CHAPTER 7

CONCLUSION

7.1 TL GLOW CURVES OF NATURAL ZIRCON

From the present studies it is found that natural TL of zircon is related to its colour. No natural TL was observed in green and dark green zircons while other samples showed a broad peak around 235°C and gamma irradiation of samples induced another peak around 130°C. The different colours of the samples are due to the differences in the alpha activity of the samples. As the colour of the sample becomes darker, their natural TL and TL sensitivity decreases. The absence of NTL in dark samples seems to be due to their metamictization caused by high alpha activity of the samples. The artificial TL glow curve of zircon sand, separated from the sands on the beaches of Kerala, consists of a sharp peak at 100°C and beyond that the TL is a broad glow peak covering the whole temperature range upto 400°C. This broad peak seems to be a combination of a number of overlapping peaks very close to each other.

7.2 RESOLUTION OF GLOW PEAKS AND THEIR KINETICS AND TRAPPING PARAMETERS

The TL glow curve of natural zircon from Kerala beach sand was resolved in the present investigations. Hoogenstratens (1953) thermal cleaning technique was used to resolve the glow peaks from room temperature to 400°C. Six glow peaks could be
resolved at temperatures 115°C, 155°C, 195°C, 255°C, 325°C and 380°C.

TL kinetics of zircons, studied in the present investigation, by glow peak shape method indicate that the TL peaks in zircon follow second order kinetics.

The trapping parameters $E$ and $\beta$ for multipeaks of zircon have been calculated by 'initial rise method' and 'glow peak shape method'. The $E$ values for the TL glow peaks (except for I peak) calculated by glow peak shape method are found to be less than the values calculated by initial rise method. The reason for this difference remains yet to be discerned.

The $E$ values increase with the increasing values of peak temperature. In a plot of $E$ values, calculated by initial rise method, against peak temperature, most of the points fall on a straight line given by the equation

$$E = \frac{T - 101}{344}$$

7.3 RADIATION EFFECT

The TL intensity of zircon increases with increasing gamma dose. In all the zircon samples, after a gamma dose of $2.4 \times 10^6$ rads, the TL emission reaches saturation, the magnitude of which seems to depend on the present alpha activity, i.e., the natural radiation damage suffered by the samples.

7.4 THERMAL TREATMENTS

In the present investigations, the temperature of 950°C, at which the recrystallization of metamict zircon takes
place, was chosen for thermal annealing of the samples. It was observed that the thermal treatment removed the colouration of most of the samples.

The effect of annealing time on the TL emission for various zircon samples shows that the magnitude of change in TL emission and its intensity depend on annealing time as well as the present alpha activity of the samples. The TL emission of the samples with alpha activity greater than 400 alphas/mg-hr show slight change with heating time while the ones with alpha activity less than 300 alpha/mg-hr show a significant change.

The TL intensity of the unheated zircon samples reduces by a factor of about \(10^6\) for the zircon sample with the alpha activity of nearly 400 alphas/mg-hr. With increasing alpha activity the TL intensity remains practically unchanged. The TL intensity of annealed samples substantially increases and this increase seems to be clearly a function of alpha activity of the zircon samples. The increase in TL emission could be more clearly indicated by plotting the TL ratio after and before annealing against the present activity of the samples. The maximum TL ratio (TLR maximum) occurs for the present alpha activity of about 100 alphas/mg-hr and approaches nearly unity around 2000 alphas/mg-hr. For the samples with low values of present alpha activity, it seems that the TL ratio increases very fast with low alpha activity.

From above observations it can be shown that the restoration of TL after annealing is dependent on the concentration of defects created by the alpha recoil nucleus event produced by decay of the radioactive impurities contained in the crystal
structure of zircon, as shown by Vaz and Gentile (1971). If it is assumed that the TL emission before heating is contributed by undamaged zircon (Zi), whereas the TL emission after heating is contributed both by undamaged zircon, as well as, the reconstituted expanded zircon phase (Zd), then the normalized TL ratio (TLr) for zircon with any value of alpha activity can be represented by:

\[
\text{TL}_r = \frac{\text{TL}_\text{exp}}{\text{TL}_\text{max}} = Zi + Zd
\]

From this equation, one can calculate the fraction of the phase that is restored by heating the undamaged zircon as a function of alpha activity. Thus, \((\text{TL}_r - Zi)\) gives a curve which matches the one obtained by Pellas for expanded zircon Zd.

It is thus clear that the heat treatment of zircons at 950°C for more than 20 hours restores the expanded zircon phase, produced by action of the alpha-recoil nucleus, to normal zircon Zi. Also, the TL ratio curve represents the relative amount of damaged zircon recovered by thermal treatment. Therefore, the non-recoverable fraction should be given by the reciprocal of the normalized TL ratio (TLr) curve. This also matches the one obtained by Pellas by adding the concentrations of the phases Zr (amorphous zircon), Zs (SiO2), and Zz (ZrO2).

The enhancement of the TL emission on thermal treatment of zircon samples is also alpha activity dependent and is due to the recovery of the deformed zircon fraction to normal zircon. This proves that higher alpha activity i.e., extent of neutronization is the reason for lowering of the sintering point of the zircon sands.
The results of DTA show a distinct variation between the different zircons and the netanict varieties. A sharp exothermic peak at 350°C is noticed for green zircons. In general all the zircons show some indication of an exothermic change at 350°C, the minimum being shown by yellow zircon sample. This peak may be due to some structural crystallization, which is confirmed by the fact that this reaction is negligible for pink and yellow varieties of zircons which have very low alpha activity. Also, previously heated samples did not show this reaction.

Visual examination of the samples after DTA tests i.e., after being heated to 1300°C, showed that brown, light green and dark green varieties of zircons were completely fused (sintered into hard lumps); brownish yellow zircon showed slight fusion whereas pink and light yellow zircons remained absolutely unaffected indicating thereby the stability of the samples with low alpha activity. This is further confirmed by the results of sintering tests as the pink and light yellow zircons did not sinter at the maximum temperature of 1350°C attained in the furnace, whereas, green zircon showed sintering at around 1250°C.

From the present investigations unsuitability of some zircon sands, due to their higher alpha activity, for industrial use is clearly borne out.

7.5 SPECTRAL CHARACTERISTICS

The TL spectrum of gamma irradiated zircon consists of many emission bands. It was interesting to note that though the TL glow curve of natural sample was different from the heated sample, the TL spectrum in each case was observed to be the same.
The only difference was in the intensity due to the sensitization after heating the sample.

A broad continuous band at 340 nm in the TL spectra of natural zircon at 100°C seems to be an emission of the host lattice. The same emission band has been reported by Incacci et al. (1980 a,b) in the TL spectra of synthetic zircons at temperatures ranging from 0°K to 350°K.

For temperatures higher than 100°C, it seems that the TL peak positions are dependent on the nature of activators. The TL spectrum of these peaks was found to be similar to that of $\text{ZrSiO}_4 : \text{Tb}^{3+}$. The emission at high temperatures in natural zircons can thus be attributed to $\text{Tb}^{3+}$ ions which enter the lattice replacing $\text{Zr}^{4+}$. During irradiation $\text{Tb}^{3+}$ reduces to $\text{Tb}^{2+}$ by capturing an electron which is ejected from the highest filled orbital of a neighbouring oxygen. By heating the sample, recombination of the electron centre $\text{Tb}^{2+}$ with a hole centre gives rise to the formation of an excited state ($\text{Tb}^{3+}$)\(^*\) which is transformed into ground state with $\text{Tb}^{3+}$ characteristic emission. The different TL peaks are due to different types of hole traps which have been formed along with the defects associated with $\text{SiO}_4^{4-}$ groups such as oxygen vacancies localized in the immediate vicinity of $\text{Tb}^{3+}$ centres.

Further investigations are necessary to reason out the difference in the trapping parameter $\tau$ as calculated by various techniques.