CHAPTER V

RESULTS AND

DISCUSSION
SECTION - A

THERMOLUMINESCENCE
A. THERMOLUMINESCENCE

It is generally accepted that no crystal, either natural or synthetic, is perfect in all respects. Certain number of inherent defects exist in the crystal which in the case of alkali halides primarily consist of cation and anion vacancies. It is believed that impurities, unavoidably present or deliberately incorporated, mainly occupy substitutional positions at alkali ion sites in the alkali halide crystal\textsuperscript{43,44}. When a multivalent impurity like Tb\textsuperscript{3+} is intentionally introduced in a monovalent crystal such as NaCl, the extra positive charge of the impurity ion will give rise to electrical imbalance in the crystal. Since the crystal as a whole should be electrically neutral, equal number of negatively charged defects must be produced in the crystal. This requirement is satisfied by the generation of positive ion or cation vacancies which can be formed with ease in alkali halides. If the impurity is divalent in nature, the divalent cations and cation vacancies exist in the crystal (i) independent of each other as free vacancies and free divalent ions ; (ii) associated in pairs to form dipoles ; or (iii) associated together in higher aggregates than pairs. All these entities have been observed in alkali halides containing divalent impurity. Because of the excess positive charge on the impurity ion and the negative charge at cation vacancy there is coulombic attraction between them which forms impurity-vacancy (I-V) pair. The I-V pair is viewed as an electric dipole. It has been reported that at room temperature a major fraction of the divalent cation and cation vacancy is present in the form of dipoles\textsuperscript{45-50}. 
The experimental work in the fields of ionic conductivity, dielectric loss, diffusion, optical coloration, and spin resonance has also confirmed close association between divalent cation and cation vacancy leading to the formation of electric dipoles.

Survey of the literature shows that in alkali halide crystals certain rare earth impurities like Eu$^{3+}$, exist in the divalent state rather than in the trivalent state. This premise is corroborated by the studies of thermoluminescence and optical absorption of Samarium (Sm$^{3+}$) doped NaCl. It was found that doping of NaCl with Sm$^{3+}$ produces Z-centres. Since divalent impurity is an integral part of the Z-centres, it is concluded that Samarium (Sm$^{3+}$) is incorporated into the alkali halide lattice in the divalent state i.e. as Sm$^{2+}$. In the present analysis it is therefore presumed that Terbium (Tb$^{3+}$) impurity enters the base material (NaCl) as Tb$^{2+}$ ions.

Thermal glow curves of Terbium doped sodium chloride specimens obtained by crystallization from aqueous solutions were examined in as-received condition and after thermal pretreatments. The effect of the variation in the Tb content of the specimen on the glow curves was also studied. The data presented also include the study of the influence on the glow curves with the change in the nature of the exciting radiation. The radiations used were beta rays from $^{90}$Sr source and gamma rays from $^{60}$Co source. The glow
curves were recorded in the temperature range 30 to 400°C and were tested for their reproducibility. Typical glow curves obtained in the measurements are presented for discussion. Following the usual practice, each peak in the TL glow curve is specified by the temperature at which it appears. It may be noted that the shape of the glow curve depends on the impurity concentration, pretreatments of the specimen etc. Hence the resolution of a peak and its position on the temperature scale are influenced by these factors. For instance, when a subsidiary peak develops in the neighbourhood of a principal glow peak, changes in the relative intensities of the components results in slight variation in the position of the principal peak. In this respect, the assignment of a particular temperature to a glow peak may appear somewhat arbitrary. In spite of this the temperatures assigned to the peak are typical and these have been used to identify the glow peaks. The glow peaks recorded in the present measurements appear at 90, 140, 200-240 region and 340°C. Out of these the glow peak at 240°C was found to have wide shift in its position and hence wherever necessary it is identified by the temperature at which it actually appears. The TL output in the glow curve measurement is indicated in amperes.

According to manufacturer's data the base material (NaCl) used contains intrinsic background impurity, major part of which is divalent impurity of Ca-group and Mg. The role of inherently present impurity in the glow curve cannot therefore be overlooked. The data presented below include thermal glow curves of "pure" or undoped NaCl alongwith NaCl:Tb specimens.
Figures : 1 and 2

Thermal glow curves of undoped NaCl specimens in as-received condition after crystallization from aqueous solution and after thermal pretreatments are presented in Figs. 1 and 2. The thermal pretreatment involved annealing and quenching from 500 and 750°C. It is seen from the data that all the specimens exhibit two well resolved glow peaks at 90 and 240°C. Each specimen was subjected to thermal cycling in which it was irradiated at room temperature, heated to around 400°C with uniform heating rate and then cooled to room temperature under ambient conditions. The same was repeated in successive thermal cycles. It is well discernible that 90°C peak is favoured if the specimen is studied in as-received condition from aqueous solution. Whereas thermal pretreatment preferentially enhances the strength of 240°C peak. Microcrystals or crystallites grown from solution will more or less behave like slowly cooled crystals with controlled number of imperfections. On the other hand, annealed and quenched microcrystals will have "squeezed-in" vacancies and also dislocations due to thermal strains.

From the earlier studies 5,61,62 with reference to correlation of the annealing of colour centres with thermoluminescence it was concluded that in heavily X-irradiated alkali halides the F centres play the role of recombination centres. The mobile entity is presumed to be the interstitial and not the F centre electron. On the other hand Gartia et al 63 proposed that F
electrons might be the mobile carriers and V centres are the recombination centres. Since the glow peaks occur at the same temperature in both the cases it is not possible to discriminate between the "electron" and "hole" peaks. One possibility could be that the background impurity ion acts as an emission centre probably because electron-hole recombination takes place in its neighbourhood.

The above given data concerning undoped NaCl clearly indicate that 90°C peak is the property of the crystallinity or perfect regions of the lattice whereas 240°C peak is the characteristic of the disturbed or strained regions of the lattice. Changes in the intensities of the two peaks due to thermal cycling are ascribed to rearrangement in the defect pattern of the specimen as a result of heating.

Figures : 3 - 6

Figs. 3 - 6 represent the experimental data for Terbium (Tb) doped NaCl specimens in which Tb concentration was varied from 100 to 1000 ppm. All the specimens were prepared by crystallization from solutions. It is of significance to note that glow curve shape of doped specimens is different from that of undoped specimen (compare Fig.1 with Figs. 3-6). Firstly, at lower Tb concentration, the intensity of 240°C peak is higher than 90°C peak (Figs. 3 & 4) or the growth induced by thermal cycling preferentially favours 240°C peak (Figs. 5 & 6). In this respect the TL behaviour of doped
specimen is opposite to the one shown by undoped specimen. Secondly, there is in general more TL emission under 240°C peak and in the temperature region above in the case of doped specimen. This is mainly observed in the first thermal cycle. Such a behaviour is conspicuous by its absence in the glow curve of undoped specimen. Thirdly, the glow peak appearing on the higher temperature side around 340°C in the glow curve of doped specimen in the first thermal cycle is erased in the second and subsequent thermal cycles. No such feature is observed in undoped specimen.

Thus, in spite of the occurrence of the two glow peaks at 90 and 240°C being in common with Tb doped and undoped NaCl specimens, the above mentioned differences clearly indicate that the incorporation of Tb impurity influences the glow curve pattern. In other words, Tb impurity has some role in the thermoluminescent behaviour of NaCl:Tb specimen.

Figures : 7 and 8

Figure 7 represents the data for NaCl:Tb specimens in which Tb concentration was varied from 2 mg to 30 mg. The specimens were annealed and quenched from 750°C, after crystallisation from solution, and were subjected to beta dose of 350 Rad. The intensity of the principal dominant glow peak at 200°C is plotted as a function of Tb concentration in Figure 8. It is clearly seen that there is consistent increase in the strength of 200°C peak with Tb concentration which reaches saturation after 10 mg concentration. The data presented obviously demonstrate that glow curve of Tb doped
NaCl markedly differs from the corresponding glow curve for undoped NaCl.

Figures : 9 - 12

One batch of Tb doped specimens prepared by crystallisation from solution was subjected to thermal treatment in which the specimen was annealed at 500°C for two hours and then quenched to room temperature. Figs. 9 through 12 represent the glow curves for such thermally pretreated specimens of varying Tb concentration. The noteworthy features observed in the data are as follows :

(i) At lowest Tb concentration (100 ppm; Fig. 9) there is a broad and diffuse emission with maximum around 340°C in the first heating run. In the second and subsequent heating runs the emission at 340°C disappears and instead a weaker emission at 275°C appears.

(ii) With the increase in Tb concentration (200 ppm and above; Figs. 10 - 12) the glow curves exhibit peak around 340°C along with peaks at 90 and 240°C in the first thermal cycle. The 340°C peak is obliterated and the emission under 240°C peak selectively gains in strength in the subsequent thermal cycles.

(iii) In all the cases the 90°C peak remains subdued.

Figures : 13 - 16

Another batch of doped specimens as-obtained from aqueous
solutions, containing different amount of Tb impurity, was annealed near the melting point (750°C) for two hours and then quenched to room temperature. The glow curve shapes for these specimens are more or less similar to the corresponding curves for the specimens quenched from 500°C except of course, enhanced TL emission for specimens quenched from 750°C.

Figures : 17 - 19

In yet another series of experiments, the thermal glow curves for doped and undoped NaCl specimens, untreated and thermally pretreated, were recorded using gamma radiation. The geometry of the experimental set-up and other experimental conditions were the same as in the case of beta irradiation. The results obtained are presented in Figs. 17-19. In all the cases the gamma dose used was 800 Rad. The data concerning thermal cycling on the shape of the glow curves induced by exposure to gamma radiation are identical with those produced by beta irradiation and hence they are not reproduced. The differences from beta irradiation are

(i) the occurrence of well resolved peak at 140°C in the case of undoped NaCl and at lower Tb concentration for NaCl:Tb specimens and

(ii) appearance of a peak at 275°C as distinct from 240°C peak at lower Tb concentration (Fig.18).

Figures : 20 and 21

Gamma irradiation of Tb doped specimens annealed at 750°C
and quenched to room temperature gives rise to glow curves in which 240°C peak is the only dominant peak. The emission in the glow curves in the temperature region below 240°C is negligible at lower Tb concentration (Fig. 20) and almost absent at higher Tb concentration.

Figures: 22 and 23

With the experimental conditions during exposure to beta and gamma radiation agreeing in all details, measurements were also made to examine the effect of the variation in the radiation dose in the glow curve shape of NaCl:Tb specimens (Tb concentration 1000 ppm) quenched from 750°C. Each glow curve was recorded with fresh specimen from the same batch of specimens prepared for the study. Comparison of the growth of the peaks in the glow curves induced by beta and gamma irradiation reveals following differences.

<table>
<thead>
<tr>
<th>Beta Irradiation</th>
<th>Gamma Irradiation</th>
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<tbody>
<tr>
<td>(i) Beta irradiated specimen exhibit well resolved peak at 90°C even during initial doses.</td>
<td>(i) In the initial range of dose upto 2400 Rad gamma irradiation does not generate 90°C peak.</td>
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<tr>
<td>(ii) The 90°C peak has growth comparable with 200°C peak in the higher range of doses of beta radiation.</td>
<td>(ii) The 90°C peak appears only at higher gamma doses first as a weak structure on the ascending slope of the 200°C</td>
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peak and later appears well defined only at highest gamma dose.

(iii) 140°C peak in the glow curves of beta irradiated specimens does not show up except as a weak shoulder for highest beta dose.

The 140°C peak appears comparatively well resolved at lower gamma dose.

(iv) For beta dose of 800 Rad the intensity of 200°C peak is of the order of $10^{-6}$ amp. For gamma dose of the same magnitude the intensity of 200°C peak is around $10^{-5}$ amp. i.e. one order higher.

For gamma dose of the same magnitude the intensity of 200°C peak is around $10^{-5}$ amp. i.e. one order higher.

**Figure : 24**

The data presented in Fig. 24 concerns with the examination of the variation of the TL output of NaCl:Tb phosphor exposed to different doses of beta and gamma radiation (Ref. Figs. 22 and 23). It is clearly seen that in both the cases the TL response is linear in the dose range upto $10^3$ Rad beyond which it becomes supralinear.

**Figure : 25**

The data in Fig. 25 demonstrates that after the initial decay the TL output of NaCl:Tb phosphor nearly remains constant over a duration of few weeks. In other words the fading of TL is negligible.
The results presented in Figs. 26 and 27 pertain to the comparison of TL output of standard TLD material (LiF TLD-100) with the TL output of NaCl:Tb. It is observed that the output of NaCl:Tb phosphor is comparable with the standard material in the case of both beta and gamma irradiation.

Measurements were carried out for the evaluation of the activation energy for 200°C peak exhibited by NaCl:Tb phosphor. The related data namely, (i) the glow curve obtained after irradiation with gamma dose followed by annealing at 167°C for 30 minutes, and (ii) the Arrhenious plot for initial rising part of 200°C peak are presented in Figs. 28 and 29 respectively. The activation energy calculated using above mentioned data was found to be 1.3 ev.

Figs. 30 and 31 represent the data used for determining the order of kinetics using isothermal decay of 200°C glow peak after an exposure of NaCl:Tb phosphor to 800 Rad gamma radiation at 147°C temperature. In the present case the thermoluminescence process is found to be of second order.

In what follows an attempt is made on the basis of the qualitative reasoning to propose models for the TL centres.
associated with the observed glow peaks. As mentioned in the beginning, there is experimental evidence to suggest that Tb\(^{3+}\) ions enter alkali halide lattice in the divalent state i.e. as Tb\(^{2+}\) ions. From the studies of divalent impurity doped alkali halides it is well established that a major fraction of the impurity is involved in the formation of Impurity-Vacancy dipoles. Based on this concept it is therefore presumed that the Tb impurity in NaCl lattice exists mainly as Tb\(^{2+}\) ion-cation vacancy dipoles.

Data presented in Figs.3 to 6 for NaCl:Tb specimens, prepared by crystallization from aqueous solutions, studied in as-received condition show the occurrence of 340°C peak in the first thermal cycle and its erasure in the following cycle. The obliteration of 340°C peak at the end of the first heating run clearly indicates that the TL centres associated with the peak consist of some kind of defect aggregates which break up during heating. It is reported in the literature that dipoles have tendency to aggregate, three together, to form metastable clusters called trimmers. However, such clusters are known to be thermally stable upto 100°C and hence the association of trimmers with 340°C peak is ruled out. It is proposed that the metastable aggregate associated with 340°C peak may be collection together of impurity ions, dipoles and vacancies in which the constituents are loosely bound. The enhancement in the intensities of 90 and 240°C peaks in the following thermal
cycles is believed to be due to utilization of the constituents freed from such clusters in the generation of the centres responsible for 90 and 240°C peaks. As can be seen from the data, there is of course, no one-to-one correspondence between the suppression of 340°C peak and the consequential enhancement of 90 and 240°C peaks. It is possible that besides aggregates giving luminescence at 340°C other types of metastable aggregates which are non-luminescent may also be involved in the process.

The results presented in Figs. 5 and 6 indicate that the strength of 90°C peak relative to 240°C peak is higher in the first cycle. In the subsequent cycles the growth of 240°C peak is favoured. The specimens examined are in as-received condition obtained by crystallization from solutions. Such specimens behave more or less like slowly cooled crystals of which the dislocation content is minimised, consisting in this case of grown-in dislocations. Since the growth of 90°C peak attains near saturation in the first heating run, it is presumed that the TL centres associated with this peak are limited in number and are located in the dislocation free or perfect regions of the lattice. In the case of divalent doped alkali halides it is known that only a small fraction of the impurity is available as single or isolated ions whereas a major fraction is involved in the formation of dipoles. Isolated or single Tb$^{2+}$ ions situated in the perfect regions are suggested to be responsible for 90°C peak. Besides single Tb$^{2+}$ ions, there is a large number of impurity-vacancy dipoles present in
the volume of the specimen. Because of their asymmetric strain the dipoles are thermally induced during thermal cycling, to diffuse towards dislocation sites and thereby reduce the strain energy. The dipoles in the dislocation regions are presumed to be responsible for 240°C peak.

Another notable feature observed in the given data is the marked shift in the higher temperature peak position from 240°C (at lower Tb Conc.) to 200°C (at higher Tb Conc.). This result can be explained on the basis of the degree of elastic interaction (due to stress field of the dislocation) between the dipole and the dislocation. Since the thermal cycling stimulates the dipoles to move closer to the dislocations, the elastic interaction between the two increases. It is presumed that the position of the 240°C peak is a function of the distance of the dipole from the dislocation. With the decrease in the distance the peak position shifts to lower temperature side. At higher Tb concentration the dipoles in the close neighbourhood or in the vicinity of the dislocations will be more numerous in number. In that case the peak position shifts to 200°C.

It is also seen from the data that 90°C peak also exhibits minor shift in position from 125 to 100°C (Fig.5). This feature can be attributed to the change towards crystallinity of the specimen due to annealing during thermal cycling.

Thus, it is inferred that the 90°C peak is due to single or isolated Tb$^{2+}$ ions located in the perfect regions of the lattice
whereas 240°C peak is associated with the dipoles in the dislocation regions of the lattice.

The specimens, as-received from aqueous solutions, when subjected to thermal treatment, in which they are annealed at 500°C for two hours and then quenched to room temperature, display altogether different thermoluminescence behaviour (Figs. 9-12). Parallelism in this behaviour is observed if instead of 500°C the temperature of quench of the specimen is raised to near melting point namely, 750°C (Figs. 13-16). The data presented demonstrate that in lightly doped thermally quenched specimen (Figs. 9, 10; 13, 14) the thermoluminescence emission during first heating run is mainly in the 340°C region. In the following cycles the TL emission in the 340°C region markedly subsides and a very weak peak at 240°C is discernible. This feature is attributed to the low impurity content in the metastable clusters associated with the 340°C peak. Because of low impurity concentration the break up of the metastable clusters at the end of first heating run does not provide scope for the creation of a sufficient number of dipoles and hence the 240°C peak appears weak. When however, the impurity concentration is high (Figs. 11, 12; 15, 16) the suppression of 340°C glow peak at the end of first heating run is in general followed by selective enhancement in the strength of 240°C peak leaving 90°C peak nearly unaffected. The preferential increase in the intensity of 240°C peak is understandable since the thermal strains produced in the specimen by quenching will result in the increase of its dislocation density. Besides this in heavily doped specimen the dipoles generated after
the disintegration of the metastable clusters will be significant in strength. Such a situation would naturally be conducive to the growth of 240°C peak. Near absence of distortion free regions in the quenched specimen should, as expected, inhibit the growth of 90°C peak.

In order to examine the effect of the nature of the exciting radiation on the shape of the glow curves of NaCl:Tb specimens, the measurements made with beta radiation were repeated for gamma radiation. In general, the results obtained with beta and gamma irradiation are nearly identical. However, the minor differences observed between the two seem to be of significance.

Fig.17 represents the glow curves for undoped NaCl specimens after exposure to gamma dose of 800 Rad. The two principal glow peaks at 90 and 240°C observed with beta irradiation also appear with gamma irradiation. However, there is a weaker peak at 140°C which is conspicuous by its absence in the case of beta irradiation.

The data presented in Figs.18 and 19 concern with the glow curves of gamma irradiated NaCl:Tb specimens in as-received condition obtained by crystallization from aqueous solutions. The occurrence of 140°C peak is very well observable in lightly doped specimens. Besides this there is also a simultaneous appearance of 275°C peak as distinct from 240°C peak when the specimen is lightly doped (Fig.18). When the specimen is heavily doped (Fig.19) the
peaks at 140 and 275°C are not observed. It is presumed that they are overshadowed by the two dominant principal glow peaks at 90 and 240°C.

The TL centres associated with 140°C peak are presumed to be Tb\textsuperscript{2+} ion-cation vacancy pairs or dipoles which, as mentioned earlier, are also supposed to be associated with the 240°C peak. The difference between the two however, is in their environments. The 140°C peak TL centres are supposed to be located in the dislocation free regions as against 240°C TL centres presumed to be situated in the dislocation regions. Because of the asymmetric strain produced in the lattice, basically the dipoles in the dislocation free regions will be limited in number which restricts the growth of 140°C peak.

It is conjectured that the 275°C peak is also a characteristic of the dipoles formed after the break-up of the metastable clusters. However, during migration towards dislocations the motion of these dipoles is arrested on the way by association due to elastic interaction with some crystalline imperfection say, a positive ion vacancy. The diffusion of a dipole in association with a positive ion vacancy becomes a difficult process. Such immobilised entities probably act as 275°C TL centres.

Gamma irradiation of Tb doped specimens annealed at 750°C and quenched to room temperature gives rise to glow curves in which 240°C glow peak is the only dominant one. The TL emission in the
glow curves in the temperature region below 240°C is negligible at lower Tb concentration (Fig. 20) and almost absent at higher Tb concentration (Fig. 21). The specimens in this case are thermally strained and in consequence their dislocation content is high. Most of the dipoles are therefore situated in the dislocation regions which enhances the strength of 240°C peak. The suppression of 90°C peak may be the result of quenching of luminescence due to the presence of other crystalline imperfections such as a pair or a higher aggregate of vacancies in the vicinity of the dipole and also because of near absence of the perfect regions in the lattice.

Glow curves presented in Figs. 22 and 23 respectively correspond to the specimens with 1000 ppm Tb concentration, annealed and quenched from 750°C, after exposure to varying doses of beta and gamma rays. Comparison of the development of peaks in the glow curves of beta and gamma irradiated specimens with dose reveal certain differences which are listed earlier (vide page 58 ). In what follows an attempt is made to offer explanations to the observed differences. The explanations are given in the order the differences are listed on page 58.

(i) The 90°C peak is attributed to the presence of isolated Tb$^{2+}$ ions (Tb$^{3+}$ presumed to be incorporated as Tb$^{2+}$ in NaCl lattice) in the perfect regions of the lattice. Exposure of the specimen to beta radiation produces free electrons and holes which in turn generates F centres (trapped electrons) and Cl° atoms (trapped holes) in the lattice. During warm up the electrons are released
from their traps which then recombine with the holes. When the recombination takes place near the Tb$^{2+}$ ion the excess energy available during recombination is transferred to the Tb$^{2+}$ ion and the ion therefore goes in the excited state. The TL emission at 90°C is believed to take place when the excited Tb$^{2+}$ ions returns to the ground state.

The electron configuration of Tb$^0$ atom is $4f^8 5d^1 6s^2$ i.e. there are two electrons in the 's' state and one electron in the lower 'd' state. The absence of 90°C peak in the glow curves of gamma irradiated specimen at lower doses is ascribed to the ionisation of Tb$^{2+}$ ion and formation of Tb$^{3+}$ ion i.e. electron in the 5d subshell is removed. Being of lesser energy, beta rays are presumed to be incapable of removing the 'd' state electron. Hence in this case the above proposed emission accompanying electron-hole recombination occurs at 90°C during warm up. However, in the case of gamma irradiation heating of the specimen leads to the release of 'd' state electron trapped outside in the lattice and its subsequent return to the Tb$^{3+}$ ion formed due to irradiation. The capture of the electron by Tb$^{3+}$ ion will of course, first generate excited Tb$^{2+}$ ion however, the transition from excited state to ground state appears in this case to be nonluminescent.

(ii) Exposure of the specimen to higher doses of radiation would increase its vacancy concentration. This would facilitate uniform dispersal of the impurity ions and thereby create isolated Tb$^{2+}$ ions more in number in the volume of the specimen. In this situation the
strength of 90°C peak will steadily increase with beta dose.

Higher dose means longer period of exposure of the specimen to the given radiation. In view of this, in the case of gamma irradiation one may expect two competitive processes operating simultaneously during prolonged exposure. In one process the Tb$^{2+}$ ions are ionised to form Tb$^{3+}$ ions and in another the Tb$^{2+}$ ions are reformed. The slow development of 90°C glow peak during gamma irradiation is believed to be due to gradual increase in the number of available Tb$^{2+}$ ions with the increase in its duration.

(iii) The occurrence of well defined peak at 140°C in the glow curves of gamma irradiated specimen at lower dose (8000 Rad) compared to that in the glow curves of beta irradiated specimen substantiates the model presented for 140°C peak. The peak is assumed to be associated with the dipoles in the dislocation free or perfect regions of the lattice. As proposed in the discussion to follow concerning TL mechanism in the occurrence of 140°C peak, the excitation of the 140°C TL centre is presumed to involve the displacement of ion. That is besides electronic an ionic process is also involved in the light emission for which the energy requirement is naturally much higher. Hence gamma irradiation preferentially favours the generation of 140°C peak.

(iv) Exposure of the specimen to the same dose of beta and gamma radiation selectively enhances the strength of 200°C peak
in the glow curves of gamma irradiated specimen. This feature is consistent with the model proposed for the TL centre associated with 200°C glow peak. This peak is presumed to be due to dipoles in the dislocation regions. In this case also the proposed TL mechanism involves ionic displacement and hence higher energy for the excitation of the TL centre. The growth of 200°C peak therefore takes place with comparative ease in the glow curves of gamma irradiated specimen.

The TL mechanism for the occurrence of glow peak at 90°C has been described above. It is proposed that the TL processes involved in the appearance of 140°C and 200°C peak are identical except that the former takes place in the dislocation free regions and the latter in the dislocation regions of the lattice. The Cl⁻ ion in the dislocation free region is properly coordinated with its six nearest neighbour cations. On the other hand, the Cl⁻ ion in the dislocation region (specially near the core) being either weakly bonded with its nearest neighbours or bonded with less than six nearest neighbours or both, is not properly coordinated. It is therefore relatively easy to displace the Cl⁻ ion in the dislocation region than to remove the same in the dislocation free region. In other words, the energy requirement for the removal of Cl⁻ ion from its regular position is higher in the case of 140°C peak than that for 200°C peak.
There is experimental evidence overwhelmingly in favour of interstitial halogen being introduced in some form along with F centres during room temperature irradiation of the alkali halides with ionising radiations. The experimental data suggest that such halogen interstitials are stabilised by forming halogen molecules or molecular ions in association with other crystalline imperfections. It is believed that F centres of different thermal stability act as recombination centres for the holes which are thermally released from traps. In the present case the 140 and 200°C peaks are presumed to have their origin in the same TL process but taking place at different temperatures. The proposed steps in the TL mechanism of 140 and 200°C peak are given below. A schematic diagram representing these steps is presented in Fig. V - 1

(i) Beta or gamma irradiation of the specimen leads to the removal of the electron from the Cl ion adjacent to the cation vacancy of the dipole.

(ii) The resulting Cl atom relaxes into the cation vacancy forming a Cl molecular complex oriented along <100> direction.

(iii) The generated anion vacancy captures an electron released in the lattice during irradiation and forms an F centre.

(iv) Since Cl molecular ion is not stable at room temperature it is presumed to lose an electron (during irradiation) to
Before Irradiation
Tb$^{2+}$ ion-vacancy dipole.

Irradiation

At room Temp.

Two cl$^o$ Atoms (After Removal of Electrons),
Tb$^{3+}$ ion and cation Vacancy

Tb$^{2+}$ ion, cl$_2$ Molecule and two F-centres.

Warm up to 140 or 200°C.

THE SEQUENCE OF STEPS IN THE OCCURENCE
OF 140°C OR 200°C GLOW PEAK.

FIG: Y-1
form a $\text{Cl}_2^o$ molecule and an isolated negative ion vacancy elsewhere in the lattice captures the electron to form another F centre. Thus, the electronic structure of the excited TL centre associated with either 140 or 200°C glow peak consist of $\text{Cl}_2^o$ molecule and two F centres.

(v) The warm up of the specimen thermally releases holes and the resulting electron-hole recombination gives rise to TL emission.
B. USE OF TL OF NaCl:Tb IN RADIATION DOSIMETRY

The preliminary information regarding radiation dosimetry has been presented earlier in Chapter - III. This section concerns with the examination of the NaCl:Tb phosphor as a dosimetry material. The basic conditions that TL phosphor must satisfy for its efficient performance as TLD material are as follows.\textsuperscript{69,70, 77-81}

(i) High TL efficiency and sensitivity,
(ii) High stability,
(iii) High concentration of trapping sites, simple trap distribution and long storage of trapped charges at normal working temperature,
(iv) Freedom from spurious TL and sufficient range of linear TL response,
(v) Matching of the spectral sensitivity of the photo detector with the spectral distribution of luminescence emission,
(vi) Resistance to radiation damage of the trapping centres, the luminescence (or emission) centres and the base material itself,

(vii) Low fading, energy independance, reproducibility, small size and low cost of the material.

The TL characteristics exhibited by Tb$^{3+}$ activated NaCl phosphors prepared under different Physical conditions after exposure to either 350 Rad beta or 800 Rad gamma dose are presented in section - A. The examination of the TL glow curve characteristics of NaCl:Tb clearly indicates that the NaCl:Tb material which is annealed for two hours in air and subsequently quenched to room temperature exhibits dominant and well defined glow peak in the temperature region 200-240°C alongwith weaker peaks at 90 and 340°C after standard dose of 350 Rad beta or 800 Rad gamma radiation given at room temperature (Figs. 9-16 and 20-21). Further, it is found that preheat treated NaCl:Tb with Tb$^{3+}$ concentration 1000 ppm gives very intense TL output only at 200°C (Figs. 12,16 and 21). Hereafter, the 750°C annealed and quenched NaCl:Tb (1000 ppm) specimen is designated as NaCl:Tb(T). Figures 26 and 27 exhibit the TL glow curves of standard dosimeter material, LiF TLD-100 and present material NaCl:Tb (T) under identical experimental conditions after the standard dose of 800 Rad gamma and 700 Rad beta radiations respectively. The comparison of the glow curves of these two specimens conclusively brings out the fact that the TL output of NaCl:Tb (T) around 200°C is comparable with that of
LiF TLD-100. The TL results of CaF$_2$ also corroborate this fact. In other words, the TL sensitivity of the material under examination is suitable for its use in dosimetric applications. This indicates the fulfilment of high TL efficiency and sensitivity, the requirement No.1 of the efficient TLD material. High temperature (200°C) peak suggests the involvement of deep electron traps which ultimately leads to the long storage of trapped charge carriers at normal working temperature. The correlated study of the estimation of activation energy for 200°C peak clearly indicates that the thermal activation energy for the proposed dosimetric peak is around 1.3 eV. (Figs. 28, 29). The energy value is a definite indication of the stability of the glow peak. Thus, the second basic consideration of an efficient TLD material namely, the stability is found to have been satisfied in the present phosphor.

In part A, it is proposed that the TL centre responsible for the occurrence of 200°C peak comprises of Tb impurity-vacancy dipole in the dislocation region. The nature of the glow curve reveals the fact that the trap is single valued and a large number of trapping sites are associated with the creation of this peak. Thus the third requirement enumerated in the list is well satisfied by the NaCl:Tb phosphors.

In the beginning it was believed that the lowest detectable exposure depends on the sensitivity of a material. Later on the dosimetry workers realised that the nature of the detector also
plays a part in deciding the lowest detectable dose. The TL reader used in the present work was highly sensitive, its characteristics being well known. It is believed that TL reader has not put any restrictions in recording even the weakest TL signal emitted by the phosphor. In the present experiments, the dose range extends from $10^1$-10$^4$ Rad. This has resulted in measurable TL signals from the phosphors, which could easily be detected by the TL reader.

Besides this, the black body radiation signals emanating from the sample and heating pan along with the factual TL from material during warm-up have also been found to be important factors in the judgement of the lowest detectable exposure along with sensitivity. TL workers have minimized the recording of incandescence signal, by using hot nitrogen gas. However, they realized that the real TL from phosphor is undetectable in the cases where the black body signals predominate the factual TL from phosphors. Thus, the incandescence signals were found to limit the lowest detectable exposure. Later on it was found that the black body radiation is very negligible below 250°C. The present TLD material exhibits its TL peak around 200°C. This temperature is sufficiently high for the adequate stability, yet low enough to be free from black body radiation during heating. In the cases of TL materials emitting light in the region other than infrared, the black body signal can be reduced by using appropriate optical filters. This has been taken care of in the present TL measurements. Further, the present material exhibited intense TL
emission around 200°C for the working dose $10^1$-$10^4$ Rad (Figs. 22, 23 and 24). The factual TL has therefore always predominated the incandescence. In spite of this the recording of the glow curves was made in nitrogen atmosphere. Hence, the black body radiation disturbance for the detection of the lowest detectable exposure is out of question in the present TL measurements.

It has been established that unirradiated specimen display some signal during read out, known as spurious or non-radiation induced TL. This TL is suggested to be the surface phenomena, most likely caused by mechanical surface effects. It is quite reasonable to believe that whatever TL the phosphor emits is the total sum of the radiation induced TL signal and spurious TL signals. The nonradiation induced TL is higher in powder samples. Like the black body radiation, the high spurious luminescence is found an important factor restricting the lowest detectable exposure. The use of a single-piece dosimeter material and/or readout in an inert atmosphere such as nitrogen have been found to alleviate the contribution of spurious TL signals in total TL output. The TL measurements for NaCl:Tb (T) specimens were carried out in nitrogen atmosphere which eliminates the spurious TL from the sample. On the other hand great care was taken in handling and preserving the samples during its use so as to be free from any mechanical deformation induced spurious TL.

The special property of the material that made it useful in TL dosimetry is the exact and precise relationship between the TL
output and the incident exposure (dose). The standard TL dosimeter materials namely, LiF and CaF$_2$, normally exhibit a linear TL response at low radiation exposures. LiF TLD-100 has a supralinear TL response for radiation dose greater than $10^3$ Rad, while CaF$_2$ exhibits this for dose greater than $10^5$ Rad. The TL glow curves of the present material have been examined after irradiating it at room temperature by the doses in the range $10^1$-$10^4$ Rad. The glow curves exhibited by the specimen are presented in Figs. 22 and 23. The TL dose responses (the TL output versus the dose in Rad) are given in Fig. 24. It is clear that the TL dose response is supralinear after $10^3$ Rad. This helps in establishing the relationship between the signal magnitude and the exposure. The TL response is found to be linear. One should recall that the dose estimation through the response of optical density of photographic film versus exposure (dose) does not have this advantage at some of the exposures. Film opacity stops growing soon after the dose of about 10 Rad. The another quality of the film (its high exposure performance) if improved upon can cover the range up to $10^3$ Rad however, it is very costly. In other words the linear or sublinear optical density dose response has been found in limited range of dose. Besides this, the reusability of the film is doubtful once it is exposed. It is interesting to note that the TL dose response of the presently proposed TLD material covers the large dose range of $10^1$-$10^3$ Rad like other TLD materials in use. The present material gives linear TL response up to $10^3$ Rad (Figs. 22, 23, 24), which is high enough to cover most of the exposures of interest to radiation users. The above discussion provides an additional support in the consideration
of the NaCl:Tb (T) phosphor as an efficient TLD material (fulfilment of requirement No. iv).

The materials which are in general use presently namely, LiF and Li₂B₄O₇, display their characteristic TL emissions in blue and yellow regions respectively. For recording the yellow light emission efficiently, it is customary to select and optimise the photomultiplier which senses the other emissions too. In such a case the detector may not register blue light very well. The photomultiplier tube (PMT) detector being more sensitive to one colour than other, the two phosphors, LiF and Li₂B₄O₇ releasing same magnitude of signal, may show different intensities of light received from them. This relates to the another interfering influence in the detection of the TL output and thereby the dose. The sensitivity of the TL dosimeter depends on the matching of the wavelength region of the TL emission and the sensitive region of the spectral response of the detector.

For the selection of an efficient TLD material, stability, sensitivity and freedom from spurious signals are not the only requirement. The energy dependence or the tissue equivalence is the another point to be examined precisely. The number of photons absorbed in a given material depends on the incident energy. Further, the experiences of the Health Physicists and Radiologists have revealed that the most convenient dosimeter is the one which absorbs radiation similar to a tissue. For the determination of the dose of radiations of high or low energy, the energy response of the
phosphor must be considered for the proper estimation of exposure. Unfortunately, the energy dependence characteristics of the present material could not be examined systematically because of limited experimental facilities available. However, in a future programme, it is proposed to examine the energy response of the present dosimetric material with requisite experimental facilities available in other laboratory.

The additional complications that have been considered in certain materials are the supralinear responses. The responses of the TL dosimeters to ionizing radiations have been examined and reported by many investigators$^{73}$. It has been established that under irradiation by low LET (Linear Energy Transfer) radiations such as gamma or beta rays, TLDs typically exhibit a linear response at low dose levels, and supralinear response at high doses. The linear component has been found to occur at exposures from $1$ to $10^3$ Rad. Usually above 500 Rad many dosimeters lose their linear response and become supralinear. However, it has been realised that the dose at which the response changes to supralinearity depends on the crystal, type of impurity doped, its annealing and irradiation history. Moreover, the degree of supralinearity itself be found energy dependent as well as dependent on the type of radiation$^{35,74}$. Further, it is known that the responses of most of the dosimeters stop growing at a certain dose. Such a situation is often observed at exposures in the neighbourhood of $10^5$-$10^6$ Rad. Hence at such high exposures, special dosimetry techniques have been used. It is found that the supralinear response in some of the crystals
disappears after annealing. Since the supralinear response is a special characteristics of high temperature peaks the supralinear response observed in the present material is believed to be due to peak 200°C appearing at high temperature. The work is in progress to find a suitable treatment which may improve the supralinear part.

Along with the stability, sensitivity, spurious signals and energy dependence the resistance to radiation damage is one more necessary requirement. A previous history of high exposure, makes the dosimeter unusable for further estimation work. In some materials, high exposures change their subsequent sensitivity, usually a reduction is observed. In such a case, the dosimeter is said to have suffered the radiation damage. This creates some permanent changes in the defect pattern which alters its TL behaviour. Figs. 22 and 23 indicate no shift in the position of 200°C peak with increase in dose. Therefore the TL phosphor under study is said to be resistive to radiation damage. It is possible that in case any changes in the NaCl:Tb (T) lattice occur due to high exposure, the same are removed due to annealing during thermal cycling to which the phosphor is subjected for TL glow curve measurement. In thermal cycling the material is warmed after the exposure with the uniform rate of heating upto 400°C and then cooled rapidly to room temperature. It is believed that the successive recording of TL brings the specimen back to its original pre-irradiation state by removing the radiation damage if any, produced by high exposures. Thus in the present case the defect pattern
remains unaltered over a wide range of exposure to beta or gamma radiation. This favours the use of NaCl:Tb (Tb) as TLD material (basic requirement No. vi).

Yet another established fact which disqualifies a material for dosimetric applications is the deterioration of the TL strength of the glow peak with time after the irradiation. This is known as fading and originates from the existence of thermal energy at room temperature. In the present case the NaCl:Tb (Tb) specimens are presumed to generate during heat treatment impurity-vacancy dipoles in the dislocation regions. It is suggested that thermal energy at room temperature is not sufficient to destroy these TL centres. The dipoles in dislocation regions being comparatively stable, the TL centre in the material under investigation will remain unaffected till the specimen is heated to a very high temperature. This would restrict the fading of the proposed dosimetry peak (200°C) in NaCl:Tb (Tb) material at room temperature. The TL output for 200°C peak of irradiated specimens has also been examined after different durations of room temperature decay. The decay time versus TL intensity of 200°C peak is presented in Fig.25. The decay time extends over few days. The results show negligible fading. This fulfils yet another consideration of an efficient TLD material. The examination of the TL glow curves, particularly with respect to 200°C peak of the material being investigated, with different concentrations of Tb impurity (Figs. 7 and 8) confirms that for all the concentrations of Tb impurity, the nature of the glow curves
remains identical. This promises the excellent reproducibility. The other listed conditions namely, desirable shape and size of the specimen, low cost of material and easy availability are additional points which enhance the claim of NaCl:Tb (T) as a dosimetry material. It is therefore proposed that solid state dosimeters prepared from NaCl:Tb (T) material may be useful in the estimation of beta or gamma doses.

The material is of course, hygroscopic and very unstable in most climatic conditions. The system has to be properly insulated from the moisture in the atmosphere. This limitation can be eliminated by shielding the phosphor from direct exposure to atmosphere. This drawback can also be minimised by doping the material with suitable co-activator. The experiments aimed at improving the usability of the system keeping in view this aspect is proposed to be undertaken in this laboratory. It is concluded that the NaCl:Tb (T) can be considered a suitable dosimetry material in the estimation of dose of beta and gamma radiations in the range of $10^1$-$10^3$ Rad.