Chapter - 2

Previous Work

2 - PREVIOUS WORK

Beryl is one of the minerals which has been studied extensively both by mineralogists and solid state physicists, because of their attractive colours, complex crystal chemistry that varies from region to region and their genesis in pegmatites and related hydrothermal deposits. Therefore, before describing details of the work carried out by the author, an effort is made to evaluate the nature and extent of work carried out on beryl by previous workers.

2.1 GENERAL

Earliest reliable account of beryl is found in Egyptian records. The deposits are located in a bleak desert, far to the SE of Cairo and the earliest date given by Little (1917) is around 3500 BC. According to Tagore (1819), who accomplished a monumental study of gemstones with special reference to their position in Indian culture, the emerald has been used amongst the Hindus from time immemorial, being held so high in esteem that even any other flawless gem assuming the form of an emerald is highly prized. Tagore devoted a number of pages to discussions on emerald and beryl, quoting from ancient Sanskrit sources and attesting to the rich fund of mineralogical knowledge possessed by the ancient inhabitants.

Birdwood (1880) in his monograph on Indian industrial arts mentions reference to emerald in ancient writings, noting especially the amulet or talismen composed of nine gems known as the *nava-ratna* or *navratan*, of which one stone is emerald, Birwood also mentions about *vedas* (ancient sacred Hindu writings), where also frequent references are made on precious stones including the beryl and emerald. The discovery of emeralds in Rajasthan in 1944 were of the same type as Egyptian and thus cannot be unequivocally stated that all the early Indian emeralds and beryls came from Rajasthan (Sinkankas and Read, 1985). According to Sinkankas (1981), this discovery suggests the possibility that the region could have supplied these gems in an earlier time. Ball's (1928) chronology of gem mining gives beryls as being produced in India by 400BC. Beck (1941) describe a hoard of beads found in the ruins of city of Taxila in Punjab, among which were beads of beryl. Regardless of where the inhabitants of India obtained their first beryls, it now appears that a brisk trade in beryls (usually emerald) developed at the same time, when ancient Egyptian mines were in operation (Sinkankas, 1981).

2.2 OCCURRENCE

First official documentation on the occurrence of gem beryl from pegmatites in India were reported by Crookshank in the year 1947 and 1948. In 1947, he identified green crystals found near Kaliguman, a small village between Amet and old fortress of Kumalgarh in S. Rajasthan as emeralds. Later a series of occurrences lying within a narrow and straight belt of rocks, emerald bearing schists were discovered by Roy in 1955. Pascoe (1950) and Krishnan (1956) also reports of beryl occurrences in their work on Geology of India and Burma. Brown (1953) mentions of an Indian source of emerald, variously given 'Cangagem' or 'Canjargum' (probably a corruption of Kangayam, town in Coimbatore, Tamil Nadu). According to him the name most likely refer to aquamarine of greenish colour. Iyer in 1948 reported presence of fine blue gem quality aquamarine from Padar area of Zanskar - Udhampur in Kashmir. Later Wadia (1958), published extensive review on the occurrence of beryl in India. During the Twenty Second International Geological Conference held in India, Dhar and Phadke (1964) documented extensively the various occurrences of beryl and other minerals in pegmatites in the proceedings of section 6 on

'Minerals and Genesis of Pegmatites'. Some noteworthy beryls producing districts reported by them were Hazirbagh, Monghyr and Gaya in Bihar; Udaipur, Bhilwara, Ajmer, Tonk and Jaipur in Rajasthan; Nellore, Srikakulam and Vishakhapatnam in A.P.; Hassan and Mysore, and minor quantities from Madras, mainly in Salem and Coimbatore districts. In Orissa, small occurrences of beryl were reported from Koraput and Sambalpur districts. According to these workers beryl is the most important accessory mineral next to mica in pegmatites in India. They also noted that, usually green muscovite bearing pegmatites carry accessory minerals, while those containing only biotite rarely show accessory minerals in appropriate quantity. Almost after three decades later, Mishra and Mohanty (1995) gave a detailed account on the occurrence of gemstones in Orissa from Easter Ghat Granulite belt. Of the three pegmatite dominant districts in Orissa, i e., Sambalpur, Bolangir and Subranapur; pegmatites in Badmal-Mursundi area of Subaranapur district are found to be rich in gem quality beryl deposits These authors, merely reported the occurrence of beryl, but mineralogical and geochemical studies were not attempted by them

2.3 STRUCTURE AND CRYSTAL CHEMISTRY

Several types of unusual beryls have been reported by many authors in different parts of the world. The first reference on unusual beryl were reported in the year 1962 by Schaller et al. from Mohana County, Arizona. This beryl differs distinctly from other known beryls in physical and chemical composition. It had the highest measured RI (1.610); had the lowest percentage of SiO_2 and Al_2O_3 and high Cs content of about 6.68% and Li = 0.23%. Later in the year 1965, Mortimer described minor elements composition of beryl in various environments. He concluded that, the beryl from pegmatites contain small amounts of Fe, Mg, Sc, Ti and V, whereas, beryl from wall rock adjacent to pegmatite generally has more of above elements. Ghera and Lucchesi (1967) reported unusual vanadium bearing beryl from Kenya. A comprehensive compilation of mineralogical and geochemical data concerning beryllium in rocks and mineral deposits was published in the year 1965 by A. A. Beus with particular reference to the Russian deposits. The original Russian version of the book was published in the year 1960 by Academy of Sciences of the USSR. Bues in his book gives a thorough analyses of the behaviour of beryllium in the genesis of rocks and mineral deposits. He reported for the first time "stuffed" beryl crystals from Russia. The main feature of this crystal he observed is the occurrence of inclusions of albite, quartz, less commonly muscovite, tourmaline and microcline, which penetrate into the beryl and in many places form the core of its crystal. Bues also reports of zoned beryls, in which the turbid, opaque lower part of the crystals changes suddenly along a plane parallel to the pinacoid, into a completely transparent beryl Kampf and Francis (1989) reported occurrence of gem quality bicoloured (aquamarine - morganite) beryl from Bananal mine, Minas Gerais, Brazil. Sander and Doff in the year 1994 documented blue sodic beryls from vein of upper Devonian conglomerates from SE Ireland, which contains extreme amounts of Na and unusually high cell edge; a, (9.2902Å).

Deciphering the structure of a mineral forms the first basic study before embarking on to any further detailed studies; and in this respect, Bragg and West are known as the pioneering workers in the field of crystal structure determination. Structure of beryl was also determined by the same authors several decades ago (1926). They opined that, beryl belongs to hexagonal system with ideal formula $Be_3Al_2Si_6O_{18}$ and space group P6/mcc. In the year 1950, Belov and Matveeva determined the parameters of beryl by the method of partial projection. Later on many workers like Bakakin et al. (1962; 1969) and Feklichev

(1963) worked extensively on the composition of beryl, character of isomorphism and position of principal isomorphic elements in the crystal structure. Bakakin et al. (1967) were the first to give an account on the volatile constituents in beryl occupying different positions in beryl lattice. Latter Bakakin et al. (1970) carried out chemical analysis, X-ray diffraction of 26 beryl crystals. On the basis of his data he recognised six standard types of beryls. He further indicated that based on diffraction patterns, a semiquantitative estimation of composition from unit cell parameters is plausible. Davir and Low (1960) reported first Electron Spin Resonance (ESR) studies. He indicated presence of Fe^{3+} ion in the structure with help ESR studies and concluded that these ions substitute distorted octahedral Al^{3+} site and also indicated its possibility in tetrahedral Be^{2+} site. Evans and Mrose (1968) and Gibbs et al. (1968) were first to work extensively on the structural refinement

Wood and Nassau (1967) in their extensive work using infrared spectroscopic studies indicated the presence of two types of water, which they described it as Type-I and Type-II, depending on the orientation of two fold axis of water; and CO_2 molecules oriented with their long axis perpendicular to the C_6 axis in the open channels of beryl lattice Later in the year 1968, Wood and Nassau gave another fundamental paper on beryl on the optical absorption studies. With the help of absorption spectroscopy they showed the presence of various transition elements in different oxidation state such as Cr^{3+}, V^{3+}, Fe^{3+}, Fe^{2+} and Mn^{2+}. in the substitution as well as in the interstitial sites and gave an account on their rolè in beryl colouration.

Goldman et al. (1978) after working on corderite (1977), a mineral structurally similar to beryl, gave a comprehensive study of the channel constituents of beryl using samples from different localities. These authors carried out electronic absorption spectra of Fe^{2+} in non - chromium beryls. They observed that the Fe^{2+} at Al site produce absorption band at 820 and 970nm (E||*c*) and Fe^{2+} at channel site produces band at 820nm ($\perp c$). Although many workers gave their optical absorption results, there was no universally point of view regarding the interpretation of absorption spectrum. Except Wood and Nassau (1968) and Goldman et al. (1978), other workers have more or less agreed to either of the above worker's view.

De Almeido Sampio Filho and Sighiholf (1973) have described the crystal chemistry of beryls from Brazil. They showed positive correlation of alkalis with cell parameters (Li to *c*-axis and Na to *a*-axis). Cerny (1975); Cenry and Turnock (1975); Cenry and Simpson (1977) and Hawthorne and Cerny (1977) studied beryls from Tanco pegmatite from Manitoba, Canada and demonstrated the relationship of RI with alkali content in beryl and crystal structure of Cs-rich beryl. According to them alkalis are confined to the 2a and 2b sites, Cs occupy at 2a site and Na at 2b site. Adams and Gardner (1974) studied single crystal vibration sepctra of beryl and dioptase. Zimmerman (1981) also studied IR spectra of H_2O and CO_2 in beryl and corderite, their kinetic factor and possible structural site. Aines and Rossman (1984) evinced from their experiment that on heating the beryl crystal above 400°C, water that is structurally bound in the channels begins to partition into an unbound state with the characteristics of gas and this results in free motion of Fe transition ions in the channel.

The first thermal behaviour of water molecules in beryl were studied by Polupanova et al. in 1985. They observed appreciable changes in the structure on heating above 1000 °C in the fundamental region (400 - 1300 cm^{-1}) due to the loss of water producing structural changes in the silicon-oxygen framework. In the year 1990, Sherrif along with Hawthorne and Cerny studied beryls using multinuclear Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) and crystal structure studies. These workers observed that in the NMR spectra, ^{29}Si signal is narrow in alkali-poor beryls and broadens with increasing alkali content and also observed two ^7Li signals, indicating Li ion occurring both as a framework constituent and as a channel species. A retired US Navy captain, John Sinkakas because of his immense interest in minerals wrote the first book on beryl entitled "*Emerald and other beryls*" in the year 1981. Later in the year 1985, Sinkankas with P. G. Read wrote the second edition title 'Beryl' containing eleven chapters.

Brown and Mills (1986) worked on the high temperature crystal structure of hydrous alkali rich beryl from Harding pegmatite, New Mexico. These authors refined the structure of hydrous Li, Cs and Na rich beryls by heating at variable temperatures, and then cell parameters were determined. They found that the *a* and *c* cell parameters were found to expand due to increase in volume of AlO_6 octahedra and $(Be, Li)O_4$ tetrahedra. Aurosichhio et al. in the year 1988, gave a fundamental paper on classification beryl based on c/a ratio and reappraisal of crystal chemistry studies on beryl.

Hofmeister (1987) and Hageman et al. (1990) gave a detailed account of the Raman spectroscopic studies on beryl in the region of 30 - 4000 cm^{-1} to explore the effect of impurities on the Raman spectrum of beryl. Manier Glavinaz and Lagache (1989) made interesting observation on IR absorption spectrum of beryl after removal of alkalis from structure by leaching experiment. He noticed that the '*a*' and '*c*' cell parameters decrease as the alkalis are progressively leached. Artioli et al. (1993) with the help of single crystal neutron diffraction studies confirmed the presence of Li substituting tetrahedral Be site and Fe in octahedral site. Again in the year 1994, Aurisichhio et al. gave another fundamental paper on classification of beryls based on IR spectroscopy studies in the structural region between 1200 - 400 cm^{-1}. Babu et al. (1994) were the first to provide characterisation of Indian beryls using FT-IR spectroscopy. Recently Babu and Sabestian (1998) gave a detailed characterisation of beryl samples from Bihar, Rajasthan, Andhra Pradesh and Kerala and also their physcial and optical parameters. They concluded that the beryl samples are alkali poor and form two distinct populations with alkali concentration of 0.594-0.863 wt% and 1.468-1.871 wt%

Charoy et al. (1996) carried out micro FT-IR, Raman and MAS NMR studies on alkali poor beryls from Serra Branca, Brazil. Their study based on ^1H MAS NMR spectrum confirmed the absence of any anisotropic movement of H_2O molecules from one orientation to other on the NMR scale.

2.4 SURFACE TOPOGRAPHY AND DEFECTS

Structural defects and growth history of natural beryl crystals were extensively studied by Scandale et al. (1979). Graziani et al. (1981), carried out X-ray topographical investigations coupled with electron probe analyses, and found good agreement between reconstruction of growth history and growth temperature and pressure ranges deduced from inclusion analyses. Scandale (1984) observed optical anomalies using basal plates of natural beryls. They discerned that, optical anomalies were found to depend on growth history and variation of impurity content and in particular optical axial plane orientations and 2V (anomalous) values were found to depend on minor element concentration difference in growth sectors. Yoshimura et al. (1985) also carried out X-ray topographic studies of growth textures on natural beryl crystals from Brazil to understand the growth defects such as dislocations, growth bands and growth sectorial features. Graziani et al. (1990) classified growth marks on pegmatite beryls into two categories as general and specific in relation to their types and distributions.

2.5 COLOUR

As mentioned earlier, the gorgeous green colour of emerald, sky blue colour of aquamarine, rose red colour in morganite and the golden yellow colour of heliodor have attracted scientist to elucidate the cause of various colours in beryl.

Variations in colour on heating beryl crystals were initially observed by number of Russian workers like Kurbatove and Kargin (1927); Grum - Grzhimailo (1940) and Gavrusevich and Arapulov (1948). They found that the yellow colours are stable upto 250 °C and on further heating to 280 °C yellow hue changed to green and from 280 °C to 300 °C it transformed to blue. Although many workers in the early 50's gave different theories to explain the cause of colour in beryl, it was only after 60's, particularly after the discovery of many advanced spectroscopic instruments and techniques, scientists could give a satisfactory explanations to beryl's complex colours. Kurt Nassau and D.L. Wood of Bell laboratory, New York were the pioneer workers on the study of cause of colour in minerals. They not only worked on the IR spectroscopy as explained earlier, but also gave a detailed account on the cause of colour in beryl using optical absorption spectroscopy. They concluded that the major cause for colour in beryl was due to the presence of bivalent and trivalent iron impurities located various sites with variable concentrations (Wood and Nassau, 1968). In the same year Wood and Nassau explained the cause of colour in red beryls from Wah Wah mountains, Utah, USA (Nassau and Wood, 1968).

Jayraman (1940) investigated blue, green, yellow beryls and concluded that Fe^{3+} and Fe^{2+} were responsible for the colour Bibhuti Mukerjee (1951) analysed seven Indian beryls of different colours and concluded that Sc is not the cause of colouration, but they are connected with crystal deformation due to a combination of factors. The study of

Srinivasan (1950) indicated that blue beryls from Nellore, A P. turned to brown on heating and to deep brown on further heating.

Samolovich et al. (1971) analysed Optical absorption (OA) and EPR spectra of beryl crystals and concluded that the yellow colour of beryl is associated with the presence of Fe^{3+} and Fe^{2+} in octahedral co-ordination and presence of Fe^{2+} in tetrahedral site results in blue colour in beryl. Nassau (1973) reported his preliminary observation on Maxixe type blue and green beryls. Later Nassau et al. (1976), with the help of optical absorption studies discerned that the deep blue colour in Maxixe type beryls is due to presence of some colour centre species. Edgar and Vance (1977) using EPR, OA and Magnetic circular dichroism studies deciphered the above colour centre species to be CO_3^- radical impurity in Maxixe type blue beryls. Subsequently Anderson (1979) also carried out EPR studies and deduced that, blue colour in Maxixe beryls is due to presence of NO_3 impurity and blue in Maxixe type beryls is due to CO_3^- free radical impurity. Thus the above authors distinguished two types of blue beryls from Maxixe Mine, Brazil based on presence of colour centres, (i) Maxixe beryls characterised by presence of NO_3 impurity produced by natural irradiation of NO_3^- and (ii) Maxixe type blue beryls formed artificial irradiation and characterised by the presence of CO_3^- impurity resulted from CO_3^{2-}. Parkin et al. (1976) carried out Mossbauer spectroscopic studies on several blue coloured gems minerals including aquamarine; he attributed blue colour in aquamarine to charge transfer (CT) process between adjacent Fe^{2+} and Fe^{3+} cations. Later Price et al. (1976) also carried out similar studies on beryls.

Blak et al.1982, worked on Brazilian blue and green beryl using ESR and optical absorption studies. Isotani et al. in the year 1989, conducted line shaped and thermal kinetic analysis of the Fe^{2+} band in Brazilian green beryl and showed that Fe^{2+} in channel site contains two orientations. Nassau (1984) and later its second edition in 1994 wrote an exclusive book on 'Gemstone Enhancement" He documents various colour enhancement techniques applied to beryl and the reaction to the same. Panjikar (1995) carried out optical absorption studies on beryls from various localities and concluded that, blue beryls from Orissa reveal absorption bands at $12{,}000 cm^{-1}$ ($\parallel c$) and at $12{,}000 cm^{-1}$ ($\perp c$), attributed to bivalent iron in tetrahedral and octahedral site.

Thus it is apparent that a considerable amount of work has already been carried out in various aspects. However, detailed studies on Indian beryls are lacking. The present thesis address the spectroscopic characterisation of beryl with particular reference to Orissan beryls.