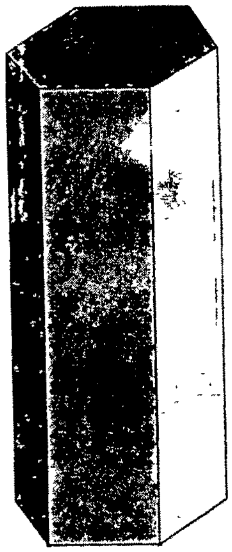

Chapter - 3

Crystal Chemistry and Properties

3 - CRYSTAL CHEMISTRY AND PROPERTIES

3.1 STRUCTURE

Beryl is a typical representative of cyclosilicate with a specific chemical formula of $Be_3Al_2Si_6O_{18}$ and it falls under the space group P6\mcc. Structure of beryl was first discovered by Bragg and West (1926). The striking structural pattern of this mineral is $[Si_6O_{18}]$ rings, which are united laterally by the beryllium (Be) ion which has a four - fold coordination with oxygen and aluminium (Al) ion that has a six - fold coordination with oxygen arranged between the rings (*Figures 3.1*) The octahedral Al^{3+} site is slightly distorted axially while the tetrahedral Be^{2+} site is highly distorted (Davir and Low, 1960; Gibbs et al , 1968). In the vertical position, the layers of beryllium - oxygen tetrahedra and the aluminium - oxygen octahedra alternate with the layers of silicon - oxygen rings $[Si_6O_{18}]$ Oppositively facing six - fold rings of silicon tetrahedra are stacked along the *c* crystallographic axis of beryl crystal resulting in widely spaced intercommunicating channels (*Figure 3.2*). Dimension of channels varies from 2.8 Å in the plane of Si_6O_{18} rings and 5.1 Å between neighbouring rings.

As a consequence of its structure, beryl can accommodate impurity species in solid solution in two sites, either interstitially within the channel or substitutionally adjacent to the channel walls within the octahedral or tetrahedral structural sites. These two types are known as interstitial solid solution and substitutional solid solution respectively. The most common transition metal ion impurities of Fe^{2+}, Fe^{3+}, V^{3+}, Mn^{2+} and Cr^{3+} generally substitute for Al^{3+} or Be^{2+} or occasionally Si^{4+} ion and are tightly bound to crystal lattice. The spectroscopic properties of such ions have been the subject of several investigations (Wood and Nassau, 1968; Price et al , 1976, Goldman et al , 1978; Parkin et al , 1977; Edgar and Vance, 1977, Mathew et al , 1998a)

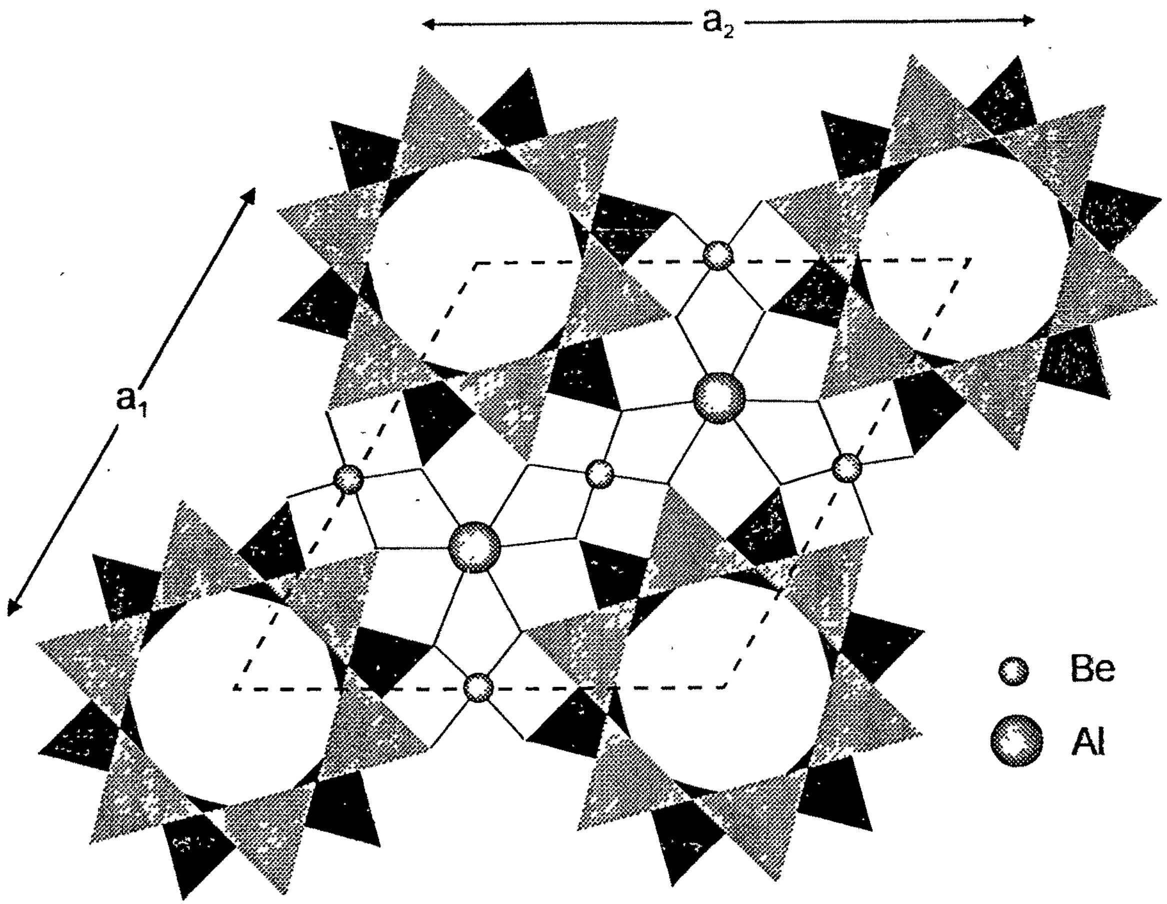

Figure 3.1 : Schematic drawing of the structure of beryl projected perpendicular to *c* - axis.

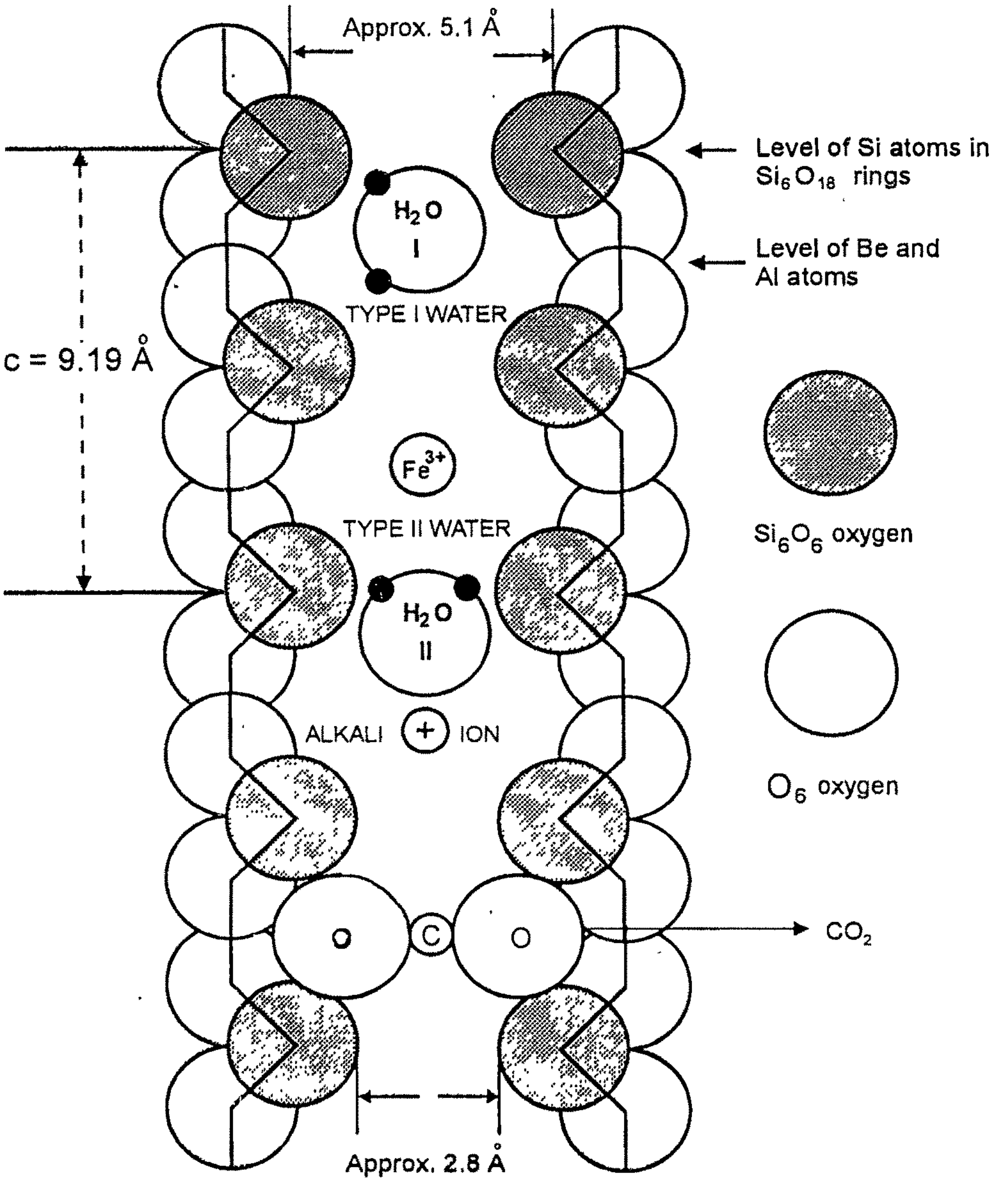

Figure 3.2 : Schematic drawing of the slice of beryl structure projected paralled to *c* - axis depicting presence two types of water molecules, transition ions and carbon dioxide (modified after Wood and Nassau, 1968).

Other impurities species, such as heavy alkali metal ions (K, Na and Cs), H_2O and CO_2 molecules commonly occupy the channels. The infrared spectra of these closely resembles those of the free molecules, suggesting that these species are only weakly bound (Van der Waals bond) to the channel walls of beryl (wood and Nassau, 1967; Aines and Rossman, 1984b; Mathew et al , 1998).

Natural beryl consists of two types of water molecules as shown in *Figure* (*3.2*). *Type - I* water molecule has its H-H direction parallel to the C_6 axis and *Type - II* water molecules has its H - H direction perpendicular to the six fold axis (Wood and Nassau, 1967). The type - II H_2O molecule, is produced due to the rotation of water molecule (type-I), located adjacent to an alkali metal ion. They are rotated from parallel to perpendicular position by the electric field of the charged alkali ion (Wood and Nassau, 1967; 1968). The water molecule is irregular in shape but is not less than 2.8 Å in one plane and 3.2 to 3 7 Å in other (Wood and Nassau, 1968) The diameter of the void within the ring is about 2 8 Å (*Figure 3.2*), the fit would of water molecule in the channel would be so tight that it would greatly modify the water molecular frequencies. However, such changes are not observed in the IR spectral studies. Thus the type-II water molecule is situated within the ring with an alkali ion nearby to rotate the molecular dipole and produce dichroism opposite to that of type-I.

Except for the smaller Li^+ ion, all other larger alkali ions are expected to enter only in the channel as enough empty space exists there (Wood and Nassau, 1968; Evans and Mrose, 1966). According to Wood and Nassau (1968) presence of channel alkali ions is made possible because of missing negative charges in the lattice produced, e.g by substitution of Fe^{2+} for Al^{3+} or by omission of Be^{2+} ion. Later several workers (Hawthorne and Cenry, 1977; Aurisichhio et al , 1988; Artioli et al., 1993) deduced through X-ray and neutron diffraction refinement that Li^+ substitutes in Be tetrahedral site and divalent ions in

Al and channel site Differential Fourier maps further discerned that the alkali cations are confined in two sites in channel (2a and 2b) The aspect of placement of iron ions in the beryl lattice is described in detail in chapter 6.

EXPERIMENTAL DETAILS

Electron probe microanalysis were carried out using SX-50 microprobe Operating conditions were 15Kv accelerating voltage, 20nA beam current and 10s counting time. Single crystal X ray diffraction was carried out on Enraf - Nonius CAD - 4. Graphite monochromatic radiation MoKα ($\lambda = 0.7107$ Å) was used as source. Twenty five reflections were used for least square refinement of cell parameters in the $20 < \theta < 25^\circ$ using CAD - 4 PC software (Enraf - Nonius, 1989). Powder XRD was carried using Philips PW 1710 diffractometer with copper target - nickel filter (CuKα).

3.2 CRYSTAL CHEMISTRY

Correlation between the crystal chemistry and lattice constants have been described by many workers (Ginzburg, 1955; Schaller, 1962; Bakakin and Belov, 1962; Feklichev, 1963, Bakakin et al., 1967). However, these were found apparently contradictory or inconclusive Fiho et al (1973) contribution to the knowledge of crystal chemistry of beryl, in particular influence on lattice constants deduced that an increase of Fe and (Fe + Mg + Mn) percentage has a positive correlation with '*a*' cell parameter. Similarly Li has positive influence on '*c*' cell parameter Positive correlation also exists between Na and parameter '*a*'.

Table 3.1a, illustrates EPMA analysis of the samples studied by the author. For comparative study chemical analysis data of Babu et al (1998) is also included (*Table 3.1b)* Sodium, the most diffusive alkali element of beryl shows fewer variations in the specimens analysed by author. However, samples of Nellore (Andhra Pradesh), Janoli, Jeevan and Bodli (Bihar) analysed (*Table 3.2)* by Babu et al. (1998) indicates high percentage of sodium. Such high sodic beryls have been reported recently by Sanders and doff (1991) from SE Ireland with RI has high as 1.60. Thus beryls from Orissa could be characterised as an alkali free beryl ($R_2O < 0.5\%$) (Hawthorne and Cenry, 1977). Thus as envisaged by Babu et al. (1998), beryls of India belongs to two distinct populations in regard to alkali contents.

The effect of complex substitutions on the lattice parameter allows to classify beryls into three series which controls its c/a ratio (Aurisichhio et al., 1988). *Octahedral beryl* - where Al $\leftrightarrow$ Me^{2+} represents the main isomorphous replacement are characterised by c/a value in the range 0.991 - 0 996 Å; the *tetrahedral beryl*, where Be $\leftrightarrow$ Li^+ is the main substitution with c/a values 0.999 - 1.000 Å; the normal beryls with c/a ratios between 0.997 and 0.998 include those where the two substitutions occur together.

Table 3.1a : Electron probe microanalysis of the beryl sample studied

Elements/ Constituents Wt%	Sample OR1 (Greenish blue)	Sample OR2 (Light yellow)	Sample OR3 (Irradiated greenish yellow)	Sample OR4 (Pale blue)	Sample OR5 (Irradiated Yellow-orange)	Sample OR6 (Greenish yellow)	Sample OR7 (Colourless)	Sample K1 (Kerala green)	Sample TN1 (Karur deep blue)
SiO_2	65.943	67.038	66.235	63.187	65.698	64.240	66.544	65.188	67.939
Al_2O_3	17.811	18.091	18.175	17.134	17.740	17.442	16.686	17.246	18.324
BeO	n. d	n. d.	n. d.	n. d.	n. d	n. d.	n. d.	n. d	n. d
FeO^t	0.680	0.543	0.589	0.519	0.545	0.744	0.537	0.752	0.473
MnO	0.006	0.006	---	---	0.025	0.012	0.037	0.006	---
CaO	0.015	0.013	0.021	0.032	0.020	0.014	0.025	0.054	0.033
MgO	0.026	0.001	0.016	0.099	0.093	0.081	0.083	0.178	0.289
Na_2O	0.0159	0.220	0.131	0.234	0.206	0.275	0.206	0.348	0.238
K_2O	0.018	0.010	0.019	0.002	0.019	0.031	---	---	0.028
Li_2O	n. d.	n. d.	n. d.	n. d.	n. d.	n. d	n. d	n. d.	n. d
Cr_2O_3	0.039	---	---	0.040	0.027	0.031	0.047	0.023	0.041
TiO_2	---	0.003	0.045	---	0.034	---	---	0.003	---
V_2O_3	0.010	---	0.042	0.050	0.032	0.012	---	---	0.014
NiO	0.005	0.033	0.007	0.040	0.022	0.016	0.033	---	0.054
CoO	0.025	0.025	0.038	---	0.056	0.056	0.025	0.025	0.072
F	0.0175	0.146	0.144	0.164	0.216	0.057	0.203	0.259	0.121
Total	84.912	86.129	85.462	81.461	84.73	83.011	84.447	84.082	87.626

Table 3.1b : EPMA analysis of beryl samples (contd.) (*Analysis of Babu et al. 1998)

Elements/ Constituents Wt%	Sample SIB1 (Siberian yellow-orange)	Sample BR1 (Brazilian colourless)	Sample R1* (Hazirbagh, Bihar)	Sample R11* (Janoli, Bihar)	Sample R12* (Bodli, Bihar)	Sample N2* (Nellore, T.N.)	Sample A1* (Attapadi)
SiO_2	66.621	67.805	65.060	65.160	65.360	64.980	64.880
Al_2O_3	18.132	18.298	18.080	17.580	17.790	17.708	17.890
BeO	n.d	n.d	12.680	12.050	11.850	11.806	13.100
FeO^t	0.661	0.549	1.200	0.320	0.680	0.850	0.690
MnO	0.056	--	0.024	0.031	0.028	0.020	0.026
CaO	0.051	0.002	0.320	0.320	0.320	0.250	0.220
MgO	0.051	0.082	0.130	0.220	0.320	0.170	0.250
Na_2O	0.399	0.330	0.760	1.530	1.510	1.510	0.690
K_2O	0.008	0.042	0.050	0.165	0.116	0.071	0.073
Li_2O	n.d	--	0.040	0.064	0.054	0.060	0.038
Cr_2O_3	0.063	--	n.d	n.d	n.d	n.d	n.d
TiO_2	--	0.012	n.d	n.d	n.d	n.d	n.d
V_2O_3	0.018	0.012	n.d	n.d	n.d	n.d	n.d
NiO	0.014	0.013	n.d	n.d	n.d	n.d	n.d
CoO	0.036	--	n.d	n.d	n.d	n.d	n.d
F	--	--	n.d	n.d	n.d	n.d	n.d
Rb	n.d	n.d	18	33	24	18	16
Cs	n.d	n.d	19	16	44	36	49
H_2O	n.d	n.d	2.140	1.630	1.880	2.180	1.690
Total	86.110	87.032	99.59	99.18	99.910	99.60	99.41

Table 3.2, represents c/a ratios of beryls studied by the author. The c/a ratio indicates that, except colourless beryl (Orissa), other coloured beryls are of octahederally substituted (details of type of substitution are given in chapter 5) whereas colourless beryls are tetrahedrally substituted. Octahedral type beryls are due to fact that the divalent metal ions increase the cation-oxygen bond distance in the octahedral (Al site). This site is, however, constrained by short edges shared by Be tetrahedron, and therefore, gets flattened in *c* direction, resulting in an increase in bond length which directly influences the values of '*a*' cell parameter (Feklichev, 1963; Aurisichhio et al , 1988). In contrast, an increase in tetrahedral cation - oxygen distance due to substitution at Be results in increase in the length of '*c*' parameter (Aurisichhio et al., 1988; 1994). Although Li concentration was not determined in the present study, the author presumes an increased tetrahedral substitution in colourless beryls is on account of high Li^+ substitution at Be^{2+} site, in accordance with other workers (Hawthorne and Cenry, 1977; Aurisichhio et al., 1988; Artiloli et al., 1994).

Thus different type of substitution in beryls of Orissa from the same locality discerns the chemical constraints of environment and formation conditions of beryls. The change in c/a ratio from 0.996 for alkali free beryls to 1.003 for lithium-caesium beryls is apparently the main cause for the change in crystal habit of beryl as a function of alkali content(Bues,1960).

Table 3.2 : Physical and Optical properties and cell constants of the beryls studied

Sl No	Sample	Sample No.	Specific gravity (SG)	Refractive Index (RI) ε	ω	Cell parameters c	a	c/a	Type of Substitution
1	*Colourless	OR7	2.66	1.568	1.572	9.199	9.176	0.9994	tetrahedral
2	*Irradiated - colourless	OR6	2.66	1.568	1.573	9.204	9.227	0.995	tetrahedral
3	*Green blue	OR1	2.66	1.570	1.575	9.199	9.207	0.9964	octahedral
4	*Greenish - yellow	OR3	2.68	1.571	1.576	9.203	9.238	0.9968	octahedral
5	*yellow	OR2	2.67	1.570	1.575	9.176	9.209	0.9950	octahedral
6	*Blue	OR4	2.67	1.570	1.576	9.208	9.239	0.9944	octahedral
7	TN blue	TN1	2.70	1.575	1.580	9.178	9.206	0.9966	octahedral
8	Siberian yellow	SIB1	2.69	1.572	1.577	9.207	9.227	0.9966	octahedral

* Samples from Orissa

3.3 CRYSTAL HABIT

Crystal habit of beryl is highly diverse, varying from slender thin prismatic to tabular, truncated pyramidal to coniform, skeletal (stuffed) crystals (Bues, 1965).

Plate 3.1 a & b, depicts beryl crystals studied by author; shows well developed habit prismatic faces. Only a few crystals revealed well developed basal pinacoid, while others were broken fragments of prismatic crystals. Pyramidal faces although present in one sample, were found highly damaged Thus well developed prismatic faces Orissan beryls indicate that, they could be alkali free beryls having total alkalis less 0.5% as envisaged by Bues (1965). In pegamatites, such long prismatic crystals of the above variety are usually found as isolated individuals or in pockets, unhindered during their growth or rarely intergrowth of two or more crystals

Unlike pegmatites, the pneumatolytic - hydrothermal deposits are characterised by slender prismatic crystals, and are characterised especially by dense intergrowth of crystals in radiating growth or dense massive crystals. The alkali rich beryls usually show stubby prisms, almost discoidal crystals flattened parallel to the *a* - axis, and frequently with numerous faces of prism and pyramids. In addition to the flattened habit, alkali beryl crystals also develop especially broad faces of the bipyramid {1121} (Bues, 1965; Sinkankas, 1985).

3.4 PHYSICAL PROPERTIES

Crystal structure of beryl confers a high degree of hardness (7.5) on the Mohs scale. The uniformity in structural strength is apparent when beryl is faceted into gems - the lapidary is unable to sense any appreciable difference on case of grinding for polishing among the

Plate 3.1a : Prismatic beryl crystals from Karur and Siberia

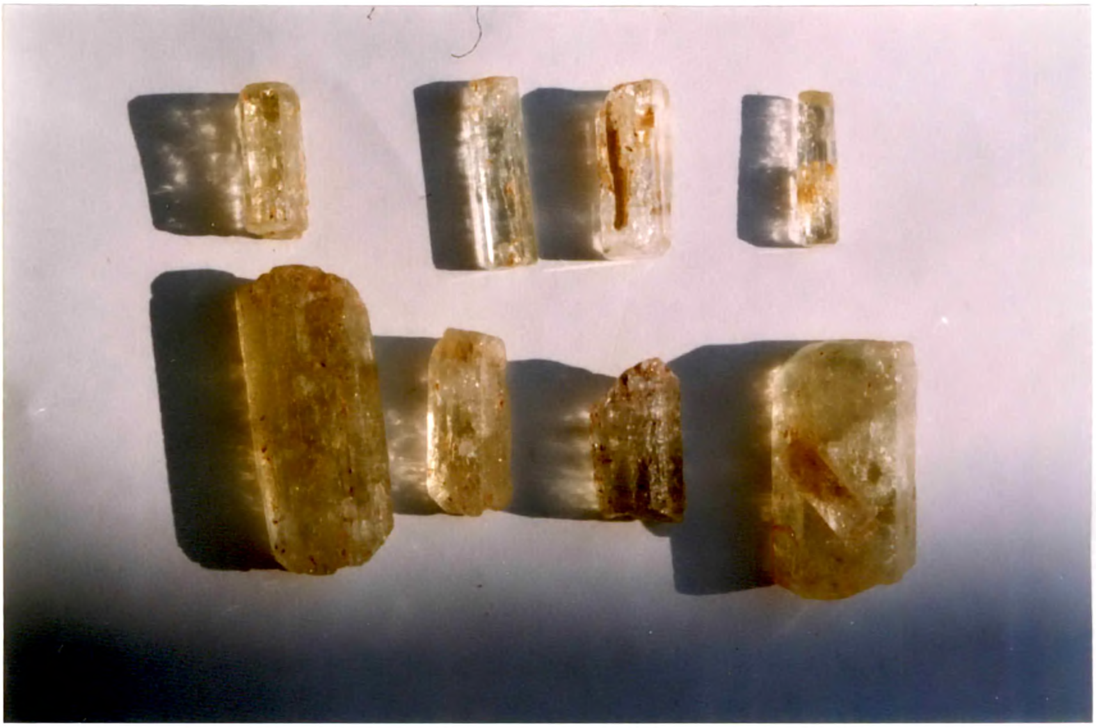

Plate 3.1b : Beryls crystals from Orissa revealing well developed prismatic habit

various crystallographic directions (Sinkankas, 1985). Similar strength is also noted in crystals that are heat treated to change colour. Considerable temperature can be applied without breakage, provided the crystal is not already cracked/cleaved or does not contain inclusions.

3.5 SPECIFIC GRAVITY AND REFRACTIVE INDEX

The specific gravity and refractive indices of beryl vary with the content of alkalis. *Figure 3.3,* indicates that the specific gravity values of all samples increase positively with refractive index of ordinary ray in accordance with earlier workers (Schaller et al., 1962, Hawthorne and Cenry, 1977). In regard to specific gravity, it is not only the alkali content that is important, but also the quantitative composition of alkalis. Alkali beryl with high lithium has a SG close to alkali free beryls (Hawthorne and Cenry, 1977). However, occurrence of sodium, especially of caesium in the channels of beryl would result in marked increase of specific gravity. SG of beryl also depends largely on the water content and on the extent to which the crystals are saturated with gas liquid inclusions.

Magnitude of refractive index is largely influenced by the alkalis and to lesser extent by the octahedral and tetrahedral substitutions and channel water (Bues, 1965; Cenry and Hawthorne, 1976). The maximum refractive index value of 1.575 observed for Orissan beryls indicate that these beryls contain low Cs (<40ppm, Hawthorne and Cenry, 1977).

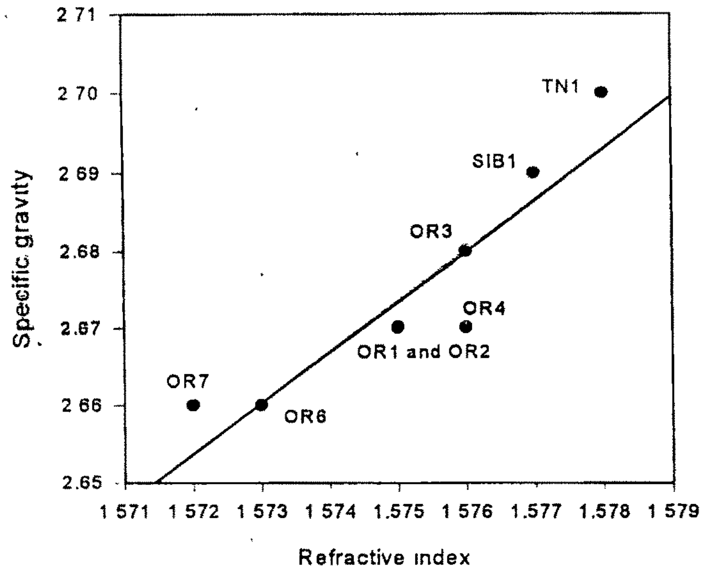

Figure 3.3 : **Showing positive correlation between specific gravity and refractive index (ω)**

3.6 INCLUSIONS

Presence of solid inclusions in pegmatitic minerals are rather uncommon. Beryl is usually found entrapped with liquid inclusions and to lesser extent with solid inclusion.

For a mineralogist/gemmologist, the presence of inclusions are of great interest, however, too many inclusions can render otherwise good gem material worthless. Certain inclusions, especially in emerald are distinctive and sometimes can even serve to identify the particular deposits from which they came (Gubelin,1974; Koivula and Gubelin, 1992). Inclusions are also used as a tool to distinguish between synthetic and natural emerald, aquamarines etc. They also provide evidence as to the geochemical environment in which the beryl crystals grew, besides temperature and pressure of formation (Roedder, 1984).

Plate 3.2a, reveal presence of petrogenetic (inclusion formed before the beryl and latter enveloped by the beryl crystal as it grew) inclusion of plagioclase and quartz in one of the Orissan beryls *Plate 3.2b*, is another example of petrogenetic inclusion of sillimanite in Orissan beryl. The pegmatites of Badmal province are seen intruded into the Khondalites (garnet-sillimanite-graphite schists) and therefore, could have got entrapped sillimanite during the growth of beryl crystal.

Beryl crystal growing rapidly in the *c* direction, results in the developments of a miniature well, the walls of which extend upward leaving hollow interior (*Plate 3.3*), Bridging of hollow interior is prevented by the rapidity of growth, because once such tube begins, it is extremely difficult for the nutrients to circulate within the tube and cause the wall to grow towards each other (Sinkankas, 1985).

Although no syngenetic (formed contemporaneously) solid inclusions were observed in the beryls from Orissa, they revealed presence of multiphase liquid inclusions as shown in *Plate 3.4*. Daughter minerals inside the cavity are mainly halite, calcite and mica. By far the commonest inclusions in all beryls is fluid, sometimes two immiscible phase, at times gas and liquid, and occasionally small daughter crystals grown within the liquid. Evidences of epigenetic solid inclusions in Orissan beryls are lacking, nevertheless, reveals presence of innumerable secondary fluid inclusions (mainly biphase/multiphase) as shown *Plates 3.5 a & b* These secondary inclusions are formed due to the intrusion of fluids along fracture plane during pocket rupture. Further necking down process begins to attain minimum surface energy, and a series of biphase/multiphase inclusions are observed along a plane (Roedder, 1984, Shepherd et al., 1985).

Plate 3.2a : Petrogenetic solid inclusion of plagioclase and quartz in beryl from Orissa

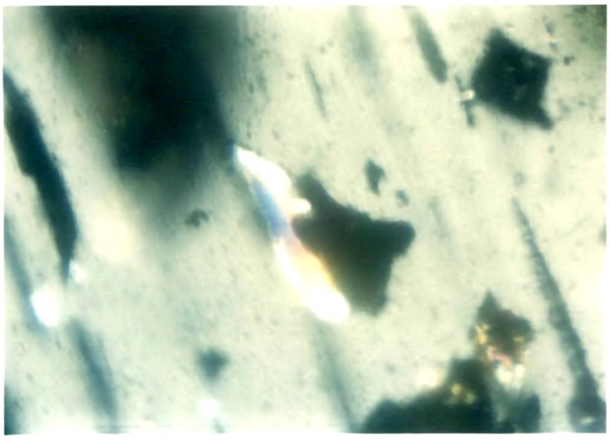

Plate 3.2b : Petrogenetic solid inclusion of sillimanite in Orissan beryl

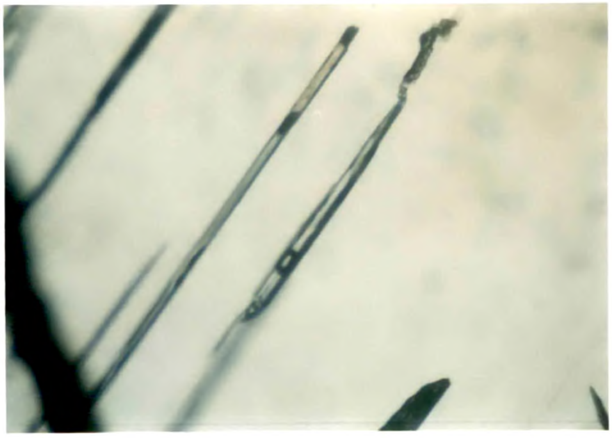

Plate 3.3 : Tubular inclusions in Orissan beryl

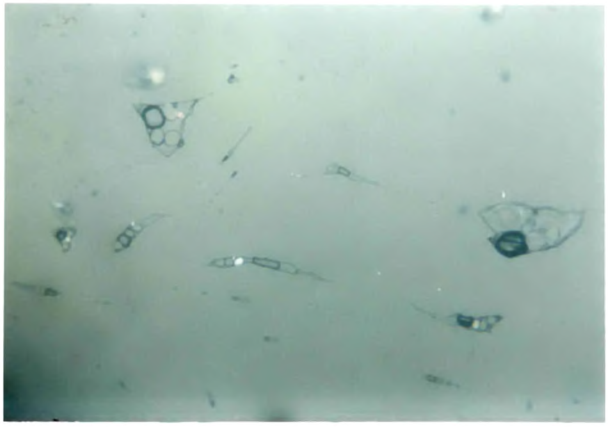

Plate 3.4 : Polyphase inclusions in Orissan beryl

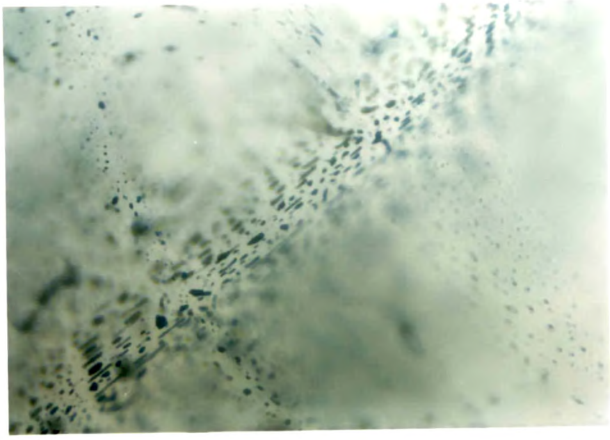

Plate 3.5a : Secondary inclusions along a fracture plane in beryl from Orissa

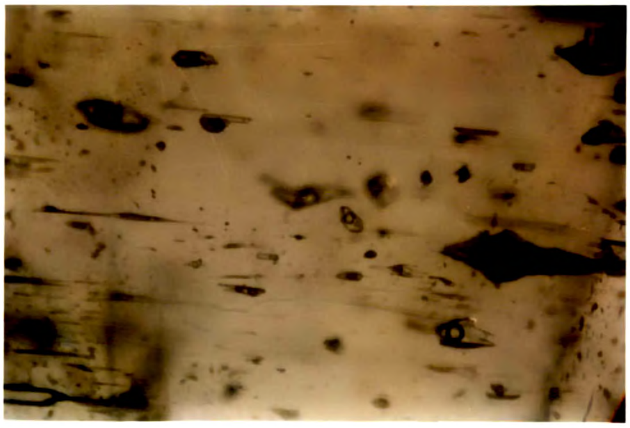

Plate 3.5b : Psuedosecondary inclusions in beryl from Orissa