DISCUSSION

Thermoluminescence (TL) is the thermally stimulated release [in the form of light] of energy stored in a material by previous excitation. The excitation can be achieved by agents like ionizing radiations, UV rays, mechanical stress, chemical reactions etc. At the end of excitation, a material may have some energy stored in it which may be released in the form of light at a latter time only when the material is warmed. [TL should not be confused with incandescence when emission occurs near the melting point of materials.] The phenomenon repeats itself any number of times when the material is subjected to excitation and heating alternately. The TL intensity emitted is strictly proportional to the initial excitation, and it is this aspect which has made a significant impact in various applications.

By far the most sensitive TL materials are the dielectric solids; however, it is a widespread phenomenon and is exhibited by an endless number of materials: Inorganic Crystals, Glasses and Ceramics, Polyethylene and Teflon, certain Biochemicals and Biological materials and so on. Inspite of intense research during the last decade or so, a unified theory of TL has not been evolved, it is impossible to predict the TL behaviour of a material from any amount of physico-chemical specifications of the material. Still, it is amazingly true that the TL technique has yielded practical success in a variety of applications in disciplines such as Radiation Dosimetry, Solid State Physics, Geology, Archaeology, Lunar Science and Forensic Science. Since the research work of the present thesis involves the use of TL of NaF and NaF:K in radiation dosimetry, a brief account of the present understanding of TL in pure and monovalent impurity doped alkali halides and their applications in radiation dosimetry are reviewed separately.

THERMOLUMINESCENCE - STATE OF UNDERSTANDING

The interaction of ionizing radiations with matter leads to various effects, some of which leave memory in the target material. These memory effects can be seen as the after-effects of the irradiation. Thermoluminescence is one of such phenomenon in the insulating solids. TL or more precisely thermally stimulated luminescence is a type of luminescence which is emitted by giving a thermal stimulation to the sample. Any luminescence requires an excitation. In the case of TL, it is usually provided by irradiating the sample with x-rays, or other ionizing radiations, like alpha, beta and gamma rays.

These radiations interact with the matter in the following three ways: (i) photoelectric effect, (ii) compton effect, and (iii) pair production. In photoelectric process X- or gamma photon imparts all its energy to an electron bound to the atom. This energetic electron while moving through the medium pulls out the electrons from the other atoms by exciting electrostatic force. Thus, the primary electron produced in the photoelectric effect produces a large number of free electrons in the medium. In compton effect, an incident photon gives out part of its energy to an electron. The so-called compton electron then produces further large scale ionization in the medium. Pair production is the conversion of a gamma photon of energy larger than 1.02 MeV into a pair of negative and positive electrons. These electrons possess a kinetic energy equal to the difference of the incident photon energy and the rest mass of the electron-positron pair. This electron-positron pair interacts with the medium to produce ionization on large scale. Alpha particle due to its large momentum can cause atomic displacements in addition to the ionization. Fast neutrons too cause atomic displacements.

Thus the effect of incidence of ionizing radiations in insulating solids can be divided into two categories: (i) atomic displacements by energetic heavy ions and by fast neutrons, and (ii) ionization. The metamictization of the mineral crystals by the effect of prolonged alpha irradiation from the primordial radioactivity is a well known effect of the former type by which the mineral crystals become obliterated in geological time length. The latter category of radiation effects in insulating solids involves the electronic displacements. In this process, the electrons and holes liberated during the incidence of ionizing radiations are trapped at defect sites in the lattice. These defects could be either in the form of lattice vacancies or impurity ions which may be intrinsically present or might be caused by incident radiations themselves. The trapping of an electron at a negative ion vacancy, for example, produces the well-known F-centre. Similarly, a hole can be trapped in the form of V_K centre. This centre is a molecular anion, in which an electron is shared between two atoms in their anion lattice position. These defect centres involving the trapping of electrons or holes are called "colour centres". Since they absorb visible light of particular colours, the manifestation of the trapping effects can be seen in the form of optical absorption bands.

Most of the molecular ions [colour centres] produced recombine immediately. Some of the molecular ions located in a particular situation in a lattice can stay in their locations for prolonged periods which depend on the stability of the configuration. The trapped electrons and holes can return to their normal position if the irradiated sample is heated gently. The heat provides the activation energy to release the trapped charge from its potential well. The detrapped charge while returning to its normal position emits energy in the form of light. This is called thermoluminescence (TL). TL is thus the release of stored energy. The specific property of TL is its emission in the form of glow peaks. The glow peaks appear when the sample's temperature is raised after having been irradiated [Excited]. The rise in temperature of the sample reduces the life of electrons/holes in the trap, which leads to their ejection out of the traps at the exponentially increasing rate. This gives rise to a quick increase in the luminescent light emission. As the number of the trapped electrons/holes starts getting exhausted, the light intensity decreases and finally falls to zero. The light emission in TL process thus, appears in the form of glow peak.

The basic facts that have been investigated in the field of luminescence of pure and impurity doped materials are:

(1) What is an emitter?

(2) What is a trapping site?

(3) What is the nature of the TL centre?

(4) What is the mechanism of TL in alkali halides?

(5) Since the constituents of luminescence centre are closely associated with the structure of the material, and the structure of material is highly sensitive to pre-treatments, the attempts have also been made to examine the effect of different physical and chemical pre-treatments on the luminescent characteristics of the pure and impurity doped alkali halides. The brief account of such basic research work is described hereafter.

Since the results obtained with crystals of simple structure and known properties in the pure state are more amenable to interpretation, alkali halides have been most widely used in the luminescent research. Their large electronic band gap ($\simeq$ 8 ev) leads to a wide range of transparency and thus a very broad spectral region is available for the study of the effects of the impurities, vacancies, and other crystalline imperfection. Great interest was therefore centred in the study of the luminescence of alkali halides activated with heavy metal impurity such as thallium (Tl).

The systematic extensive theoretical and experimental work of Phole and his collaborators[7], Williams[8-10] and others[11-21] have clearly indicated that the luminescence centres in thallium doped alkali halides proposed so far are:

(i) isolated substitutional Tl^+ ion,

(ii) pairs of Tl^+ ions called dimers in which two Tl^+ ions occupy nearest neighbour alkali ion positions,

(iii) negatively charged complex ions of the type $(TlXn)^-$ in the dislocation regions where X denotes the halide, and

(iv) TlX-molecule formed by localized strain.

Thermally stimulated luminescence of KCl:Tl exhibited two principal glow peaks. Johnson and Williams[10] have concluded from their study that the two metastable states $3P_0$ and $3P_2$ within Tl^+ ion act as trapping sites for the electrons and are responsible for the two principal glow peaks around 200 and 300°K. However, it was shown[14] that the same two glow peaks were also observed in KCl doped with impurity other than Tl. In other words, the trapping sites for the electrons were not within Tl^+ ion but were due to crystalline imperfections other than impurity ion. The trapping sites were subsequently identified as negative ion vacancies[19-20].

Since the KCl:Tl phosphor exhibits long term phosphorescence and yet there is no photoconductivity, it was concluded that there is a close spatial association between the Tl^+ ion and its companion negative ion vacancy. In thermoluminescence centre so formed the Tl^+ ion acts as the emission centre, whereas the negative ion vacancy as the trapping site. The trapped electron returns to its parent Tl^+ ion by tunneling process. The TL mechanism is suggested to involve the following steps:

Before irradiation $Tl^+ + \boxed{-ve}$ ion vacancy
After irradiation Tl^{++} + F centre
After warm-up F centre $\longrightarrow$ $\boxed{-ve}$ ion vacancy + $\bar{e}$
$\bar{e} + Tl^{++} \longrightarrow Tl^+(^3P_1) \longrightarrow Tl^+(^1S_0) + h\nu$

The F centres are believed to be important component in the formation of TL-centres in thallium activated alkali halides.

In the last decade the systematic studies have been made on thermoluminescence properties of cesium halide activated with monovalent and divalent cation impurities by S. Selvasekarapandian et al[22-26] to understand the actual TL process, and to find out the exact nature of emitter and trapping site of TL centre. They have observbed in their work, a few glow peaks in X-or gamma-irradiated $CsBr:Cu^+$ and $CsCl:Cu^+$, and have attributed them to $F-Cu^+$ centres, a part of the glow peaks due to thermal decay of F-centres. Further, they found that the gamma-irradiated $CsBr:Ag^+$ and $CsCl:Ag^+$ crystals display additional glow peaks compared to undoped samples. From their optical absorption and TL studies, they ascribed these additional peaks to Ag^0 and Ag^{++} centres. They further suggested that TL arises from the radiative recombination of an electron or hole released thermally from its trap. On this premise, they made an attempt to give mechanism of TL.

From the observed experimental luminescence properties of thallium doped NaCl, NaBr, NaI, NH_4Cl, NH_4Br, KBr, KI and LiCl etc.[14,19,27-35] researchers have concluded that in general, luminescence centre comprises of an emitter [probably metallic impurity ion] and a trapping site [point defect], very closely associated with each other. The same luminescence centre is responsible for the occurrence of phosphorescence and thermoluminescence exhibited by the above materials.

Large number of scientists working in field of luminescence of pure and impurity doped alkali halides have investigated that peak position in the glow curve/emission spectrum is influenced by factors such as Heating Rate, Extent of Initial Excitation [e.g. radiation dose] etc. It was found that TL characteristics of any material could be specified by the TL glow curve at a given dose, heating rate and the TL emission spectrum at a given temperature. Further, it has been realized that the TL phenomenon is sensitive to variety of factors such as

(i) impurities in the material

(ii) pre and post thermal and/or mechanical and/or irradiation treatments to the material, and

(iii) LET of radiation used for excitation etc.

According to the present state of understanding the above factors change the defect pattern and impurity distribution in the host matrix. Therefore, different people attributed these new changes in the host lattice to the observed significant changes in the TL properties of the pre-treated material.

In view of the above description, it is believed that like thallium doped alkali halides, in NaF:K system, K^+ ion takes substitutional position of Na^+ ion in the host lattice. On this premise, the TL centre responsible for the observed TL characteristics is suggested to be comprised of an emitter, K^+ ion, and a nearby trapping site - a negative ion vacancy. $\boxed{K^+ \mid -}$. It is presumed that the exposure to ionizing radiation either excites the electron; which gets trapped at the metastable level within the impurity ion or separates the electron from the present K^+ impurity ion and electron so released is then trapped at crystalline imperfection other than the impurity ion [forming F-type of colour centre]. Liberation of the captured electrons during heating and their recombinations with holes at impurity centres results in the emission of the light photons. Bearing in mind the relevant literature referred above on monovalent thallium doped alkali halides, and the proposed above TL-centre model for NaF:K system, the observed TL behaviours and the explanation for the change in TL characteristics of different glow peaks of NaF and NaF:K are included in the following section.

A Basic TL Characteristics of Pure and K^+ Doped NaF

I TL Peaks of Pure NaF

(a) 120°C glow peak

(b) 150°C glow peak

(a) 120°C glow peak

It is clearly seen from figures 2 to 5 that virgin Sodium Fluoride powder displays well defined peak at 120°C along with high temperature peak at 360°C after a test beta dose [2.1×10^3 rads] in the first thermal cycle. Reference to K^+ doped specimens is made since this peak is also observed in the glow curve for these specimens. In the case of NaF:K specimens however, the intensity of this peak does not grow with the increase in K^+ concentration (Figs.2, 6, 10, 14, 18 and 28). It is important to note that the peak at 120°C is observed as a well defined ioslated peak only in undoped virgin NaF [Figures 2, 6, 10, 14 and 18]. No synthetic or natural material is absolutely pure, however, ultrapure it is made. Some impurities in trace quantity are inherently present. It is therefore, reasonable to assume that 120°C peak may be associated with the unavoidably present inherent impurities in the base material namely, Sodium Fluoride. Since the peak is observed in all the undoped specimens, and further, since the material in the as-obtained condition, from the manufacturers (virgin) could be supposed to have been annealed and cooled slowly, it might also be concluded that the peak at 120°C is associated with the crystallinity of the material.

According to the maker's data, the impurities present in the NaF material are; Insoluble matter (0.005%), Free acid-HF (0.04%), Chloride-Cl (0.002%), Fluorosilicate-SiF6 (0.12%), Phosphate - PO_4 [0.0005%], Sulphate-SO_4[0.005%], Iron-Fe(0.002%), Heavy metals-Pb(0.002%), and Potassium-K(0.01%). Amongst these, Fluorosilicate (SiF6) and Potassium (K) are present in 0.12% and 0.01% respectively. It is therefore suggested that 120°C glow peak is associated with these inherent impurities. A complex formed by negative ion vacancy adjacent to the impurity in the perfect region of NaF matrix is assumed to form the TL-centre responsible for the glow peak at 120°C. The concept of volume consideration strengthens the association of negative ion vacancy with the impurity ion to form TL-centre.

It is observed that the glow curve displayed by virgin NaF is highly sensitive to thermal treatment. Annealing the NaF specimens at elevated temperatures say; 200, 400 and 600°C for two hours and suddenly cooling the same to room temperature in open air has indicated drastic changes in the nature of the glow curve. The well defined isolated peak observed at 120°C in pure untreated NaF specimen suppresses in the intensity, it appears as hump, and a new peak developes at 150°C under application of preheat treatment to virgin NaF [Curve-1, Figures 2 to 5 and 22]. When the temperature of quench is around 400°C [Curve-1, Fig.4], the peak at 150°C appears as dominant, isolated one along with hump at 120°C. The peak at 360°C occurs with some change in its intensity in all the three cases. It is worth noting that the two small broad peaks at 120 and 190°C appear when the temperature of quench is raised to 600°C [Fig.22]. In 600°C air-quenched NaF specimens, the peak at 360°C disappears completely. It is clearly observed from the data presented in figures 2 to 5 that thermal treatment changes the shape of the glow curve significantly. It is also clear that elevation in the annealing temperature from 200 to 400°C, and further to 600°C makes the higher and higher temperature peaks well defined and distinct. Unlike other pre-treated specimens the peak at 360°C disappears in the case of 600°C air quenched NaF specimens.

These experimental results can be interpreted on the premise of the model suggested for the glow peak at 120°C. The thermal treatment increases the vacancy concentration as well as redissolves the precipitated inherent impurity. Besides this, the thermal strains produced during rapid cooling generates the dislocations and increases the dislocation content in the material matrix. Further, it is believed that the said change in defect pattern is highly sensitive to the quenching rate and different for different annealing temperatures. It is suggested that the thermal treatment does not preferentially produce TL-centres related to 120°C but instead generates large number of TL-centres associated with higher temperature peaks. It is also presumed that the TL-centres related to 120, 150, 190 and 360°C peaks have genetic relation and their components may be identical

- A complex formed by inherent impurity in vicinity of negative ion vacancy. The only difference is that the complex is located in different environments for different glow peaks.

It is observed in the present experiments (Fig.2) that successive thermal cycling changes the glow curve pattern exhibited by virgin NaF. In the second thermal cycle, the well defined peak at 120°C reappears as hump and peaks at 150 and 360°C come up distinctly. Thereafter, in the further successive heating runs, the glow curve pattern remains more or less identical with minor changes in the intensity. It is very significant to note that the change in nature and the intensity of the glow curve after completion of first heating run is more significant in thermally pre-treated specimens than in the case of untreated specimens. These experimental results can also be explained on the basis of the content of vacancy, vacancy pair, dislocation and dislocation debris present in the NaF matrix and the rate of redistribution of them, as well as inherent impurities in the NaF material under the different thermal shocks produced during air-quenching the material from various higher quenching temperatures. It is very well established that higher quenching temperature promises higher density of vacancy, higher aggregates of inherent impurity, and dislocation. This situation favours generation of TL-centres responsible for 150 and 360°C glow peaks, which is observed in the present work (Figures 2-5).

The increase in the incident beta dose excites larger and larger number of TL-centre for 120°C peak available in the NaF matrix. This finally results in the increase in the intensity of 120°C glow peak. The preset results corroborate this fact (Fig.31).

The complex - Inherent Impurity - Vacancy, $\boxed{\text{In-Vacancy}}$, in defect free region is proposed as TL-centre model for 120°C glow peak. The heat treatment relatively reduces the number of such TL-centre in defect free region and increases the same in disturbed region. Therefore, the peak intensity related to $\boxed{\text{In - V}}$ complex in free region (120°C) is expected to be reduced, which is seen in Fig.2. The rise in intensity of 120°C peak observed with successive heating runs or pre-heat treatments may be due to overlaping of strong high temperature (150 or 190°C) peak with 120°C [Figs.3, 4 and 5]. Thus proposed TL-centre explains most of the characteristics of 120°C glow peak.

(b) 150°C glow peak

The examination of the TL properties of NaF and NaF:K with different K^+ concentrations in untreated and pre-heat treated conditions, after irradiation with standard beta dose [2.1×10^3 rads] clearly shows that the peak of 150°C does not appear in any of the NaF:K specimens [Figures 1-21]. It appears only in pure NaF [Figures 2to 4]. Further, this peak is seen well developed, isolated and dominant one in pure NaF either after completion of the first thermal cycle [Fig.2] or in the first thermal cycle of 400°C air-quenched NaF. It is important to note that even in the first thermal cycle, it is absent in pure virgin NaF, it starts appearing as hump in 200°C air-quenched NaF and come out as dominant peak in 400°C annealed and suddenly air-cooled NaF [Fig.2-4 and 22]. It is remarkable to note that once again it disappears in the 600°C air-quenched NaF specimens [Figures 5 and 22].

The above mentioned experimental results clearly suggest that the peak at 150°C in NaF is the property of pure NaF. Further, it appears either after pre-thermal treatment at 400°C or after execution of first heating run in untreated NaF. One should bear in mind that durng first thermal cycle the beta irradiated pure substance of NaF is heated to 400°C and then air-cooled rapidly to room temperature for recording the second glow curve. This procedure itself is as good as execution of annealing the specimen at 400°C and suddenly air-cooling to room temperature. In short in both the cases, the NaF undergoes pre-heat treatment of rapid air-cooling from 400°C temperature to room temperature. In view of this, and as described in the previous section [(I) a], it is suggested that the TL-centres involved in the occurrence of 150°C are of identical nature to that suggested for 120°C glow peak, but they are located in the disturbed region of the NaF matrix, most probably, situated a few lattic distance away from the dislocation. The defect pattern and dislocation density in NaF lattice depend on the temperature of quench. The higher the temperature of quench, higher is the density of vacancy and the dislocation. It is negligible or zero in the virgin pure NaF, minimum in 200°C air-quenched material, moderate in 400°C air-quenched material, and maximum in the specimens, suddenly air-cooled from 600°C temperature. Since the dominance of the 150°C glow peak is seen in the material air-quenched from 400°C, the suggestion made for TL-centre, $\boxed{\mathrm{In}}\!\boxed{-}$ complex, located few lattice distance away from dislocation for 150°C glow peak is reasonable and suitable. This also explains why does the peak remain absent in virgin and 600°C air-quenched NaF specimens. The mechanism of occurrence of the 150°C is identical to that of 120°C and 360°C glow peaks and is described elsewhere.

The change in the intensity [increase] of the 150°C glow peak is observed in recording of consecutive heating runs. It is believed that the change in the defect pattern and redistribution of inherent impurity brought out by the heat treatment accomplished during execution of successive thermal cycling, are responsible for the observed change in the intensity of 150°C peak with successive thermal cycling.

The intensity of the 150°C peak is observed to be increasing with the increase in the incident beta dose [Figures 31A and 31B]. This experimental result can be interpreted very clearly on the same line of arguments that have been proposed to explain the growth of the intensity of 120°C peak with increase in beta dose in previous section [(I)a].

II Thermally Stimulated Luminescence Glow Peaks in NaF:K

(a) 165°C glow peak

(b) 190, 230 and 300°C glow peaks

(a) 165°C glow peak

The examination of the TL glow curves presented in Figures 1-22 clearly indicates that the peak at 165°C is totally absent in the untreated and pre-heat treated pure NaF. The peak around 165°C is seen only after the introduction of monovalent cation impurity (K^+). Besides this, it appears in the beginning as a small peak and its intensity rises with the increase in K^+ concentration. The intensity becomes optimum at 1000 ppm concentration of K^+ in NaF:K specimens [first curves 6, 10, 14, 18, figures 4, 22, 23, 24]. Thereafter, it falls for further increase in the K^+ concentration. The absentia of this peak in pure NaF, its presence and intensity dependence on concentration of monovalent impurity K^+ in NaF:K specimen, clearly encourage the author to suggest that the peak at 165°C is the property of the K^+ ion impurity in NaF. Further it is suggested that a complex formed by K^+ ion in close association with other crystalline imperfection namely, anion vacancy $\boxed{K^+ \,|\, -}$ is the TL-centre associated with the 165°C glow peak.

Since the peak is seen selectively prominent one, either after the completion of the first thermal cycle or after the execution of pre-heat treatment of annealing the NaF:K at 400°C for two hours and subsequently cooled rapidly in air to room temperature [figures 23-26, 7, 8, 11, 12, 15, 16 & 19]. Under this situation one expects large number of dislocations and vacancies produced on account of thermal strain. It is presumed that $\boxed{K^{+}}\boxed{-}$ complex located in the dislocation region is responsible for the generation of TL peak around 165°C in NaF:K specimens. This is possible, becuase of the large size of K^{+} ion compared to Na^{+} ion [$K^{+} = 1.33A^{o}$, $Na^{+} = 0.95A^{o}$]. It is energetically advantageous for the K^{+} ion to migrate to the dislocation site and thus reduce the strain energy in the specimen. Since the K^{+} ion is situated substitutionally at the site of Na^{+} ion in NaF host lattice and is bigger in size than Na^{+} ion, mechanically it prefers its location very close to negative ion vacancy. It is more suitably accommodated in the vicinity of anion vacancy.

Thermal cycling effect on the behaviour of 165°C peak has been studied in detail in one of the experiments. It is observed from figures 6, 10, 14 and 18 that the as-obtained NaF:K specimens exhibit slight change in the intensity of the peak with the consecutive thermal cycles. Except as-obtained NaF:K phosphors [Figures 6, 10, 14 & 18] all other 200 and 400°C air-quenched NaF:K specimens with different K^{+} concentrations, 200, 500, 1000 and 2000 ppm [Figures 7, 8, 11, 12, 15, 16, 19 and 20] show significant rise in the intensity of the 165°C glow peak with successive heating runs. It is believed that the change in the defect pattern, redistribution and diffusion of vacancy and the impurity in the host lattice produced by thermal cycling may be responsible for the observed change in the intensity of the glow peak. The materials of NaF:K with above mentioned four different concentrations of K^+ impurity have also been examined for their TL behaviours to know effect of pre-heat treatment from different elevated temperatures namely, 200, 400, and 600°C. The results presented in figures 23, 24, 25 and 26 clearly indicate that the peak at 165°C is seen well defined isolated, dominant one with optimum intensity, when the specimen is quenched from 400°C. This feature can also be explained on the basis of above proposed hypothesis of change in defect pattern and redistribution of impurity and vacancies in NaF matrix. It should be mentioned here that the non-occurrence of 165°C peak in most of the 600°C air-quenched specimens is on account of the production of other higher pair and aggregates of K^+ ions instead of single $\boxed{K^+ \mid -}$ complex.

The rise in the intensity of the glow peak upto 1000 ppm concentration of K^+ in NaF:K specimens and sudden fall in the intensity when the concentration is 2000 ppm or more (Figure 41) can be explained as follows. The proposed TL-centre for the 165°C glow peak is $\boxed{K^+ \mid -}$ complex situated in dislocation region. The increase in K^+ concentration generates larger and larger number of such complex. This promises the growth in the intensity of the peak related with $\boxed{K^+ \mid -}$ complex, i.e. 165°C peak. When the concentration becomes higher than 1000°C, concentration quenching takes place and instead of single, pairs and higher aggregates of K^+ ions may be generated. This favours other peaks and results in the reduction in intensity of the 165°C peak which is associated with single K^+ ions.

The effect of incident radiation dose on the behaviour of the 165°C peak hasbeen studied in yet another experiment. It is found that the intensity of the peak grows with the increase in the incident beta dose [Figures 33, 34, 35 and 36]. It is suggested that the increase in the incident beta dose excites more and more number of $\boxed{K^+ \,|\, -}$ complex. This in turn displays larger and larger TL output at 165°C.

Figures 40A-40D clearly show that the behaviour of 165°C glow peak does not change with the application of external magnetic field at any stage. The survey of literature brings out the fact that the magnetic field applied in the present experiments is insufficient to produce and change the defect pattern and impurity distribution in the NaF matrix.

The proposed mechanism for the occurrence of thermoluminescence emission at 165°C is given below.

The excitation of the NaF:K (T) phosphor with beta radiation at room temperature transfers the electron from a neighbouring F^- ion to the negative ion of the nearby anion vacancy. In doing so, a hole located at F^0 atom gets captured at the adjacent cation vacancy and the electron is trapped at the anion vacancy of the proposed TL-centre. Heating the material

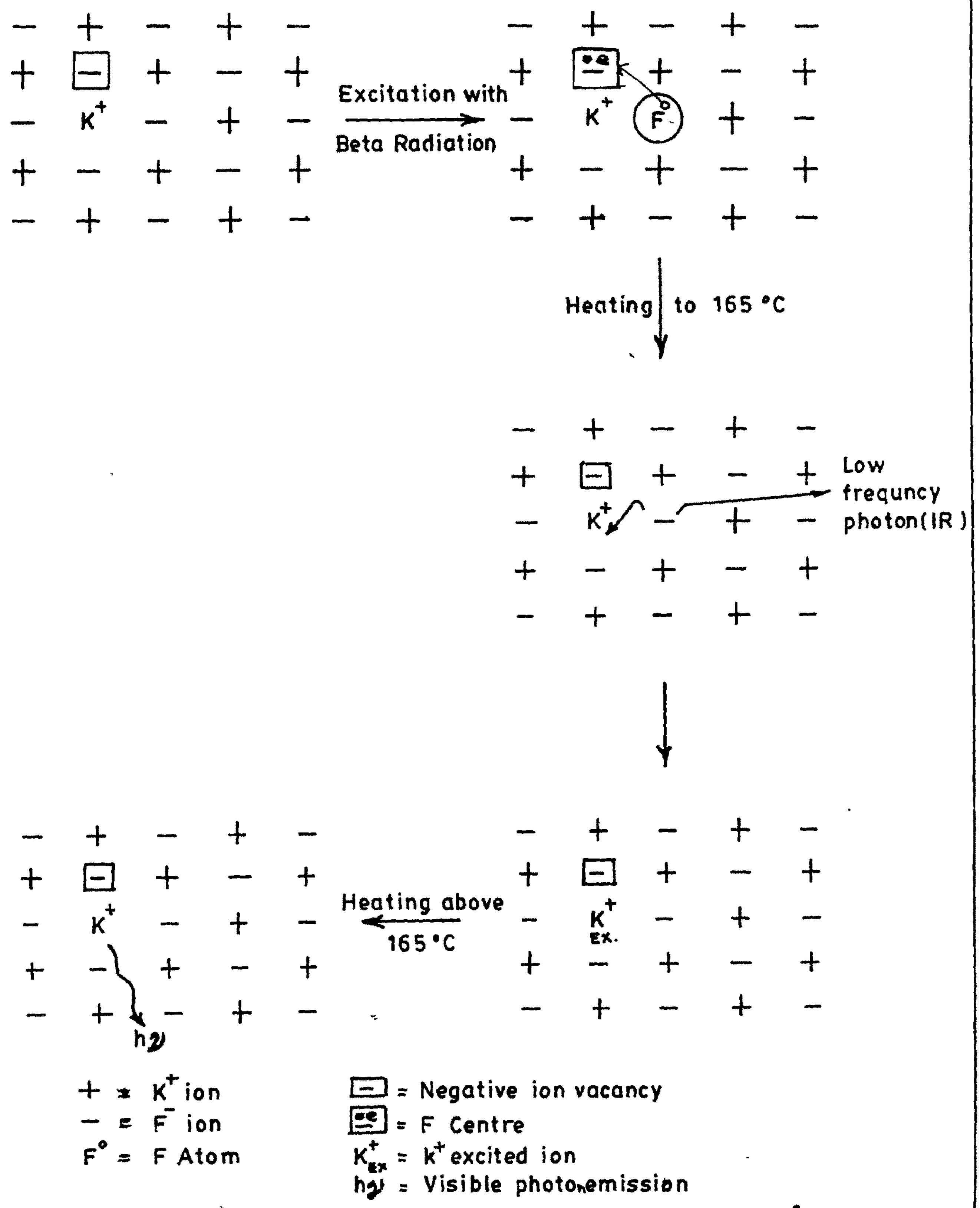

FIG. V-1 STEPS INVOLVED IN TL MECHANISM OF 165°C GLOW PEAK to 165°C with uniform heating rate results in the emission of low energy photons through recombination of electron and hole at the hole site . This infra red radiation dissipates as lattice vibration in the host lattice of NaF. The excess energy, thus released excites the K^+ ion, one of the constituents of TL-centre proposed for 165°C peak. The excited K^+ ion comes down to its ground state by emitting the characteristic emission of the impurity ion (K^+). The steps involved in the mechanism of TL emission at 165°C in NaF:K(T) phosphor are described in figure V.1.

Kinetics and Trapping Parameters of 165°C glow peak

The present phosphor under investigation NaF:K, exhibited number of glow peaks, namely; 165, 230, 300 and 360°C after a standard beta dose of 2.1×10^3 rads. The individual peak appears as well defined one in a special physical and chemical condition of the NaF:K material. It has been found that the 400°C air-quenched NaF:K (1000 ppm) specimens [(NaF:K(T)], exhibit well defined, isolated and very prominent peak at 165°C. Since the information of activation energy and order of kinetics facilitate the selection of phosphor in different TL application, the attempts have been made to compute them through one of the methods. The results obtained are presented in the following table.

According to the experiences of TL radiation dosimetry people the fading rate of the glow peak at given temperature

Parameters of 165°C glow peak

Peak Temp. (Tm)°K	Low Temp. Half-width (T)°K	High Temp. Half-width (δ)°K	Full Half-width (ω)°K	Geometrical factor $\mu_g = \delta/\omega$
438	37	27	64	0.4218

Activation Energy 'E' = 0.661 ev
Frequency Factor 'S' = 1.11×10^{6} sec^{-1}
Order of Kinetics : First Order

depends on the value of activation energy and order of kinetics. Like standard commercially available dosimetry phosphor LiF-TLD-100, the order of kinetics for 165°C glow peak in the present material is not unity. The activation energy of the peak is also high. These facts promise low fading and high thermal stability of the 165°C peak which encourage the author to believe that the present material, NaF:K(T) may be of use in radiation dosimetry. In order to investigate the utility of NaF:K(T) phosphor in radiation dosimetry, the detailed study of the dosimetric properties of 165°C TL peak has been made in the present work and presented in the Section-B.

(b) 190, 230 and 300°C glow peaks

It is very clear from TL results exhibited in figures 1 to 22 that 190°C peak is the special property of 600°C air-quenched pure and potassium doped NaF phosphors. It is very interesting to note that the relative intensity of 190°C glow peak is low compared to that of 120°C peak in 600°C air-quenched pure NaF [Figures 5 and 22]. The relative intensities of these two peaks become more or less identical in lightly doped 600°C air-quenched NaF:K (K^+ = 200 ppm], figures 9 and 23. It is important to note that the relative intensity of 190°C glow peak becomes more than that of 120°C, if the content of K^+ impurity in NaF:K specimens is higher than 200 ppm.[Figures 13, 17, 21, 24-26 and 30]. In other words, the peak at 190°C appears predominantly in 600°C air-quenched NaF:K specimens which contain higher concentration of K^+ impurity . In the case of NaF:K specimens with higher concentration of K^+, the generation of pairs and or higher aggregates of K^+ impurity ions will naturally become more pronounced compared to single isolated K^+ impurity ion. On the other hand, the aggregations of monovalent K^+ impurity ions proceed in two stages, the initial fast aggregation of impurity ions into cluster of more than three, followed by a slower aggregation into two (pairs) or three K^+ ions. It is also well known that the aggregation with higher number of K^+ ions will be more thermally stable than those with lower number [pairs of K^+ ions] as they occupy position such that the interaction between them is significant. Therefore, it is suggested that the pairs of two K^+ ions may be responsible for 190°C glow peak whereas the higher aggregates namely, three (trimer), four(tetramer) and five (pentamer) K^+ ions may be respectively associated with the 230, 300 and 360°C glow peaks. Since all these peaks appear well defined in 600°C air-quenched NaF and NaF:K specimens, and in such thermally treated phosphors, the density of dislocation and vacancy are expected to be high. It is believed that these pairs and higher aggregates of K^+ ions related with these peaks are located in dislocation region. The results obtained in the cases of pre-heat treated NaF:K specimens (figures 23-26) also confirm the above proposed hypothesis. The similar type of behaviour of these peaks with very low intensity is observed in thermally treated pure NaF [fig.22]. It is believed that this may be due to unavoidably inherently present very very low content of potassium impurity (as per makers data) in the NaF host material.

TL glow curves presented in figures 5, 9, 13, 17 and 21 report the recording of successive thermal cycling of 600°C air-quenched pure and potassium doped NaF. It is found that the intensity of the glow curve [peaks 120, 190, 230 and 300°C] rises with the successive thermal cycles. The increase in the intensity is observed significant after completion of the first thermal cycle. It is proposed that during recording of first heating run the specimen undergoes heat-treatment of annealing and rapid cooling from 400°C in open air. The thermal shocks produced in the material induce the change in the defect pattern and number of single, pair and higher aggregates of K^+ ions. It is believed that this new situation is responsible for the observed change in shape and intensity of 120, 190, 230 and 300°C glow peaks. Once the defect pattern and redistribution of impurity K^+ ions take place due to first heating run the repeatation of the further thermal cycles may not produce significant change in the defect pattern. This explains why the change in intensity of the glow curve is remarkable in the second heating run only.

The results obtained in the cases of pre-heat treated NaF:K specimens [figures 23-26] also corroborate the above proposed hypothesis. It is clearly seen in these figures that as-obtained NaF:K phosphor exhibits weak peaks at 120 and 165°C along with dominant one at 360°C temperature; if the specimens have been pre-heat treated at 200, 400 and 600°C in air and subsequently examined for TL behaviours, it has been found that the peak at 360°C changed its shape and intensity with the rise in the temperature of pre-heat treatment (say 200 and 400°C). When the temperature of pre-heat treatment has been fixed at 600°C, the 360°C peak totally disappeared and peaks around 190, 230 and 300°C appeared separately. It is presumed that the thermal strains produced during rapid cooling of the material from 600°C are sufficient enough to break up the complex - more than four K^+ ions with nearby negative ion vacancy, proposed for occurrence of 360°C peak. This in turn produces other complexes which involve association of single, two, and three K^+ ions. As suggested in the discussion of 360°C glow peak, the present discussion also brings out the fact that 360°C, 190, 230 and 300°C are related genetically.

It is well known fact that dislocation cores are negatively charged below 500°C. It is established that positively charged negative ion vacancies form the sheath around the dislocation which results the negative charge on the dislocation. Therefore, it is quite reasonable to propose that the complex [pair of K^+ ions - negative ion vacancy], should be located in the vicinity of the dislocation to have a negative ion vacancy as its component. It is suggested that the TL peaks observed in the present work at 190, 230 and 300°C in NaF:K specimens may be associated with similar type of complex [pair of K^+ ions - negative ion vacancy], situated in different environment. It is believed that the negative ion vacancy located as nearest (n). next nearest (nn), and next next nearest (nnn), neighbours to the pair of K^+ ions in the dislocation region may be responsible for the origin of the above observed glow peaks in NaF:K specimens. This also results different thermal stabilities. It is suggested that the type of situation namely, pair of K^+ ions associated with negative ion vacancy at next (n) site may be responsible for the occurrence of 300°C glow peak. Further, it is presumed that second and third, types; (nn) and (nnn) sites of location at negative ion vacancies in the dislocation region may be responsible respectively for the occurrence of 230 and 190°C glow peaks. The changes observed in the intensities and shape of these peaks with successive thermal cycling and pre-heat treatments can be explained on the basis of creation, destruction of dislocation and point defects and impurity redistribution in the NaF lattice due to thermal strains produced on account of execution of heat treatments.

III Glow Peaks Related to NaF and NaF:K

(a) 360°C glow peak

The peak around 360°C has been studied extensively by large number of investigators[36-39] in different alkali halides. Kathuria et al[36] studied pure and impurity doped LiF specimens for the said peak, while Joshi et al[21,40] examined the same for pure and different impurities doped KCl and NaCl, using different sources of excitation. On the basis of their work, they established following facts for 360°C peak in pure and impurity doped LiF, KCl and NaCl.

(i) The peak does appear in the first heating run even without excitation of alkali halides specimens.

(ii) It does not regenerate in the second thermal cycle with or without irradiation.

(iii) The pre-heat treatment does not result significant change in the position and intensity of the peak.

(iv) The different types of exciting radiations [UV, X-, beta-, gamma and alpha-rays], alkali halides, and impurities [mono-, di-, and trivalent] do not change intensity and position of the peak significantly.

The above facts led them to propose that the excitation of centre responsible for 360°C glow peak is mainly initiated by non-radiative means, particularly, mechanical pressure during handling of the specimens.

In the present work, a dominant peak around 360°C is observed in NaF alkali halide. Like other alkali halides [NaCl, KCl, and LiF], the peak is seen present without any irradiation and also found absent in the second and further successive heating runs [Figs.1A and 1B]. These experimental results led the author to suggest that the peak observed around 360°C in NaF and NaF:K specimens is also the spurious TL peak. And as proposed by earlier workers, it is excited by mechanical pressure exerted during handling and spreading the phosphor uniformly on specimen holder to record the thermal glow curves. The mechanism for the observed spurious 360°C peak in NaF and

NaF:K phosphors is more or less identical to that already suggested for 360°C spurious peak in other alkali halides and given elsewhere[36-40].

It is believed that in the first heating run, the material is heated to 400°C and subsequently cooled rapidly to room temperature to examine the second TL run. In doing this, the specimen is not disturbed mechanically or any other means. This undisturbed condition of the specimen ruled out the possibility of any type of mechanical excitation of the material. And hence, the peak related to mechanical excitation; i.e. spurious peak around 360°C, should not occur in the second and onwards successive thermal cycles. This is corroborated by the fact observed for 360°C peak in the present work [Figs.1A and 1B]. Thus the proposed model for spurious peak around 360°C explains the change in intensity with successive heating runs.

Inspite of considering above mentioned facts of spurious TL peak around 360°C in most of the alkali halides, including the present one, the following interesting experimental observations in NaF can not be kept aside.

In the present experiments, the peak at 360°C is found absent in the second and further successive thermal cycles, when TL has been recorded without any excitation of NaF material [Figs.1A and 1B]. On other side, it is important to note that unlike earlier reports, the peak around 360°C does appear in second and other consecutive heating runs in irradiated pure and K^+ doped NaF [Fis. 2, 3, 4, 6-8, 10-12, 14-16, 18-20]. Looking to the previously reported fact of non-occurrence of 360°C spurious peak in second and second onwards successive cycles in un-irradiated and irradiated pure as well as impurity doped alkali halides on one side. And its appearance in all the three successive cycles in the present experiments with irradiated NaF and NaF:K specimens. It is reasonable to suggest that there is co-existence of two separate peaks, namely; spurious (S) and real Radiation Induced (RI) peaks in the temperature region around 360°C. There may be overlaping of these two peaks around 360°C temperature.

In order to investigate this dual nature of the peak around 360°C, series of experiments have been made in the present work. TL glow curves were recorded without any excitation for as-obtained NaF, as well as 200, 400 and 600°C air-quenched NaF specimens. The glow curves recorded are presented in Figs.1A and 1B. It is clearly seen that in non-excited material, the peak around 360°C appears only in the first heating run and remains absent in other successive thermal cycles. Its intensity has been found to be reduced with the rise in the quenching temperatures and finally found to be disappeared completely when the temperature of quench was kept 400 or 600°C [curves 1 in all specimens, figures 1A and 1B]. In the cases of irradiated NaF materials, the peak around 360°C has been found well resolved and well defined in all the three conditions of NaF, namely, as-obtained, 200 and 400°C air-quenched one [Figs.2-4, and 22. It is of great importance to note that the peak remained absent when the NaF was air-quenched from 600°C. The NaF:K specimens also exhibited more or less identical type of experimental results [Figs.23, 24, 25, 26 and 30].

The specimens of NaF air-quenched from 400°C, for which the spurious TL peak has been found absent or with negligible intensity have been selected for further investigation of nature of RI glow peak in the region around 360°C. In one of the experiments, such specimens were irradiated with different doses of beta-radiation and studied for their TL behaviours in identical experimental conditions. The results obtained for the first thermal cycles, under the influence of various beta doses are presented in figure 31B. It is distinctly seen that no peak originates around 360°C till the magnitude of incident beta dose is 4.66×10^2 rads. [including spurious peak]. Above this beta dose, the peak around 360°C starts appearing as a hump, and then slowly come up as well defined peak when incident dose is 2.1×10^3 rads. Thereafter, the intensity of this peak grows with the increase in the incident beta dose. Similar types of results are also observed in 400°C air-quenched NaF:K specimens [Figs.33-36]. One should bear in mind that the existence of proposed spurious peak around 360°C is totally out of question as 400°C air-quenched specimens are selected for the observations [Figs.1B]. Therefore, the present experimental facts suggest beyond any doubt that the origin of the peak around 360°C in these specimens is purely radiation induced, and it is different from spurious TL peak. This strengthens the author's proposal of two separate peaks, namely; spurious (S) and real RI one, around 360°C.

The figures 31A and 31B exhibit that the RI peak around 360°C in NaF appears as well defined dominant one when the incident beta dose is 2.1×10^3 rads. Therefore, for the systematic examination of this RI peak, the materials of NaF and NaF:K are excited all the time with standard beta dose 2.1×10^3 rads. The effect of successive thermal cycles on the RI peak around 360°C has been studied for all the specimens. It is clearly seen from figures 2, 3 and 4 that the peak stabilizes itself after experiencing some change in the intensity during second successive thermal cycles. The TL results reported for NaF:K with different K^+ concentrations, figures 6, 10, 14 and 18 also support this experimental feature. The sudden change in the intensity of RI glow peak is observed after completion of the first heating run ofcourse, which afterwards stabilizes itself. On the premise of the proposed hypothesis, this may be due to removal of spurious TL peak around 360°C This also justifies the occurrence of two separate peaks, namely, 'S' and RI peaks in the temperature region around 360°C.

Since the RI peak is found in the 400°C air-quenched specimens and sometime after execution of the first thermal cycle [which is also as good as cooling rapidly the material from 400°C in open air], it is proposed that the peak results from the centre which comprises of the higher aggregation of impurity ions [inherent or deliberately added] namely, pentamer. Further, the non-occurrence of this peak up to the critical beta dose 4.66×10^2 rads indicates that the pentamer requires higher dose to generate radiative transitions. These facts suggest that the pentamers must be located in the dislocation region of the host lattice. It is believed that the change in the vacancy and dislocation contents produced on account of thermal strains generated during execution of first thermal cycle or 400°C air-quenching pre-treatment, may facilitate the formation of K^+ ion (or inherent impurity ion] higher aggregates, namely pentamer. The change in number of K^+ ion pentamer is suggested to be responsible for the observed change in intensity and nature of glow curve with successive thermal cycle or with pre-heat treatments.

From figures 27, 28 and 29, it is observed that the RI peak intensity initially grows with the increase in the concentration of K^+ impurity ion in NaF. It reaches to optimum value for 1000 ppm concentration of K^+ impurity, and then suddenly falls down for further increase in the concentration. The dependence of intensity of RI peak on K^+ impurity also supports the above proposal of higher aggregate centre (pentamer) rather than single impurity centre responsible for occurrence of the RI peak around 360°C. It is quite reasonable that in the case of pure NaF, the inherent impurity, and in the case of NaF:K specimens, the deliberately introduced K^+ impurity form the higher aggregates. The decrease in the height of RI peak beyond optimum concentration (1000 ppm) may be the effect of concentration quenching [figures 27, 28 and 29].

The specimens of NaF and NaF:K with four different K^+ concentrations, annealed and rapidly cooled to room temperature from 600°C in open air, have also been studied for their TL characteristics. The examination of these results [figures 5, 9, 13 and 17] reveals the fact that neither spurious nor the RI peak around 360°C appear in any of the specimens. Besides this, the peaks in lower temperature region, namely, 120, 190, 230 and 300°C come up in the second and other successive TL runs. It is also seen that in pure material the relative intensity of 120°C peak is more while in doped NaF, that of 190°C is significant. The first cycles of figures 5, 9, 13 and 17 clearly indicate that the peak at 190°C comes up on account of destruction of 360°C glow peak. This brings out the fact that there exist genetic relation amongst 360°C and other peaks in 120-300°C region. It is suggested that the TL centres associated with 360°C glow peak [close association of large number of impurity ions, pentamer], break-up during 600°C pre-thermal treatment and thermal cycling which obliterate the 360°C peak, and creates other centres, namely, single K^+ ion,pair of K^+ ions, trimer and tetramer of K^+ ions which result 120, 190, 230 and 300°C glow peaks.

The effect of application of magnetic field on the behaviours of RI peak has also been studied for 400°C air-quenched NaF:K (1000 ppm) specimens. The results demonstrated in figures 40A-40D bring out the fact that the magnetic field does not change the peak position, shape and intensity of the RI peak. According to present proposal, RI peak results from higher aggregates of K^+ ions which are located in disturbed regions of host lattice. The external magnetic field is believed to be insufficient to break-up this higher aggregate cmplex. Hence it may not change the TL centres associated with RI peak around 360°C. This in turn does not permit significant change in the intensity and nature of RI glow peak. Thus, the present model suggested for RI peak interpretes most of its observed properties. In general, it is concluded that two separate peaks, namely spurious (S) and RI glow peaks appear around 360°C in the present NaF and NaF:K phosphors. Between them, the former one originates on mechanical excitation while latter one results on excitation with ionizing radiation. The spurious one is found to be erased under the application of 400°C annealing and rapid cooling thermal pre-treatment in air [Figs.1A & 1B], while the RI peak around 360°C is found thermally stable under the same treatment [Figures 2-4, 6-8, 10-12, 14-16 and 18-20].

The peak around 340-360°C has also been studied in greater detail by Mrs.Akolekar et al[39] in the cases of pure and

Ba doped KCl. From their experimental results they indicated that the peak around 340-360°C in pure and Ba doped KCl is not spurious one. However, they could not throw more light as they did not report TL glow curves of KCl and KCl:Ba without irradiation. It is important to note that the present work on 360°C TL glow peak and the proposed suggestions support the experimental results and interpretations given by Mrs. Akolekar et al.

B Application of TL of NaF and NaF:K to Radiation Dosimetry

(a) Brief account of use of TL in Radiation Dosimetry

The measurement of thermally stimulated emitted light serves as a measure of the accumulated amount of irradiation absorbed by the sample prior to its heating. It was reported in literature[41] that the TL phenomenon was first applied in 1897 by Hoffman[42]. In the second half of the twentieth century, large number of workers gave much importance to TL and its applications in various fields. The two main applications of thermoluminescence are thermoluminescence dosimetry (TLD) and TL dating of archaeological and geological samples. Several materials exhibit the property of TL. New materials are investigated every year. The applications of TLDs in various fields are expanding and progressing. Large number of research papers are published yearly on TL dosimetry, discussing new materials and their developments to achieve better and better accuracy for various possible radiations measurement.

Daniel[43] was the first person to propose the phenomenon of TL for radiation dosimetry in 1950. Daniel and Heckelsberg et al[44] developed the instrumentation for TL dosimetry in 1957. Daniel group was the first to use LiF to measure radiation doses in 1966[45]. Ginther and Kirk[46] have shown that CaF_2:Mn could be used for TLD. Nonsenko et al[47] and Schayes et al[48] have established that other materials like $CaSO_4$:Mn and natural CaF_2 are also suitable for dose estimation. Many other groups have since then found variety of materials useful for different specific dosimetry applications - very low and very high doses as well as the detection and assessment of different type of radiations. For example, LiF and $LiF_2B_4O_7$:Mn can be used to measure the dose of thermal neutrons[49]. Cameron et al (1968)[49] have also described a method to distinguish between gamma-rays and thermal neutron in the mixed field of the two. Kastner et al[50] developed the LiF-TLD-100 in such a manner which could be used for detection of beta particles of different energies.

In order to standardize the criteria of selection of any TL phosphor as an efficient TLD material, large number of investigators have undertaken and examined TLD through different aspects in different radiation laboratories all over the world. From their experimental results they have established the following essential basic requirements that TL material should satisfy for its efficient performance as TLD phosphor.

(i) High concentration of trapping sites, simple trap distribution and long storage of trapped charges at normal working temperature (large trap depth).

(ii) High TL efficiency and sensitivity.

(iii) Resistance to radiation damage of trapping centres, the luminescence centres and the base material itself.

(iv) Matching of the spectral sensitivity of the photodetector (3000-5000A^{0}) with the spectral distribution of luminescence emission.

(v) Freedom from spurious TL and sufficient range of linear TL response.

(vi) Low fading, energy independence, reproducibility, small size and low cost of materials.

Attix[51] and Becker[52] have reviewed the use of TL dosimeters for personal and environmental monitoring, which is practiced all over the world in the different Health Physics laboratories. It has been reported that the luminescence material is the heart of the fabrication of the personal dosimeter. Minerals like quartz and feldspar as well as many organic and inorganic chemicals exhibit TL. A very few of them obey the above mentioned basic requirements listed for an efficient dosimeter.

A list of the most useful materials in real practice has been made by Becker (1973)[53], specifying almost all information regarding the manufacturer, the trade name, the appropriate reference, and the activator which seems to be responsible for the TL of interest. Harvey[54] and Aitken[55] found out that different materials are suitable for estimations of different dose ranges. They reported that LiF is most suitable for measurement of high doses, while, CaF_2 is suitable to evaluate very low doses.

TL has been used for radiation dosimetry under various circumstances, for example Crosby et al[56] employed LiF dosimetry in vivo measurements of transmission through bone and lung. Recently, a thin $CaSO_4$:Dy teflon TL dosimeters have been developed by Lakshmanan et al[57] for beta dosimetry in personal monitoring, capable of registering very low dose.

LiF:Mg:Ti [trade name TLD-100, 600, or 700 mostly in ribbon or chips form] made by Harshaw Chemical Company continues to be the most important TLD in many countries from the monitoring of photons, electrons as well as albedo neutrons and charged particles although it is intriguing to see that the annealing characteristics of this material is still a subject of investigation[58,59]. Its other complicated characteristics, namely, its multipeaked glow curve has been turned into advantage with computerized deconvolution of the different glow peaks using a software programme and computer, Harshaw automatic TLD badge reader incorporates such a software programme[60]. With this development it is now possible to reduce fading errors, lower minimum detectable dose limit, discriminate the LET of the radiation and even determine approximately the time of exposure.

Several other countries make their own LiF:Mg:Ti, mostly in pellet form or in teflon matrix, with almost similar properties as that of LiF-TLD-100.

LiF:Mg, Cu, Ti is a new sensitive tissue equivalent material which is fast catching worldwide attention since the past few years. It was first invented by Nakajima[61] from Japan in 1978 and is 30 times more sensitive than LiF:Mg:Ti to gamma rays. This material is now available in chip form Radiation Detector Works, China as well[62]. Low dose measurements, better tissue equivalents to photons below 150 KeV, absence of supralinearity and very low sensitivity to thermal or fast neutrons are some of the advantages of this material which make it a promising alternative to LiF:TLD-100 in personnel and environmental dosimetry, dosimetry of gamma rays in mixed fields and clinical dosimetry in dose range below 10Gy[63].

Besides this, other people developed the $Li_2B_4O_7$:Mn for radiation estimation. They found certain limitations, namely, hygroscopicity and TL emission in the red region. Takenuga from Japan[64] explored the $Li_2B_4O_7$:Cu in such a manner that the above stated limitations have been minimized. He claimed that TL sensitivity of $Li_2B_4O_7$:Cu is three times higher than LiF-TLD-100 and it has a linear TL response with close and a near tissue equivalence to photons. In powder form [finely dispersed on a solid base] $Li_2B_4O_7$:Cu is available commercially and used widely for personnel dosimetry in many countries. This system was developed and marketed by National Panasonic Ltd., Japan. An optical heating provides a fast readout and company claims that its TLD badges are reusable for upto 1000 times. Casel, E has listed[65] the relevant characteristics of fire TLD commercial systems tested recently.

B.A.R.C. India has developed indigenously $CaSO_4$:Dy system in 1974 for their personnel dosimetry[66]. They have claimed that method of preparation is very simple and it has been adopted by many countries. Prokic[67] of Yugoslavia made pellets from $CaSO_4$:Dy powder with a suitable binder and used for radiation dosimetry. Lakshmanan et al[68] developed $CaSO_4$:Dy Teflon [Trade name of PTFE by Dupont Nemours Ltd] matrix, and recently, incorporated a transparent mica sheet as the antibuckling devices which can read the dose in the range 0.06-0.14 mGY.

USSR Scientists[69] explored recently Anion-defect alpha-Al_2O_3:C TL detector. TL sensitivity of this phosphors is found 50 times higher than that of LiF:Mg:Ti. The another system developed by Mohril[70] is the $K_2Ca_2(SO_4)_3$:Eu which is reported to be 5 times more sensitive than $CaSO_4$:Dy. Its main TL peak at 150°C is reported not to fade at room temperature. S. Selvase Karapandian[71] has put efforts in last five years to develop different impurities activated Cesium halides as TLD material.

In last ten years T.R. Joshi[21], Mahajan[72,75], Dhake[73,77], Nehate[74,76], Chaudhari[40] and Srinivas[78] have developed the impurity doped sodium and potassium chloride as dosimetry materials. They claimed that the materials are very cheap, easily available and better sensitive than commercially available LiF. E.E. Heywood et al[79] reported that the high sensitivity, ideal glow characteristics and low cost could make NaCl phosphor, a commonly used TL material provided few limitations could be minimized. He has also used NaCl for dose estimation in the treatment of Carcinoma Cervix.

It is very clear from the above mentioned descirption that the field of development of new improved and high sensitive TLD phosphor is very active, essential and it is a promising field for young researchers to investigate and provide better and better TL materials for different types of radiation applications. Luminescence and thermally stimulated luminescence study of NaF have been reported earlier. However, few workers have reported on the examination of NaF in pure and doped form in view of their application in radiation dosimetry. The present work arose out of the consideration whether pure and K^+ doped NaF materials are suitable for dosimetry purpose or not.

(b) Application of TL of NaF(T) and NaF:K(T) in radiation dosimetry

Sodium fluoride has received considerable attention as a material with potential for optical information storage[80,81]. Zhao Jianai and others have reported the experimental results of

TL and TSC of colour centres in NaF and NaF:Mg^{+2} crystals irradiated by electron beam with heavy doses[82]. They have reported six glow peaks in the TL glow curve of undoped NaF namely, 97, 142, 160, 210, 254 and 372°C. The results obtained in the first part of the thesis suggest that NaF and NaF:K materials are quite sensitive to beta radiation. It has been found from basic TL study that NaF(T) and NaF:K(T) [400°C air-quenched NaF and NaF:K (1000 ppm) respectively] display very well isolated dominant peaks respectively at 150 and 165°C. Since the peak at 165°C is the property of K$^+$ impurity and is at higher temperature than 150°C glow peak related to pure NaF(T), the specimens of NaF:K(T) are selected for the examination of different dosimetric properties to investigate their suitability in beta radiation dosimetry. In what follows the experimental results are given below:

It has been mentioned earlier that the TL centres associated with 165°C peak in NaF:K(T) involve K$^+$ ion-anion vacancy pair $\boxed{K^+ \mid -}$, located in the dislocation region. The glow curve shape clearly shows that the trap is single valued and a large number of them is involved in the production of the peak at 165°C. The peak temperature is also high which suggests the involvement of deeper traps. This satisfies the first basic requirement of high concentration of trapping sites, simple trap distribution and long storage of trapped charges at normal working temperature.

The comparison of TL glow curves of NaF(T) and NaF:K(T) clearly brings out the fact that for any particular does the overall intensity of the glow curve is significantly high in the case of NaF:K(T) compared to that of NaF(T) phosphor [Figs.32 and 35]. Not only this, but it has been found that the intensity of glow curve is quite comparable with that of glow curves exhibited by other standard materials like, NaCl:Tl(T), NaCl:Ca(T), NaCl:Ba(T) and LiF-TLD-100 under identical experimental conditions after the exposure to standard beta dose [$2.1\text{x}10^3$ rads]. This clearly points out that the TL sensitivity of the present material under examination is suitable for its application in radiation dosimetry. The material NaF:K(T) is better than NaF(T). In other words the material NaF:K(T) fulfills the another basic condition, namely, high TL efficieny and sensitivity [condition No.ii].

Yet another established fact which disqualifies the material for dosimetric uses is the resistance to radiation damage. It is well known fact that the interaction of radiation with very high dose with material changes the defect pattern in the host material by producing vacancies, pairs and clusters of vacancies, and dislocation during irradiation. This finally disturbes the TL-centres associated with a dosimeter peak. The change in number of TL-centres and their environments result in the change in the peak temperature and shape of the glow peak. It is basically highly essential that the glow peak shape and temperature must remain unaffected in a good dosimeter material.

If this is not the case, the phosphor is useless for radiation dosimetry. The present phosphor, NaF:K(T) with the dominant peak at 165°C, has been examined in this respect. The results observed exhibited in figure 35, clearly shows that the present material preserves the nature and peak temperature position of the glow curve throughout the dose range $29\text{-}1.44\text{x}10^4$ rads. This brings out that the material of NaF:K(T) does not suffer radiation damage on account of high beta exposures. This satisfies the requirement No.iii stated earlier in the main list, which recommends the use of the material as TLD phosphor.

The commercially available dosimeter materials, LiF and $Li_2B_4O_7$ display their characteristic TL emissions in blue and yellow regions respectively. It is realized and established that to record these signals efficiently, the detector selected must be sensitive in this wavelength regions. If it is not so, then detector will sense the TL signals incorrectly. And it will not give correct estimation of dose even though the phosphor posseses high TL efficiency. In other words, 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. As mentioned in part A the TL emission exhibited by NaF:K(T) is in 400-480 nm region. This TL emission from the material falls in the sensitive region of the detector used in th present experiments. This favours the condition No.iv listed in this section.

The main important TL property which makes the phosphor useful in TL radiation dosetry is the precise and accurate relationship between the TL intensity of the particular peak and the incident radiation dose. A linear TL output versus incident dose in the region of interest of radiation users made the LiF and CaF_2 popular and useful in TLD. The growth of TL intensity of 165°C glow peak under excitation with different increasing doses of beta radiation is examined and presented in figure 35. The plot of the intensity of TL at 165°C glow peak versus the incident beta dose is found to be linear in the range 29 to $1.4x10^4$ rads [Fig.38A]. This is considered to be high enough to cover most of the range of exposures of interest to beta radiation users. The plots of TL output versus doses have also been examined for the peaks around 120, 150 and 360°C. The response for 360°C is sub-linear (38B) and the peak is suggested to be spurious one. On other side, the TL output versus dose responses for 120 and 150°C peaks are found non-linear [figures 32A-32B] since the intensity of the 165°C is found optimum and the TL versus dose response is also seen linear, the dosimetric properties of this peak has been examined in detail and those of 120, 150 and 360°C peaks have not been considered for systematic dosimetric study. Being free from spurious TL and possessing sufficient range of linear TL response, the NaF:K(T) material under present investigation has provided an additional support for its consideration as an efficient TLD material [satisfaction of condition No.V].

It has been realized well that the fading rate of the glow peak at a given temperature is closely associated with the magnitude of activation energy and order of kinetics. As per the calculation made in the previous section, the values of activation energy and order of kinetics for 165°C peak in the case of NaF:K(T) specimens are respectively 0.661 ev and first order. They are in order with the magnitudes computed for standard LiF material. This promises the high stability and low fading at room temperature. In order to investigate the fading, the loss in the TL intensity of the 165°C peak under the room temperature decay during the time interval between stopping of excitation and starting of the recording of the glow curve, has also been studied. The different durations of room temperature decay versus TL intensity of 165°C peak exhibited by NaF:(K)T specimens under excitation with standard beta dose, 2.1×10^3 rads, is presented in figure 39. It is seen from the figure that TL intensity of the peak does not change significantly for the decay time ranges from 1 sec. to few weeks. This indicates the negligible fading and which satisfies the condition no.VI from the main list.

Along with the stability, sensitivity, spurious signals, resistance to radiation damage, linear TL response etc., the resistance to damage induced on account of magnetic field is one of the most necessary requirements. In practical dosimeter applications and personal monitoring the Department of Atomic Energy Radiation protection persons send the fresh dosimeters by post to different centres in the country. They collect them back at regular interval of time from different centers to estimate how much radiation dose is received by that person of that center who is working in radiation field. Thus, before they read the dosimeters through TL reader for determination of radiation dose, the dosimeters pass through so many persons, places, and environment in transit. Therefore, chances are there for such dosimeters to come under high magnetic fields. In such circumstances, the material of dosimeters may suffer damage due to high magnetic field as it suffers in the case of high radiation exposures. In order to investigate the withstanding capacity of the NaF:K(T) dosimeter material, the TL glow curves have been examined under the influence of different magnetic field employed before and after excitation of material with beta radiation. The experimental data are presented in Figures 40A-40D. It is distinctly seen that the nature, the intensity and the peak position of the dosimetry peak at 165°C in the present material remains unaltered over a wide range of magnetic field. This promises the excellent withstanding capacity of the present phosphor against high magnetic field, just like the radiation field.

In addition to this, the other earlier stated fundamental requirements, namely, reproducibility, low cost of material, easy availability, desirable shape and size of the specimen, are the special points which strengthen the claim of NaF:K(T) phosphor as a dosimeter material. The material is ofcourse hygroscopic and very unstable in moist climate. However, our experimental results of TL glow curves exhibited by the material of NaF:K(T) with different amount of deliberately added water contents encourage the author to suggest without any hesitation that solid state dosimeters prepared from NaF:K(T) phosphor can be useful in the estimation of doses of beta radiation. On other side, the limitation of hygroscopicity can be eliminated by shielding the phosphor from direct exposure to atmosphere. Besides this, doping the material with suitable co-activator can minimize this drawback.