - 747 and 681 cm^{-1} bands are also due to Be-O (Adams and Gardner, 1974, Hofmeister, 1988) In the normal FT-IR spectra of yellow, blue and green

Orissan beryls (*Figures 5.10a to 5.12a*) show clear absorption band at 747 cm^{-1}, however, in colourless beryls (*Figure 5.9a*) it is observed as shoulder. This, the author presume is due to probable substitution of Be by Li, since as the alkali content increases, the beryllium content decreases (Bakakin et al., 1970). The spectral region from 1200 - 600 cm^{-1} contains bands due to vibration of SiO_4 and BeO_4 tetrahedra. The presence of Na and Ca in beryl does not cause any change in the above region, since Na and Ca are larger ions with ionic radii 0.98 and 1 04Å respectively Therefore, they occupy sites in channels. The larger ions such as K and Cs (1 33 and 1.65Å) stretch the structure in the direction parallel to the rings and compress the other structural elements, particularly BeO_4 tetrahedra (Plyusnina, 1964). Thus it is evident that changes in the 1200 - 600 cm^{-1} frequency indicate some chemical changes in the beryl samples under study

According to Aurisichhio *et al.* (1994), presence of shoulders at 700 and 560 cm^{-1} bands are evidences of tetrahedrally substituted beryl. In the present study as shown in *Figures 5.9a to 5.12a*, these two bands were not discerned in a normal FT-IR spectrum. However, on carrying out Fourier Self Deconvolution (FSD; Kauppinen et al., 1981) (*Figures 5.9b to 5.12b*), both the above bands are seen as shoulders (*Figures 5.9b to 5.11b*). An increase in absorbance of IR intensity is possible when there is a progressive entry of cations into tetrahedral site, but not into octahedral site (Aurisichhio et al., 1994). In the samples under study except for colourless beryl, other beryls (yellow and blue) reveal only small shoulders, whereas colourless sample shows prominent absorbance This elucidates that in yellow and blue beryls form Orissa there is partial substitution of actions in tetrahedral site, while in colourless there is greater substitution and absence of tetrahedral substitutions in green beryls As shown in *Figure 5.13a*, the FSD trace of colourless beryl (goshenite) indicates 700 cm^{-1} as shoulder shifted towards 714 cm^{-1}. FSD trace of other coloured beryls (*Figures 5.13b* & c) indicate shoulders close to 700 cm^{-1}

Zone (iii)

Two absorption bands at 524 - 527 and 491 - 496 cm^{-1} seen in spectra (*Figures 5.9a to 5.12a*) are assigned to Al-O vibration. The slight shift of the present bands from Aurisichhio *et al.*(1994) assignment (535 and 500 cm^{-1}) indicates the degree of distortion of the polyhedron. This occurs when larger bivalent ions like Fe^{2+} or Mg^{2+} substitutes for Al^{3+} ion (Plyusnina, 1964; Mathew et al., 1998b). This substitution results in an increase of volume of the polyhedron to accommodate the ions with larger radii. Thus it leads to elongation of Me-O (metal-oxygen) distances, resulting in distortion of the polyhedron. On further detailed FSD analysis between 600 - 500 cm^{-1}, the 521 cm^{-1} band observed in normal FT-IR spectra of colourless (*goshenite*) beryl (*Figure 5.9a*) is seen to have resolved into 555 and 524 cm^{-1} bands (*Figure 5.14a*). The 555 cm^{-1} band is closer 560 cm^{-1} band observed by Aurisichhio *et al.*(1994), which they assigned to substitutional tetrahedral site. In the blue beryl (*aquamarine*) FSD spectrum (*Figure 5.14b*), it is observed that 521 cm^{-1} band is a combination of three absorption bands at 558, 535 and 521 cm^{-1} bands. Yellow beryl (*heliodor*) FSD spectrum (*Figure 5.14c*), is observed to be a combination of 557, 535 and 522 cm^{-1} As shown in *Figure 5.14d*, the FSD spectrum of green beryl indicates no resolution of 521 cm^{-1} band.

From the above observation of FSD spectra between range (600 - 500 cm^{-1}) it can be deduced that in colourless beryl, there is a strong absorption close to 560 cm^{-1}, whereas in yellow and blue, it is observed as only shoulders and green beryls do not discern any such

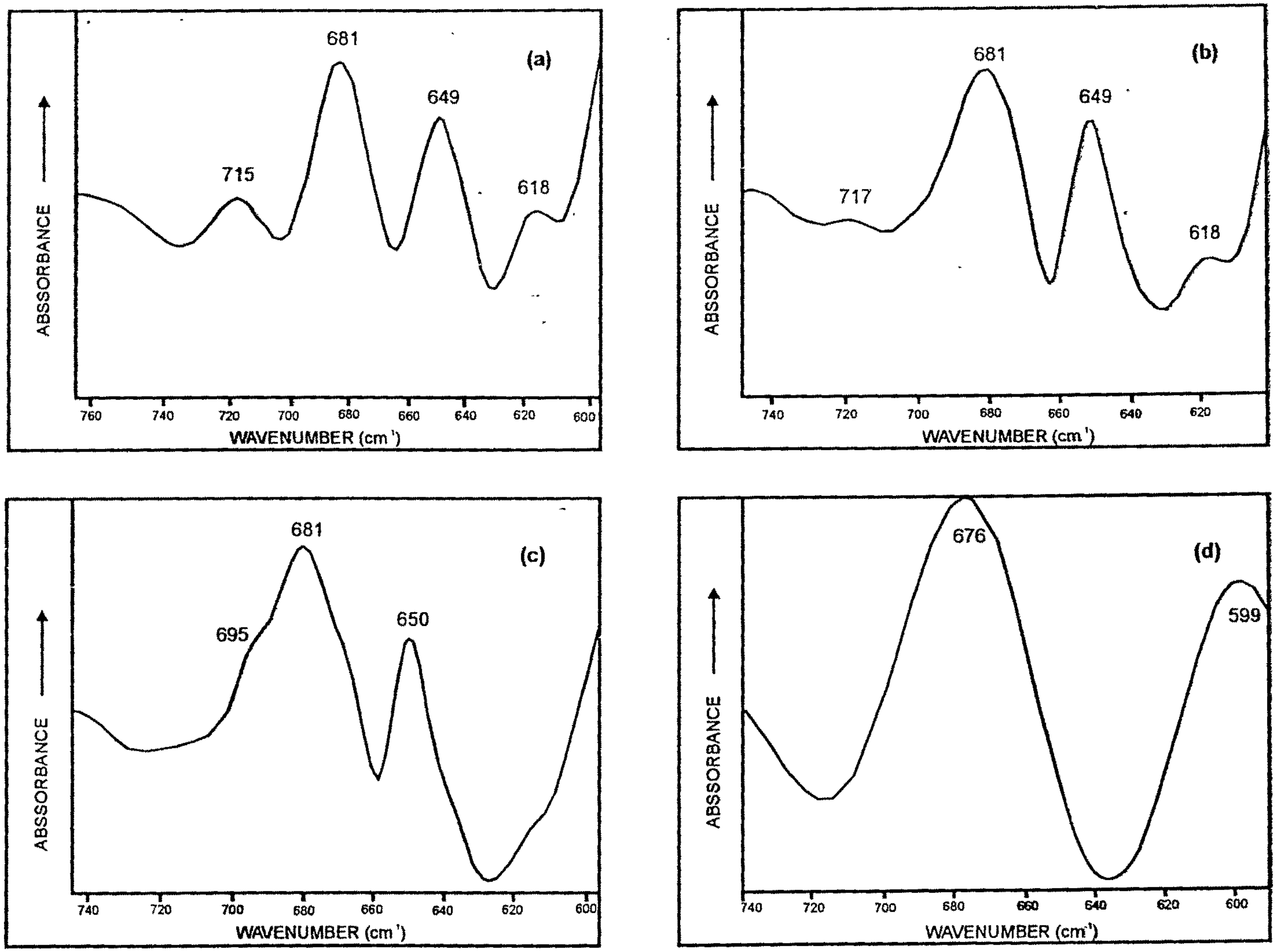


Figure 5.13 : Fourier self deconvolution spectra in the range (760 -600 cm^{-1}) of a) goshenite, b)aquamarine, c) heliodor and d) green beryl

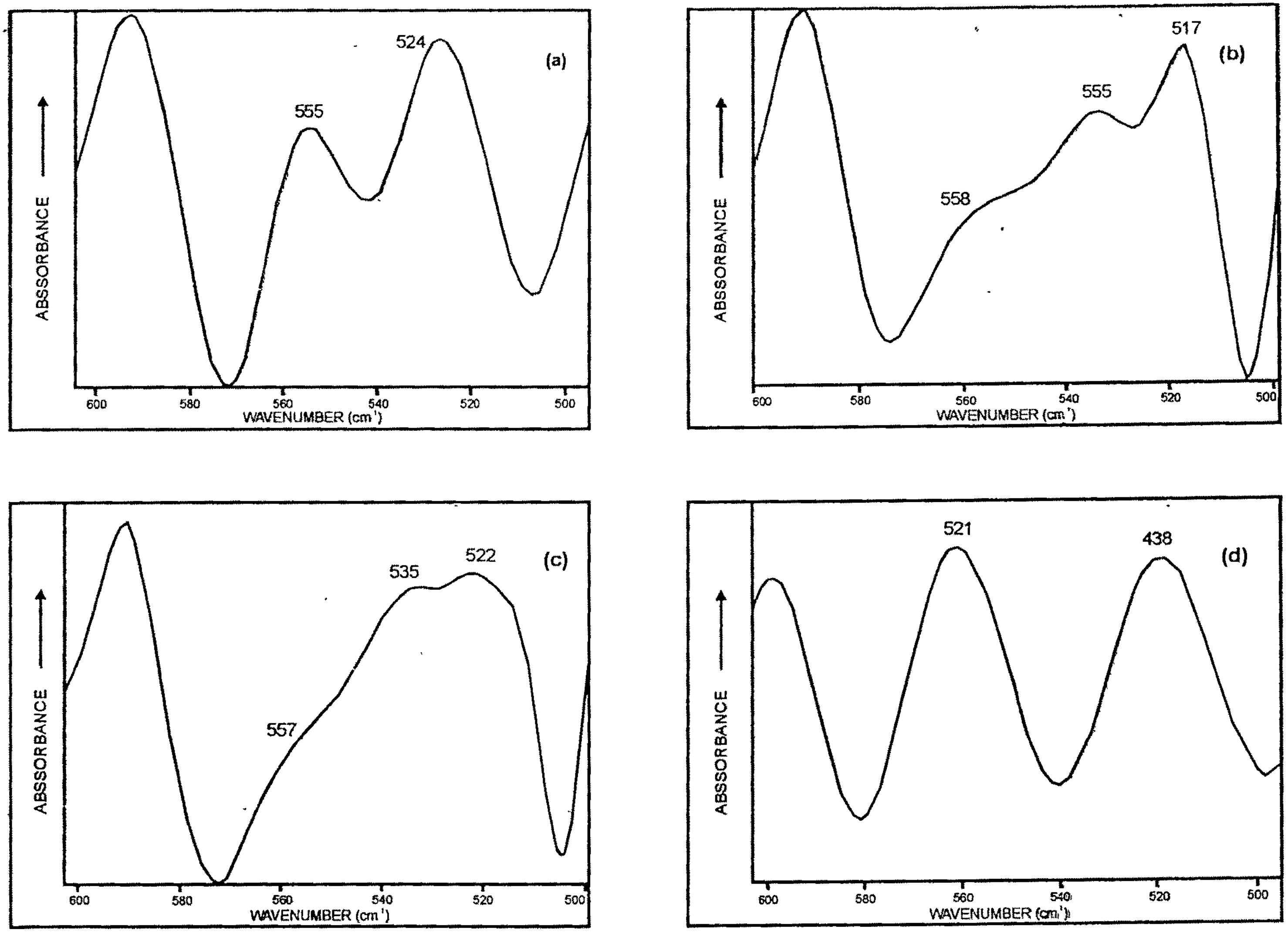


Figure 5.14 : Fourier self deconvolution spectra in the range (600 - 500 cm^{-1}) of a) goshenite, b) aquamarine, c) heliodor and d) green beryl

feature This clearly corroborates that (i) *in colourless beryl there is major tetrahedral substitutions;* (ii) *there is a minor amount of tetrahedral substitution in yellow and blue* and (iii) *in green there is only pure octahedral substitution.* This is well supported by the single crystal and powder X-rd result (*Table 5.4*).

For comparison, powder FT-IR spectra of beryls from various other Indian localities like TN, Kerala and Bihar from India and samples of Siberia and Brazil were also studied. The TN, Kerala and Bihar beryls discern weak shoulders at 700 and 560 cm^{-1}, indicating partial tetrahedral and more of octahedral substitution. Among the Siberian and Brazilian beryls, the Siberian yellow beryl reveals partial tetrahedral substitution indicated by bands at 712 and 556 cm^{-1}, while Brazilian beryl shows a purely octahedral type of substitutions.

5.2.3 THERMAL EXPERIMENTS

Generally studies of minerals and their properties are carried out at room temperature (25 °C) However, such a study would only provide limited insight into the properties of minerals and more exciting informations can be obtained at elevated temperatures. It is known that trace water in silicates can induce considerable effect on the properties of minerals (e g Aines and Rossman, 1984b, 1985; Hobbs, 1981; Karanth et al., 1998). Since hydrous components in minerals are reactive and mobile, the high temperature speciation and their position in the structure may not be the same as at room temperature. Aines and Rossman (1984b) have studied high temperature behaviour of water and CO_2 in minerals like corderite and beryl. In the present thesis, the author has attempted to study the behaviour H_2O behaviour at elevated temperatures of Indian beryls. Unlike in Aines and Rossman (1984b) who heated the sample insitu in a high temperature infrared spectrometer, the author due to lack of adequate facility has heated the sample outside in an electric furnace and then cooled to room temperature to observe the spectra.

Figures 5.15 a & b, depicts Aines and Rossman (1984b) high temperature studies on beryl crystals They indicated that above 300 °C, the intensity of the original peak is diminished and a new component in the form of a broad band of equal intensity in both polarisation is observed around 3650 cm^{-1}. With an increase in temperature the intensity of this broad band also increases at the expense of *type - I* and *type - II* water molecules. According to these authors two types of water begins to partition represented by broad band at elevated temperatures.

In the present study the author observed that, on heating beryl crystals (100μm) from room temperature to 800 °C did not reveal any decrease in intensity of H_2O band, however, indicates increase in intensity with slight broadening of the spectra, attributed to increase in range of O-H. .O distances in the environment of H_2O molecules due to thermal motion (*Figure 5.16*). This indicates, that after heating the crystal to higher temperatures and then allowing to cool to room temperature for obtaining the spectra, results in returning of two water types to its original state Thus it is well evident that the H_2O molecules are tightly entrapped in the structural channels Aines and Rossman (1984b), argued that the rapid loss of *type - I* water indicates that it has entered the structural channel at lower temperatures. However, according to the present author, this as the only reason cannot be considered, as it is well known that the *type - II* water molecule is due to the rotation of H_2O molecules by the adjacent alkali ions which are able to rotate the H_2O from perpendicular to the parallel position by the effect of the electric field of the alkali cation (Wood and Nassau, 1967; Zimerman, 1981; Manier-Glavinaz, 1989). Therefore, *type - II* water molecules lie strongly

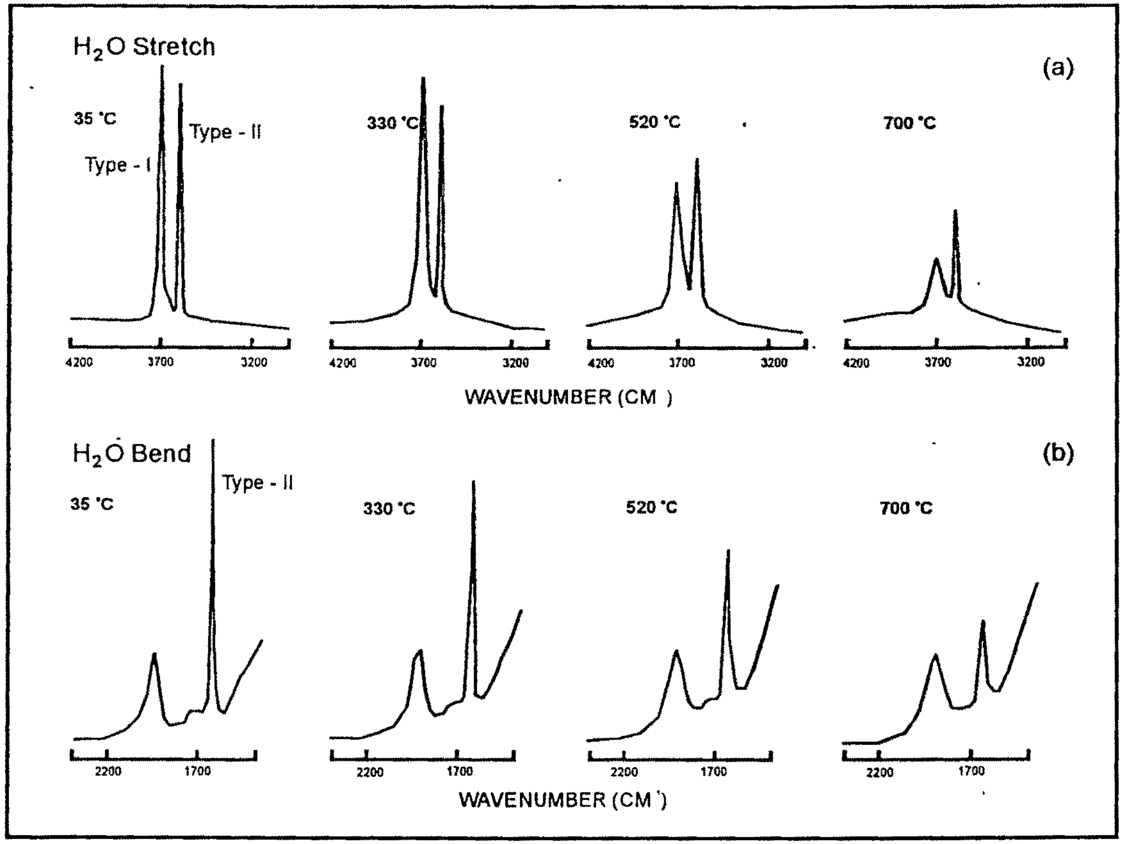


Figure 5.15 : Infrared spectra of single crystal beryl (E||c) at variable temperatures. a) O - H stretching region and b) H - O - H bending region (after Aines and Rossman, 1984b)

attracted towards alkali cation, whereas the *type - I* water is free and therefore, free to get dislodged on heating before *type - II* water molecule.

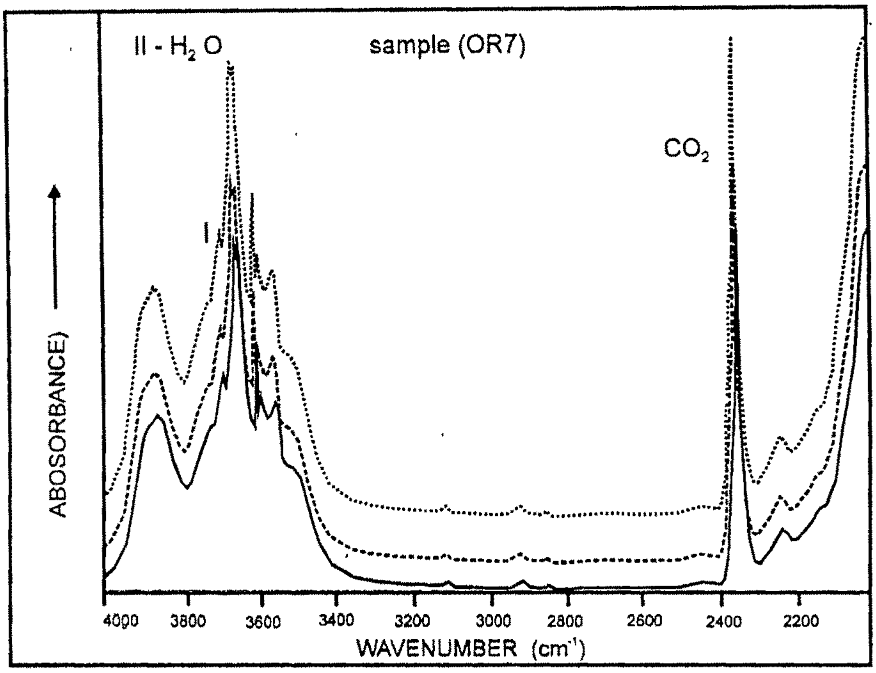


Figure 5.16 : Unpolarised FT-IR spectra depicting heating experiment carried out room temperature (continous line), 500 °C (dahsed line) and 800 °C (dotted line) on single crystal

Figure 5.15b, represents Aines and Rossman (1984b) high temperature investigation in the bending mode region around 1600 cm^{-1} Similar to stretching mode, the deformation mode also reveals decrease in intensity on heating The author in the present study observed certain peculiar behaviour in this region on heating, although no decrease in intensity is evident On heating from RT to 500 °C, the bands at 1600 cm^{-1} show an increase in intensity due to thermal vibration, whereas no significant change is observed for 1635 cm^{-1} band (*Figure 5.17a*). The band at 1562 cm^{-1} shows an increase in intensity and shifts towards 1554

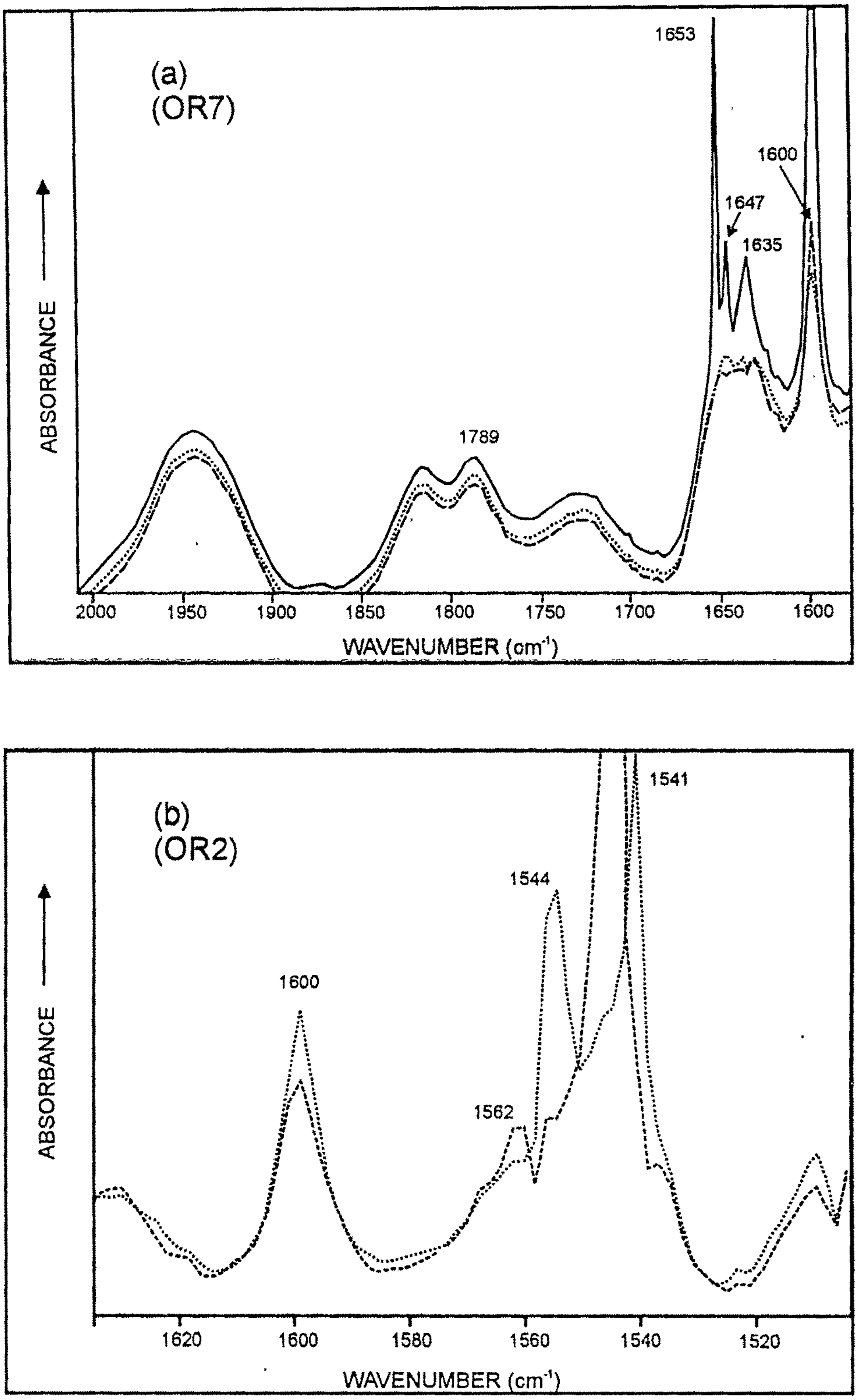


Figure 5.17 : Single crystal (100um) FT-IR spectra depicting behaviour of bending mode region on heating at variable temperature. RT (dashed line), 500 °C (dottedline) and 800°C (continous line)

cm^{-1} whereas the band 1545 cm^{-1} shifts towards 1541 cm^{-1} with a decrease in intensity (*Figure 5.17b*) Charoy et al., 1996 attributed band at 1545 cm^{-1} to the CO_2 (V_3) molecule in psuedocarbonate structure because of its interaction with one of the oxygen atoms of the silicon tetrahedral ring. However, the present author presumes this to be another bending mode of H_2O species, since asymmetric (V_3) of CO_2 is observed only in the range of 2400 - 2300 cm^{-1} (Aines and Rossman, 1984b).

The most important feature observed by the author is around 1635 cm^{-1} where *type - II* water molecule bending mode vibrates On heating to 800 °C for three hours, the 1635 cm^{-1} peak shows a little increase in intensity and some amount of broadening A new sharp peak is observed at 1647 cm^{-1} and an intense sharp peak at 1653 cm^{-1}. The band at 1600 cm^{-1} also increases in intensity. The presence of broad increased band at 1635 cm^{-1}, a new band at 1647 cm^{-1} and peak at 1653 cm^{-1} indicates a possible rearrangement of *type - II* H_2O molecule on heating and shift towards higher energy (1635 to 1653 cm^{-1}) due to possible shift of the molecule from its original position in the channel. Thus although on heating above 500 °C, there is a decrease in intensity of all vibration modes as envisaged by Aines and Rossman (1984b), the above studies by the present author elucidates that before a decrease in intensity, a whole lot of dynamic rearrangement occur in the structural channel of beryl structure.

A temperature dependent Proton NMR studies is warranted to deduce such complex behaviours, which the author was not able to carry out.

The beryl samples under study were heated upto 1000 °C for 10 hrs. Except for slight decrease in intensity, there was no complete dehydration, indicating that Indian beryls requires higher temperatures (>1000 °C) for dehydration. However, on heating above 1000 °C, the samples are found to break and crack into pieces. This is possibly due to pressure exerted by volume expansion in the channels of beryl structure due to water molecules.

5.3 RAMAN SPECTROSCOPIC STUDIES

As discussed earlier natural beryl crystals possess a variety of impurities, which may occupy either crystallographic sites of atom of the host crystal or in the channels. Raman spectroscopy allows and easy access to polarised spectra in contrast to IR spectroscopy which requires either very thin samples or reflectivity measurements. Very little characterisation has been carried out on beryl using Raman spectroscopy. Narayanan (1950) provided a low frequency spectrum of beryl with meagre details. More recent Raman studies in conjunction with IR spectroscopy have confirmed the occurrence of major active modes of vibration predicted by factor group analysis (Gervais and Piriou, 1972; Hofmeister, 1988).

Polarised Raman spectra (*Figures 5.18 a & b*) were recorded at room temperature on gem quality perfect hexagonal beryl crystals, using Ramnor HG2S, multichannel spectrometer equipped with a *Spectra Physics Argon Ion Laser* (514.5nm exciting line). spectra were acquired over the characteristic Raman frequency of Si-O, Al-O, Be-O, H_2O and CO_2.

It is observed by the author that the unpolarised spectra in both orientation (normal or parallel to *c* axis), the H_2O show similar intensity and position at 3615 and shoulder at 3605 cm^{-1} (*Figure 5.18a & b)*, suggesting at least two orientations in roughly equal proportions for H_2O molecule (Charoy, et al , 1996). However, on recording polarised spectra, intensity of H_2O is observed strong along $E\|c$ (*Figure 5 18a*) which drops in intensity along $E\perp c$ (*Figure 5.18b*). Along this direction weak absorption is observed at 3705 and 3675 cm^{-1} attributed to

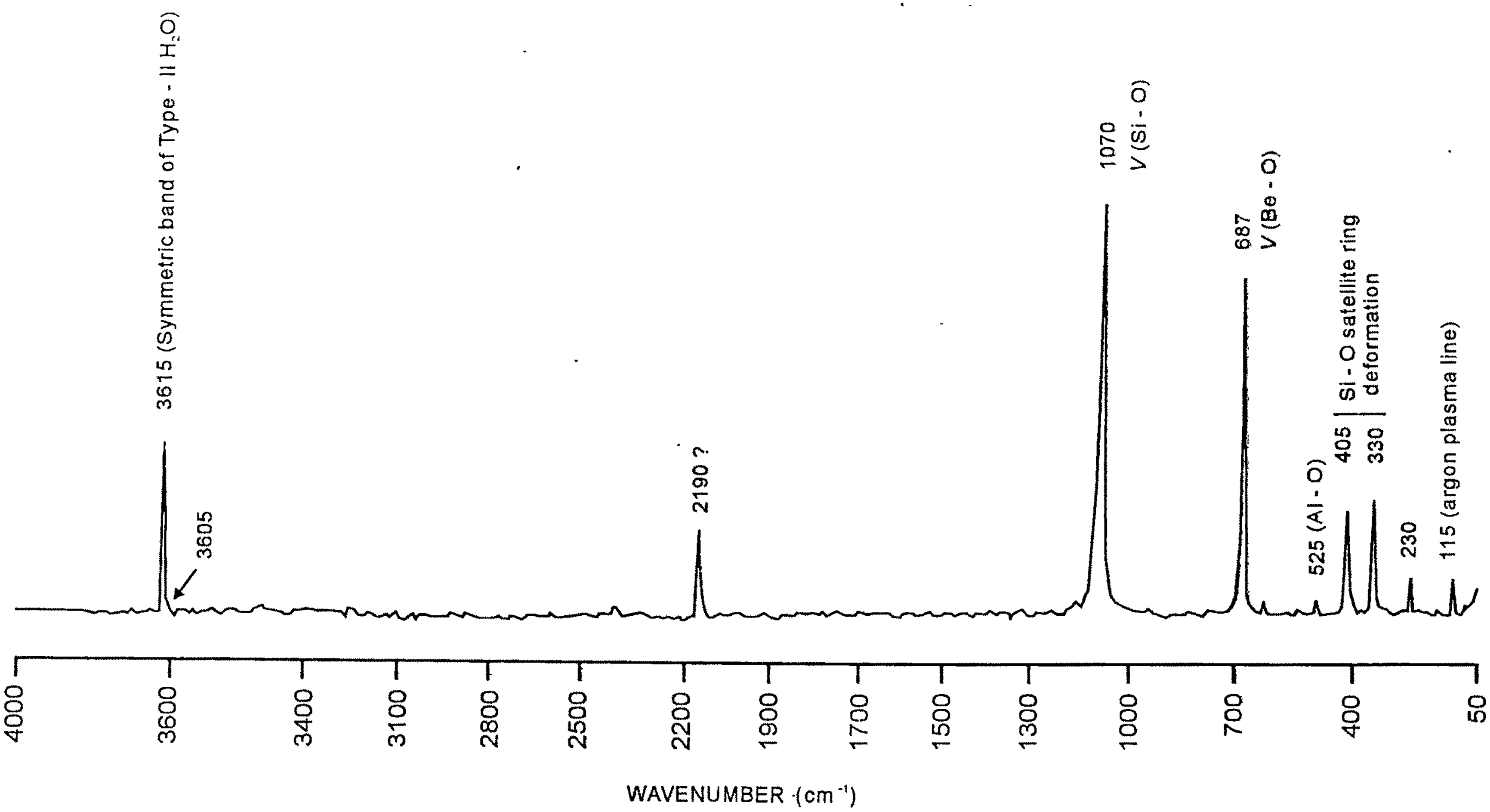


Figure 5.18a : Polarised Raman spectra of beryl along E II *c* (spacing between divisions are not equal)

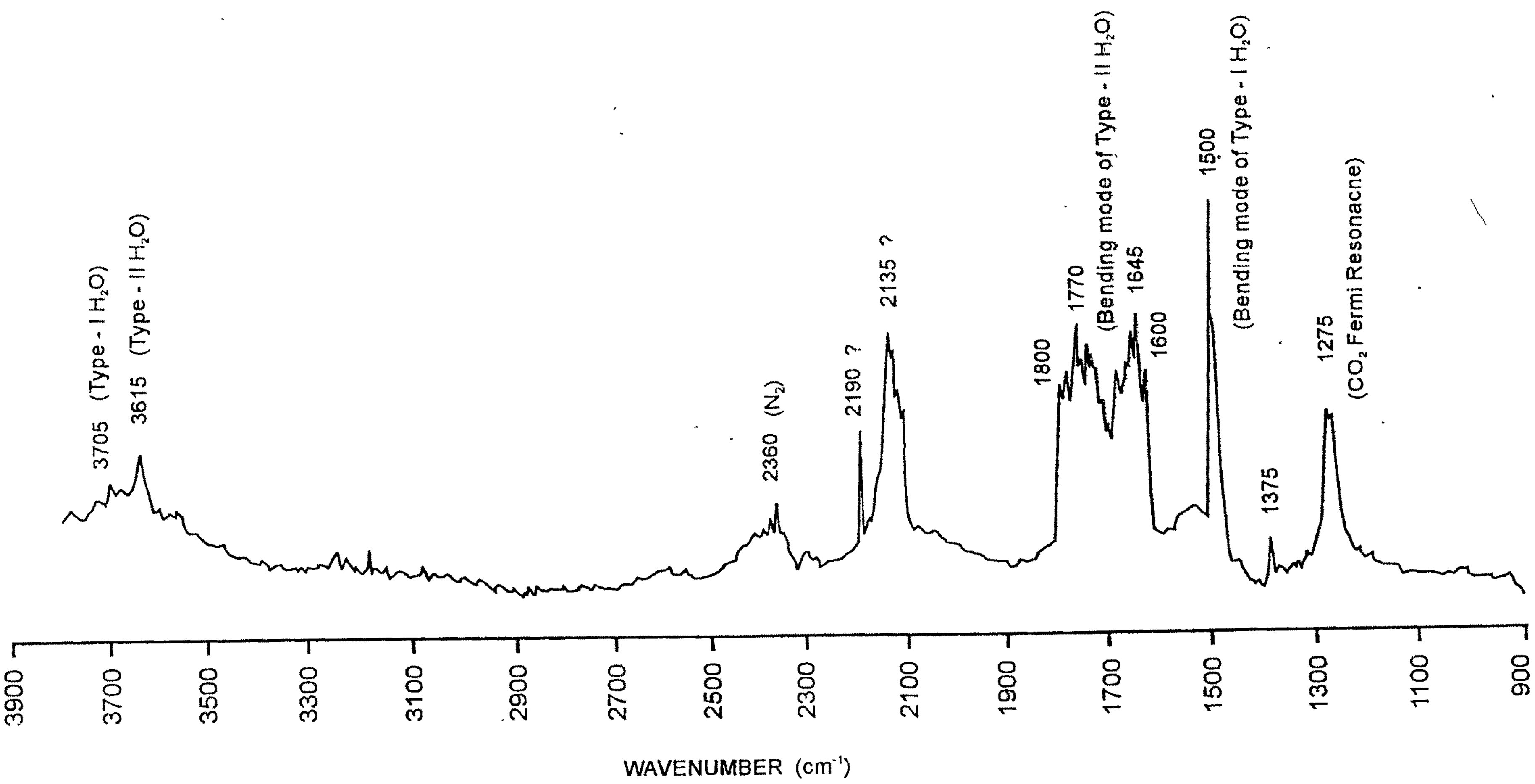


Figure 5.18b : Polarised Raman spectra of beryl illustrating various channel constitutents along E⊥*c*.

type - I H_2O and bands at 3615 and 3605 cm^{-1} to *type - II* H_2O molecule in accordance with the FT-IR spectra (*Figures 5.5a to d*).

Both types of water molecule are present in different orientations in the channel and is therefore expected to show intense bands in both polarisation direction, however, the polarised spectra (*Figures 5.18a & b*) show intense band of *type - II* H_2O molecules in both polarisation This behaviour is yet to be understood. The band present at 2135 cm^{-1} in both polarisation is being reported for the first time by the present author, however, its assignment remains ambiguous.

The CO_2 peak is represented by peaks at 1275 and 1375 cm^{-1} seen polarised only along E⊥*c* (*Figure 5.18b*). As stated earlier, the V_2 (bending mode) and V_3 (asymmetrical mode) vibrations of CO_2 are Raman inactive (Charoy et al., 1996). However, problem arises when intensities of overtone and combination bands are close to those of fundamentals (*Fermi Resonance*) According to Nakamoto (1963) the first overtones of the V_2 and V_1 vibrations of CO_2 can interact to form two strong Raman lines at 1388 and 1286 cm^{-1} In the present study by the author only a strong band at 1275 cm^{-1} (V_1) and weak at 1375 ($2V_2$) are observed, which the author presumes is the Fermi Resonance of CO_2 as described by Charoy et al. (1994). Complete absence of CO_2 Raman band along E||*c* (*Figure 5.18a*) again corroborates the earlier observation based on IR spectra, that the CO_2 molecule is oriented normal to the channel axis The 1070 cm^{-1} along E||*c* (*Figure 5.18a*) represents symmetric stretching vibration of Si-O, while 405 and 330 cm^{-1} represents Si-O ring deformation. Peak at 687 cm^{-1} (*Figure 5.18a*) indicates Be-O stretching vibration (Hofmeister, 1988; Charoy et al., 1996). The attributes of 230 cm^{-1} along E||*c* is not known.

The bending mode vibration of *type - II* H_2O molecule is observed at 1630 cm^{-1} polarised only along E⊥*c* (*Figure 5.18b*) However, in addition to the 1630, several peaks are observed between 1800 - 1645 cm^{-1} Bending mode of *type - II* H_2O molecule is expected around 1600 cm^{-1} in accordance with the IR spectra, but the Raman spectra show no feature around 1600 cm^{-1}. Instead a sharp peak is observed at 1500 cm^{-1} along E⊥*c*. This the author presumes could be the bending mode of *type - II* H_2O, however, its shift of 100 cm^{-1} (in FT-IR it occurs at 1600 cm^{-1}) is not understood. Similarly the attributes of intense peaks between 2110 - 2155 cm^{-1} is also not known. The peak at 2360 - 2350 cm^{-1} probably arises from the vibration of N_2 molecules (Macmillan and Hofmeister, 1988).

Thus present investigation reveals that Raman spectroscopy is quite sensitive to the crystal chemistry of beryl. Polarised Raman measurements discerns a variety of Raman bands not observed in IR spectra. The presence of various unknown peaks warrant detail analysis using Raman studies for the complete characterisation of beryl The volatile characteristics can shed light on the physical conditions prevailing during the growth of the beryl crystal.

As discussed earlier, heating experiments upto 1000 °C did not reveal any significant change in the behaviour of water molecule. The author therefor, carried out thermoanalytical techniques to decipher loss of volatile species and also to observe any change physical and chemical properties on heating.

5.4 THERMOANALYTICAL METHODS

Many physical and chemical properties are temperature dependent. There are some properties when measured as a function of temperature provide useful analytical information. Techniques used to obtain such information on some property as a function of temperature are called thermoanalytical methods The interpretation of thermal analysis provides assistance in relating the features of the *property - temperature curve* (peaks, discontinuities, changes in slope etc.) to possible thermal events in the sample i e chemical reactions or physical transitions resulting from the change in sample temperature.

The Thermoanayltical analysis were carried using *Sieko 5100 DTTG* instrument.

5.4.1 THERMOGRAVIMETRIC ANALYSIS (TGA)

This is a technique in which change in weight of a substance, in an environment heated at controlled rate is recorded as a function of its temperature When weight is plotted against temperature a curve characteristic of the substance studied is obtained. Such curve is called Thermogravimetric (TG) curve of *thermogram.*

Figure 5.19, represents TG analysis of powdered beryl sample. The TG curve reveals a horizontal line on step wise heating from room temperature to 1000 °C Result of this experiment again supports the author's earlier observation that the volatiles are tightly wedged in the channels of beryl lattice. On heating, the water molecules behave as unbound state (gaseous) and at the same time, they are not driven out of the channels as described by Aines and Rossman (1984b). Therefore, it does not affect the TG curve. The molecules that remain in unbound state on heating return to original state on cooling

5.4.2 DIFFERENTIAL THERMAL ANALYSIS (DTA)

This technique of thermal analysis is based upon the detection of changes in the specific heat content of the sample with temperature The specific heat of a material changes

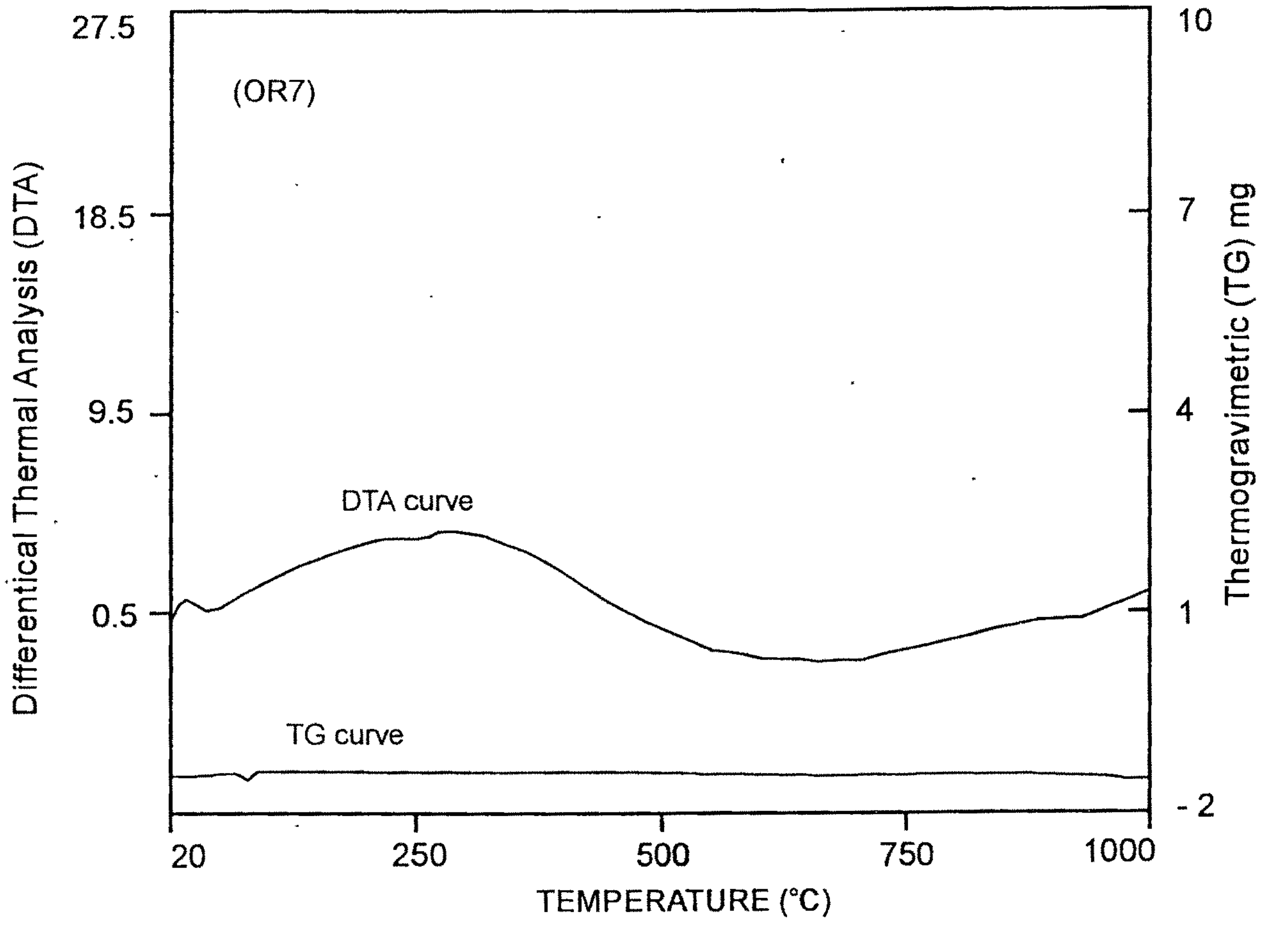


Figure 5 19 : Thermogravimetric (TG) and Differential thermal analysis (DTA) of powdered beryl slowly with temperature in a particular state, but alters discontinuously at a change of state. With increase in temperature, the supply of thermal energy may induce physical or chemical reaction in sample e g melting or decomposition (phase transition) change in enthalpy, latent heat of fusion, heat of reaction. Such changes may be detected by thermal analysis.

In differential thermal analysis (DTA), to deduce accurately the small difference between the temperature of sample taken for analysis and programmed sample temperature, the sample and the reference material are heated separately in identical environment *Figure 5.19*, depicts DTA curved of beryl powder. The curve reveals no significant changes in physical as well as chemical process on heating. The small peak observed around room temperature is due to initial displacement of the baseline from the zero differential temperature arising from the mismatching of thermal properties of the sample and reference material. The broad curves at 200 and 760 °C are due to the baseline and not related to any change in the sample form (Prof. Sunder Murthy personal comm).