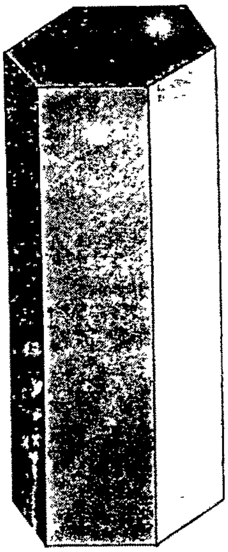

Chapter - 7

Conclusions

7 - CONCLUSIONS

Above studies on gem varieties of beryls from Orissa reflect on , i) environment at the time of growth, (ii) structure, (iii) composition, (iv) volatile constituents, (v) cause of colour and (iv) safer method of enhancing colour of beryls.

Based on these studies following conclusions have been drawn by the author.

7.1 CHEMICAL COMPOSITION

As discussed in chapter 3, chemical analysis of beryls from Orissa and Tamil Nadu indicate them to be of alkali poor type ($R_2O < 5\%$), while, beryls from Bihar, Andhra Pradesh and Kerala indicates presence of high sodium content. Thus beryls of India appear to belongs to two distinct populations in regard to alkali content.

7.2 SURFACE MICROTOPOGRAPHICAL STUDIES

Studies and discussions in chapter 4 have disclosed following facts:

1 Majority of crystals grow by two-dimensional nucleation (2DNG) or Kossel - Stranski Volmer mechanism, spreading and piling up of growth layers and also by spiral growth mechanism or BCF (Burton - Caberra - Frank) mechanism (Sunagawa, 1984).

2 Hexagonal growth layers (dihexagonal dipyramid of second order and basal pinacoid) seem to initiate growth layer, atleast in early stages of growth.

3 In the later stages of growth rhombus shaped growth layers (only hexagonal dipyramid of second order) are observed.

4. Extremely tiny hexagonal shaped and rhombus shaped shallow one layered growth hillocks are observed Presence of growth hillocks suggests independent growth takes place on prism faces of natural beryl crystal. Dense population of growth hillock is attributed to extensive nucleation.
5. Crowded etch pits are due to densely populated defects, atleast in certain cases.
6. Intergrowth patterns indicate presence of densely populated growth hillocks and growth pyramids.

7.3 SPECTROSCOPIC STUDIES

Spectroscopic investigation using FT-IR, Raman, ESR, OA and Mossbauer studies (chapter 5 & 6) discerns the usefulness of employing the spectroscopic techniques in deciphering the various structural details of a mineral, which a simple X-ray diffraction is not able to provide.

7.3.1 VIBRATIONAL SPECTROSCOPIC STUDIES (IR and Raman)

1) Beryls of Badmal mines of Orissa is a combination of tetrahedral and octahedral type substitution. Incorporation of major proportion of Lithium in colourless beryl indicates, that they probably have formed in the lepidolite zone of the zoned pegmatite, while other coloured beryls are formed in the zones poor in Lithium mica.
2) Beryls from a single locality may have different c/a ratio or type of substitution and therefore, such study calls for caution of analysing all coloured beryls before arriving at a generalised conclusion on the type of substitutions in beryl. From the normal FT-IR spectra, the beryls of Orissa appear to be of 'octahderally substituted' type; however, on deconvolution reveals them to be 'tetrahedrally' or 'normally' substituted. Thus deconvolution studies on normal FT-IR spectra provide further

improved resolution of infrared spectra. This again coupled with low temperature studies would provide greater insight on the type of substitutions in beryl. The present extended study also reveals that TN, Kerala, Bihar and Siberian beryls show more of 'normal type', while Brazilian beryls are purely 'octahedral'.

3) Studies on volatile constituents reveal presence of H_2O and CO_2 in the structural channels of beryl crystals, which reflect the volatile constituents of parent melts. Since CO_2 often acts as diluant which inturn lowers water activity and generates anhydrous conditions in magmatic and metamorphic environments. Dominant presence of type - II H_2O indicates considerable proportion of alkalis occupying channel site. However, as evidenced from chemical analysis it does not indicate that beryls from Orissa to be of high alkaline affinity. Thus, a majority of the available alkalis in these beryls have occupied channels, but not the substitutional sites. The low alkali content in these beryls indicates that they might have been precipitated from acidic fluids. The wide range of compositional variation displayed by beryls from various geological settings is a consequence of alkalis and structural water, which have profound effect on the stability of the mineral.

7.3.2 COLOUR

Spectroscopic investigation using ESR, OA and Mossbauer studies reveals that although colourless beryl contains appreciable concentration of paramagnetic ions; but are they are not occupying the colour producing sites. However, on artificial irradiation using electron beam accelerators, the colourless beryl from Orissa transforms to green and yellowish orange colours. On heating to 300 °C, the above green colour transforms to yellow, and on further heating to 400 °C renders them blue hue. The present blue shade obtained from colourless beryl (*plates 6.2a & 6.2b*) is almost of the same hue as the natural blue beryl. Thus the present study by the author indicates the importance of gem enhancement in elevating the colour of uncoloured or feebly coloured stones to more desirable blue ones and thus increasing demand in the market.

Spectroscopic investigation on irradiated (colourless) beryl reveals that they are on account of the formation of defect centre (Maxixe type) and radiational oxidation of Fe^{2+} ion at octahedral Al site and associated ultraviolet charge transfer process. One heating to 300 °C, the defect centres decay resulting in the loss of blue hue and thus rendering beryl yellow colour. On further heating at controlled conditions to 400 °C results in pale blue hue in beryl. This is because at 300 °C blue hue due to defect centre disappears and on controlled heating to 400 °C, due to the oxidation - reduction phenomena of Fe ion facilitates intervalence charge transfer between Fe^{2+} and Fe^{3+} ion and thus once again renders blue colour. Subsequent heating to higher temperatures (> 500 °C) results in reduction of Fe^{3+} at Al site to Fe^{2+} and associate retreat of UVCT to shorter wavelength. This results in again colourless shade to beryl.

Blue colour in beryls is on account of intervalence charge transfer process of electron from Fe^{2+} to Fe^{3+} (metal - metal) ion. The presence of broad band in the region of VIS - NIR along *e* -ray in blue beryls indicates that the charge transfer vectors lies in the plane E||*c*. Broadness of band is due to the combination of Fe^{2+} crystal field transition and IVCT process. The charge transfer transitions occur in mineral spectra together with crystal field transition (Smith, 1978). The energy of a charge transfer process is related to the ionization potential of the donor cation (Fe^{2+}) and electron affinity of the acceptor cation (Fe^{3+}). These charge transfers in silicates results from metal - metal bonding acrossed shared polyhedral edges . The bonding results from the overlap of Fe^{2+} (t_{2g}) and Fe^{3+} (t_{2g}) d - orbitals (Sherman, 1987). Large half widths of the order of 300 - 2000 cm^{-1}

(Smith and Strens, 1976) are generally considered as the most reliable characteristic of charge transfer transition (Mattinson & Robinson, 1987).

Present study by the author elucidates that the presence of Fe^{2+} ion alone in channel site, as advocated by Nassau (1994) for blue colour in beryl, does not seem to be true The Fe^{3+} ion involved the charge transfer could be occupying a site near to the Al site; probably an interstitial or tetrahedral site, although presence of tetrahedral Fe^{3+} ($g =$ 4 3) is discerned in the ESR spectra, however, was not able be discerned in the optical and Mossbauer spectra, because of low concentration.

The yellow colour in beryl is on account of the presence of sufficient amount of Fe^{3+} ion (> 30%of the total iron) in octahedral Al site and the resulting ultraviolet charge transfer process between Fe^{3+} and its O^{2-} ligand.

Green hue in beryl is due to the combination of yellow due to UVCT and blue due to IVCT. On heating above 400 °C, Fe^{3+} ions at octahedral Al site reduce to Fe^{2+} ion and thus loses its yellow hue, leaving behind in blue colour in beryl.

The energy of the electron beam applied to enhance the colour of beryl is hardly 1.7 Mev, and therefore chances for induced radioactivity (> 8.0 Mev, induce radioactivity; R S Deshpande, BARC, personal comm.) does not arise. *Such enhanced stone thus can be safely used in the jewellery.*

It is quite possible that various shades of green and yellowish -orange beryl may have formed in nature from colourless beryl are due to natural irradiation during the course of geological time and subsequent heating of the host body might have resulted in the development of various shades of colour in beryl.