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CENTRO DE PROTEÇÃO RADIOLÓGICA E DOSIMETRIA
Área de Materiais Dosimétricos

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K. S. V. Nambi[**]

PREFACE

Although the phenomenon of Thermoluminescence (TL) was known for nearly three centuries, the basic mathematical understanding was first provided by Randall and Wilkins only in 1945 and its applications as a research tool was proposed subsequently in 1953 by Farrington Daniels. The last two decades have witnessed a rapid development in this field with perhaps more slant on applications as evidenced by five international conferences on applications in Radiation Dosimetry and one meeting on applications in Geology. There is also a published proceedings of a national symposium on TL and its applications. There had been considerable efforts in trying to develop enough understanding of the phenomenon both mathematically and physically and these reports are scattered over a spectrum of scientific journals. It is worth mentioning here that TL is perhaps an unique Physical phenomenon that has embraced lot more scientific disciplines than any other process known today; yet there has been no single effort to present all its aspects together in a place. This review attempts to fill this need and provides a kind of upto-date stock-taking in this field. As bibliographies are already available, no attempt has been made to provide an exhaustive list of references, but chosen carefully with more emphasis on basic aspects and later publications. All the possible applications of the phenomenon are briefly described at the end and an optimistic picture of the future trends in this field is projected. A review of latest information on TL instrumentation and phosphors is also included and that this report will prove valuable even for persons getting started in this field.

I – INTRODUCTION

I.1 – The Phenomenon

Thermoluminescence (TL) is a misnomer in the conventional sense of the names of luminescence processes like Cathodo-luminescence, Chemi-luminescence, Electro-luminescence and Bio-luminescence; heat is not an excitation agent in TL but only a stimulant. The excitation is achieved by any conventional agent like ionising radiations, UV rays, mechanical vibrations, stress, chemical reactions and so on. Thus Thermoluminescence is the phenomenon of luminescent emission after removal of the excitation under conditions of increasing temperature. Phosphorescence at any temperature after the cessation of the excitation, is nothing but isothermal decay of TL at that temperature; hence TL should be defined as the thermally stimulated release (in the form of optical radiation) of energy stored in a material by previous excitation. It is also necessary to distinguish clearly between thermoluminescence and incandescence emissions from a material being heated: the luminescence usually lies in a spectral region where the material is non absorbing; the incandescence emissivity is strongest where absortivity of the material is the maximum. There is also a wide gap between the temperatures of occurrances of these two emissions, incandescence occurring at very high temperatures near the melting point of the respective material The highest temperature at which TL has been reported for any solid is around 650°C. Normally it is understood that no TL can be observed at temperatures far lower than the excitation temperature, there are however exceptions and these are

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(*) A compilation of series of lectures delivered for an Advanced Course in the Area of Nuclear Technology at the Instituto de Energia Atômica, São Paulo, Brazil during 1976 (Review completed in February 1977.)

(**) Health Physics Division, Bhabha Atomic Research Centre, Bombay, India distinguished as cryo-luminescence and cooling-down luminescence It is heartening to note that in recent times the phenomenon of TL is being correctly referred as Thermally stimulated luminescence (TSL) The review in the present report will be restricted to radiation induced thermally stimulated luminescence and its applications.

The first observation of TL recorded in literature can be dated as far back as 1663 when Robert Boyle reported to the Royal Society in London on observing a strange glimmering light when he warmed a diamond in the dark(24,140). Even as early as 1895, the underlying physical process of thermal release of stored, radiation induced luminescence was used for detection of ionising radiation. However it is only during the last two decades progress on TL research and applications accelerated very rapidly and at the moment the accumulated TL publications number well over 2.000 with an annual increase rate of about 200(14)

I.2 – The Materials

By far the most sensitive TL materials are the dielectric solids. However it is a widespread phenomenon and is exhibited by a host of minerals; inorganic crystals, glasses and ceramics, organic compounds such as polymers including polyethylene and teflon; certain biochemicals and biological materials etc. It is almost impossible to predict the TL characteristics of a material from any amount of physico-chemical specifications of the material.

The phenomenon can be most easily observed by warming a rock piece of a natural fluorite in the dark. The colour and intensity of the luminescence observed will depend upon the kind of fluorite piece heated. Certain varieties of fluorites available in countries like Brazil, Belgium, France, Germany, India and Japan are known to exhibit enormous TL. Energy had been stored in such minerals due to cosmic irradiation as well as self irradiation from minute radioactive impurities like U, Th & K, through the entire geological age. After the first heating when the TL emission has ceased, it can once again be induced by artificial irradiations in the laboratory with any convenient X or gamma ray source.

The most widely studied materials for their TL behaviour are those that are used in radiation dosimetric applications: CaF_2, LiF, $CaSO_4$, Mg_2SiO_4, BeO, $Li_2B_4O_7$ etc. The presence of minute quantities of certain elements like the lanthanides, Mn, Mg, Ti etc either individually or otherwise, have been found to be necessary to enhance the TL efficiency of most of these materials: CaF_2 (Mn), CaF_2 (Dy); $CaSO_4$ (Mn); $CaSO_4$ (Dy); $CaSO_4$ (Tm); $CaSO_4$ (Mn,Pb); LiF (Mg,Ti); BeO(Na); $Li_2B_4O_7$ (Mn), Mg_2SiO_4 (Tb) etc. Most of these phosphors can be easily prepared in the laboratory (Cf. sec. 2.1) and are also available commercially. Some of the minerals have also been studied extensively for their TL characteristics because of their applications in Archaeology or Geology: Quartz, Fluorites, limestones, Calcites, Anhydrites, Al_2O_3 etc. Attempts have recently been made on the TL studies of human bones with a view for applications in Archaeology & Forensic Science.

I.3 – Measurements

A simple experimental arrangement (figure 1) to measure TL can be a light-tight housing inside which a small sample of the TL material can be heated in front of a photomultiplier and a power supply and D.C. amplifier to operate the photomultiplier and measure its current output. The output of the D.C. amplifier can be conveniently fed to a recorder to obtain a continous record of the luminescence measured against a time scale convertible to a temperature scale if the heating pattern could be independantly or simultaneously measured. A heat-suppressing filter interposed between the sample and the photomultiplier face will greatly improve the signal to noise ratio of the detected luminescence.

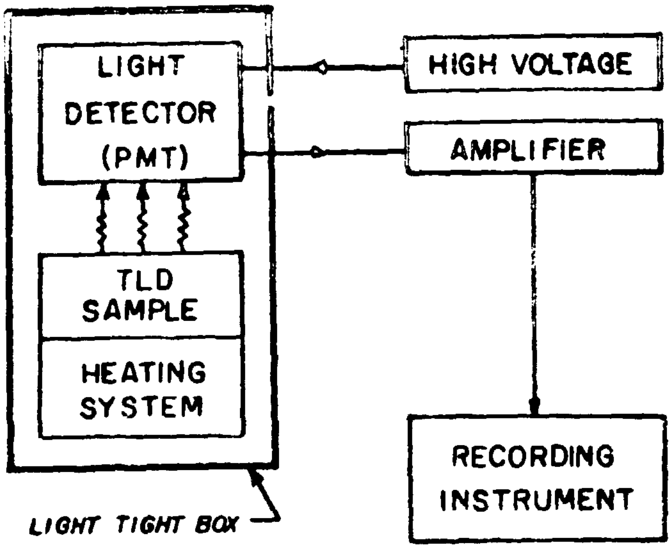


Figure 1 – Schematics of the basic requirements of an experimental arrangement to measure TL (Cameron, J.R., 1968 – ref. /33/).

The pattern of luminescence output vs. temperature is called the thermoluminescence glow curve. It should be remembered that by luminescence it is meant, the total light output. The spectral quality of the luminescence (ie. light output vs. wavelenght) at any particular temp. during the heating will be called the thermoluminescence emission spectrum. Both the TL glow curve and the spectral emission curve may exhibit many peaks depending upon the nature of the material whose TL is being measured. These are respectively called glow peaks or glow maxima and spectral emission peaks or maxima. Figure 2 & 3 give the TL glow curve and TL emission spectrum obtained from an Indian Fluorite sample.

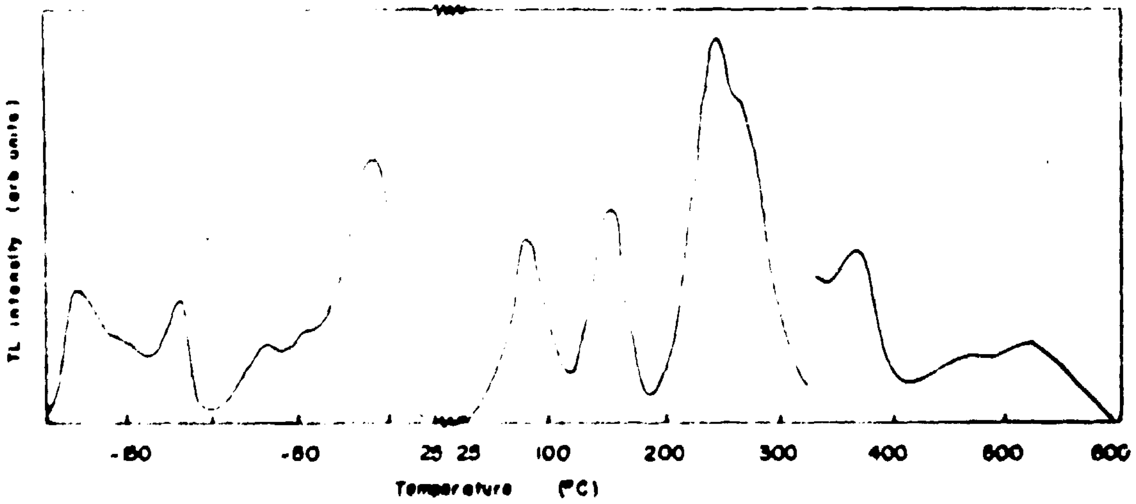


Figure 2 – TL glow curve of an Indian Fluorite sample after gamma irradiation at LNT (Sunta, C.M., 1971 – ref. /196/).

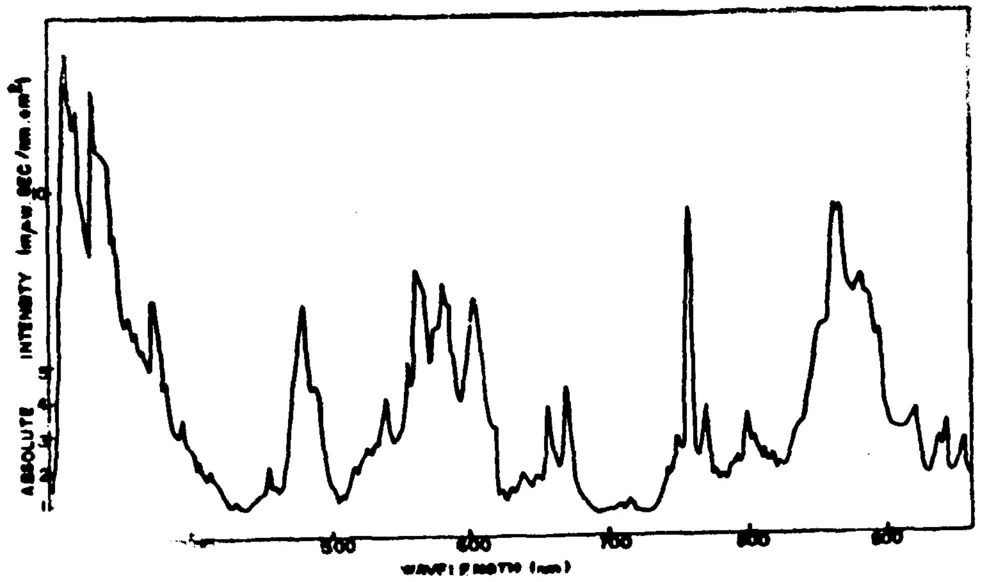


Figure 3 – TL emission spectrum of an Indian Fluorite sample (Nambi, K.S.V., 1975 – ref. /141/).

If a monochromator or a band pass filter is placed between the TL sample and the photomultiplier, a TL glow curve of a particular emission wavelength could be obtained. This is called a monochromatic TL glow curve. Figure 4 gives monochromatic glow curves of an Indiao fluorite sample recorded up to about 325°C.

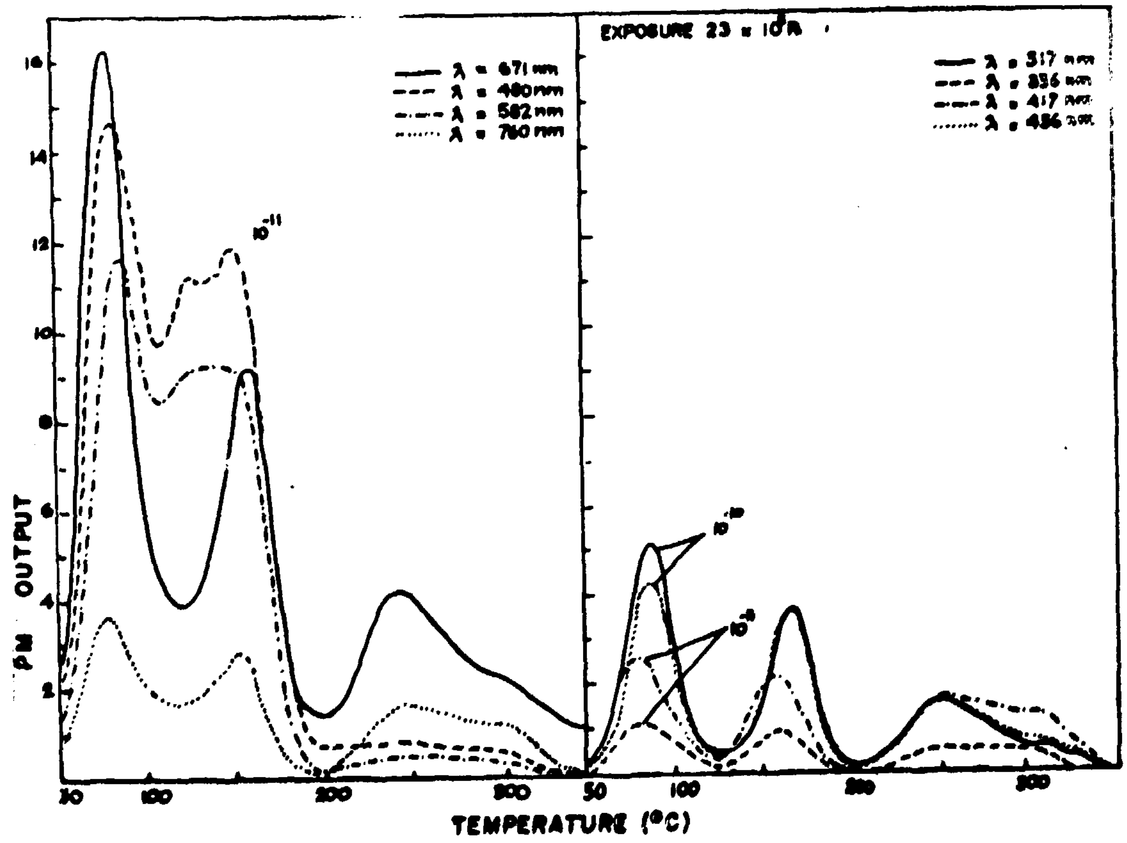


Figure 4 – Monochromatic TL glow curves of natural CaF_2 (Bhasin, B.F., 1975 – ref. /17/).

The physical significance of the nature of curve is usually explained as follows:

When the material is "excited", equal numbers of electrons and holes are "liberated" within it and some of them may become "trapped" at certain "centres" in the material (§. sec. III) ie energy is "stored" in the material. These storage sites are called electron or hole traps according to the nature of the electrical carrier being trapped. Under normal storage conditions these traps may be quite stable even for years. However by proper "stimulation" (either thermal or optical) their probability of getting detrapped (§. sec. IV.1) can be enormously increased and the trapped charge carriers can come back to their original stable configuration. This process is usually accompanied by release of energy most of which is thermal but in some materials a fraction appears also as optical radiation (§ sec. VIII). This is what is observed as TL. If several traps of different depths are involved in the process in the same material, then it is evident that the "detrapping" will occur at different temperatures and consequently the light emitted will be in the form of several "bursts" of light and will be reflected as several glow peaks in the glow curve. When light is emitted, the nature of the emitting species and its "surrounding" is reflected in the spectral quality of the TL emission as shown by the TL spectral emission curve. The spectral emission peaks may correspond either different species or different energy states of the same species or different environs of the same species (§. sec. IX).

The peak locations either in the glow curve or the spectral emission curve are fairly constant for a given material and the light sum under the peak may be found proportional to the extent of the initial excitation (eg. radiation dose, §. sec. X.6). The glow peak temperature is a measure of the thermal activation energy needed for the detrapping (§. sec. V).

The rate of heating while measuring TL also affects the glow peak temperatures, the intensities and the shape of the glow curve (§. sec. IV) but not the emission spectrum.

Hence it can be stated that the TL characteristics of any material can be specified by the TL glow curve (with heating rate specified) and the TL emission spectrum (with the temperature specified). Of course, both are related to a specific excitation of the material.

However, it should be borne in mind that the phenomenon of TL is sensitive to a variety of other factors such as: impurities in the material, pre-and post-treatments to the material (eg. pre or post-exposure thermal treatment at a particular temp. for a particular time interval), LET of the radiation used for excitation, the integrated level to which the material was subjected to the excitation, the experimental arrangement used for measuring the luminescence etc (§. sec. VI & VIII).

Inspite of the many parameters that could complicate the TL emission from a material, it is amazingly true that the phenomenon finds successful practical applications in many disciplines today (§. sec. X) while research is continuously on to find a satisfactory explanation of the observed TL phenomenon in general terms.

II – TECHNIQUES

II.1 – Phosphor Preparation

The essence of the problem of preparation of an artificial TL phosphor boils down to finding a technique to "dope" a material effectively with a proven activator impurity. Such a technique can be very elaborate and sophisticated as will be needed in the case of basic studies involving single crystals or special applications involving extruded ribbons, glasses and the like. On the other hand for applications such as in radiation dosimetry where polycrystalline powders are sufficient to use, very inexpensive yet reasonably reproducible techniques could be successfully employed. In this review more emphasis is given to the later.

II.1.a – Preparation of Single Crystals of TL Phosphors

The techniques of growing a single crystal are all well known and documented. The most important methods are those due to Bridgemann and Stockberger. Depending upon the TL material being grown special design features are called for, however(164). The starting material has to be very pure and it is common practice to use methods such as vacuum distilation, zone refinement etc, to purify a given material. The activator impurity element (or a convenient compound of the element) should be pure as well and should be dry mixed thoroughly with the base material (may be the mixture is preheated before loading into the crystal-growing furnace). It is highly desirable to operate the furnace in good vacuum or in an inert atmosphere with no traces of water vapour or oxygen. For better reproducibility, the heating and cooling patterns should be under good and accurate control.

The making of extruded rods/ribbons from a molten material is an industrially feasible standard technique now and will not be discussed here.

CaF_2 and LiF TL phosphors have been made by either of the two processes mentioned above.

II.1.b – Preparation of Polycrystalline TL Phosphors

One of the easiest methods which has been successfully employed in preparing TL phosphors like CaF_2:Mn & $CaSO_4$:Mn is to dry-mix finely powdered constituents of the phosphor and fire under inert atmosphere or vacuum(91). However a more efficient doping method would be to coprecipitate the base material and the activator (for eg. CaF_2 and MnF_2 from a chloride solution with Ammonium Fluoride) followed by drying and firing at high temperature in an inert atmosphere or vacuum(74).

The most interesting and useful phosphor, $CaSO_4$ (Dy) is easily prepared by dissolving the powder mixture of $CaSO_4$:$2H_2O$ and Dy_2O_3 in conc. H_2SO_4 acid and slowly evaporating the acid to dryness. The fine polycrystalline-residue obtained can be ground, sieved and annealed at 700°C for 1 or 2 hours before use as a TL phosphor (see ref. 182 for optimal preparation condition and annealing temperature).

The preparation of thermoluminescent Mg_2SiO_4 (Tb) or Al_2O_3 (Na) require fusing at very high temperature (~ 2000°C) and a technique using graphite/platinum crucible and a "gas-blow torch" can be effectively used(19).

As for as LiF is concerned only the single crystal grown with the necessary activator seem to exhibit maximum sensitivity. However, most of the commercially available LiF powders, after a heavy pre-gamma irradiation and subsequent annealing exhibit sufficient TL sensitivity(112). Fairly sensitive LiF polycrystalline powder can be prepared by coprecipitating the activator (Mg,Ti) and LiF form their chloride solution by adding HF and heating the dried precipitate at about 600°C for an hour or so in vacuum or inert atmosphere.

II.1.c – Preparation of TL Glasses and Phosphor – Embedded Teflon Discs

Glasses and teflon embedded discs of TL phosphors have definite advantages in large scale applications and for ease of handling although the sensitivity is usually less. The successful TL glasses so far reported in literature are either phosphate – or silicate – based. A typical TL glass composition is: 29% Li_2O, 12% Al_2O_3, 59% SiO_2 and 0.002% Tb(73).

For preparation of teflon discs loaded with TL phosphors like CaF_2, $CaSO_4$ and LiF, the phosphor powder in a typical ratio of 1:5 by weight and a low temperature moulding technique is employed(111).

Another interesting method which is useful in dosimetric applications using highly sensitive phosphors like CaF_2 and $CaSO_4$, is to mix the phosphor with pure KCl or KBr in a typical ratio of 1:2 by weight and cold-press about 200 mgm. of the mixture into a pellet of about 1 cm dia. and 1 mm thickness. Fairly transparent rigid discs are obtained which can be handled quite freely and heated repeatedly(156).

Table I gives an idea about the activator and background impurity concentrations specified in literature for some of the well known TL phosphors.

Table I

Impurities and TL Sensitivities Reported in Literature
for some well Known TL Phosphors

TL Phosphor	Impurity (conc. in ppm)	Impurity responsible for TL	Relative TL sensitivity to gamma irradiations
LiF	Al – 20 Ca – 6 Mg – 300 Ti – 5	Mg, Ti	1.0
CaF_2	Na, Mg, Al, Cr & Mn (total) < 60 Lanthanides (total) > 60	Lanthanides especially Ce, Sm, Gd, Dy, Er & Tb	13.0
$CaSO_4$	Mn, Zn, Pb, Cd & Sb (total) < 36 Dy : 870 other Lanthanides : < 30	Dy	39.0
Al_2O_3	Na : 100 Si, Ca, Fe, Ti & Mg (total) : 300	Na ?	5.0

II.2 – Instrumentation

Many types of TL Readers are available commercially(14) and these are mostly suited for applications in Radiation Dosimetry. There are clear advantages especially for basic research work, with a self-designed, home-built equipment which is not at all difficult to make even with a low budget.

The design and operating considerations can be conveniently divided into four parts:

II.2.1 – Sample Detector Housing

This contains essentially the photomultiplier, the filters and the sample holder (invariably a small heater pan) the encasement being light-tight. The choise of the photomultiplier has to be judicious depending upon the emission characteristics of the TL material being investigated. Signal to noise ratio can be greatly improved by (i) cooling the PM tube (ii) choosing proper heat filters (iii) providing a light-guide between the sample & the PM tube (iv) using a 90° reflection to detect the luminescenee rather than directly from the sample being heated, and (v) using a diaphragm over the sample so that the PM tube "sees" only the sample and not other parts of the heater also It is common experience that an inert atmosphere or vacuum in the sample chamber helps reduce spurious signals (§. sec.VII) and hence provision for an inlet – outlet arrangement in this housing will be a desirable feature. There has been an interesting suggestion to use hot N_2gas in a jet to heat the TL crystal or phosphor encased in a glass capillary and this has been successfully employed at least in Radiation Dosimetry. This method, while reducing the spurious TL occurrance, improves also the signal to noise ratio as the infra red background is very much reduced

II.2.2 – Heating System

In principle many possibilities exist to heat the TL material: electrical resistance heating, hot gas-jet heating, infra red heating, RF heating, magnetic induction heating, ultrasonic heating and so on The easiest and most widely used is that based on electrical resistance heating Kanthal alloy has been used extensively as the heater pan by many TL workers and is not found to give rise to its own spurious luminescence (Many materials including platinum even after a short exposure to light, give rise to luminescence when heated). Non linear, but reproducible heating patterns could be easily achieved by passing a fixed current though the heater-resistor and various heating patterns with different high temperature limits could be achieved by changing the value of the current. Such a simple system – say using a variac to supply the heater voltage – is quite useful and inexpensive especially for dosimetric applications and even in basic investigations However for research studies, a linear heating always provides advantages (§ sec. IV & V) and this can be done either mechanically (say by attaching synchronous motor to the variac(143)) or electronically(68) A sophisticated temperature programmer in a TL reader unit can have facilities like: choice of any linear heating rate, isothermal hold, automatic cut off at any desired temperature, programmed cooling and so on (figure 5).

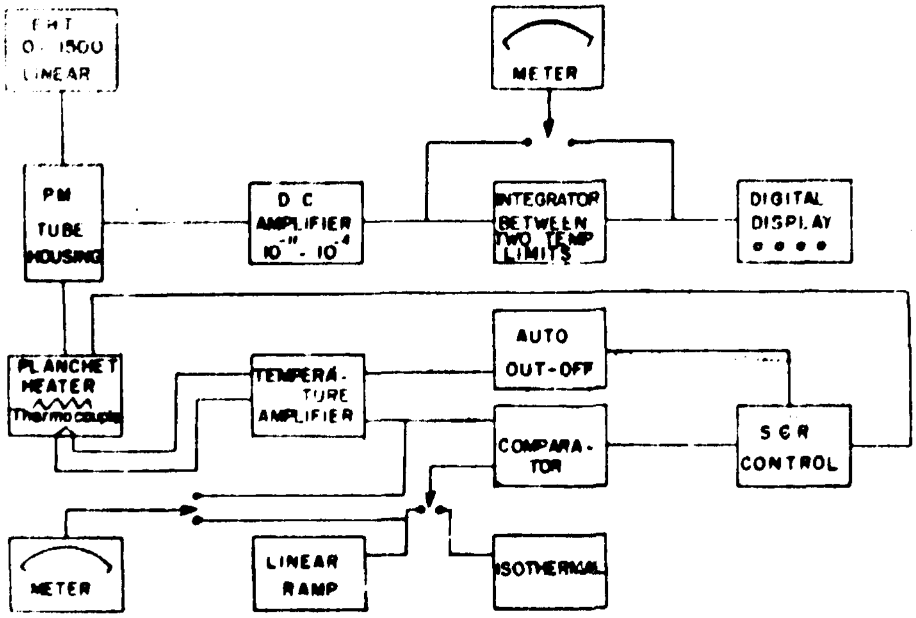


Figure 5 – Block Diagram of a sophisticated TL Reader Unit

II.2.3 – Signal Detector System

This can be a simple D C amplifier coupled to a current recorder or sophisticated with a digittal printed readout and a plotter A whole spectrum of variations are possible in between the two extremes mentioned above The basic detection can be either a dc measurement or a pulse measurement. The dc mode itself can be converted into a count rate measurement easily with a capacitor – neon lamp combination or in a better manner using a chopper whith an added arrangement to remove the noise signal completely. In the pulse-molde, usually called the photon counting, the charge pulses of individual electrons generated in the PM tube are counted and this has a much higher signal to noise ratio of detection(113,188). The signal whether in the dc mode or pulse mode can always be integrated over any specified interval in the TL glowcurve using an integrator coupled suitably with the heating system

For examples of sophisticated TL readers useful for research studies which can be built in the laboratory or bought commercially see references 17 and 37.

II.2.4 – Techniques

II.2.4.1 – Sample Temperature Measurement

Generally speaking, TL materials are rather poor thermal conductors and usually, for measurement of TL temperatures, thermo-couples are spot-welded either at the top or bottom of the heater pan on which the TL material is loaded for the study. Obviously the indicated temperature is not representative of the material at all. In fact all published data on TL suffer from this criticism and no wonder, many times one comes across serious disagreements in glow curve data of one and the same material. As thumb rule, the temperature diference between two faces during a heating process can be estimated as

$$\Delta T = \frac{q\ L^{2}\ .\ C\ .\ \rho}{K}$$

where:

q = heating rate

L = sample thickness

ρ = density

C = specific heat and

K = thermal conductivity

For most of the purposes it is sufficient to have a heating system which is reproducible and a temperature indication which is very close to that of the sample. This is easily achieved by having the heat capacity of the TL phosphor at a minimum compared to that of the heater and the thermal and electrical time constants should match In case of powder samples, a small quantity of the powder (approx. 5 mgms) spread evenly on the heater pan almost to a single-grain layer, serves the best compromise. In the case of a crystal block or a cold-pressed disc it may be necessary to provide thermocouples at the top and bottom surfaces and measure the average temperature of the material. For measurement of actual temperatures there has been an interesting suggestion(152) to mix equal amounts of fine TL powder and fine pure gold dust, cold press it to a strong disc and snugly fit in mechanically a fine thermocouple bead by drilling a blind hole in the disc.

II 2.4.2 – Checking-up for Constant Instrument Sensitivity

The day-to-day sensitivity of a TL instrument may fluctuate owing to factors such as voltage variations, PM tube fatigue, electronic instabilities, extremities in ambient weather and deposition of dirt and vapour on optical parts. The overall response of the instrument can be checked by one of the three ways: (i) using a standard TL dosimeter pre-irradiated to a convenient standard dose (ii) using a standard light source-usually an inorganic or plastic scintillator mixed with a minute radioactive source of long half life and (iii) a light emitting diode connected to a regulated current source. There are however problems like instability of the light source itself due to various factors, mismatch of the spectral emission characteristics of reference light source and the TL material under study etc. The use of a set of LEDs with different emitting colours seems to offer the best choise(177).

II.2.4.3 – Low Temperature TL Measurement

In basic research studies especially involving organic materials, measurement of TL from say liquid nitrogen temperature onward is a necessity and the sample-detector housing has to be designed carefully(205) Sample loading at low temperatures presents considerable difficulties and no inovation has yet been made in this direction. Also, use of a single linear programming for the entire temperature range of interest in ionic solids, say 77°K to 1000°K is still not in vogue although such a programming should be easily attainable.

II.2.4.4 – TL Spectral Measurement

Basically there are at least four techniques that are being used: (i) use of band pass filters between sample and detector while taking the glow curve and constructing the TL emission spectrum(117) (ii) periodical spectral scanning during a glow curve measurement and reconstruction of the TL emission spectrum at any desired temperature of the glow curve(101) (iii) spectral scanning during isothermal decay of a glow peak and correcting for the intensity by decay estimates(195) and (iv) construction of the spectrum for any temperature of emission from the monochromatic TL glow curves(141). While method (iv) is the most sensitive and absolute, method (iii) is most convenient and quick. All the methods excepting method (i) need a monochromator to be interposed between the sample and detector.

II.2.4.5 – Precision of the TL Measurement

An estimation of the precision of the TL Reader used is complicated by three independent variables: sensitivity of the instrument, self-consistency of the TL emission itself from the material being studied and the accuracy of the "activating exposure" given to the material. It is however possible to estimate the precision of the instrument by taking a large number of repeat readings after the same exposure and applying the theory of analysis of variance to the data(122,163).

II.2.4.6 – Automation in TL Reading

In large scale applications as in Radiation Dosimetry, considerable progress has been made in completely automatising the TL reading instrument to handle thousands of TL dosimeters with identification codes and print out of the corresponding doses automatically(83). There has been just one report(123) of an automatic TL instrument which is sophisticated and is of immense use in research studies: as the TL material is being linearly heated, the light emitted is spectrographically analysed over uv-red range at a constant fast scanning rate and the data are computer-processed to provide a 3-D picture of the TL intensity distribution against wavelength as well as temperature.

II.2.4.7 – Automatic Background Signal Elimination

A double beam detection technique has been proposed(106) for measurements of low level TL where-in two similar samples (one "irradiated" and another "clean") are heated simultaneously with identical heating rates and the difference in the outputs of two identical photomultipliers facing the samples, are automatically plotted in a recorder. This method has been claimed to be of immense help in detecting low level-high temperature TL usually exhibited by geological samples.

III – UNDERSTANDING THE TL PHENOMENON

III.1 – On the Basis of Band Theory of Solids

The phenomenon of TL is usually qualitatively explained with the aid of the band picture of the solid with respect to its electronic energy levels. The forbidden band gap can be imagined to contain some acceptor/donor metastable levels which are basically responsible for the observed TL.

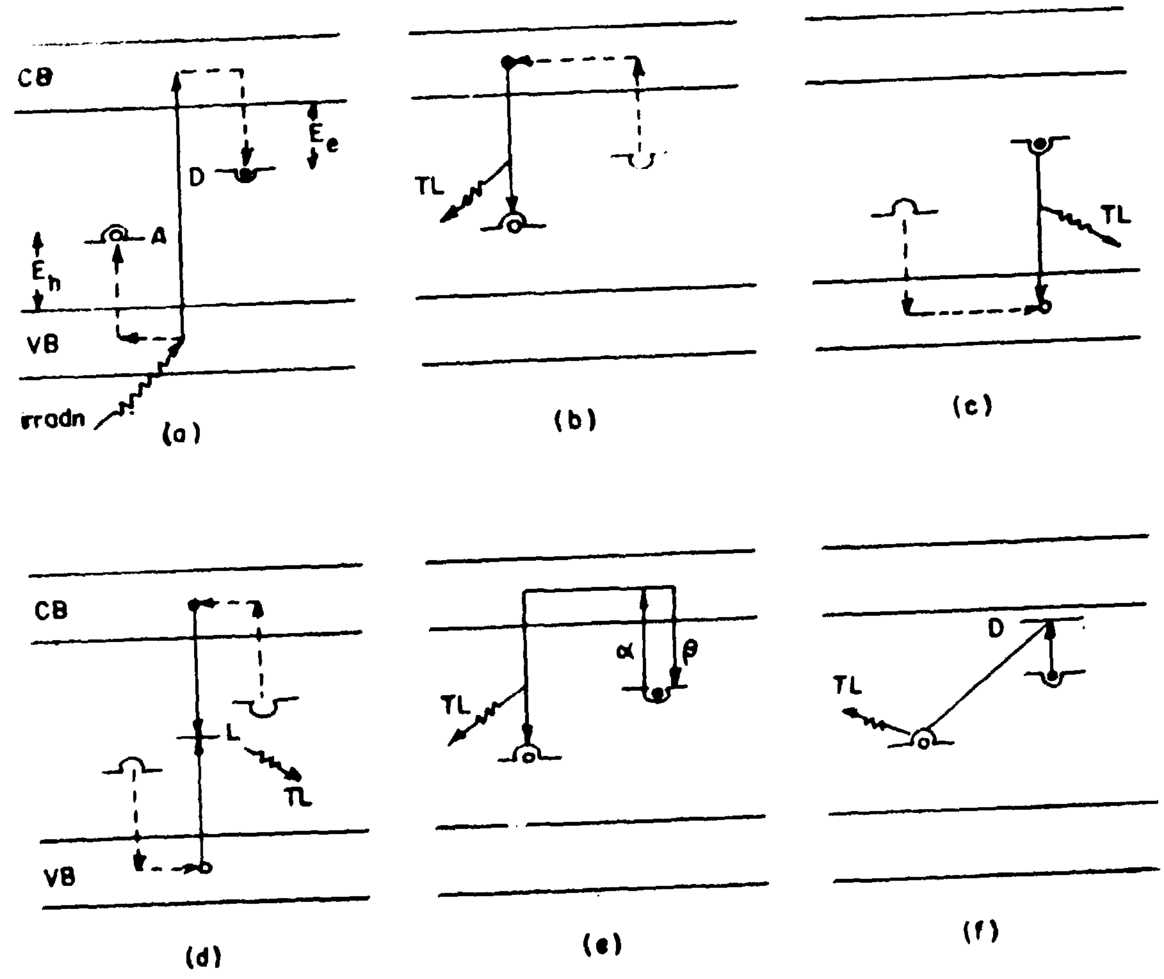


Figure 6 – Band model diagrams for the TL process in an insulating crystal (a) – upon irradiation; (b) – (f) alternative processes upon heating.

As illustrated in figure 5, interaction of ionizing radiation with the solid results in transfer of sufficient energy to electrons in the valence band (VB) for transfering them to conduction band (CB). This process usually requires energies around 10 ev (in a typical ionic crystal) and is effected by secondary electrons which are produced in the environment of the primary photo-electron of the charged particle tracks A good number of these "liberated" electrons return immediately to the ground state accompanied/unaccompanied by light emission (causing phosphorescence/internal heating). However a fraction of these can be captured at donor levels D with the corresponding holes at acceptor levels A

If the traps are not very deep. detrapping and recombination may already occur at a substantial rate around room temperature resulting in a short half life of the stored energy. This is called phosphorescence usually but strictly it is room temperature thermoluminescence.

Only if the traps are deep enough to result in sufficient storage stability at RT (half-lives of trapped electrons of at least several months normally corresponding to glow peak temperature greater than about 150°C), the effect becomes of dosimetric interest

The donor/acceptor levels are simply metastable states associated with crystal defects (including impurities). As the crystal is being heated either the electron or the hole – whichever is trapped with less energy-will be thermally ejected out of the trap and the corresponding TL glow peak temperature will be a measure of E_e or E_h respectively – the thermal deactivation energy. The released charge carrier can recombine at the still trapped counter part emitting the TL as shown in (b) & (c) of figure 6 If electrons are detrapped and recombine at the hole trapped at the acceptor level, the TL glow curve will represent the thermal activation energy of the electron traps and the TL spectral emission curve will characterise the hole centre and vice versa In many phosphors it is possible that the electrons and holes are detrapped more or less simultaneously and they recombine at an entirely new site (figure 6d), called the luminescence centre or recombination centre The TL glow curve will in this case represent an effective thermal activation energy needed by the trapped electron/hole to surmount a potential barrier between the trap and recombination centre

In reality, a trapped charge carrier when detrapped has a finite probability of getting retrapped (β in figure 6) When this retrapping probability is significant, the shape of the glow curve is different from the case when it is absent Also the recombination probability for the detrapped charge carrier may in most cases change with time (i.e., as the heating proceeds) depending on the number of available unused recombination centres Such a process is called a second order or bimolecular process usually while the simplest case where the recombination has a constant probability with time, is called a first order or mono-molecular process. There are also practical situations where the detrapped charge carriers recombine directly without having to be excited into the conduction/valence bands. This is a case of TL involving isolated luminescence centre and the process follows first order kinetics (figure 6f).

All the foregoing discussions take into account only the ionisation effects of the excitation irradiation; one should not however forget about the displacement effects resulting from elastic/inelastic collisions of the atoms of the phosphor with the impinging radiation. This effect is more significant for the case of particulate radiations (table II) The important thing about this displacement effect is that atoms are physically moved which results in the creation of interstitials and vacancies. In relation to TL, these constitute defects which have the potential to influence the trapping and emission processes.

Table II

Displaced Atoms Produced in "Thick" Materials with $Z < 30$ by each Incident Particle or Gamma Ray. (Levy, P. W. in Thermoluminescence in Geological Materials, Ed. Mc Dougall D. J., Academic Press, 1968)

Radiation	Energy	Number of displacements	
	MeV	theoretical	experimental
alfa	0 – 5	50 – 200	30 – 100
beta	0 – 5	$2 \times 10^{-2} - 2 \times 10^{-1}$	$10^{-2} - 10^{-1}$
gamma	0 – 3	2×10^{-3}	10^{-3}
neutron	0 – 5	400 – 1800	40 – 200
fission fragments	80	$10^3 - 10^4$	
cosmic rays	> 10	50 – 200 for each 5 MeV > 10 MeV	

III.2 – Understanding TL on Configurational Coordinate Diagrams

When TL occurs within an isolated luminescence centre, the process is usually more meaningfully described on the Configuration Coordinate diagram[49]. The energy of the trapping state in interaction with the lattice is given by a Configurational Coordinate curve $U^T(r)$ when the system is in the ground state and by $U^L(r)$ when it is raised to an excited state from which a luminescence transition may take place. The ground state of the system before the trapping took place is represented by $U^G(r)$. It is convenient to imagine the curves $U^G(r)$ and $U^L(r)$ to be representative of the potential energy of the system 'trap + lattice' while $U^T(r)$ that of the shallow excited level of the trapping state.

The entire process of excitation, trapping and thermally stimulated emission can be described as shown in figure (7).

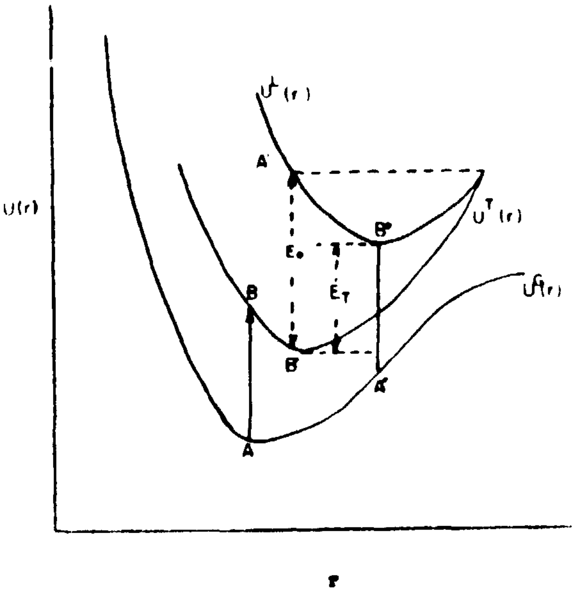


Figure 7 – Thermal and Optical activation of a trap and TL emission on a configurational coordinate diagram:

AB – *excitation leading to trapping at B'*
B'A – forbidden transition
E_0 – optical activation energy
E_T – Thermal activation energy
B"A" – TL emission

This model gives a more clear picture about the detrapping especially regarding the thermal and optical activation energy diferences There has been arguments favouring the use of the C.C. diagrams even in the cases where the detrapped electron enters the conduction band before the luminescence transition occurs. The ionisation continuum is considered to be given by all energies lying above the curve $U^L(r)$ which represents the potential energy of the system "trap + lattice" when the electron has just left the trap and is in the conduction band.

III.3 – Understanding TL on the Basis of the Observed Physicochemical Effects

Explanations of the TL phenomenon on the basis of band theory of solids or Configurational Coordinate diagrams are only intuitive models to help understand the phenomenon in general rather than to answer all the observations made on the TL of all the phosphors. It is possible to construct a self consistent picture for the TL process in individual phosphors purely based on experimental observations A good example is the case of Thermoluminescence exhibited by CaF_2 (RE) and $CaSO_4$ (RE) phosphors(133,144).

By irradiation it is considered that an electron is removed from F^- and $(SO_4)^{--}$ ions respectively and is trapped by the RE^{3+} impurity ions; A hole is imagined to be trapped at the fluorine and sulfate sites respectively in a variety of configurations like F^o, F_2^- etc and SO_4^-, SO_3^- etc. These trapped holes are thermally less stable than the trapped electrons at the rareearth sites. After the irradiation, when the phosphor is warmed, the holes are released in stages from various configurations resulting in a set of thermal activation energies as observed in the multipeak TL glow-curves exhibited by these phosphors. The "released" holes recombine with the trapped electrons at the rareearth sites leaving the rareearth ions in excited states These excited rareearth ions emit their characteristic luminescence while returning to their ground states The emission maxima observed in the TL spectral emission curves of these phosphor correspond to the different excited electronic levels of the RE^{3+} ions.

Thus the whole TL process can be represente by the following equations:

$$[RE^{3+}] + \ldots + F^- + \ldots \xrightarrow{\text{irradiation}} [RE^{2+}] + \ldots + F^o + \ldots$$

$$\text{or} \qquad\qquad\qquad\qquad \text{or}$$

$$[RE^{3+}] + \ldots + F^- + F^- + \ldots \xrightarrow{\text{irradiation}} [RE^{2+}] + \ldots + F_2^- + \ldots$$

$$[RE^{2+}] + \ldots + F^o + \ldots \xrightarrow{\text{heating}} \begin{array}[t]{l} [RE^{3+}]^* \\ \downarrow \dashrightarrow TL \\ [RE^{3+}] \end{array} + \ldots + F^- + \ldots \text{ etc}$$

(The dots in the equation denote that RE and F ions involved in such valence reduction-oxidation processes are not nearest neighbours in the crystal lattice).

IV – MATHEMATICAL TREATMENT OF THE TL PROBLEM

IV.1 – Detrapping of Charge Carriers from Metastable Levels

Whenever a trapped charge carrier (electron or hole) is considered to be released by thermal activation (as in TL) the usual and perhaps the only available mathematical approach is to consider the probability of finding these in a particular potential energy arrangement with a Maxwellian statistical distribution of energies at various temperatures. If a trap is considered as a potential well, then E is called the trap depth and as the temperature is increased, the probability of finding the trapped carriers with this energy E (so that they can escape) increases exponentially by: $e^{-E/kT}$ where k is the Boltzman constant. There are however certain difficulties in understanding the situation assuming thermodynamic equilibrium considerations(200). Semi-classically, assuming phonon interactions, the problem of thermal activation of trapped charge carriers can be worked out(49) to give the probability rate of escape as

$$p = s\,e^{-E/kT} \tag{1}$$

It is more appropriate to understand this probability rate as the inverse of the life time of the charge carrier in the metastable state at temperature T, ie,

$$\tau^{-1} = p = s\,e^{-E/kT} \tag{2}$$

The factor "s" has the dimension $\sec^{-1}$ and is hence called the frequency factor. In many phosphors this factor is only slowly varying with temperature and can be considered a constant for a particular trap. The factor s is sometimes found to be dependent on the initial concentration of the carriers in a trap. When the frequency factor is not treated as a constant it is referred as the "pre-exponential factor" which is comprised of the frequency factor and concentration or temperature dependant terms (§ sec.IV.2). The frequency factor is physically understood in best of imaginations the folowing way: if one considers the trap as a potential well then value "s" represents the product of the number of times an electron hits the walls (in a attempt to escape from the well) and the wall reflection coefficient. It then follows that value of s should be of the order of, or less than, the vibrational frequency of the crystal. However in practice one does come across situations where s takes values differing from lattice phonon frequencies by many orders of magnitude. This is attributable to fuctuations in local environments of the trap such as produced by a nearby impurity causing changes in the frequency of the localised phonons. Values of s in the range of $10^8 \sim 10^{11}$ are normally encountered in TL phosphors and it is instructive to understand the variation in the "lifetimes" of trapped carriers in a particular trap characterised by a particular frequency factor (see table III).

Table III

Relationship between the Life-Time and
Observation Temperature for a
Charge-Carrier in a Trap
Characterised by E = 0.65 eV
and $s = 10^9 \sec^{-1}$ (49)

Temperature of observation T°C	Life-time τ
−100 °C	1600 days
− 50 °C	1 day
18 °C	3 min
50 °C	4 sec
100 °C	0.25 sec

IV.2 — The Simple Theory of Randall & Wilkins

Randall & Wilkins(162) provided the simplest mathematical representation for the luminescence glow peaks without any overlapping. The basic assumptions they made were that once an electron escapes from a trap there is no significant probability for it to get retrapped and that the luminescence intensity at any temperature is directly proportional to rate at which the detrapping occurs. During heating, if n is the concentration of filled traps at any time t (temperature = T) then the intensity of TL is given by

$$I \propto \frac{dn}{dt} \quad \text{or} \quad I = -c.\, dn/dt \tag{3}$$

where c is a proportionality factor which can be conveniently set to unity without any loss of generality as long as it remains constant with temperature and the minus sign indicates decrease of n with time (temperature). Assuming a linear heating rate q ie $T = T_o + qt$ where T_o is the initial temperature, it can be shown (by making use of eqn.1) that

$$n = n_o \exp\left[-\int_{T_o}^{T} \frac{s}{q}\, e^{-\frac{E}{kT'}}\, dT' \right] \tag{4}$$

or

$$I = n_o s\, e^{-\frac{E}{kT}} \exp\left[-\int_{T_o}^{T} \frac{s}{q}\, e^{-\frac{E}{kT'}}\, dT' \right] \tag{5}$$

The equation becomes easily solvable if one could use a heating rate such that $q = -\frac{d}{dt}\left(\frac{1}{T}\right)$. In any case it is easily seen that the intensity builds up as T increases, reaches a maximum for particular value of T_m and then falls off for any further increased heating. By setting $dI/dT = 0$ at $T = T_m$ one obtains the important relationship,

$$\frac{q.E}{kT_m^2} = s\, e^{-E/kT_m} \tag{6}$$

There are quite a few interesting implications borne out of Randall-Wilkins formalism:

i) At a constant heating rate q, T_m shifts towards higher temperatures as E increases or s decreases (figures 8 & 9). The area under the glow peak in each case is however strictly proportional to the concentration of the trapped electrons at the start of the experiment.

ii) For a given trap (ie constant E & s values, T_m shifts to higher temperatures as q increases (figure 10).

iii) The temperature T^* at which the probability of electron escape is $1\,\text{sec}^{-1}$ is somewhat higher than the temperature T_m at which the glow maxima occurs (figure 11). It can be easily shown that there exists a heating rate q^* for which T^* and T_m will concide and the trap depth will be given by

$$E = q^* k\, (\log s)^2 \tag{7}$$

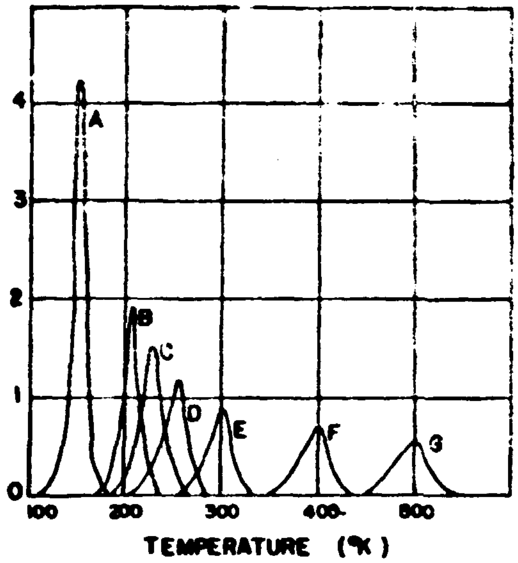


Figure 8 – Theoretical TL glow curves for phosphors with a single trap depth and no retrapping, heated at a constant rate of 2.5°K/s (Garlick, G. F. J., 1948 – ref./71/).

A) E = 0.3 eV and s = 10^9 s^{-1}
B) E = 0.4 eV and s = 10^9 s^{-1}
C) E = 0.4 eV and s = 10^8 s^{-1}
D) E = 0.4 eV and s = 10^7 s^{-1}
E) E = 0.6 eV and s = 10^9 s^{-1}
F) E = 0.8 eV and s = 10^9 s^{-1}
G) E = 0.4 eV and s = 10^6 s^{-1}

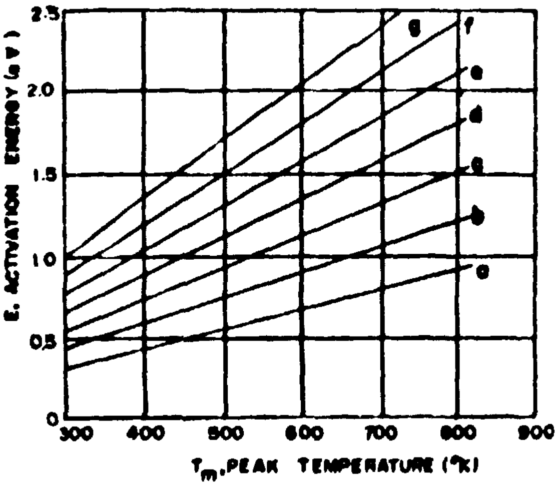


Figure 9 – Diagram displaying the relationship among s, E and T_m normalised to a heating rate of 1°K sec^{-1} (Becker, K., 1973 – ref./14/).

a) 10^4 s^{-1}
b) 10^6 s^{-1}
c) 10^8 s^{-1}
d) 10^{10} s^{-1}
e) 10^{12} s^{-1}
f) 10^{14} s^{-1}
g) 10^{16} s^{-1}

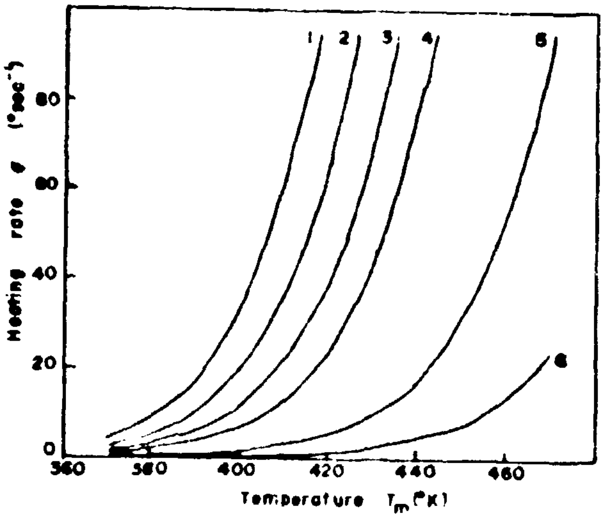


Figure 10 – T_m of a glow peak as a function of heating rate for different trap depths with $s = 10^{10}$ sec^{-1}:

E/K varies from 9000°K (curve 1) – 10800°K (curve 6) in steps of 200°K; 1 eV equivalent to 11600°K (Bräunlich, P., 1968 – ref./26/).

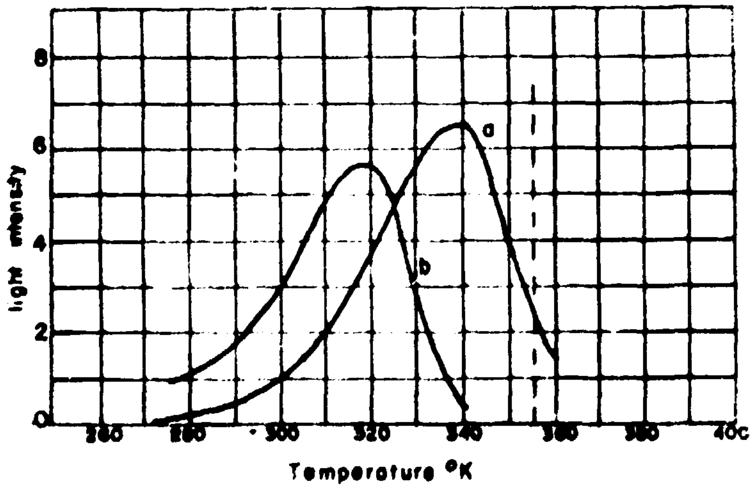


Figure 11 – Theoretical glow curve for a single trap depth and for two heating rates: a) 2.5°/s and b) 0.5°/s; E = 0.67 eV and $s = 2.9 \times 10^9$ sec^{-1}; at 356°K the decay period of the trapped electron is 1 sec (Randall, J. T., 1945 – ref./162/).

For a frequency factor of the order of 10^{10} sec^{-1} and trap depth of 1 ev, such a matching will occur for $q = 116$ deg . sec^{-1}.

Various authors have extended the Randall-Wilkins theory, to "general" order kinetics and also to cases where the frequency factor may be temperature-dependent. Such a general equation may be given by(168)

$$I = -C\,\frac{dn}{dt} = C \,.\, s'' \,.\, T^{a} \,.\, n^{b} \,.\, \exp\left(\frac{-E}{kT}\right) \tag{8}$$

where $-2 \leqslant a \leqslant +2$ and $1 < b \leqslant 2$, the order of kinetics. If the frequency factor is temperature-independent, $a = 0$ and $s''T^{a} = s'$ called the pre-exponential factor in sec^{-1} $cm^{3(b-1)}$. The solution to equation (8) can be written as:

$$I = s'n_o^b \exp\left(\frac{-E}{kT}\right) \left\{ \left[\frac{(b-1)s'n_o^{\,(b-1)}}{q}\right] \int_{T_o}^{T} \exp\left(\frac{-E}{kT'}\right. .\, dT') + 1 \right\}^{-\frac{b}{b-1}} \tag{8a}$$

Although this equation is not valid for $b = 1$, it reduces to equation (5) when $b \rightarrow 1$. By equating the derivative of this equation to zero at $T = T_m$, the peak temperature, one gets the condition,

$$\frac{(b-1)s}{q} \int_{T_o}^{T} \exp\left(-\frac{E}{kT}\right).\, dT + 1 = \frac{(s \,.\, b \,.\, k \,.\, T_m^2)}{q.E}\, e^{-\left(\frac{E}{kT_m}\right)} \tag{8b}$$

This equation gives valuable information on the dose dependence, if any, on the peak temperature shift.

If the detrapping is considered a rate process(67), the rate being specified by dc/dT where $c = (n_o - n) / n$, the zero negative order kinetics will exhibit ever-accelerating values for dc/dT; orders between 0 and 1 go through a maximum rate and in ideal cases reach completion at a finite temperature; for orders > 1, increasing order results in a more gradual asymptotic approach to the temperature axis after the maximum is reached (figure 12).

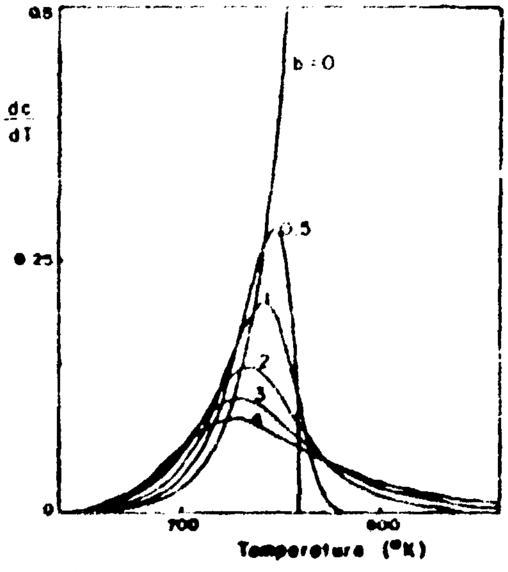


Figure 12 – Effect of the order of kinetcs (b) on the rate (dc/dT) of a process (Flynn, J.H., 1966 – ref. /67/).

There has been a singular experimental observation of an order of kinetics < 1 (0.7 in the case of some KCl and KBr samples) and this has been elegantly explained as due to a first order radiative process and a zero order non-radiative process which accounts for 30% of total decay[125,158].

An attempt has been made[212] to introduce a temperature dependent recombination probability factor $\gamma \propto \exp(W/kT)$ where W is an energy depth characterising a non-radiative process. The Randall-Wilkins equation (5) in this case becomes

$$I = k \, . \, n_o \, . \, s \, . \, e^{\frac{(W-E)}{kT}} \exp\left[\int_{T_o}^{T} \frac{s}{q} \, e^{-\frac{E}{kT'}} \, . \, dT' \right] \tag{9}$$

IV.3 – Kinetic Equations and Solutions

IV.3.1 – TL Accompanied by Conductivity

A much more generalised and physically understandable approach which makes use of the charge neutrality condition of the phosphor is to write down a set of linear simultaneous equations to account for a single TL peak. The most general case can be represented by (see figure 13)

$$\left.\begin{aligned} dn/dt &= \alpha \, . \, h - \beta \, . \, n\,(H-h) - \gamma \, . \, n \, . \, f \\ dp/dt &= \delta \, . \, f - \beta^* . \, p\,(A-f) - \gamma^* . \, p \, . \, h \\ dh/dt &= -\alpha \, . \, h + \beta \, . \, n\,(H-h) - \gamma^* . \, p \, . \, h \\ df/dt &= -\delta \, . \, f + \beta^* . \, p\,(A-f) - \gamma \, . \, n \, . \, f \end{aligned}\right\} \tag{10}$$

where H = concentration of electron traps of depth E; h = concentration of electrons trapped; n = concentration of electrons in the conduction band; f = concentration of trapped holes; p = concentration of holes in the valence band and, α, β, γ, δ, β^*, γ^*, are transfer probabilities as shown in figure with $\alpha = s \, . \, \exp(-E/kT)$.

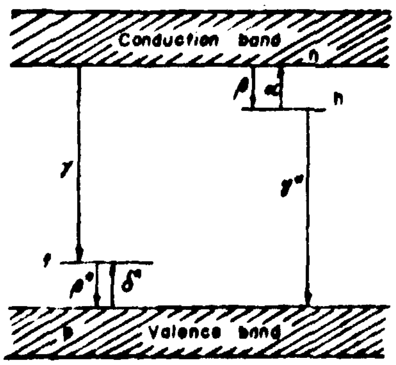


Figure 13 – Energy level scheme proposed by Schön.

These equations of course do not take into account any interaction with the presence of other types of traps. The neutrality condition demands that,

$$p + f = n + h \qquad (11)$$

The TL intensity is given by the number of radiative transitions per sec. per cm^3 of the crystal and is therefore proportional to the recombination rate:

$$\left.\begin{array}{ll} & I = \gamma . n . f \\ \text{or} & \\ & I = \gamma^{*} . h . p \\ \text{or} & \\ & I = \gamma . n . f + \gamma^{*} . h . p \end{array}\right\} \qquad (12)$$

Analytical solutions to equations (10) are not obtainable without making at least two basic assumptions:

$$n << h \text{ and } dn/dt << dh/dt \qquad (13)$$

A typical solution for the case of large retrapping of conduction eletrons and small retrapping of holes in the valance band is given by$^{(27)}$:

$$I \simeq \frac{h_o^2}{H} . \gamma . N_c . \exp\left[- \frac{E}{kT} - \frac{2\delta_o^*}{q} \int_{T_o}^{T} \exp\left(- \frac{E_A}{kT'} \right) . dT' \right] \qquad (14)$$

where E_A is the hole trap depth; q is the linear heating rate and N_c is the density of states near the bottom of the conduction band given by

$$n . H = h . N_c . \exp\left(- \frac{E}{kT} \right) \qquad (15)$$

An empirical approach assuming general order kinetics was attempted$^{(42)}$ to get the TL intensity from balance equations similar to (10). This approach helped in at least explaining satisfactorily the occurrance of shape changes in the glow peak.

Recently attempts have been made$^{(105)}$ to solve the equations (10) numerically without assuming conditions given in (13). It was found that conditions (13) are satisfied if the number of active traps are $> 10^{15}$ cm^{-3}.

IV.3.2 – TL Unaccompanied by Conductivity

An alternative situation may exist where the thermally activated charge carrier is in an excited state in the forbidden gap rather than the conduction/valance band. The set of balance equations can be written in an appropriate manner similar to eq. (9) and the intensity evaluated$^{(82)}$ under the same conditions (13).

Yet another possibility is when the transition is within one localized centre. That is, the traps and recombination centres form associated pairs. The thermal stimulation raises the trapped carrier to a level from where it can either be retrapped or emit luminescence by falling to the ground state of the centre. The kinetics in this case are formulated by the following equations[110].

$$\begin{aligned} I &= -\frac{df}{dt} = \gamma \,.\, n && \S \\ -\frac{dn}{dt} &= h \,.\, s \,.\, \exp\left(\frac{-E}{kT}\right) - s \,.\, n. && \S \qquad (16) \\ f &= n + h && \S \end{aligned}$$

where $\gamma\,(\mathrm{sec}^{-1})$ is the recombination probability of the excited electron and n refers to the concentration of excited electrons. Under the same conditions (13), the TL intensity can be written as,

$$I = \left[\frac{\gamma \,.\, s}{\gamma + s}\right] . \, f \,.\, \exp\left(\frac{-E}{kT}\right) \qquad (17)$$

IV.4 – Statistical Model/Fermi Level Analysis

All mathematical models discussed so far assume only discrete energies for the traps. In real crystal however there may be cases of a distribution of these trapping energies existing in the lattice and this may be the cause for overlapping of peaks in the TL glow curve. Such a case may be mathematically tackled by a statistical model with a quasicontinuous impurity level distribution and considering transitions from these levels into the conduction/valance band[29]. However a formula for the TL intensity as a function of temperature cannot be derived as the trap distribution H(E) is usually not known. Solutions may be found assuming certain distribution functions for H(E). In case of fast retrapping, a quasi-thermal equilibrium between conduction electrons, n and the electrons in the traps with a quasi-Fermi level F_q results:

$$n = N_c \exp\left[-\frac{E_c - F_q}{kT}\right] \qquad (18)$$

where N_c is the density of states in conduction band near E_c.

The level F_q is a function of T and moves toward the equilibrium level during heating and finally merges when no more TL can be observed. Thermoluminescence intensity is given by,

$$I = n \int_{E_v}^{F_q} \gamma\,(S_E - s_E)\, dE \qquad (18a)$$

and the number of trapping states is given by,

$$H = \int_{F_q}^{E_c} S_E \,.\, dE \qquad (18b)$$

where E_v is the energy position of to top of valance band;

γ is the recombination coefficient for the electron with empty luminescence centres;

S_E is the number of defect levels per unit energy range and s_E is the number of occupied centres per unit energy range. Such a consideration can lead to an unique experimental determination of the distribution function H(E) for the trap[30].

IV.5 – TL Growth Curves

Almost all efforts in mathematical treatment of the TL problem have been restricted to the analysis of thermal activation of the trapped carriers. The initial phase in the TL process namely the storage of energy by means of trapping of charge carriers has never been attempted as part of any of the TL models. If one is interested in relating the TL intensity with the initial irradiation (as is necessary in applications) such a mathematical representation of the TL growth curve will be very helpful. Moreover any physical understanding which may be borne out of such mathematical models can ultimately lead to development of materials which may be efficient in storing energy – a primary requirement for a sensitive TL phosphor.

There has been an attempt[131] to develop a TL intensity growth equation for the case of internal alpha irradiation of calcite crystal in analogy with F-centre growth equation for alkali halides. It was assumed that the lattice contains two types of traps initially and that by irradiation one of the types can be generated besides the traps getting filled with charge carriers.

Furthermore, it was assumed that the generation of traps by irradiation can at best be of the order of the initial trap density implying that the traps are somehow associated with impurities or defects of fixed concentration in the starting material. The appropriate rate equations are given by,

$$\begin{aligned} \frac{dn}{dt} &= \delta\,(n_o - n) \qquad \S \\ \frac{dN}{dt} &= \beta\,(S + N_o - N) \qquad \S \qquad (19) \\ \frac{dS}{dt} &= \gamma\,(S_o - S) \qquad \S \end{aligned}$$

where n and N are colour centre densities after irradiation for time t; S is the concentration of newly generated traps; n_o and N_o are the concentrations of traps initially present; S_o is the initial number of sites at which new traps can be generated; δ and β are the rate constants for filling traps and γ is the rate constant for generating new traps. Solutions for these equations can be written as,

$$u = 1 - \frac{I}{I_s} = 1 - \frac{(n + N)}{(n_o + N_o + S_o)}$$

$$= \left[\frac{n_o}{(n_o + N_o + S_o)} \right] \exp(-\delta t) + \left[\frac{\left(\frac{-\gamma S_o + N_o}{\beta - \gamma} \right)}{(n_o + N_o + S_o)} \right] \exp(-\beta t)$$

$$+ \left[\frac{\left(\frac{S_o \beta}{\beta - \gamma} \right)}{(n_o + N_o + S_o)} \right] \exp(-\gamma t)$$

$$u = a\exp(-\delta t) + b\exp(-\beta t) + c\exp(-\gamma t) \tag{20}$$

where I is the glow peak intensity after irradiation for time t; I_s is the saturation value of I for large t and a, b, c are constants with $a + b + c = 1$. In samples where new traps are not created by irradiation, the equation reduces to:

$$u = a\exp(-\delta t) + b\exp(-\beta t) \tag{21}$$

$$\text{with } a + b = 1$$

A more or less similar attempt was made(36) on LiF, the most widely used TL phosphor in radiation dosimetry. There are three important experimentally observed characteristics of this phosphor: i) for sufficiently low levels of irradiations, the TL increases linearly; ii) at higher values of irradiation the TL increases supralinearly, but the glow peak shape remains the same; and iii) at still higher values of irradiation the TL output saturates even though the shape of the peak may be changing. The mathematical model assumes an initial number of unfilled traps N_o, creation of traps by irradiation with a proportionality constant α, filling of traps by irradiation with a proportionality constant β and a maximum number of traps N_F. The TL intensity build-up in such a case is given by,

$$I = \left(\frac{N_o\beta}{\alpha-\beta}\right)\left(e^{-\beta R} - e^{-\alpha R}\right) + \left(\frac{N_F}{\alpha-\beta}\right)\left[\alpha(1-e^{-\beta R}) - \beta(1-e^{-\alpha R})\right] \tag{22}$$

where R is the irradiation level in roentgens. For LiF, complete matching with the experimental data has been obtained with

$$\left.\begin{array}{ll} N_o = 1.2 \times 10^{15} \text{ traps cm}^{-3}; & \beta = 1.1 \times 10^{-5}\ R^{-1}; \\ N_F = 6.0 \times 10^{15} \text{ traps cm}^{-3}; & \alpha = 1.0 \times 10^{-4}\ R^{-1} \end{array}\right\} \tag{23}$$

Note that the values obtained for N_o and N_F are in the range values that have been predicted for the validity of the usually advocated mathematical equations for the TL glow curve (§ sec.IV.3.1). The presence of any other type of trap that could compete with the trap under consideration for the process of filling-up during irradiation, could also be taken into account and the equation (22) suitably modified(34) giving satisfactory results. An interesting, semi-mathematical approach called the track-interaction model was later proposed(8) for LiF which essentially assumes that traps and recombination centres are produced along a track during irradiation and that for high levels of irradiation the tracks overlap. This model seem to be the most satisfactory one today.

V – EXPERIMENTAL METHODS OF DETERMINING TL PARAMETERS

The TL characteristics of any material is customarily labelled by a few parameters such as the order of kinetics obeyed by the TL process, the activation energy or trap depth and the frequency factor. There are many approaches practised to determine these experimentally(43,45,184,203); however there is very little evidence that consistent quantitative information especially on trap depth and frequency factor could be obtained by the TL methods(192). As exact TL kinetic equations can be formed and solutions obtained(105), the inescapable conclusion is that TL analysis can be meaningful only if the defect structure of the solid is known and some associated, temperature-dependant parameters such as mobility, luminescence efficiency, band structure etc are reasonably well known. Fortunately such as impractical requirement does not come in the way of successfully employing the TL technique in various applications (§ sec. X) as the phenomenon is extremely efficient and reproducible in many materials.

Most often a multi-peak TL glow curve is encountered in practice and it is necessary to isolate the peak under study from the overlapping neighbouring peaks before starting any analysis. The most widely used method is a "cleaning technique" proposed by Hoogenstraaten(84) which involves a properly chosen thermal treatment to remove all lower temperature peaks below the peak under study. Recently experimental techniques have been proposed(72,167) to isolate TL glow peaks of alkali halides by high temperature irradiation or room temperature optical bleaching or photo-stimulation with appropriate frequency.

This section lists about eight categories of the TL parameters evaluation methods which cover almost the entire spectrum of approaches being practised today.

V.1 – The Initial Rise Method

This is the simplest procedure to obtain an estimate of the trap depth and is independent of the order of kinetics involved(71). The method basically assumes the following: i) in the early rising range of temperatures, ie. $T << T_m$, the rate of change of trapped carrier population is negligible (and hence intensity strictly proportional to $\exp(-E/kT)$; ii) the frequency factor essentially remains the same at all temperatures; and, iii) there is no overlap of glow peaks belonging to different trapping levels. Thus this method would mean finding,

$$E_{i.r} = -k \frac{d(\ln I)}{d(\frac{1}{T})} \tag{24}$$

In case the factor s is temperature dependant by the factor T^a, the actual trap depth will be given by,

$$E = E_{i.r} - a \cdot k \cdot T \tag{25}$$

This relationship clearly demonstrates the fact that glow peaks belonging to the same trap (like F-centres in the TL of NaCl) will give rise to increasing $E_{i.r}$ values for higher temperature glow peaks(4).

The experimental procedure can be elegantly followed this way: The material to be investigated can be divided into two parts after the irradiation; one part can be used to record the full TL glow peak under evaluation; the other part can be heated repeatedly many number of times in such a way that each heating is terminated at a temperature where the TL intensity reached is hardly 1% of the peak intensity recorded in the first experiment. The $\ln I$ vs. $1/T$ plots are made for each heating cycle thus constituting a set of straight lines (§ sec IV 2) in the same graph (Arrehenius diagram). The slope of those lines which are parallel in consecutive runs is equated to E/k and E is evaluated. There are however theoretical and experimental considerations that limit the applicability of this method(26,80). One of the important conditions to be satisfied for the initial rise method to be accurate is given by,

$$R \cdot h_o \left(\frac{2}{Z_o - 1} \right) << f_o \tag{26}$$

where R is retrapping factor and Z_o is the filling ratio of traps at temperature T_o; f_o is the concentration of unoccupied recombination centres at temperature T_o and h_o is the density of trapped electrons at temperature T_o. This condition in other words laids down two more requirements than the three assumptions listed earlier, viz., iv) the traps are not filled to saturation and v) the retrapping is negligible.

An automatically operating apparatus for the analysis of glow peaks using the initial rise method has been described by Gobrecht and Hofmann(75). The authors show that the trap density H(E) can also be determined by this method (see figure 14). Yet another extension of this method is discussed in section 5.6.

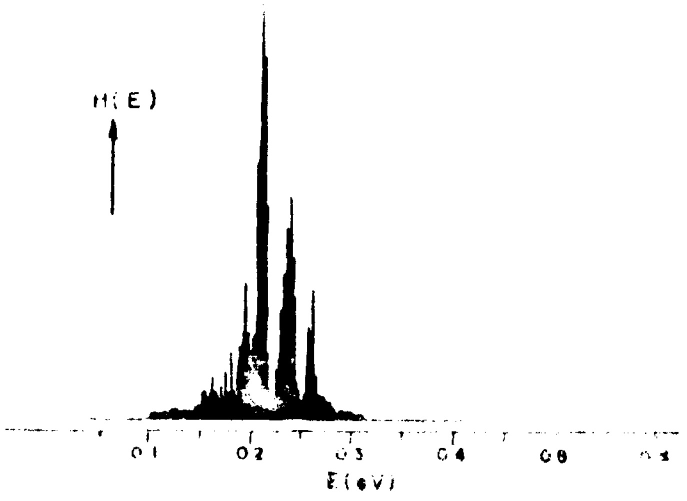


Figure 14 – Trap spectrum of ZnS:Cu phosphor using Hofmann's trap spectrograph (Gobrecht, H., 1966 – ref. /75/).

V.2 – Method Using Different Heating Rates

This method is based on equation (6). Using two different linear heating rates q_1 and q_2 and finding the corresponding peak temperatures T_{m1} and T_{m2}, one can calculate the trap depth as(22,28):

$$E = \left[\frac{k \cdot T_{m1} \cdot T_{m2}}{(T_{m1} - T_{m2})} \right] \ln \left[\left(\frac{q_1}{q_2} \right) \left(\frac{T_{m2}}{T_{m1}} \right)^2 \right] \qquad (27)$$

Another way(81,84) is to use several different heating rates and plotting $\ln \left(\frac{T_m^2}{q} \right)$ versus $\frac{1}{T_m}$ which should yield a straight line with slope $\frac{E}{k}$. It should be mentioned here that with reference to equation (9), this method would yield E rather than E-W as was obtained by the initial rise method. Thus, use of both these methods can lead to a good estimate of W.

An approximate estimate of E can be readily obtained even by plotting $\ln \left(\frac{1}{q} \right)$ versus $\left(\frac{1}{T_m} \right)$ which should yield a straight line whose slope is $\frac{E}{k}$ (57).

It has been recently pointed out(46) that equation (6) is valid for any heating rate (not necessarily linear) if one replaces q by q_m, the instantaneous heating rate at T_m. It has also been shown that for the general order case, one can plot $\ln \left| I_m^{b-1} \left(\frac{T_m^2}{q} \right)^b \right|$ versus $\frac{1}{T_m}$ and get a straight line with slope $\frac{E}{q}$ while, the $\ln \left(\frac{q_m}{T_m^2} \right)$ versus $\frac{1}{T_m}$ plot would still yield a E value to a good approximation.

The method of determining E using different heating rates has the advantage of being insensitive to retrapping effects apart from being simple. If temperature measurement can be achieved within 1°K accuracy, E values can be estimated within 5%.

V.3 – Method Based on Glow Curve Shape

T_m, T_1 and T_2 which are respectively the peak temperature and temperatures on either side of T_m corresponding to half the peak intensity (see figure 15), are dependant upon the shape of the glow peak and there are several equations developed to relate E with all or some of these temperatures.

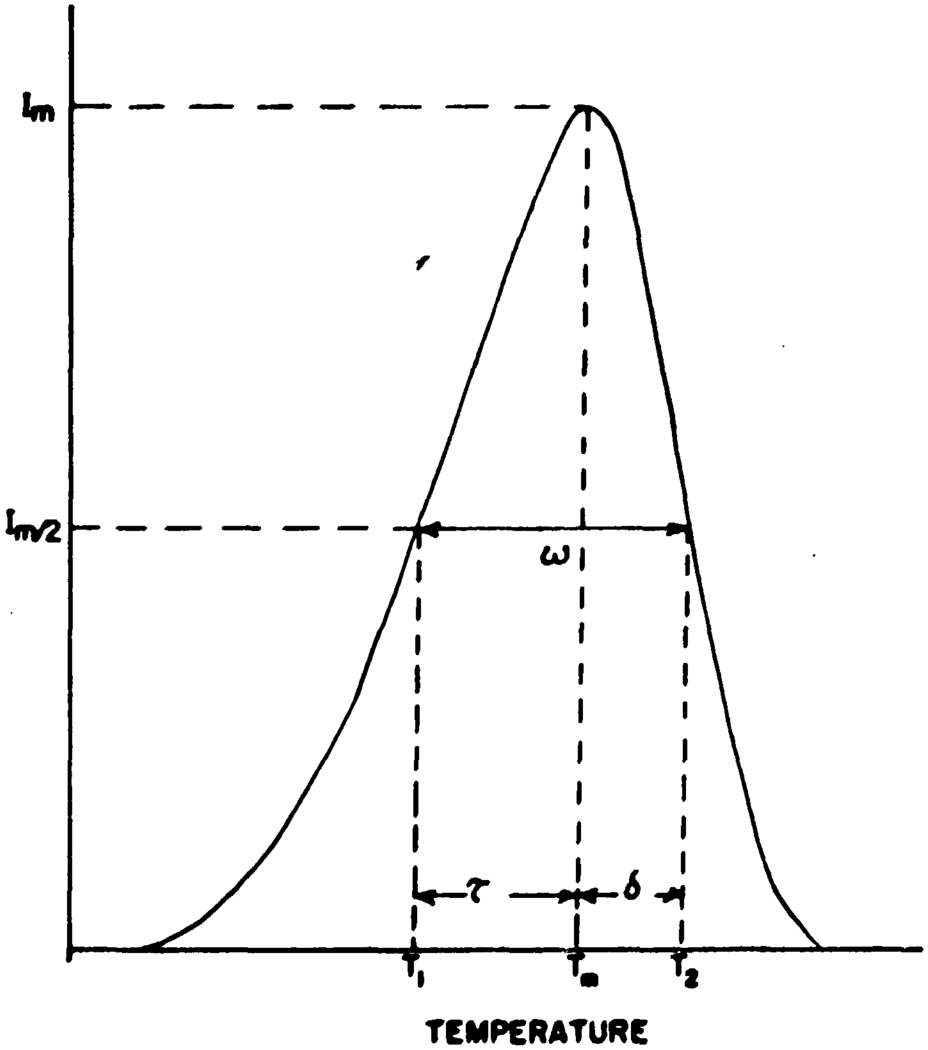


Figure 15 – Definition of various parameters for methods which use the shape of the glow curve for determining trap depth.

For the case of first order kinetics, using only the ascending part of a glow peak, it can be shown(79) that,

$$E = \frac{1.51\,k\,.\,T_m\,.\,T_1}{(T_m - T_1)} \qquad (28)$$

For the same case, using only the descending part of the glow peak, it has been shown(118) that,

$$E = \frac{k.T_m^2}{(T_2 - T_m)} \qquad (29)$$

The above equations have been found to yield values within ± 5%. There has been correction factors suggested(44) to improve the accuracy still further. These equations have their merit in that they are quite useful in providing an alternative in case of overlapping of the peak by the neighbour peaks.

A more important approach(82) has been to use both T_1 and T_2 and evaluate the trap depth as well as the order of kinetics involved. Here, the symmetry of the glow peak is measured in terms of T_1, T_2 and T_m as:

$$\mu_g = \frac{\delta}{\omega} = \frac{(T_2 - T_m)}{T_2 - T_1} \qquad (30)$$

It has been shown that,

$$\mu_g < \frac{(1 + \Delta)}{e} \text{ for first order kinetics}$$

and

$$\mu_g > \frac{(1 + \Delta)}{e} \text{ for second order kinetics} \qquad (31)$$

where $\Delta = 2kT_m/E$

The E values for the two processes are given by,

$$E_1 = [\frac{1.72\,k\,.\,T_m^2}{\tau}]\,(1 - 2.58\,\Delta)$$

and,

$$E_2 = [\frac{2\,k\,.\,T_m^2}{\tau}]\,(1 - 3\,\Delta) \qquad (32)$$

where $\tau = T_m - T_1$

Here the E values can be obtained only by iterative calculations. Neglecting Δ, equations (31) and (32) do yield informations to a good approximation.

A good estimation of E for the two kinetic processes are empirically given by$^{(44)}$:

$$E_1 = 2kT_m \left[\left(\frac{1.25T_m}{T_2 - T_1} \right) - 1 \right] \qquad §$$

and, (33)

$$E_2 = 2kT_m \left[\left(\frac{1.76T_m}{T_2 - T_1} \right) - 1 \right] \qquad §$$

A calculated graph of μ_g and order of kinetics b is given in ref. $^{(42)}$.

All the aforesaid formulations assume s to be independant of temperature. If s is considered to be equal to BT^a where B is a constant and $-2 \leqslant a \leqslant +2$, the E value for a first order process is given by$^{(103)}$:

$$E = k \,.\, T_m \left\{ \left[\left(1.2 \frac{\delta}{\tau}\right) - 0.54 \right] \left[\left(\frac{T_2 - T_1}{T_m} \right) \right] + 0.0055 - \left[\frac{1}{2} \left(\frac{\delta}{\tau} - 0.75 \right) \right]^2 \right\}^{-1} \tag{34}$$

A complete discussion on the accuracy and operating conditions for all the above formulations is given in ref. $^{(153)}$.

V.4 – Inflection Point Method

A method has been proposed$^{(110)}$ making use of the fact that the second derivative of the TL intensity with respect to temperature is zero at the inflection points. In the Randall-Wilkins formula for the TL intensity, the inflection points T_i are positive real roots of$^{(26)}$:

$$\left(\frac{E}{k \,.\, T_m^2} \right) \exp \left[\frac{2E}{k} \left(\frac{1}{T_m} - \frac{1}{T_i} \right) - \left(\frac{3E}{kT_i^2 T_m^2} \right) \exp \left[\frac{E}{k} \left(\frac{1}{T_m} - \frac{1}{T_i} \right) \right] - \frac{2}{T_i^3} + \frac{E}{kT_i^4} = 0 \tag{35}$$

This gives,

$$E = \frac{(kT_m T_i)}{|T_i - T_m|} \ln \frac{A}{Q} \tag{36}$$

where $Q = \left(\frac{T_i}{T_m} \right)^2$ and $A = 0.77$ and 2.66 respectively for $T_i < T_m$ and $T_i > T_m$.

The frequency factor is given by,

$$s = q \left[\frac{X}{YT} \right]_m \quad \text{where } X = E/kT \text{ and } Y = \exp \left(-\frac{E}{kT} \right) \qquad (37)$$

This method has the advantage of fine resolution even in case of closely lying peaks and E and s values can be obtained for all peaks from a single glow curve.

V.5 – Isothermal Decay Method

Strictly speaking, this is not a TL method but neverthless is a general technique to determine E and s. The experimental procedure consists in quickly heating the sample (after the initial excitation) to a specific temperature and measuring the phosphorescence decay by maintaining the sample isothermally at this temperature(207). It can be shown that the slope of the linear plot between $\ln I(t)$ and t is given by,

$$m = s \exp\left(-\frac{E}{kT}\right) \qquad (38)$$

By obtaining the slopes at two different temperatures, E can be calculated from:

$$\ln\left(\frac{m_1}{m_2}\right) = -\left(\frac{E}{k}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (39)$$

and hence s also can be evaluated. In the case of exponentially temperature-dependant recombination probability, viz. equation (9), this method should yield the value of E rather than E-W.

Even in the case of general order kinetics, the isothermal decay method can be applied successfully(125,158,203): the plot of $\left[\frac{I_o}{I}\right]^{(1-1/b)}$ versus time t, should be a straight line and activation energy E can be directly obtained from Boltzmann plots of the slopes. This method incidentally gives an estimate of the order of kinetics also and is perhaps the only method unaffected by temperature dependant factors such as frequency factor, quantum efficiency and the emission spectra.

V.6 – Area Measurement Method

This method essentially stems from the fact that the filled trap density at any temperature T is proportional to the remaining area of the glow peak, S_T. Such a consideration leads to(124):

$$\ln \left[I(T) \frac{(1 + \xi S_T)}{S_T^2} \right] = -\left(\frac{E}{k}\right)\left(\frac{1}{T}\right) + \text{constant} \qquad (40)$$

This is of the form, $y = \left(-\frac{E}{k}\right) x + \mu$ and the unknown parameter ξ can be evaluated numerically for the condition that the correlation coefficient, $\rho = \text{covariance}(x,y) / (v(x)v(y))^2 = 1$. E then can be calculated from the slope of the straight line plot between y and 1/T.

A simpler procedure which is an extension of the initial rise method but also involving the area measurement has been recently proposed[5]. The conventional Arrehenius diagram is modified with each value of I(T) normalised to the total area of the saturated glow peak ie. $\ln(\frac{I}{S_o})$ is plotted against 1/T for the full glow peak where S_o is the area of the saturated glow peak. Such a normalised glow peak has a straight line portion for larger values of 1/T as in the initial rise method (see figure 16) and is governed by:

$$\ln\left(\frac{I}{S_o}\right) = \left(-\frac{E}{k}\right)\left(\frac{1}{T}\right) + \eta \tag{41}$$

and the frequency factor is given by, $s = q \, . \, e^{\eta}$ (42)

Another simple method applicable only to monomolecular processes with temperature-independant 's' has been in vogue in the analysis of ionic thermocurrent curves[31]. There is no reason why this cannot be applied to the case of TL also. The method is simple in that a single measurement can lead to the determination of both E and s and is heating rate independant. The relevant relationship employed is given by:

$$\ln\left[\int_{t(T)}^{\infty} T(t)\,dt'\right] - \ln I(T) = \ln\tau_o + \frac{E}{KT} = \ln\tau(T) \tag{43}$$

As the integral on the left side is nothing but the area of the glow curve between temperatures T and ∞, the life time $\tau(T)$ can be easily obtained for various values of T. The plot of $\ln\tau(T)$ against 1/T yields a straight line with slope $\frac{E}{k}$ and the intercept = $\ln\tau_o$. Thus E and s can be determined.

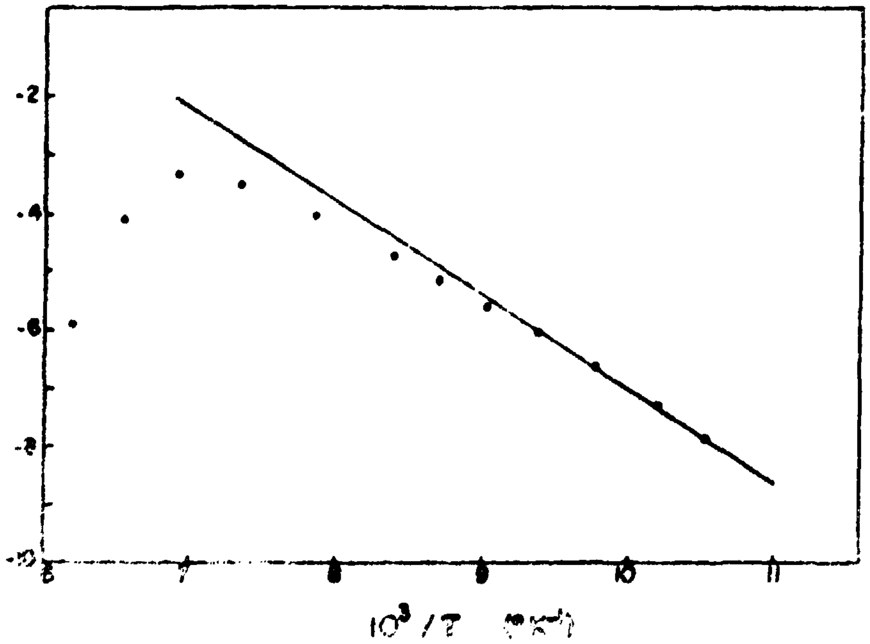


Figure 16 – Logarithmic plot of normalised TL intensity *versus* 1/T for the case of AgCL phosphor (Aramu, F., 1975 – ref. /5/).

V.7 – Curve-Fitting Method

This method involves numerical computation based on a specific model and assuming certain initial approximate values for parameters like E and s. An interative procedure is then adopted to obtain the best least square fit with experimentally obtained glow curve.

The kinetic equations and solutions which are generally adopted for such a fitting have already been discussed in sec. 4.3. Some of the attempts to fit data on TL of phosphors like NaCl, KBr and MgO can be found in references(137,181).

V.8 – Fermi Level Analysis

This is essentially based on isothermal decay measurements but the analysis is done differently (§ sec.IV.4). This method is restricted to cases where there is fast retrapping present during heating. This technique has so far been applied only on thermally stimulated conductivity data, but there is no reason why this cannot be applied to the case of TL also. This method has the added advantage that the trap depth distribution can also be elegantly obtained(29,30).

VI – FACTORS AFFECTING TL

VI.1 – Effect of Impurities

We are concerned with those impurities in a phosphor whose presence affects the TL sensitivity of the phosphor in one way or other. An impurity which "causes" TL in an otherwise "dead" phosphor is often called an "activator"; that which "quenches" or "kills" the otherwise present luminescence in a phosphor is called a "poison"; that which "increases" the already present luminescence due to an activator is called a "sensitiser". Sometimes the presence of two kinds of dopants may be necessary to observe the particular luminescence but the exact role may not be known; these are often referred as activator and co-activator in the phosphor. Traditionally in a luminescence process, an activator is the luminescence emission centre; a poison prevents energy transfer to the emission centre and a sensitiser increases the energy absorption for conversion into useful luminescence emission. In the case of TL, the role played by an activator may be more than just being the emission centre; its presence may create more traps responsible for the TL. Thus three distinct categories of activators may be distinguished as for as TL is concerned:

(i) causes increased trapping: eg. Mg in LiF(126)

(ii) causes increased emission: eg. Mn in $CaCO_3$(130)

(iii) causes both increased trapping and emission: eg. Dy in $CaSO_4$(144)

For the other roles of an impurity mentioned in the beginning, the following examples may be cited for the case of TL phosphors:

Poison: O or OH in LiF, CaF_2 etc(138)

Sensitiser: Ce in CaF_2:Mn(22)

activator co-activator: Mg and Ti in LiF(126)

An important aspect about the role of activation is the phenomenon of concentration quenching: an activator atom, to be an affective emission centre, has to be guaranteed with a minimum 'free lattice space' around it without another activator atom of the same type being present; hence as the activator concentration increases in the crystal, the luminescence increases at first, reaches a maximum at an optimum concentration corresponding to the above mentioned minimum lattice parameter and then starts diminishing for further increases in the concentration. A typical concentration quenching curve and the law obeyed in the case of TL of $CaSO_4$:Dy phosphor is given[144] in figure (17).

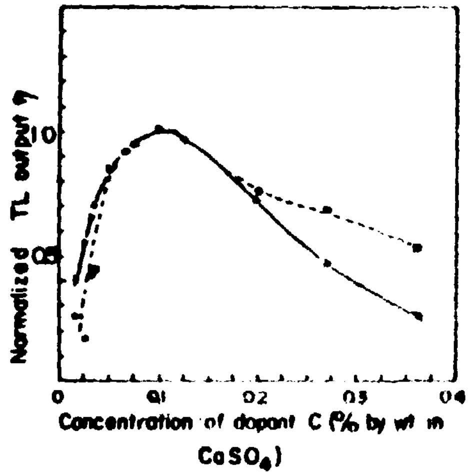


Figure 17 – Theoretical fit [$\eta = \dfrac{K}{(1 + c^{-1}\ e^{nc})}$ where K = 100, = 0.037 and n = 1000] for the concentration quenching observed in Dy(o) and Tm(□) deped $CaSO_4$ phosphors: – calculated and ---- experimental. (Nambi, K. S. V., 1974 – ref. /144/).

Typical optimum concentration levels of activators in some of the more famous phosphors were given in sec. 1.2. It is to be borne in mind that TL is an extremely structure-sensitive phenomenon and hence the "background impurities" in the phosphor is a critical factor in the TL emission[142,145].

VI.2 – Effect of Thermal Treatments

In general, TL properties exhibited by a phosphor very much depend upon the kind of "thermal annealing" experienced by it prior to the irradiation/excitation. (Obviously any post-excitation thermal treatment erases the TL signal at least up to the treatment temperature on the TL glow curve). Annealing is any process which reduces internal strain and surface energy. It is also generally true that more defects are produced at higher temperatures of annealing. The number of defects retained by the crystal lattice very much also depends on the cooling rate employed to cool the crystal to the ambient temperature from the annealing temperature. As the defects are quite often directly involved in the TL process, it is easily seen that TL should be closely related to the thermal annealing history of the crystal. Such being the case, it is obvious that a "standard annealing" procedure be adopted for reproducible results in TL studies. One such procedure traditionally followed in the case of LiF phosphors is to heat the phosphor at 400°C for 1 hour and then at 80°C for about 24 hours[220]. Such an annealing procedure is however not necessary if no defects are formed or annealed during the TL read-out procedure. This is normally the case when high-melting-point phosphors like CaF_2, $CaSO_4$ etc are involved. Caution is neverthless required to "erase" the phosphor completely in any read-out cycle as these phosphors exhibit TL glow peaks even up to temperatures as high as 650°C; any unerased TL signal – called residual TL – may interfere with further TL measurements from the same sample[197]. Hence normally it is advised that these TL phosphors be annealed at about 600°C sufficiently prior to use. This is not actually "annealing" but only an "erasing" treatment.

In some cases the TL sensitivity changes by the annealing treatment which can be identified with certain crystalline phase-changes in the phosphor. A typical example is that of quartz(146). It has been observed that the TL output for the same gamma irradiation goes through two maxima with temperature of pre-irradiation annealing (figure 18). These temperatures also correspond to the well known inversion temperatures of quartz at which the crystalline phase changes from alpha to beta and beta to gamma respectively. These changes are more pronounced when the sample is quickly quenched to the ambient from the annealing temperature (figure 19). This is perhaps due to "freezing in" some kind of mixed phase defects.

Many phosphors, particularly the non-oxide ones, if heated in air-especially in humid air – at high temperatures become less sensitive to TL due to OH poisoning(188). Hence vacuum or inert atmospheric heating should be preferred for high temperature annealing treatments. Natural fluorite TL phosphors seem to yield enhanced TL for vaccum annealing at an optimum temperature of about 850°C(146).

VI.3 – Effect of Irradiation Dose

In many phosphors the TL properties change considerably depending upon the total irradiation experienced in its earlier history. The changes are significant when this integral dose is quite high and given in an acute exposure. The effect can be easily studied by first heavily irradiating the phosphor, removing the TL by heating and then studying the TL properties at lower levels of irradiation doses. The more significant effects of such heavy irradiation are: i) TL sensitisation; ii) TL damage and iii) TL spectral changes. The generation of these three kinds of effects are shown in a flow-chart in figure (20).

VI.3.1 – TL Sensitisation

The sensitisation (ie. increase in TL sensitivity) can be arbitrarily differentiated into two kinds: real and apparent. The apparent sensitisation is the sensitisation of lower temperature peaks after a pre-heavy irradiation and partial bleaching ie. residual TL corresponding to higher temperature peaks being present in the phosphor always; this is caused by the removal of the filling and/or, luminescence competitions from the deeper traps (figure 21).

While the radiation-induced (real) sensitisation is best exhibited by quartz (figure 22), the residual TL-induced sensitisation is a property of almost all the TL phosphors (see for example figure 23) and has been thoroughly investigated in the case of LiF(35,47,196,199).

While the "real" sensitisation in quartz can be partly desensitised by heat treatment or UV irradiation(54), the "apparent" sensitisation in LiF can be completely removed and the phosphor brought back to the original sensitivity by a proper thermal treatment(196).

The sensitisation observed in LiF is linked with the supralinearity exhibited by the virgin phosphor at higher doses. There have been at least three basically different explanations offered so far and these are described briefly below as it helps in visualising the possible TL processes in a phosphor in general terms.

The effect observed in LiF can be summarised as: i) The TL output is linear at low doses and is supralinear at doses above about 1000 R; ii) The amount of supralinearity is inversely related to the LET of the irradiation (for LET effects in detail, see sec. 6.4) iii) If the sample is pre-irradiated with a dose $> 10^4$ R and annealed at 280°C, the TL sensitivity is increased to the previous supra linear level even for doses less than 1000 R ie. sensitisation; and, iv) If however the sample was annealed at 400°C after the sensitising exposure ($> 10^4$ R), the phosphor comes back to the virgin state. The different explanations offered are:

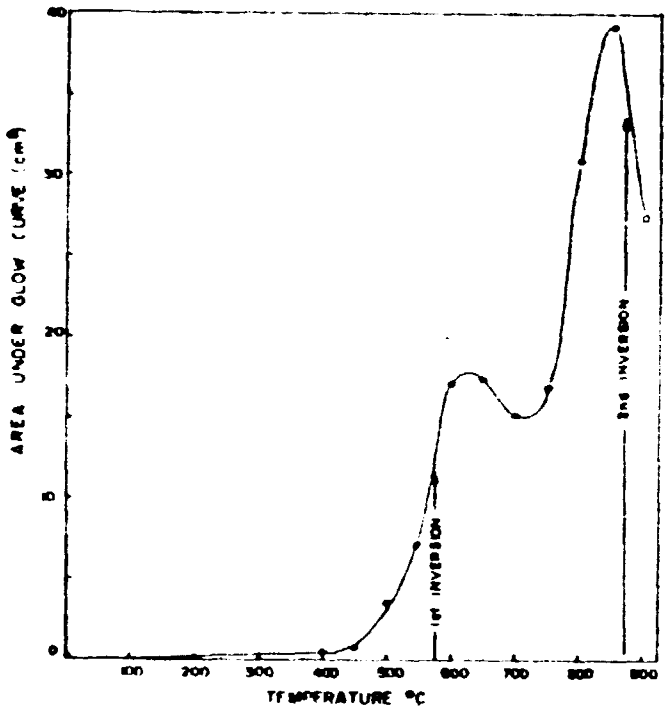


Figure 18 – Change in TL sensitivity of quartz due to pre-exposure heating – at each temperature the sample was heated for 90 mins. and cooled quickly to RT and then gamma irradiated to about 10^5 R. (David, M., 1977 – ref./146/).

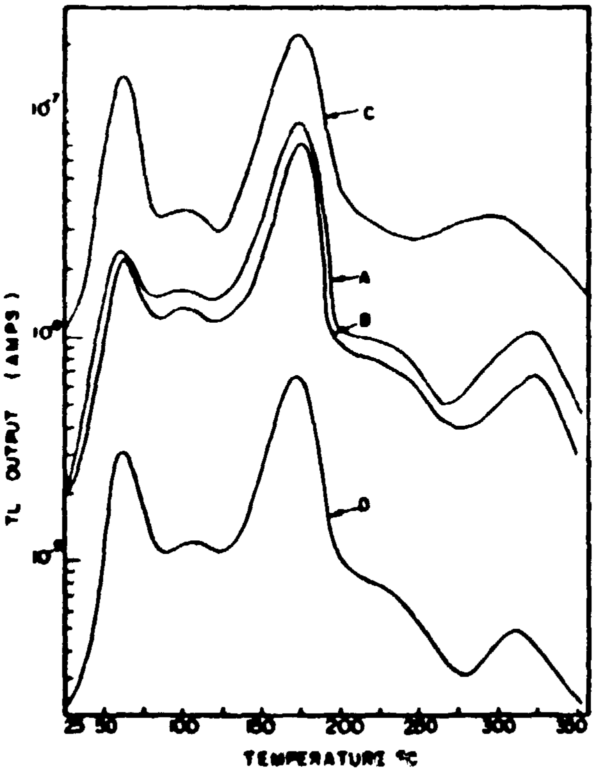


Figure 19 – Effect of cooling rates on thermal sensitisation of natural quartz: Test dose: 10^5 R)

1. sample annealed at 400°C – a) cooled in air b) cooled inside the furnace;
2. sample annealed at 600°C – a) cooled in air b) cooled inside the furnace.

(David, M., 1977 – ref./146/).

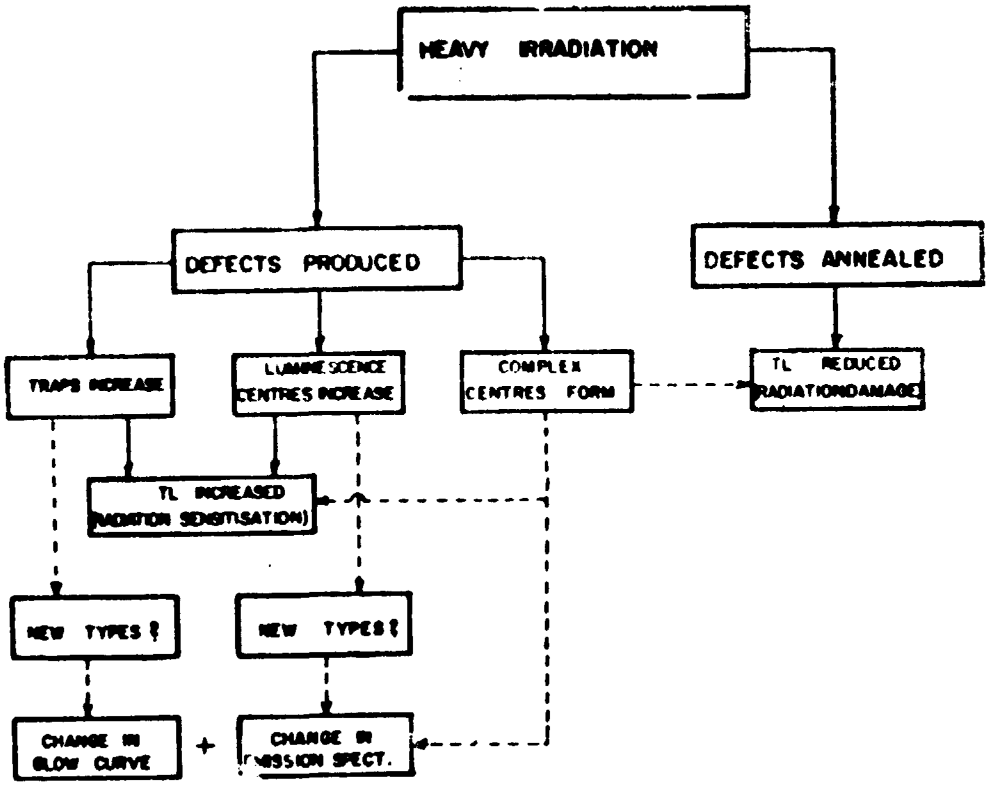


Figure 20 – Flow chart showing the effects of pre-heavy irradiation on TL phosphors.

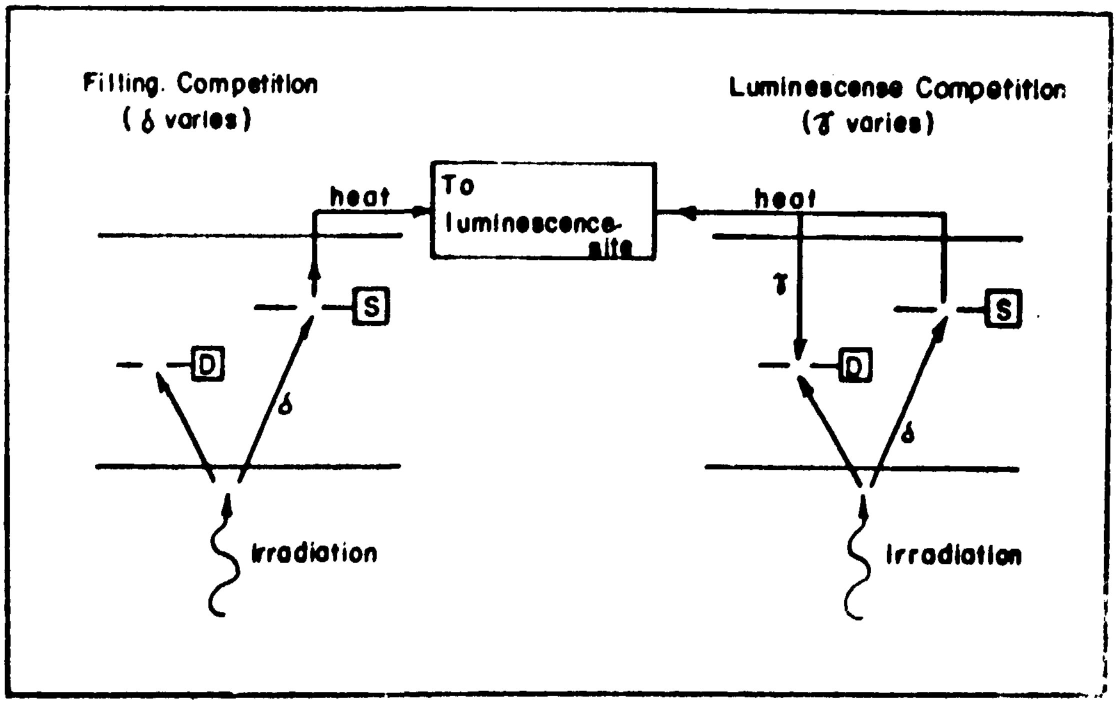


Figure 21 – Schematic illustration to explain the alterations in trapping and emission efficiencies caused by filling of deep traps.
S – Shallow traps; D – Deep traps

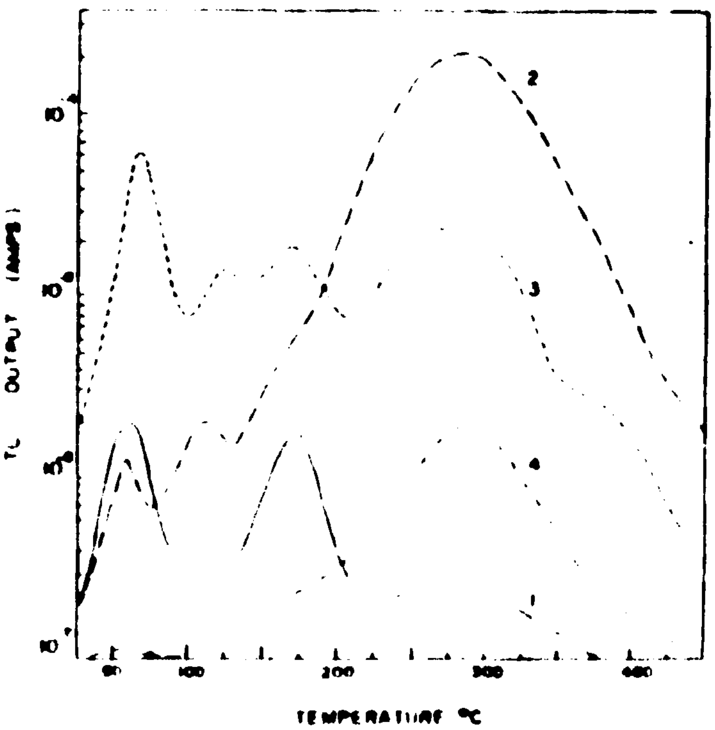


Figure 22 – De-sensitisation of radiation-sensitised quartz sample by heat and uv exposure: 1) virgin sample heated at 450°C for 60 mins. 2) sample, given a pre-gamma exposure of 10^7 R and heated again at 450°C for 60 mins. 3) sample 2, heated at 900°C for 90 mins. and heated at 450°C for 60 mins. 4) sample 2, exposed to UV for 190 hrs, and then heated at 450°C for 60 mins. (Test dose: 10^4 R) (David, M., 1977 – ref./146/).

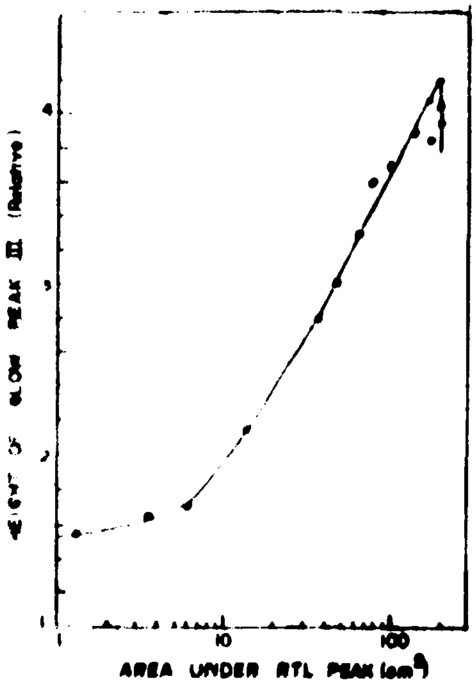


Figure 23 – RTL induced sensitisation in natural CaF_2 (Sunta, C. M., 1971 – ref./196/).

a) **Zimmerman's model**(35): It is hypothesised that more traps and/or luminescence centres could be created by the irradiation and the effect becomes significant only for doses $> 10^3$ R. This model fails to explain the LET relationship with supralinearity.

b) **Suntharalingam's model**(199): It is hypothesised that high temperature deep traps exist in very small numbers in the phosphor and their capture cross section is very high compared to the lower temperature traps. Although this model, referred quite often as the competing trap hypothesis, gained support with the experimental observation of high temperature deep traps in LiF, it failed completely in the face of a crucial observation that the high temperature peak continues to build up even after 1000 R irradiation where the beginning of supralinearity is observed(196).

c) **Claffy's model**(47): It is hypothesised that electrons and holes belonging to the same track are responsible for the TL at low doses (linear region); at higher doses due to overlap of tracks, there is considerable increase in luminescent recombinations and hence more TL. This model, also called the interacting track hypothesis, explains all the observations and gains further support from the later observations(196) that all the peaks exhibit supralinearity, the amount of supralinearity increasing with increasing temperature of the peak. (At higher temperatures the mobility of the charge carriers increases and hence there should be further enhancement in the recombinations). It is also seen that in general, low Z phosphors like LiF, $Li_2B_4O_7$ etc exhibit this supralinearity behaviour while the high Z phosphors like CaF_2, $CaSO_4$ etc do not show this effect to any appreciable degree. It is possible that track interactions can already be strong even at low doses for high Z phosphors and since these do show the "apparent" sensitisation phenomenon, the track interaction model is perhaps the true picture.

VI.3.2 – TL Spectral Changes

Spectral changes in the TL emission have also been observed with increasing doses(21,94,194). While in LiF the spectrum shifts towards longer wavelengths with increasing irradiation, in fluorite phosphor, there are changes in the UV region (figure 24). Such changes are usually accounted for, by one of the following arguments:

a) If the luminescence centres are hole centres, at lower doses, those centres nearer to the valence band will be filled more; hence as the dose increases, the more distant centres get activated more in number and the spectrum exhibits pronounced emission at longer wavelengths.

b) The spatial nearness of electron and hole centres (one of them being the luminescence centre) increases at increasing doses of irradiation and spectral emission could change corresponding to these if they are a new species.

c) At higher doses luminescence aggregate centres are formed and hence the emission could change.

d) Creation of new types of luminescence centres (including crystal symetry changes around the activator) at increased irradiation doses can cause a change in the emission spectrum.

VI.3.3 – Damage of TL

At increased doses of irradiation crystal damages (like production of voids, aggregates, strain locations etc) can occur which can reduce the TL output (figure 25) with or without a change in the TL emission spectrum. This has been demonstrated(95) in detail in the case of LiF phosphor.

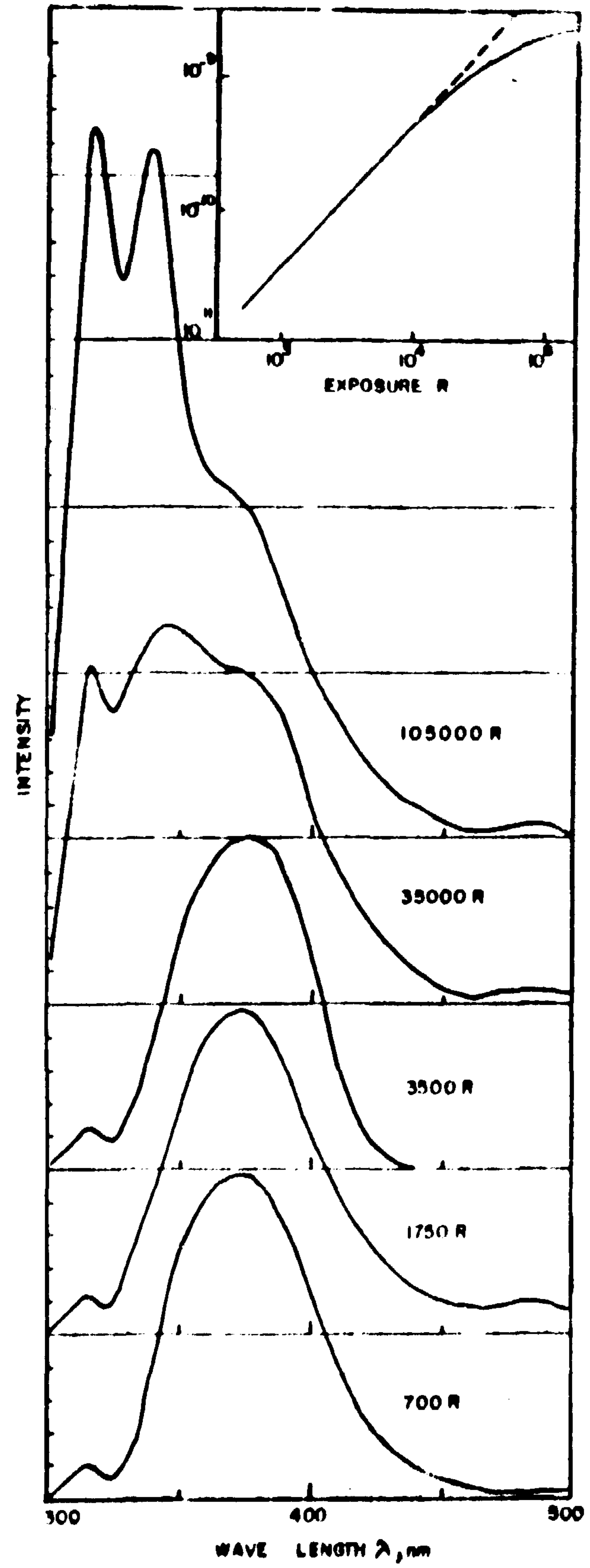


Figure 24 – Dose dependance of TL spectrum of natural CaF_2 (Sunta, C. M., 1971 – ref./194/).

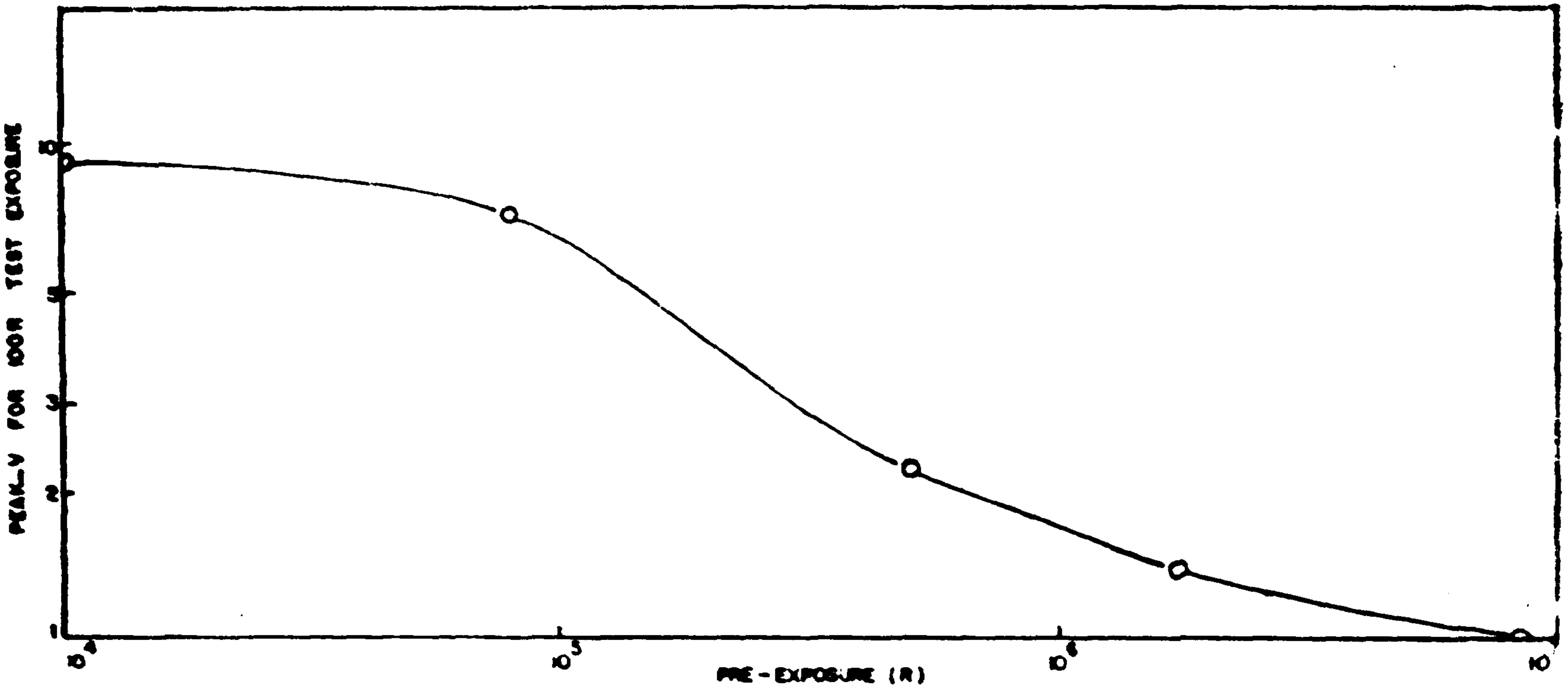


Figure 25 – Radiation induced damage in LiF TLD-100 (Jain, V. K., 1974 – ref./95/)

VI.4 – Effect of LET of Irradiation

The ionization capacity of a radiation in a medium is usually signified by the linear energy transferred to the medium by the incident energy (LET expressed in KeV/μ). The usual LET response which is observed in most of the TL detectors is decrease of sensitivity with increase of LET of the incident radiation. There are also exceptions like BeO as shown in figure (26).

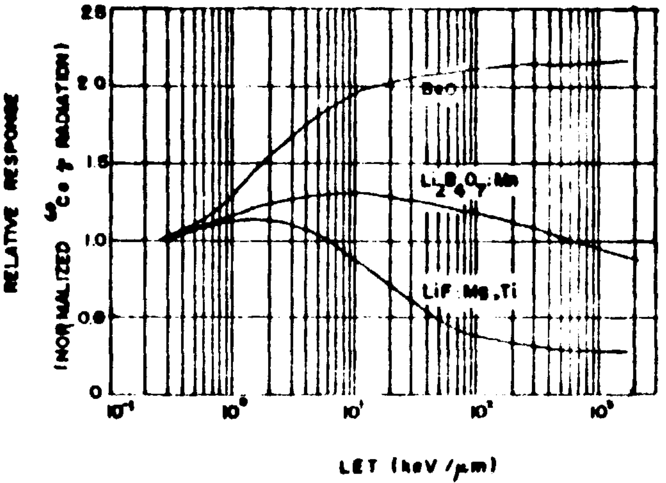


Figure 26 – Relative TL response of three TL phosphors (normalised to gamma radiation) to high energy protons as a function of LET (Becker, K., 1974 – ref. /13/).

There are probably several possible explanations that could be offered(13): thermal effects along the track resulting in reduced stability of trapped carriers; higher recombination probabilities in the extremely high local dose-rate field along the track; production of new centres due to ionic displacements etc. But the primary reason appears to be saturation of available centres in a narrow channel along the track with or without structural changes depending upon the crystal lattice characteristics. In the case of the high LET radiation, there is saturation and "wastage" of energy and the response to a particular LET radiation will hence be directly dependant upon the saturation capability of the particular TL phosphor. This has been experimentally verified(217) by measuring the relative alpha (high LET radiation) induced TL efficiencies in various TL phosphors with different saturation capabilities for the low LET beta radiation (figure 27).

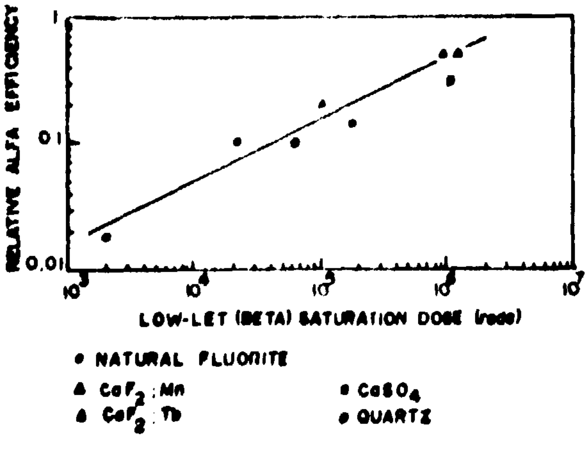


Figure 27 – Measured relative alpha radiation efficiencies in various TL phosphors as a function of the beta radiation dose required to reach saturation (Zimmerman, D. W., 1972 – ref. /217/).

Assuming the same saturation principle stated above, it has been theoretically derived(92) that the TL yield is related to the LET by:

$$\eta\,(\mathrm{TL}) = \Sigma_i\, a_i \, \frac{(1 - e^{\rho_i L})}{\rho_i L} \tag{44}$$

where,

$$\rho_i = \frac{W_i}{\lambda k_o Q} \quad \text{and} \quad \Sigma\, a_i = 1$$

Q is effective cross section of one ion column;

a_i is a factor showing the contribution of each type of trap to the TL yield;

λ is the probability for immediate electron-hole recombination;

W_i is the probability for capture in a trap of type i;

k_o is the mean energy for producing one hole.

For the case of TLD-700 (LiF), this works out(159) to be,

$$\eta\,(\mathrm{TL}) = \frac{5.025 \times 10^6}{L}\,(\tau/R) \tag{45}$$

where,

τ is the TL sensitivity in arbitrary units per unit incident fluence of high LET radiation; and R = TL sensitivity in same TL units per unit roentgen exposure to Co-60 gamma rays.

This formula has yielded theoretical LET response curves matching very well with the experimentally obtained curves using various energies of highly charged ion beams for the irradiation.

Sometimes LET effects manifest in the form of changes in the glow curve(116), response pattern with increasing irradiation doses, TL emission spectrum(157), fading rate etc and the observed response may be a combined result of these (figures 28 & 29).

In general it may be said that in a phosphor where higher temperature peaks are observed only at high doses of low LET radiation, the same may be observed even at low doses for high LET radiation. (Because of dense ionisation of high LET radiation, the relative filling up of all kinds of traps remains the same at low as well as high doses).

VI.5 – Effect of UV Rays

The effect of ultra violet irradiation on TL phosphors has been mostly pursued from the point of view of its applications in measuring UV exposures and not many investigations have been reported enlightning the basic physical processes involved. A somewhat successful explanation has been provided(107,108) only in the case of alkali halides especially NaCl, KCl and KBr.

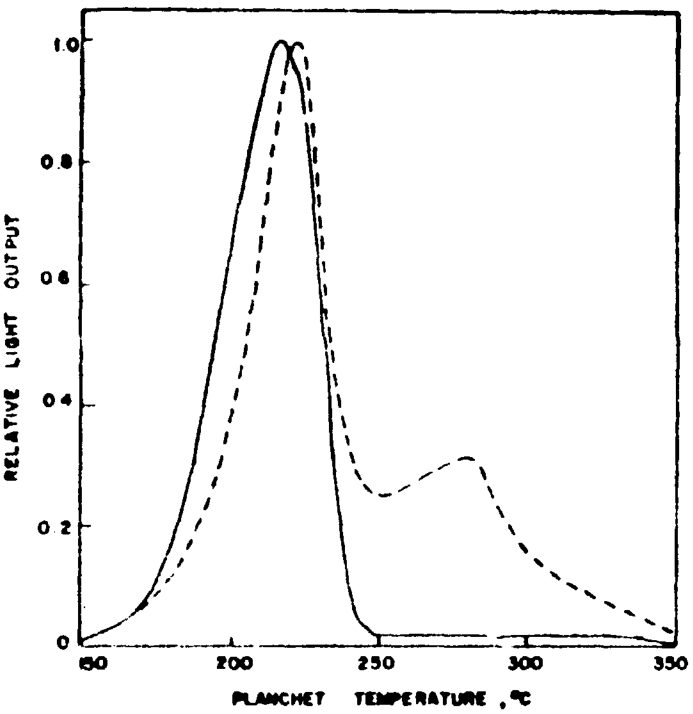


Figure 28 – Typical TL glow curves of LiF TLD-100 for alpha and gamma irradiations (Lucas, A. C., 1968 – ref./116/).

——— gama irradiation; – – – – alpha irradiation.

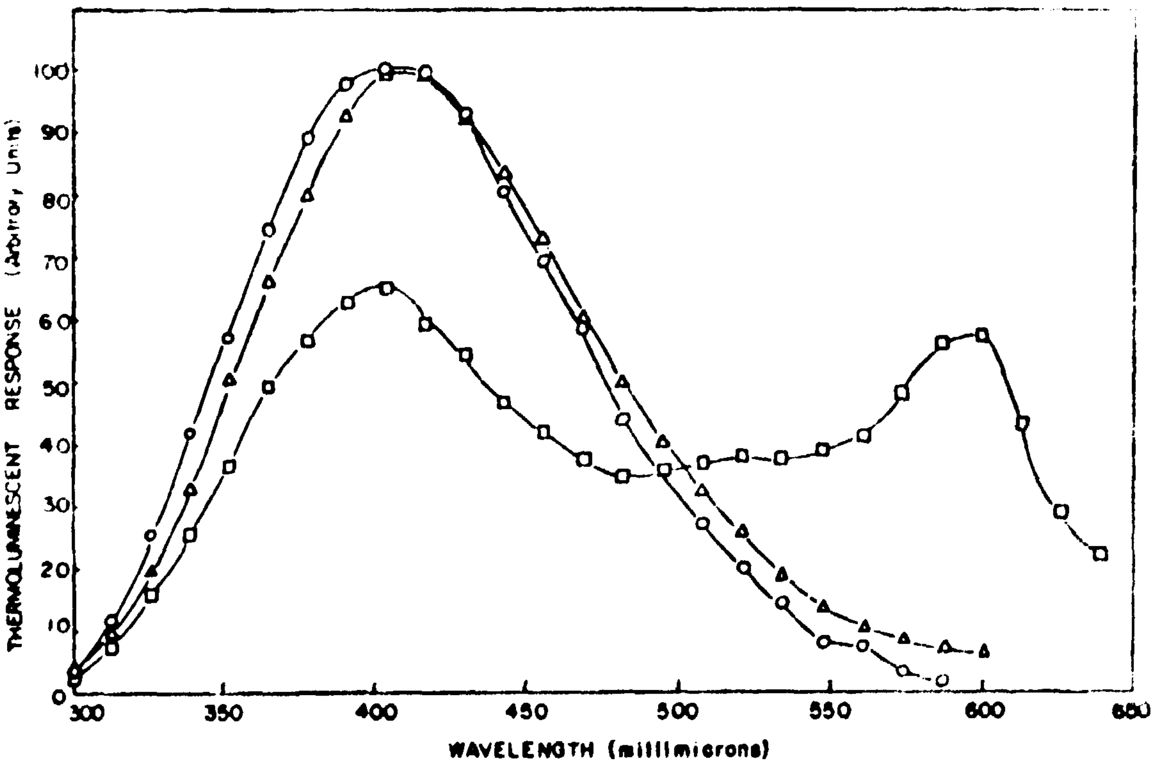


Figure 29 – TL spectral response of LiF TLD for alpha, beta and gamma irradiations (Oltman, B. G. 1968 – ref./157/).

——— ^{90}Sr beta exposed; – – –^{137}Cs gamma exposed; – □ – □ – ^{244}Cm alpha exposed.

An excitonic process of defect creation by UV irradiation has been found to lead to mathematical expressions which explain satisfactorily the wavelength dependance of the UV excited TL in these phosphors; very short wavelength light has been found to excite the phosphor by ionisation.

From the point of view of effects produced which are useful in various applications, it is convenient to consider three categories:

VI.5.1 – Intrinsic UV response/UV induced TL

Upon UV excitation by an appropriate frequency, a valence electron of the lattice or a ground state electron of an impurity atom is excited to a metastable state; upon subsequent thermal stimulation, luminescence is emitted as it would, after a X- or gamma-irradiation and heating. The TL glowcurves obtained after the two kinds of excitation are not usually the same (figure 30) and in general the TL sensitivity to UV excitation is very small. The TL glowcurve shape and the sensitivity are also wavelength dependant (figure 31).

Among the more sensitive TL phosphors, Mg_2SiO_4:Tb is the only case whose intrinsic UV response is quite high(18). Other equally gamma sensitive phosphors like $CaSO_4$ exhibit a UV sensitivity almost 10^4 times smaller; $CaSO_4$ (Dy) has been reported(38) however to have sufficient intrinsic response as to be able to measure 253.7 nm UV exposures in the range of 400 to 4×10^4 erg . mm^{-2}. CaF_2 (Dy) has been reported(10,11) to become UV sensitive after a high temperature (900°C) treatment in humid air.

VI.5.2 – UV Induced TL Bleaching and Desensitisation

If an already irradiated TL phosphor is exposed to UV rays one may observe some bleaching (or erasure) effect in the gamma induced TL. The bleaching efficiency is usually not the same for all the glow peaks as each peak may have a different λ dependence for the bleaching effect. The mechanism involved is that electrons in metastable levels (trapped by the prior gamma irradiation) are freed by the UV excitation.

A more important effect is the desensitisation effect by UV irradiation. This is in fact a damage effect in the sense that TL sensitivity increased artificially by irradiation or thermal treatment of a phosphor can be reversed at least partially by exposure to UV rays(54,221). If the luminescence centres are the activated hole centres as has been argued in the case of TL of natural quartz(221), the sensitisation process can be expected to leave a large number of activated luminescence centres; the UV irradiation may be expected to neutralise these activated centres by the excitation of valence electrons and hence the desensitisation occurs.

VI.5.3 – UV Induced Transfer TL

This is in fact a special case of UV bleaching; however it is considered here that when an electron is freed from a metastable level it has a good chance to get retrapped at some other level (a different trap). Thus a redistribution of the trapped carrier population takes place among the various types of traps present in the phosphor and a TL glow curve is generated with different relative intensities among the various peaks. The effect is best seen in a phosphor which has been heavily gamma irradiated and partially drained by insufficient heating (ie, TL corresponding to deeper traps are remaining residual in the sample). When such a sample is exposed to UV light, electrons are freed from these deeper traps and a good fraction of them are retrapped at shallower traps. Hence when the TL is read after the UV exposure, one finds a reduction in the high temperature peak and a regeneration of the lower temperature peaks. This has been best demonstrated(193) in the case of fluorite TL phosphor (figure 32).

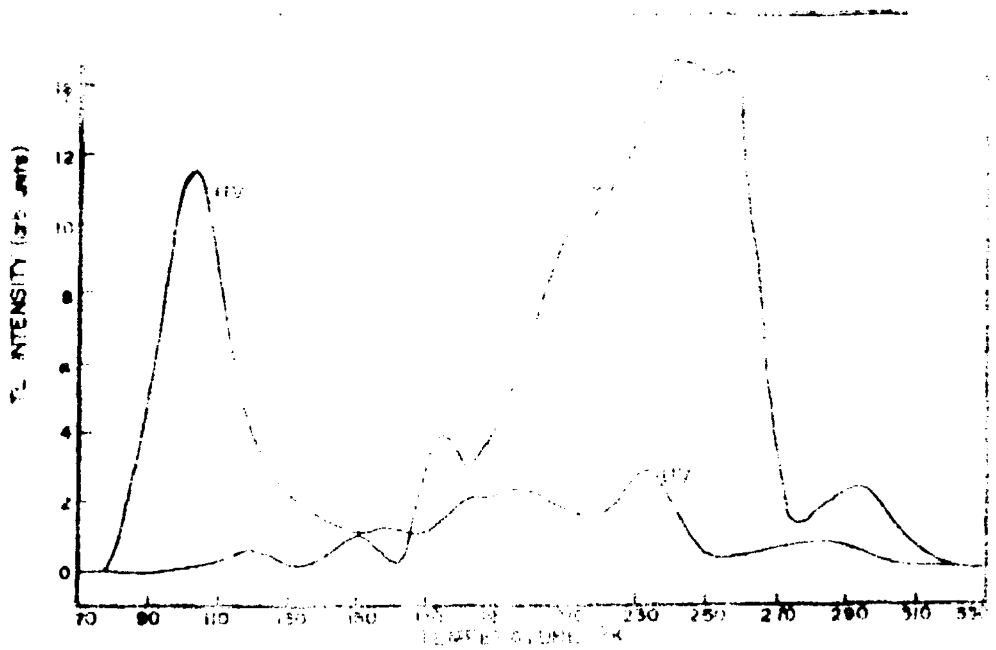


Figure 30 – TL of KBr after X (scale 1/100) and UV (1600 Å) irradiations at 80°K (Kristianpoller, N., 1970 – ref./107,108/.

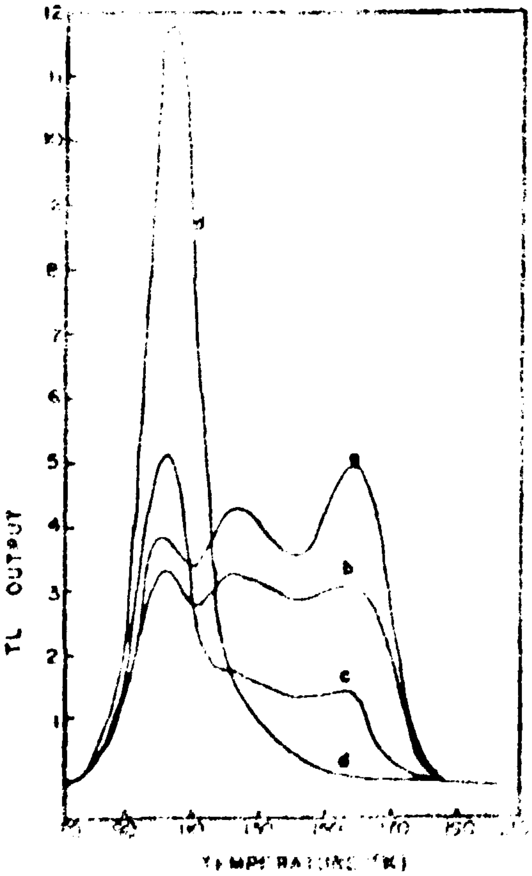


Figure 31 – TL of KBr after UV irradiation at 80°K withh a) 1870 Å, b) 1895 Å, c) 1920 Å and d) 2030 Å (Kristianpoller, N., 1970 – ref./107,108/.

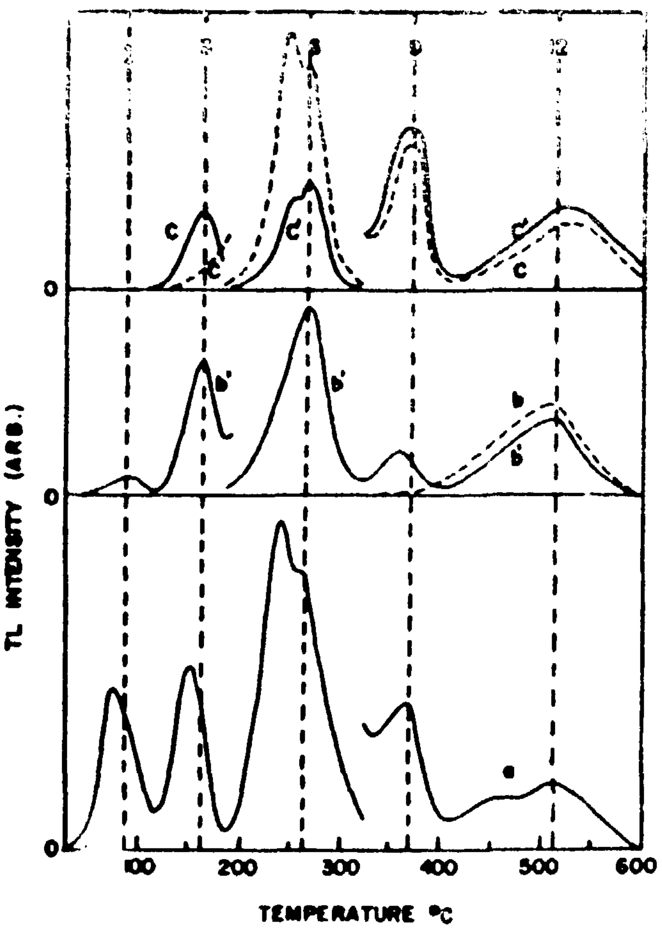


Figure 32 – Light induced transfer TL studies in fluorite phosphor (Sunta, C. M., 1970 – ref./193/). TL glow curves: a) after 5000 R gamma irradiation; b) residual TL prior to UV exposure; b') TL after UV exposure; c) residual TL before exposure to light of λ > 500.0 nm and c') TL after exposure to light of λ > 500.0 nm.

The phenomenon of UV transfer is quite efficient in most of the TL phosphors and can be successfully employed to measure even low levels of UV exposure (§ sec. 10.6). It is to be remembered that this effect is also extremely λ-dependant.

VI.6 – Effects of Stress, Crystallisation and Particle Size

These effects have been pursued in detail in the case of TL exhibited by geological samples; factors such as stress, crystallisation, decomposition and particle size are almost inseparable in these cases and hence are considered together in this section.

VI.6.1 – Effects of Stress

The application of stress can arise out of operations such as crushing, grinding, packing, pellettising etc. The different deformation processes which may arise out of such operations can be micro-cracking, formation and annihilation of crystal dislocations, intergranular gliding, rupturing, pressure twinning and so on. These can ultimately affect the TL exhibited by the specimen in many ways:

During pressure application there are dislocation loops and vacancies which can excite valence electrons (or de-excite any trapped electron) during their translation in plastic flow. The excited valence electrons if get trapped, give rise to TL which can be observed as a direct consequence of applied stress. If de-excitation of trapped electrons occurs, then obviously there will be a decrease in the observed TL as compared to the same irradiated sample prior to the stress application. Such effects are not readily seen in the artificial phosphors usually employed in TL studies; but are clearly observed(50) to affect the natural TL (arising out of internal and external irradiation from different sources over geological times) exhibited by mineral samples. $CaCO_3$ minerals constitute an important example in this respect (figure 33).

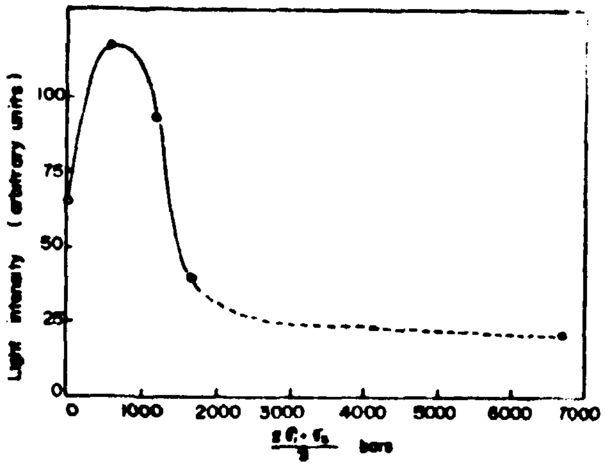


Figure 33 – Variation of the area of natural TL glow curves with mean pressures applied prior to the reading; sample: Mosset marble (D'Albissin, M., 1968 – ref /50/).

In some minerals due to pressure application, permanent lattice defects could be formed which can directly aid or kill the TL process in the material. This leads to what is known as sensitisation/desensitisation of TL material by stress application (figure 34).

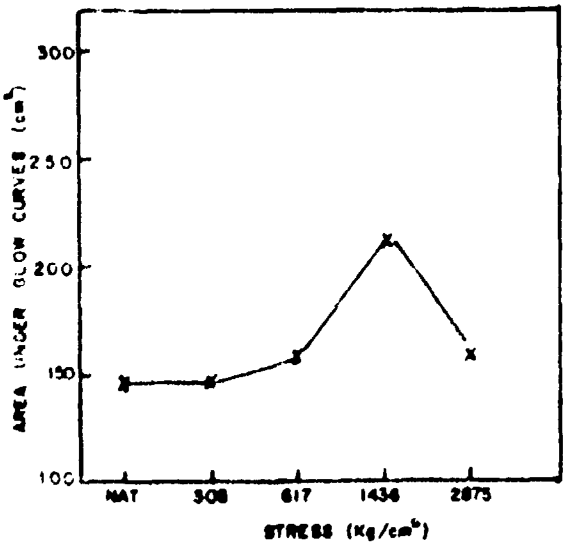


Figure 34 – Effect of stress on the TL of natural quartz. (David, M., 1977 – ref. /146/).

In all these stress effects, there is always a critical pressure value at which crystal damage sets in giving rise to decreased TL outputs. The extent of a particular effect observed for a particular stress in a given sample is also greatly related ot the particle sizes in the sample(114).

VI.6.2 – Crystallisation and Decomposition Effects

Some of the physico-chemical processes like crystallisation and decompositon may result in storage of energy in the material which may in turn appear as TL when heated. Also the crystallisation temperature as well as other physico-chemical conditions decide essentially the type and quantity of lattice defects present in the crystal and this in turn decides the TL sensitivity of the material. Thus it can be easily understood why a laboratory made TL phosphor exhibits TL even before any irradiation and also why the same phosphor prepared under even slightly differing conditions exhibit widely different sensitivities. In $CaCO_3$ minerals, the amount of Mg impurity present has a direct correlation with the crystallisation temperature and this in turn has been seen to affect the TL sensitivity; high temperature calcites are often found to possess more of the Mg impurity and exhibit more TL than low temperature calcites(23). The combined effect of stress and crystallisation have been clearly demonstrated(172) in the case of low temperature TL of ice crystals (figure 35).

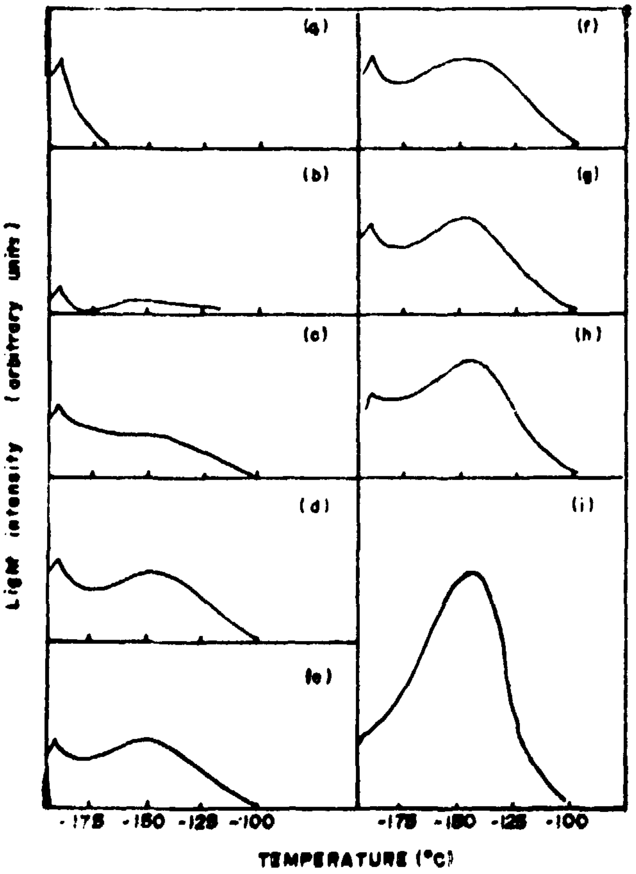


Figure 35 – TL glow curves of natural ice samples with different crystallisations: a) ice frozen in liquid air; b) fresh snow; c) old snow showing recrystallisation; d) frost crystals from a crevasse; e) crevasse filling; f) compacted firn; g) glacier ice with random bubbles; h) glacer ice with aligned bubbles and i) glacier ice with shear and flow structures. (Ronca, L.B., 1968 – ref. /172/).

VI.6.3 – The Effect of Particle Size

This assumes importance when TL of powder samples are studied. The size of the particle influences tremendously the excitation of a phosphor (eg. UV irradiation[38]) as well as the emission output by scattering and self-absorption characteristics. The effect has perhaps been well investigated only for LiF phosphor[32,185,216]. Theoretically at least, the particle size effect should be the same in all materials and extremely energy dependant in the 20-30 KeV range for smaller size particle[32]. This is borne out of energy balance considerations between total electron energy leaving a grain and that entering it (including that generated within) during irradiation. There has been an interesting observation[98] in LiF that in repeated irradiations and TL read-out thermal cycles, the particle size distribution changes considerably so as to change the TL sensitivity altogether.

VI.7 – Storage Effect

This is essentially a "fading" effect on the TL (of a previously irradiated phosphor) at a constant temperature (ambient or otherwise). There are special cases however where there is a slight increase rather than decrease in the TL output and hence the effect in general will be referred as storage effect.

The "spontaneous escape" of a charge carrier from a trap constitutes "fading". By spontaneity one usually means "ambient temperature". In contrast, the escape from traps at higher temperatures (held constant) is usually referred as "isothermal decay". In TL, the faded TL intensity is proportional to 'n', the number of trapped electrons, while during an isothermal decay, the measured TL intensity is proportional to $\frac{dn}{dt}$. In general it can be said that deeper the trap, smaller will be the fading at a given temperature (sec. IV.1).

The fading characteristics of a phosphor can be best described by the life-time, τ of the particular trapping state wherein greater τ value will mean less fading. There has been an interesting finding[190] in TL phosphors like $CaSO_4$:Mn and Al_2O_3:Cr that an optimum concentration exists for the activator whereby maximum stability of the trapped carriers are achieved and that these optimum concentrations were the same for maximum TL yield too (figure 36).

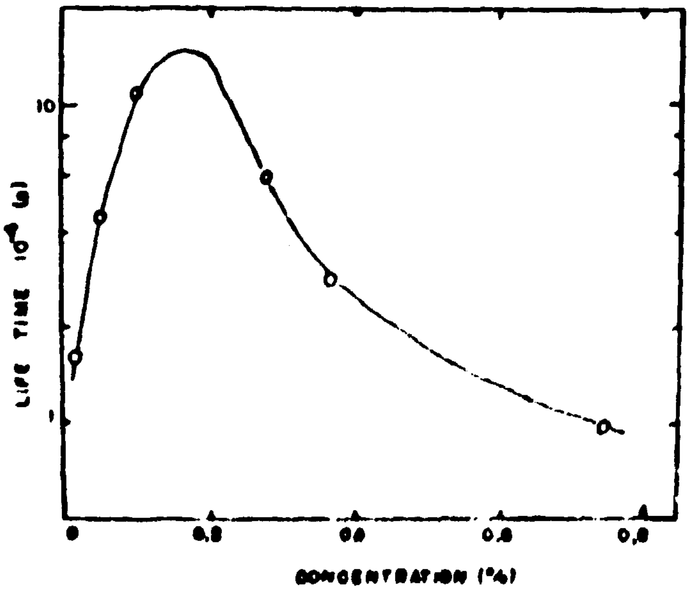


Figure 36 – Rate of fading in dependence on the concentration of Cr in Al_2O_3 (Cr) phosphor (Spurny, Z., 1971 – ref. /190/).

There is an important implication arising out of yet another finding in $CaSO_4$ phosphors that Dy and Tm activators exhibit same optimum concentration and trap depth values$^{(144)}$ but induce different fading characteristics$^{(12)}$. It can then rightly be said that fading characteristics of a phosphor is modified by the presence of impurities.

Another manifestation of the effect could be a continous shift in the peak temperature to the higher side as the peak fades. This has been explained in terms of a continous distribution of trap depth and the model has yielded satisfactory agreement with the experimental findings in fluorite phosphor$^{(210)}$.

There is a type of fading which is of non-thermal origin: even a high temperature peak in some materials is seen to decay independant of the storage temperature. Thus, a glow peak of CaF_2:Mn occuring at about 320°C seems to have the same fading (4 ~ 7%) for storage temperature widely varying between -18°C to +65°C$^{(213)}$. The process involved is not governed by the usual Boltzmann's factor; some of the possible causes are:

a) Chemical processes such as hydration of surface regions resulting in destruction of traps;

b) a tunnelling effect which can be mostly a non thermal process.

Another type of abnormal fading which could be seen mostly during short interval after irradiation-hence called short term fading — is perhaps due to a combination of the usual thermal decay and a tunnelling transfer among traps$^{(189)}$. Typically such an abnormal fading exhibits a small "build-up" during the initial part of the otherwise normal decay curve (figure 37).

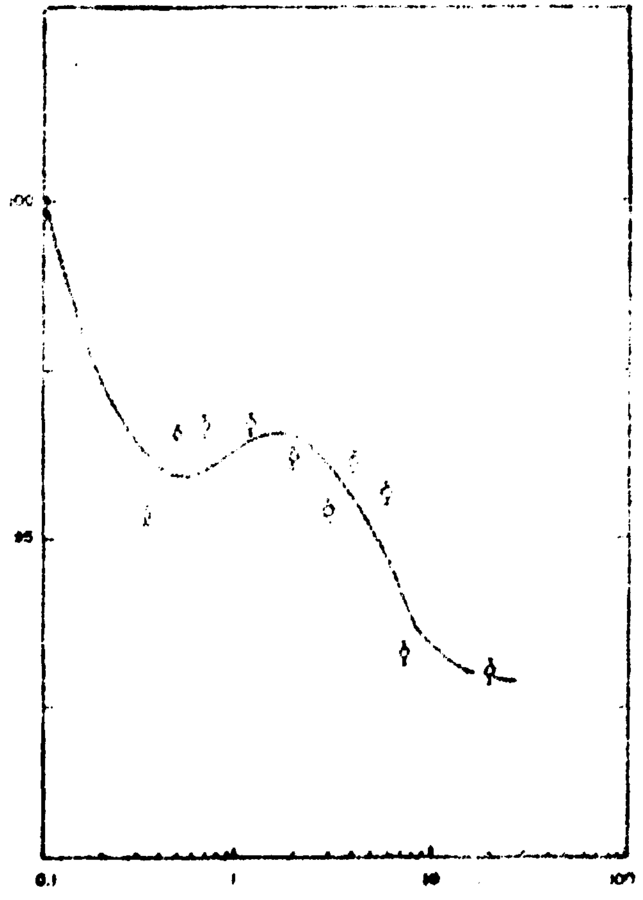


Figure 37 — Short-term fading curve of LiF TLD-100 (Spurny, Z., 1974 — ref. /189/).

VI.8 – Thermal Quenching Effects

The luminescence efficiency is generally a temperature sensitive factor, efficiency decreasing with increase of temperature. This is so because of a competition between radiative transitions (which are almost temperature-independant) and non-radiative transitions – de-excitation of material by thermal agitation – which increases with temperature. In the case of a TL phosphor having one kind of luminescence centre and several thermal activation energies, this will mean that the higher temperature peaks are observed under decreased luminescence efficiency conditions dictated by thermal quenching.

One of the easiest means(76,77) to study the thermal quenching effect in TL phosphors is to observe the variations in the radio-luminescence intensity when the phosphor is held at various temperatures during the irradiation. This method is applicable to TL processes of only those phosphors whose RL and TL emission spectra are identical.

A direct measurement(76,77) of thermal quenching of TL is somewhat possible by employing two extremely different heating rates for the same irradiation of the phosphor and measuring the total light emitted in each case. At high heating rates, the luminescence peak appears at higher temperatures (§.IV.2) and hence should be affected by thermal quenching if present. Of the more famous TL phosphors investigated(76,77), LiF and CaF_2:Mn exhibited strong thermal quenching effects while natural CaF_2 and $Li_2B_4O_7$:Mn did not (figure 38.).

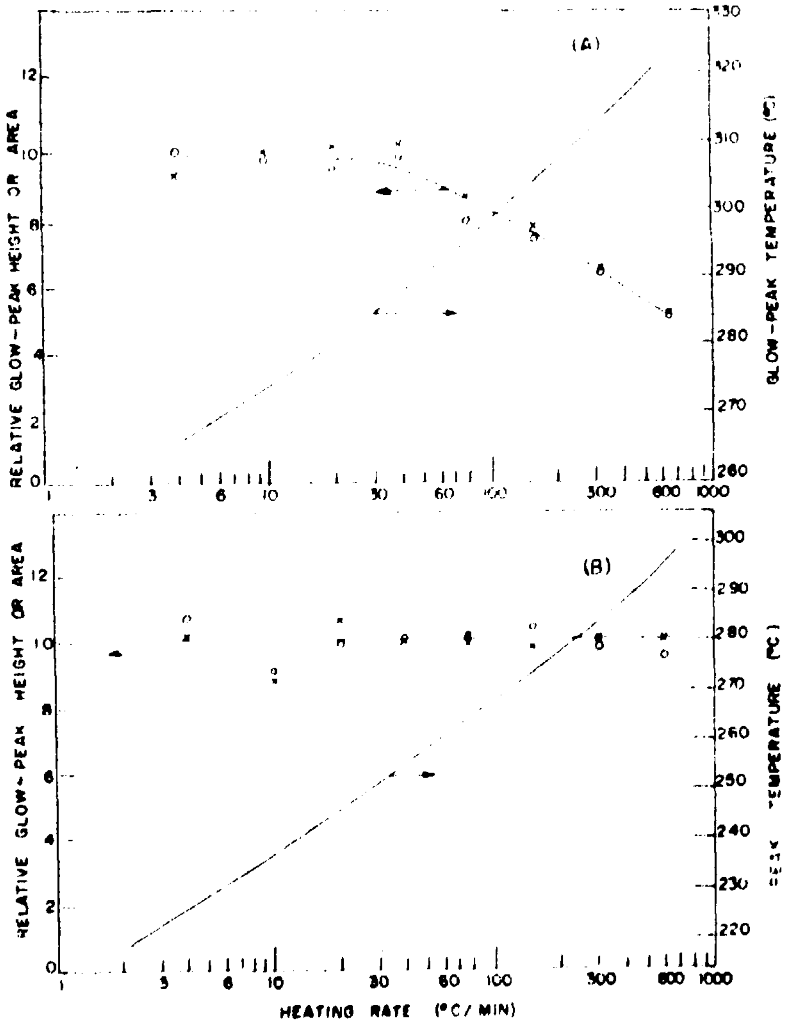


Figure 38 – TL intensities and peak temperatures of CaF_2:Mn (A) and natural CaF_2 (B) for various heating rates after a fixed gamma exposure (Gorbics, S. A., 1968 – ref. /76,77/).

VI.9 – Electro-Static Effects

It has been observed$^{(135)}$ that application of high electric fields (of the order of 10^5 V/cm) on a TL phosphor during the heating enhances the TL output and sometimes affects the nature of the emission too. This effect is thought to be due to either of the following two factors: i) field ionisation of electron traps or ii) acceleration of electrons after thermal release from traps and subsequent impact ionisation. If the first factor prevails, one could observe TL even without heating. In most of the materials however, the second factor is operative. Occasionally, there can be a quenching effect too of this applied electric field. The mechanism seems to be quite different in this case as the enhancement and quenching effects are in some cases observable in the same phosphor irradiated to different kinds of radiations like X- and UV rays.

Extensive work on this interesting effect has not yet been undertaken on any of the well known TL phosphors; the only work reported so far is on ZnS phosphor at low temperatures.

VI.10 – Effect of Infra-red Stimulation

The possibility of achieving the release of stored energy by infra-red stimulation rather than thermal stimulation (as in conventional TL) has been realised very efficiently only in the case of alkaline earth sulphide phosphors with double activators. The famous example is SrS (Eu,Sm) or SrS (Ce,Sm). In both these phosphors, the maximum emission occurs for the same wavelength of IR stimulation ($\sim 1.0\,\mu$) which corresponds to sensitising action of Sm$^{(155)}$. It is thought$^{(104)}$ that Sm^{3+} ions provide electron traps by converting into Sm^{2+} ions upon irradiation and that thermal or IR stimulation leads to ionisation of Sm^{2+} to Sm^{3+}; the TL emissions observed correspond to Ce^{3+} and Eu^{2+} emissions as the case may be. It is interesting however to not (figure 39) that the conventional TL glow curves of these two phosphors have peaks at two different temperatures: 420°K and 650°K; it is simply presumed that in the former case, there is thermal quenching at 650°K. The IR stimulated glow curve on the other hand will look alike (figure 40) and has the advantage of no thermal quenching effects being present (and hence stimulation efficiency maximum).

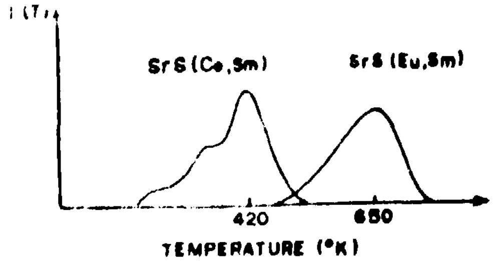


Figure 39 – TL glow curves of SrS(Eu,Sm) and SrS(Ce,Sm) phosphor (Curie, D., 1960 – ref. /49/).

Unfortunately however such effects are seen efficiently only in phosphors with shallow traps where fading is quite high$^{(174)}$. If one accepts the philosophy of multi-phonon induced ladder-like process for the detrapping (§ sec. IV.1), then one could speculate that a correct combination of the intensity and wavelength for the IR stimulation should be successful even in the case of deeper traps.

VII – SPURIOUS TL

There has been some confusion in literature regarding spurious TL; distinctions have been made with names like Tribo TL, Adsorption TL, Piezo TL etc and occasionally these have also been dealt with under the common name of spurious TL. If our prime interest is only radiation induced, thermally stimulated luminescence, then we can define spurious TL as non-radiation induced and unintentional and categorise in into two: those, related and not related, to trapped carriers. A survey of 1883 materials has yielded a statistics that 50% of inorganic and 30% of organic substances can yield tribo luminescence(78).

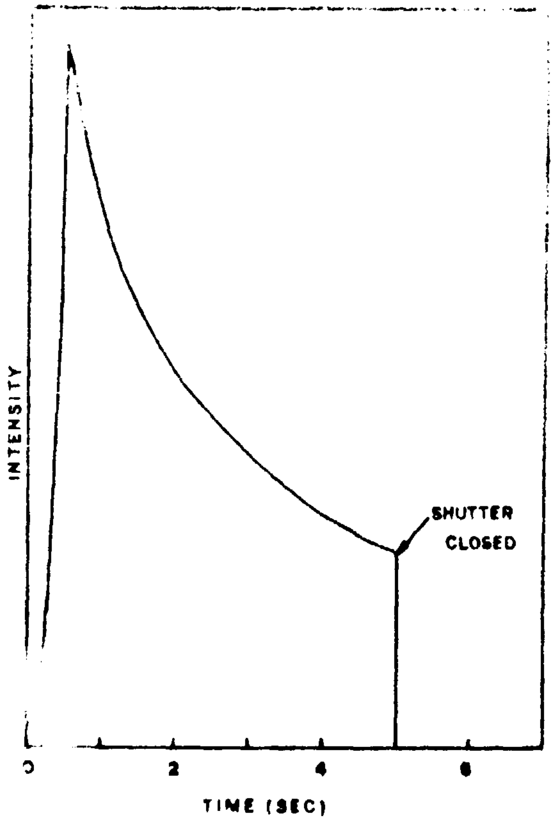


Figure 40 – Typical IR stimulated glow curve of an alkaline earth sulphide phosphor (Sanborn, E. N., 1965 – ref./174/).

VII.1 – Spurious TL Related to Trapped Carriers

VII.1a – Tribo TL, Piezo TL etc

Here, the manifestations are mostly due to stress effects and electrostatic effects. Some of the sample preparation and handling procedures like grinding, pellesting, rubbing, shaking, scratching etc can induce mechanical excitations in the phosphor. Charge carriers are liberated and trapped much the same way as during irradiation and this in turn can give rise to TL in proportion to the mechanical excitation. However this kind of TL attains saturation rather quickly and is very strongly dependant on particle size(2).

VII.1b – Adsorption TL

This is due to a chemisorption process of gaseous ions with semicondutor surfaces and is nearly eliminated under vaccum reading of TL. The effect is reduced under an inert atmosphere while it is pronounced in presence of oxygen or water vapour, being proportional to the exposure and the pressure. The process of chemisorption gives rise to free electrons or holes which recombine with the respective counterpart provided by the semiconductor at high temperature. In many cases, the spectral emission is that of pure electron-hole recombinations(16,120).

Almost all the TL phosphors exhibit tribo TL and ZnS phosphor exhibiting good piezo TL. MgO and $CaCO_3$ are good examples for the case of adsorption TL.

VII.2 – Spurious TL Not Related to Trapped Carriers

VII.2a – Decomposition Luminescence, Decrepitation Luminescence, Combustion Luminescence etc

This phenomenon is related to the chemical stability of the material while being heated. Inf the material either oxidises or decomposes permenantly in one heating, it is obvious that a spurious TL may be recorded only during the first read-out cycle; if the material undergoes phase transformations reversibly during the heating cycles, then the corresponding spurious TL if any, will be reproducible. It is thought that chemical transformations at a particular temperature give rise to molecular excitations which may be luminescent. Some of the materials which exhibit such effects are $CaCO_3$, $KClO_3$ etc(97). None of the well known TLD phosphors like LiF, CaF_2, $CaSO_4$ etc are prone to this effect.

VII.2b – Desorption Luminescence, Ionised Gas-Induced Luminescence etc

This is exhibited by almost all the TL phosphors especially when heated in air(100). Mostly the emission occurs in the region of 300°C – 400°C and the intensity is very much reduced in a continuously flowing nitrogen atmosphere. The emission spectra are more or less similar for all phosphors peaking broadly around 500 nm(62).

There have been arguments(151-201) that both, movement of the powder before (such as pouring into the heating tray) and the presence of oxygen during, read-out, are necessary to observe such spurious TL. Surface trapping states are assumed responsible for this; but none of the models are conclusive yet.

There is an interesting feature in LiF(169) that spurious TL induced by various excitations such as grinding, shaking, air-exposure etc. give peak emission at different temperatures higher than the usual radiation-induced TL peak (figure 41).

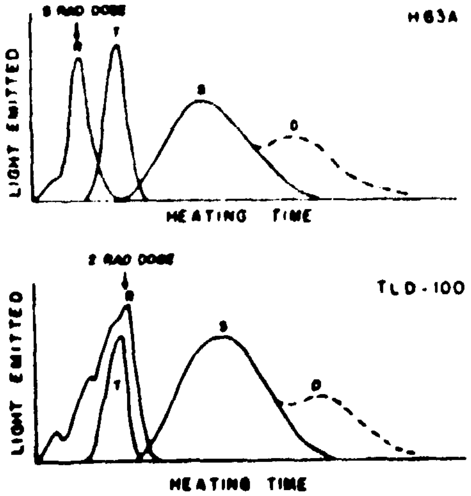


Figure 41 – TL glow curves of two samples of LiF for various types of excitations (Rhyner, C. R., 1965 ref. /169/). R – Radiation induced; T – Tribo (mechanical grinding) induced; S – Shaking induced; D – Duration (adsorption) induced.

VIII – INTRINSIC EFFICIENCY OF VARIOUS TL PHOSPHORS

Intrinsic efficiency of a TL phosphor is usually taken to be the percentage emission of the absorbed energy in the form of TL. It is to be remembered that when a phosphor is exposed to radiation, energy is 'absorbed' and only a fraction of it is 'stored'; again when the phosphor is heated, only a fraction of the stored energy appears as TL. During 'absorption', a portion of the energy is immediately emitted as 'radio-luminescence' while yet another portion appears as radiationless transitions (heat). During the 'readout', only a fraction of the stored energy is converted into TL, the remaining being in the form of radiationless transitions (figure 42).

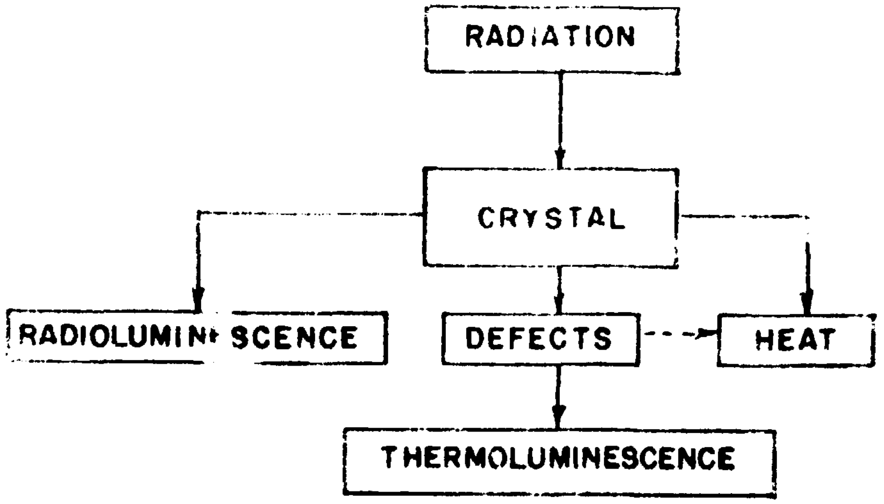


Figure 42 – Absorbed energy transformation in a TL phosphor.

In TL studies the quantities which can be measured in practice are the absorbed energy by the TL phosphor and the energy emitted as TL. All other processes in the schematic flow chart constitute a 'black box' and it is a matter of convenience that intrinsic efficiency of a TL phosphor is defined as above. It is evident that for a TL material to be efficient, the net fraction removed by the 'black box' should be as minimum as possible. Some Russian workers have estimated that a maximum possible intrinsic efficiency value of about 25 ~ 35% can be obtained in optimal TL phosphors(186). Such a value is in fact experimentally obtained for the case of $CaSO_4$:Dy phosphor(141) and there are indications that Mg_2SiO_4:Tb phosphor may have a still higher efficiency. Some of the typical values reported for the intrinsic efficiencies (at high doses) and relative TL outputs (at low doses) for various TL phosphors are given in Tables IV and V.

Table IV

Intrinsic TL Efficiencies (at High Doses) of Various
Phosphors Reported in Literature(141)

TL phosphor	Intrinsic efficiency (%)
1. TLD-100 (LiF)	0.005, 0.072, 0.13, 0.062
2. $Li_2B_4O_7$:Mn	0.3
3. $CaSO_4$:Mn	1.2, 1.5
4. $CaSO_4$:Mn:Pb	4.0
5. CaF_2:Mn	1.3, 0.44
6. $CaSO_4$:Dy	35.0

Table V

Relative TL outputs of Various Phosphors
(at low doses)[19]

TL phosphor	Relative TL output at the same dose
1. TLD-100 (LiF)	1.00
2. $Li_2B_4O_7$:Mn	0.47
3. CaF_2:Mn	8.00
4. CaF_2 (natural)	13.00
5. $CaSO_4$:Mn	37.00
6. $CaSO_4$:Dy	39.00
7. Mg_2SiO_4:Tb	79.00

It should however be mentioned that the accuracy of the values mentioned above is rather poor. This is mostly due to the fact that absolute TL spectral intensity measurements are very difficult to make with the phenomenon being transient in nature. If the phosphor is heated very slowly as to keep the intensity more or less the same during a rapid spectral scan, then the intensity involved is very low and the computations for the intensity losses in between consecutive scans are rather inaccurate. The most sensitive method seems to be the one in which spectral glow curves are recorded from individual portions of the irradiated phosphor at regular wavelength intervals and construct the TL spectral emission curve which can then be corrected for the absolute spectral response of the detector system used[117,141]. In general, it is easier to determine the absolute intensities in the case of phosphors with single broad band emission than for those having a large number of sharp emission lines (§ sec.II.2).

IX – STUDY OF DEFECTS BY TL CORRELATION MEASUREMENT

Understanding of the phenomenon of thermoluminescence involves a study of solid state defects – their formation, distribution and interaction among themselves and with the lattice. Optical measurements like absorption and fluorescence help us to understand the underlying electronic processes; a defect, if paramagnetic, can be studied in some detail with regard to its crystal surroundings through electron spin resonance measurements; complexes including aggregates and precipitates if formed, can be interpreted from conductivity data; a TSEE-TL correlation may reveal the presence of electron traps; a correlation with radio-luminescence and photoluminescence spectra may reveal some clues regarding the luminescence centres and so on.

In principle the correlations are best established by following the behaviours with increases in irradiation as well as after various stages of bleaching (photo-bleaching, isothermal decay, fading etc).

Some of the important correlations reported so far in literature are summarised below:

IX.1 – Optical Absorption and TL Correlation

Significant results have been obtained from optical absorption and TL correlation studies in materials like calcite[130], alkali halides[93], CaF_2[166] and LiF[47,127]. The findings on LiF are summarised below.

The typical TL glow curves and optical absorption spectra of gamma irradiated LiF (TLD-100) are presented in figures (43) and (44).

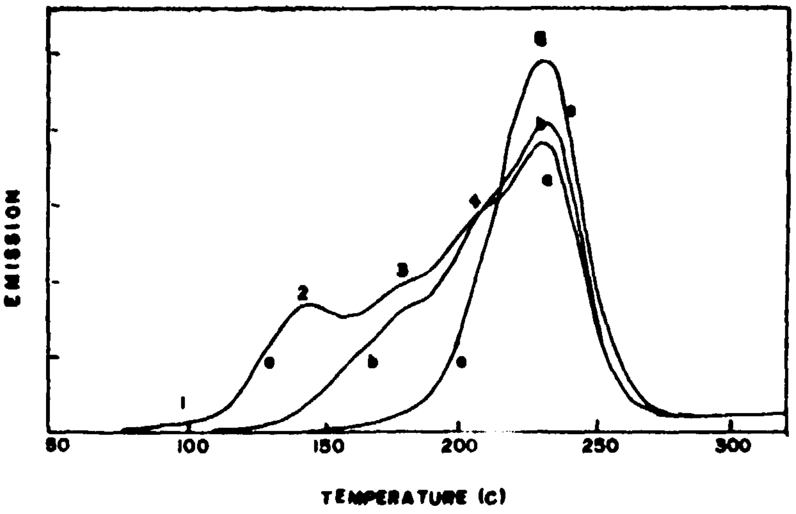


Figure 43 – TL glow curves of gamma irradiated LiF TLD-100: a) immediately after the irradiation; b) TL remaining after annealing at 100°C for 10 mins; c) TL remaining after annealing at 100°C for 60 mins. (Mayhugh, M. R., 1968 – ref. /127/).

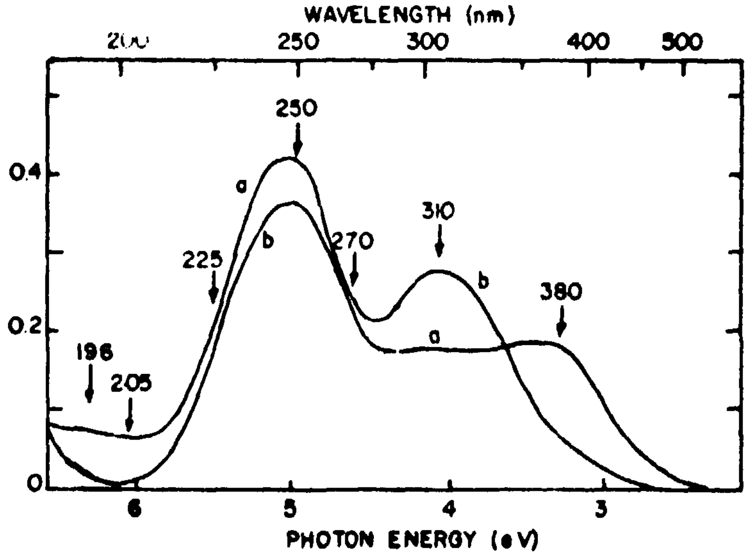


Figure 44 – Optical absorption spectra of gamma irradiated LiF: a) immediately after irradiation; b) absorption remaining after annealing at 100°C for 30 mins. (Mayhugh, M. R., 1968 ref. /127/).

The results show clearly a strong correlation between the most sensitive TL peak at ~200°C (called dosimetry peak V) and the 310 nm absorption band. This is further strengthened by results obtained by a successive annealing experiment at 150°C (figure 45).

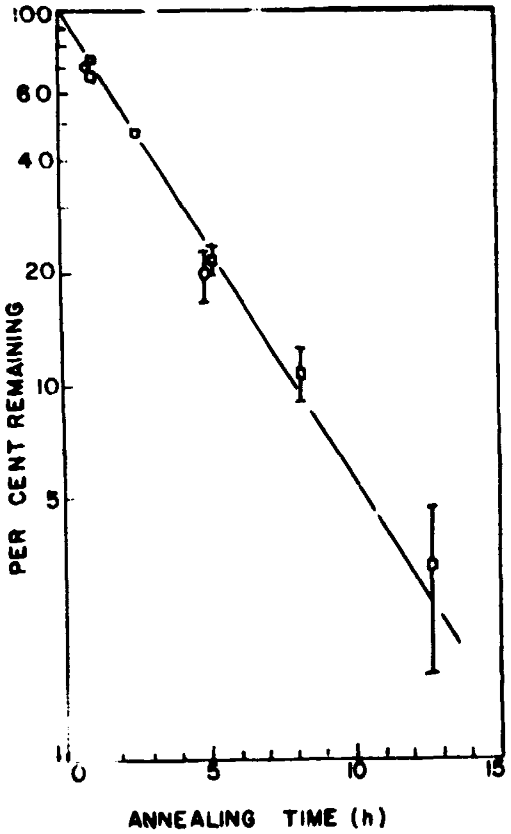


Figure 45 – The heights of TL glow peak 5 and the 310 nm absorption band as a function of annealing time at 150°C of gamma irradiated, 100°C annealed LiF TLD-100 sample (Mayhugh, M. R., 1968 – ref. /127/. O – 310 nm band; ☐ – TL peak 5.

By working on pure and Mg doped LiF crystals it has been possible to identify the 250 nm band with F centres and the 310 nm band with Mg impurity; the TL and optical absorption build-up with increasing irradiation (figure 46) indicates that both F centres and Mg centres are involved in TL. By UV bleaching experiments it could be shown that all are electron traps and that F centres are associated with luminescence centres in the TL of LiF. The usual sensitisation procedure (§ sec. VI.2 & 3) leaves a large number of F centres as residual in the sample and this results in increased sensitivity for subsequent irradiations. More recent studies(126) have led to the identification on the corresponding hole centres also viz. a 113 nm band characterising a V_3 centre and a 200 nm band characterising a V_K centre and a simplified band model has been proposed for the TL in LiF:Mg:Ti (figure 47).

Upon irradiation, electrons and holes are trapped at F and V_3 centres respectively with some of the electrons trapped at Mg centres which are relatively thermally unstable compared to F centres. Thermal stimulation releases electrons from Mg centres which annihilate V_3 centres to form V_K centres; the holes at V_K centres have mobility and combine with a tunnelling F–electron at a luminescence site (may be the Ti impurity).

This model satisfactorily explains all the radiation induced effects observed in the TL of LiF.

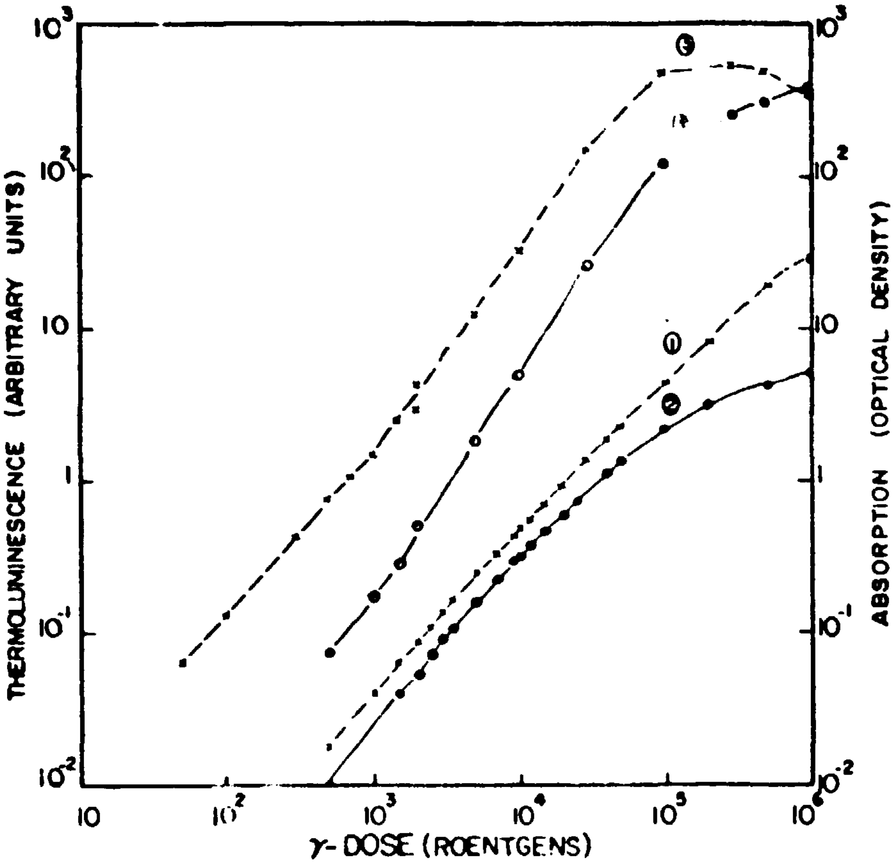


Figure 46 – Radiation-induced changes in optical absorption and TL of LiF TLD-100 with increasing irradiation (Claffy, E. W., 1968 ref./47/). 1) F (250nm) absorption; 2) Mg (310 nm) absorption; 3) 210°C TL peak; 4) 285°C TL peak.

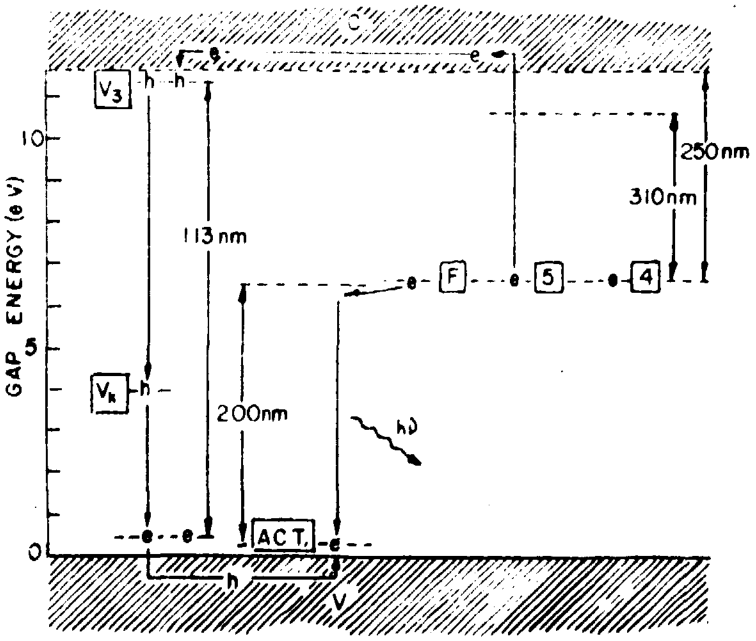
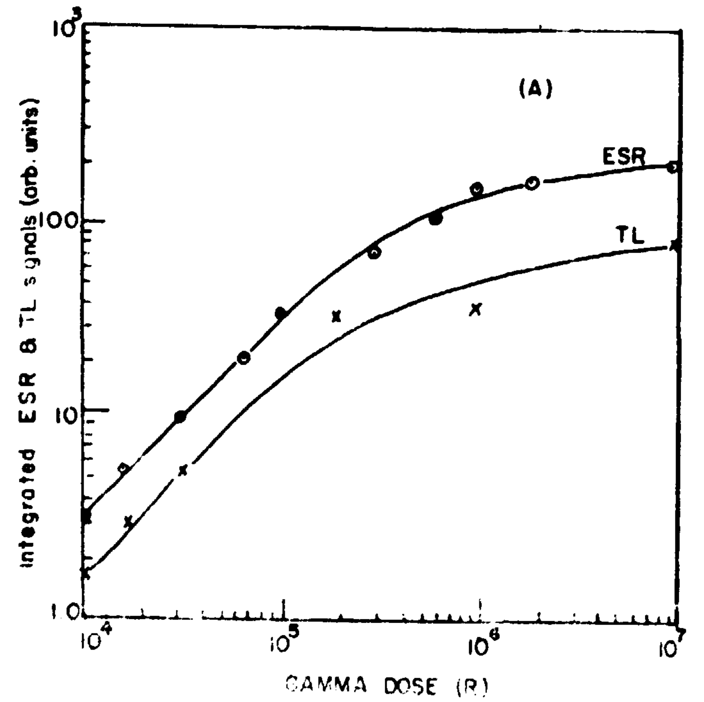


Figure 47 – Simplified band model of TL in LiF:Mg, Ti (Mayhugh, M. R., 1970 – ref./126/).

IX.2 – ESR and TL Correlation

Very useful inferences have been obtained by ESR-TL correlation measurements in phosphors like CaF_2 and $CaSO_4$[144,147]. Quantitative inferences are difficult to make as the sensitivity factors of the two methods bear a ratio of nearly 10^6 (TL being more sensitive). The findings on $CaSO_4$ (RE) phosphors are briefly summarised below:

The ESR spectra of all the $CaSO_4$ (RE) phosphors are the same irrespective of the kind of RE dopant chosen and no signal is obtained prior to irradiation; there are however relative intensity differences for the ESR intensities obtained in each case. The signals have been identified with hole centres with configurations like SO_4^-, SO_3^-, O_2^- and so on; the TL glow curves are also the same with only relative intensity differences; hence a conclusion could be drawn that perhaps the traps associated with the TL glow curves are the hole centres. The correlation is further confirmed by the near-parallelism exhibited by the growth and decay curves of the ESR and TL intensities (figure 48).



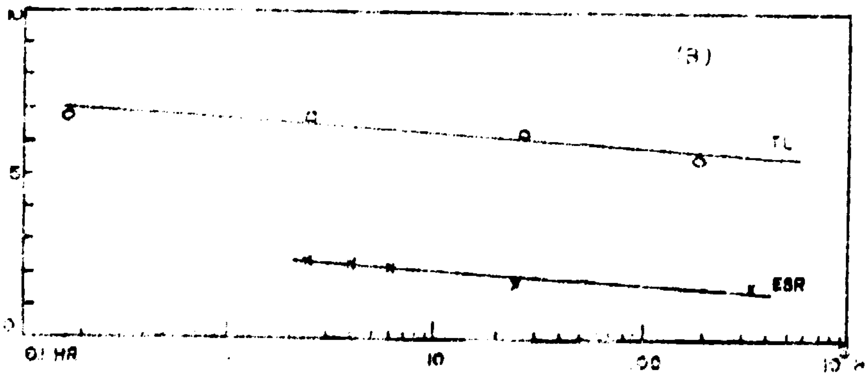


Figure 48 – Gamma dose build-up (A) and room temperature decay (B) curves for ESR and TL intensities of $CaSO_4$ (RE) phosphors.

The different thermal activation energies required for the release of holes is established by the successive thermal annealing of the ESR spectrum which exhibited prefential annealing stages corresponding to the thermal instabilities of the different centres (figure 49).

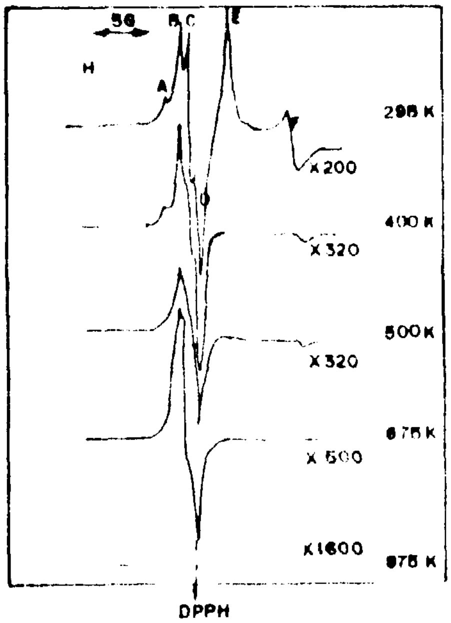


Figure 49 – Typical thermal annealing characteristics of ESR signals of gamma irradiated $CaSO_4$ (RE) TL phosphors (Nambi, K. S. V., 1974 – ref. /144/).

From the variations in the ESR intensities obtained for the phosphors with different RE dopants it could also be concluded that the RE ions influence the stability of the hole centres to different extents. The TL emission spectra of $CaSO_4$ (RE) phosphors are characterised by the sharp fluorescence emission lines of the respective RE^{3+} dopant ions. Thus is could be inferred that the TL process in $CaSO_4$ (RE) phosphors involves $RE^{3+} \underset{\text{heat}}{\overset{\text{irradiate}}{\rightleftarrows}} RE^{2+}$ reversible reactions with simultaneous trapping and release respectively of holes at the sulphate sites.

More recently such correlations have been studied(70,180) in $SrCl_2$ and BeO phosphors also.

IX.3 – TSEE and TL Correlations

On the basis of currently available understanding of the thermally stimulated detrapping processes in ionic solids (figure 50), a correlation between a TL peak and TSEE peak occurring at the same temperature may be taken to indicate the presence of electron traps contributing to the TL at that temperature(14).

Quite interesting observations have been made in the very famous TL phosphors like $CaSO_4$(191), CaF_2(161), BeO(69) and LiF(208). The findings on $CaSO_4$ and BeO are cited briefly below.

While pure $CaSO_4$ gives no TL but sufficient TSEE, $CaSO_4$:Mn gives both TL and TSEE at the same temperature. Thus it is indicated that Mn is the TL emission centre and does not possibly play the role of an electron trap. $CaSO_4$ (Pb) is found to give maximum TSEE of all the dopants studied and obviously $CaSO_4$:Mn:Pb resulted in a better phosphor(215).

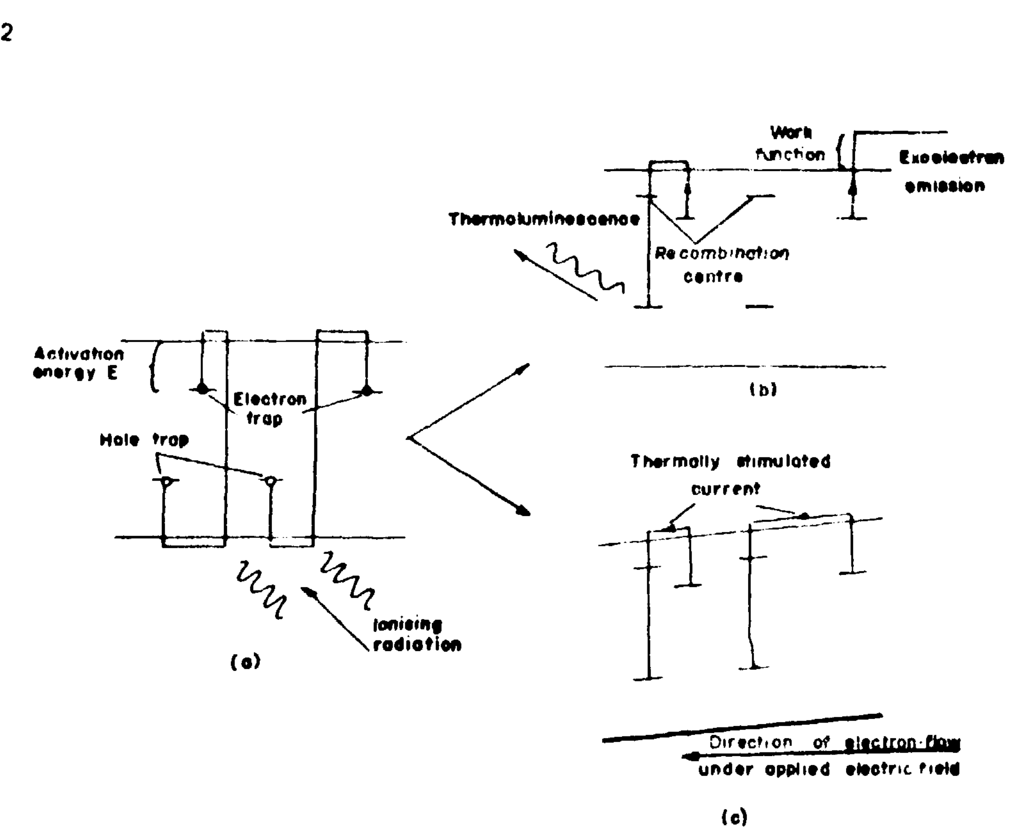


Figure 50 – Simplified schematic diagrams of the basic detrapping processes occurring in an irradiated ionic solid: a) ionization and trapping, b) thermally stimulated luminescence and exoelectron emissions and c) thermally stimulated increase in conductivity with an applied electric field (Bowlt,C., 1976 – ref./24/).

In TSEE-TL correlation studies a distinction has to be made between "surface" traps and "volume" traps and sometimes the absence of a correlation between these two processes could be simply due to this.

In the case of BeO, the TL and TSEE peaks have no correlation at all (figures 51 and 52) and the LET dependence of the two phenomena are so different that the ratio of TL and TSEE peaks from the same BeO dosimeter can be advantageously calibrated to indicate the LET of the irradiation besides the dose.

IX.4 – TSC, ITC and TL Correlations

Equilibrium relationships between lattice defects including dipole formations can be experimentally understood using techniques such as electrical conductivity, ionic currents and dielectric loss. In relation to TL, thermally stimulated electrical conductivity (TSC) and ionic thermocurrent (ITC) measurements have yielded useful information on the nature of the defect affecting the TL phenomenon(192). Figure (50) indicates that occurence of TSC and TL peaks at the same temperature would mean electron traps being resposible for the TL process. Such correlation studies have been successfully attempted in LiF(213) and CaS(209) phosphors. The salient features of these studies in LiF are summarised below:

Figures (53) and (54) show the TL and TSC annealing data as a function of temperature of annealing for both pure LiF and LiF (Mg) phosphors.

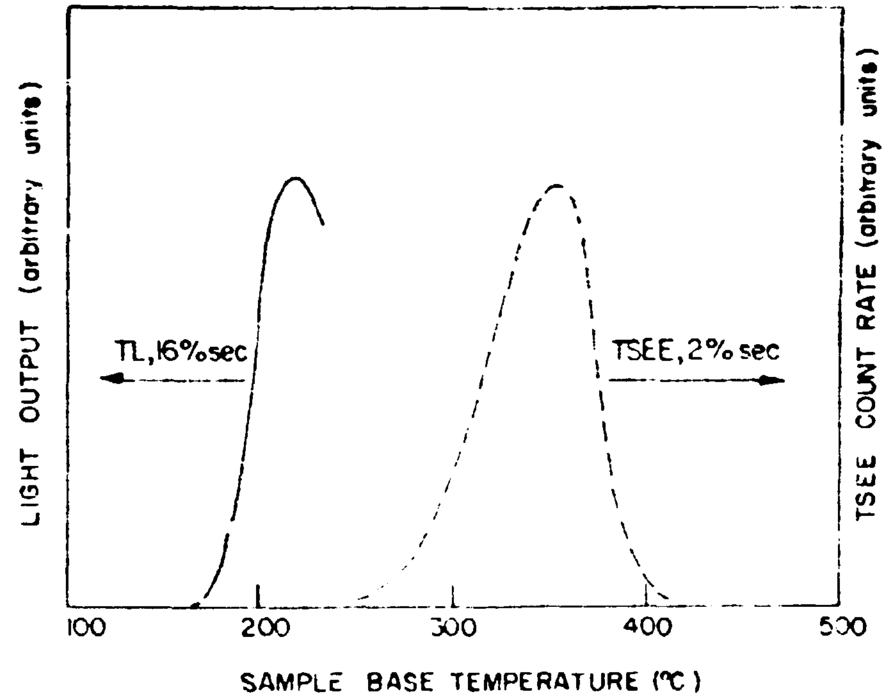


Figure 51 – TL and TSEE of BeO dosimeter after gamma irradiation: same dosimeter read on different readers (Gammage, R. G., 1974 – ref./69/).

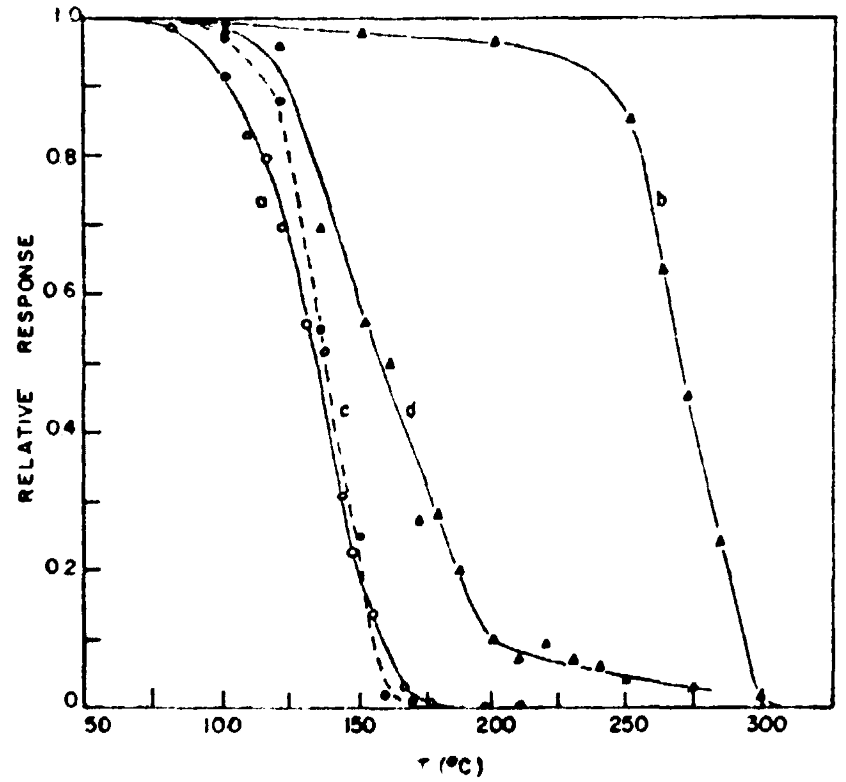


Figure 52 – Fading of TL, TSEE and EPR signals of gamma irradiated BeO as a function of annealing temperature for 30 mins. (Gammage, R. B., 1974 – ref./69/).
a) TL b) TSEE c) hole centre (ESR) d) Al^{2+} centre (ESR)

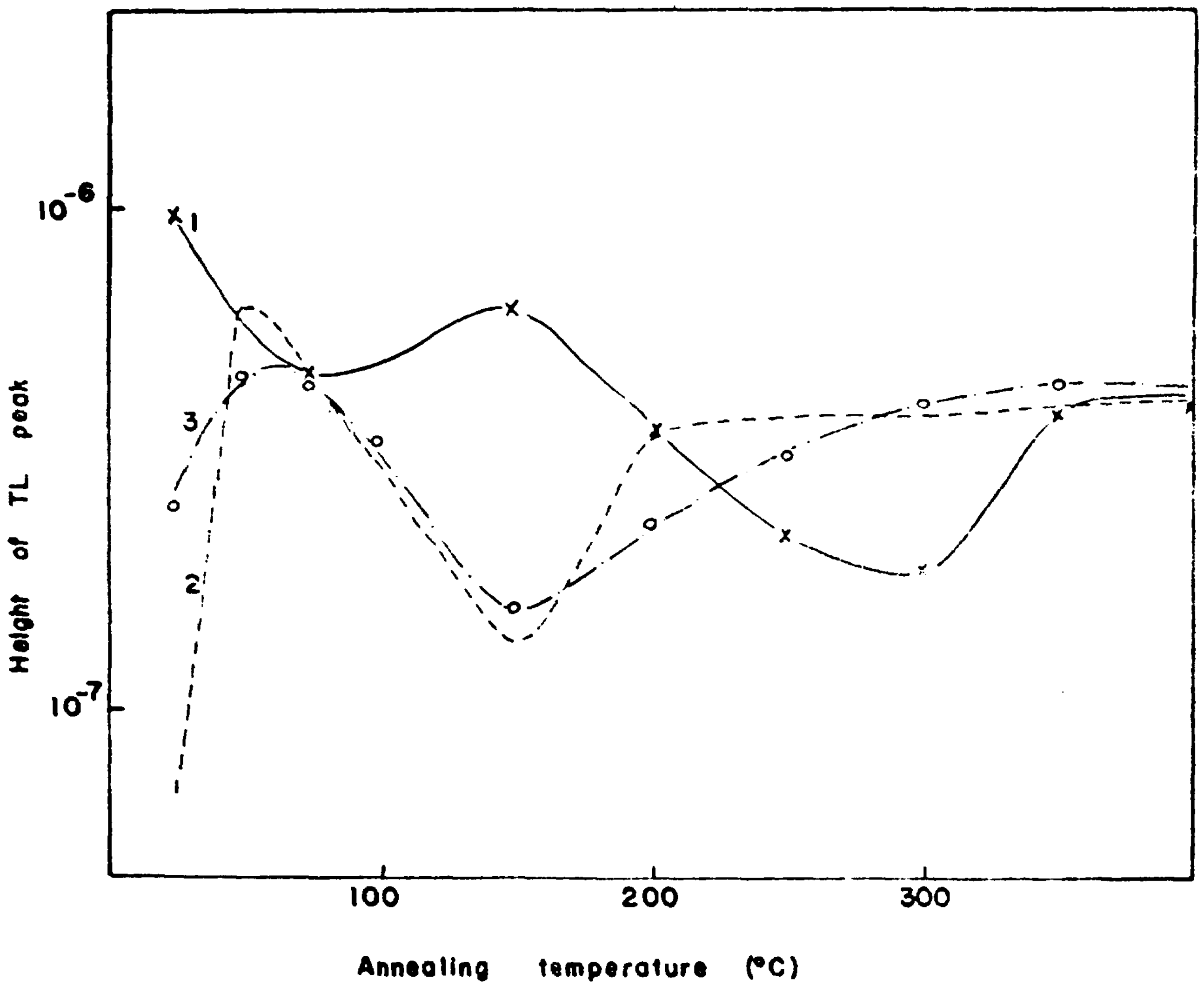


Figure 53 – Height of TL peak 5 versus annealing temperature of LiF:Mg 1) 0.004% Mg 2) 0.01 % Mg 3) 0.04% Mg (Pure LiF does not give TL peak 5) (Rao, S. M. D., 1974 – ref. /150/).

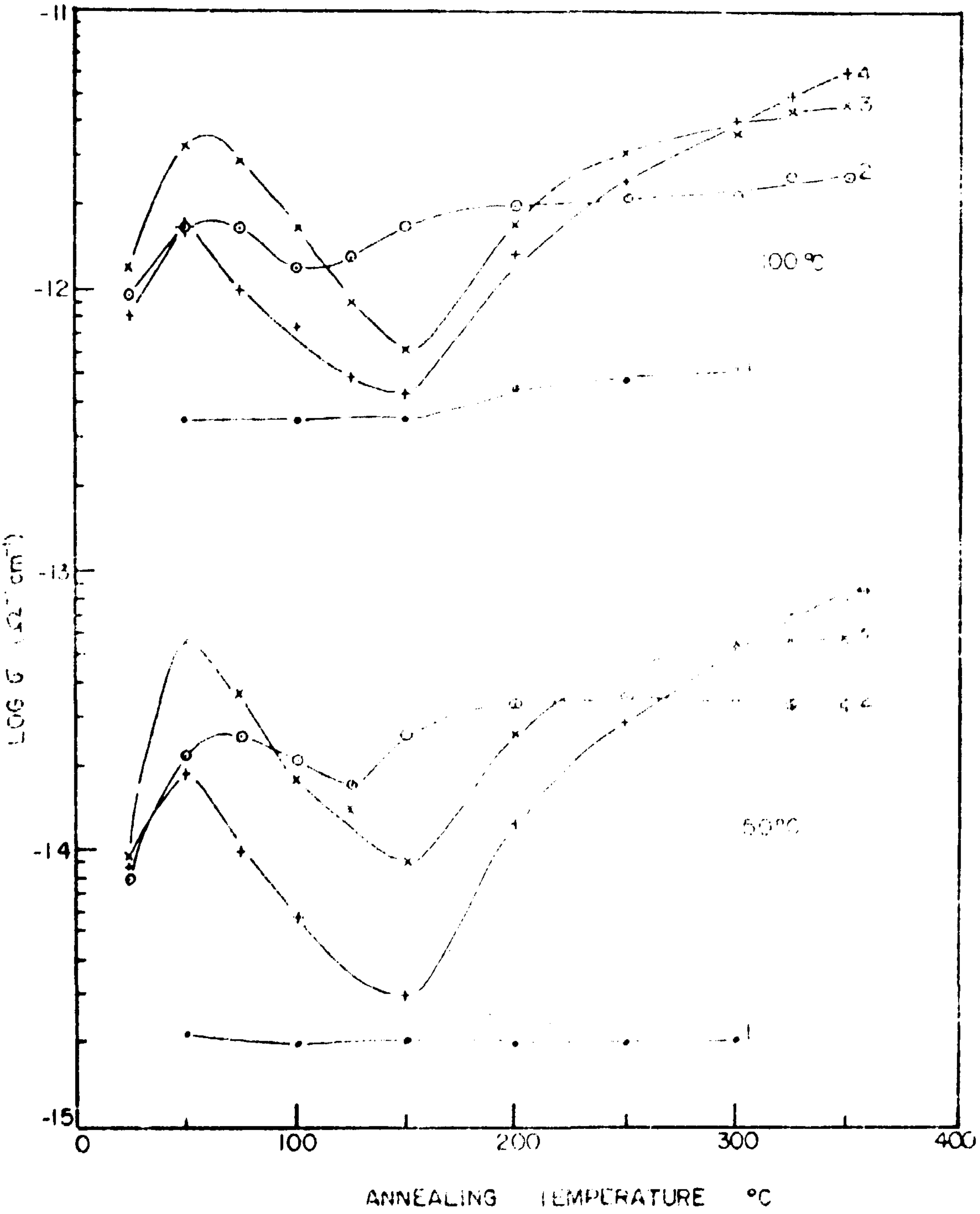


Figure 54 – Variation of conductivity with annealing temperature for 1) Pure LiF, 2) LiF:0.004%Mg, 3) LiF:0.019%Mg, 4) LiF:0.04%Mg (Rao, S. M. D., 1974 – ref./165/).

The parallel decrease in TSC and TL around 150°C annealing has been identified to the formation of neutral Mg atoms; for higher temperatures of annealing more of precipitated Mg is dissolved and hence TSC as well as the TL increases; but beyond a certain limit, the formation of impurity-vacancy dipoles and higher orders assumes more and more importance which causes the observed increase in conductivity but a saturated TL output. All theses defects have been argued to have the potential of influencing the TL behaviour in LiF.

IX.5 – Phosphorescence (PH), Radioluminescence (RL), Photoluminescence (PL), and Thermoluminescence (TL) Correlations

Useful informations on the nature of luminescence centres are always derived from the spectral characteristics; but TL spectral measurements – especially any quantitative estimates – are difficult to make (§ sec. II.2 & 8) because of the transient nature of the phenomenon. The same phosphor, if it exhibits the same spectral characteristics under steady states such as during phosphorescence decay at ambient temperature (PH), fluorescence during irradiation (RL), luminescence during photo-excitation (PL), then useful conclusion can be drawn regarding the luminescence centres involved in the TL process. Such studies have been successfully carried out in TL phosphors like LiF, Quartz(221), alkaline earth sulphates(119) and CaF_2 (RE)(208). Very significant conclusions have been drawn on the radiation induced sensitisation exhibited by LiF (TLD-100) which are summarised below:

TL and TSEE correlations revealed that the sensitisation is connected with increase in luminescence emission rather than increased trapping (figures 55 and 56). The PL, RL and TL spectra are qualitatively the same indicating involvement of the same luminescence centres in all the three; with increase of TL sensitivity after sensitisation (§ sec. VI.3), the RL intensity increased but the PL intensity decreased. This indicates that sensitisation increases the number of activated centres (luminescence centres "filled" by irradiation and which take part in the TL) with a reduction in the available unactivated centres ('empty' luminescence centres which can emit fluorescence only by photo-activation). Thus a very important understanding could be developed regarding the sensitisation process in the TL of LiF phosphors.

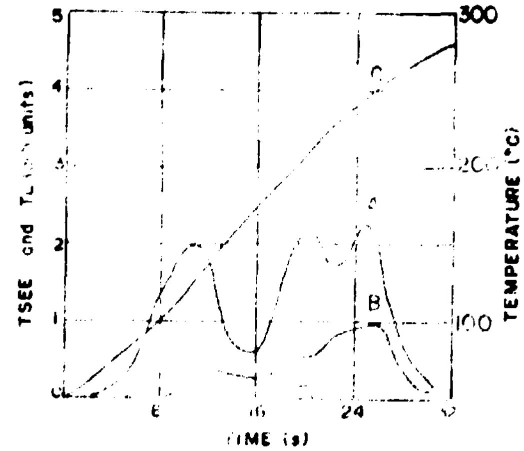


Figure 55 – TSEE(A) and TL(B) glow curves of virgin TLD-100 after gamma irradiation; (C) is the temperature curve. (Zimmerman, J., 1971 – ref. /221/).

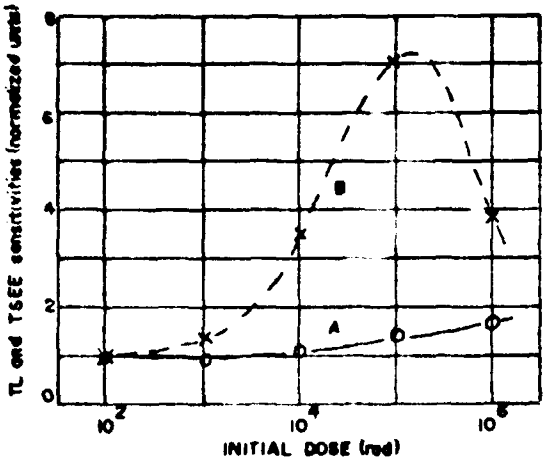


Figure 56 – Variation with initial dose of TSEE(A) and TL(B) sensitivities of peak V in TLD-100; each sample had been heated at 280°C for 60 mins. after the initial irradiation and then TL sensitivity tested at a dose of 2 rads (Zimmerman, J., 1971 – ref. /221/).

X – APPLICATIONS OF TL

TL is perhaps one of those rare physical phenomenon which is more successfully applied than understood. Its application potential was first proposed in 1953(52) and since then with the development of better instrumentation and basic understanding, its applications have engulfed a whole spectrum of disciplines such as Archaeology, Biology & Biochemistry, Forensic Sciences, Geology, Radiation Dosimetry, Radiation Physics, Solid State Physics, Space Science, Spectroscopic Analysis, TL photography and so on. The publications covering these are well collected in various Conference Proceedings listed separately at the end of this review.

The important aspects of these applications are briefly summarized in the following sections:

X.1 – Archaelogy

Thermoluminescence techniques have been found to be successful in dating ancient potteries and other mineralic, once heated artefacts and offer a quick, reliable method to detect art forgeries. The subject matter has been very well reviewed in some recent publications(1,40,132,134).

The starting of the "TL clock" is considered to be the time of firing of the pottery specimen. Whatever TL had been stored in the material due to internal and external irradiation over geological times is considered to be erased during the firing the temperature being anywhere around 1000°C. Thus the age arrived at by measuring the TL accumulated since the time of firing of the specimen is truly representative of the archaeological age from the historian's point of view.

The TL from the specimens is mostly due to some TL sensitive mineral inclusion in the main clay matrix of the sample. The internal irradiation is from the radioactive emanations of U, Th and K contents in the clay composition and the external irradiation is from the radioactive contents of the surroundings and the cosmic background at the burial site. Typically the total irradiation rate is of the order of 1 rad per year of which the major part is due to the internal component, about 20% is due to the soil irradiation and a few percent from cosmic rays. Once the accumulated TL in the specimen has been measured and expressed in terms of absorbed dose (rads) by proper calibration techniques and if the total irradiation rate (rads/year) for the specimen could be estimated, the archaelogical age can be obtained by simply dividing the former by the latter. In practice however, there are many complicating factors like variation in the TL response to alpha, beta and gamma component of the irradiation, thermal and non-thermal fading characteristics, non-linear TL dose build-up behaviour, inhomogenous distribution of the mineral in the clay matrix, presence of a heterogenous mixture of minerals contributting to the TL and so on. There are also experimental difficulties in measuring the naturally accumulated TL signal which is usually low and has to be detected against competing infra-red and spurious signals (Figure 57).

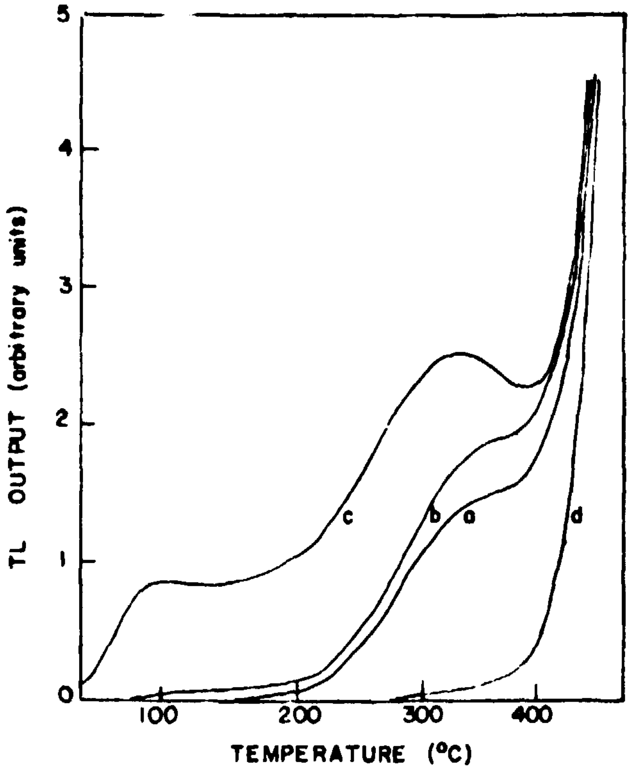


Figure 57 – Typical TL glow curve runs of an Indian Pottery Sample: a) natural TL; b) NTL +45 30R of alpha irradiation; c) NTL + 20 70R of gamma irradiation and d) Thermal noise (Sasidharan, R., 1975 – ref. /178/).

There are about five independent methods advocated so far for the estimation of the archaeological age:

i) Inclusion dating technique$^{(63,64)}$, where coarse (quartz) grains of about 100 μm diameter are separated from the clay matrix, the alpha exposed surface of the grains is removed by etching with HF and then TL estimations are made:

$$\text{Age} = \frac{(\text{ED})_{\text{Incl.}}}{D_\beta + D_\gamma + D_c}$$

where ED is the equivalent dose of the archaeologically accumulated TL signal, D_β, D_γ & D_c are beta, gamma and cosmic components of annual irradiation dose received by grains.

This method has the simplicity that it avoids the measurements of alpha components which is usually more difficult and the disadvantage that it is very sensitive to the cosmic component which is usually not known accurately.

ii) Fine grains dating technique(218,219), where fine grains ($< 10\,\mu m$) are separated and the TL estimates are made:

$$\text{Age} = \frac{(\text{ED})_{\text{FG}}}{kD_\alpha + D_\beta + D_\gamma + D_c}$$

where k is the TL sensitivity factor for alpha irradiation compared to beta, gamma irradiations.

[There can also be a subtraction dating technique where

$$\text{Age} = \frac{(\text{ED})_{\text{FG}} - (\text{ED})_{\text{Incl.}}}{kD_\alpha}$$

and this avoids the necessity to know the cosmic component of the annual archaeological irradiation].

iii) Predose dating technique(65), where the radiation induced sensitivity changes in the 110°C TL peak of quartz (§ sec.VI.3) is made use of, to estimate the archaelogically accumulated TL dose. While all arguments pertaining to the inclusion method apply here also, this method has the advantage that the TL measurements can be made with more accuracy as the measurement of the high temperature, low sensitive TL peak is avoided; also this technique is the most suitable for younger artefacts where the high temperature TL peak may not have developed to any decipherable degree.

iv) Simulation dating technique(41), in which the obtained archaeological TL signal is simulated again by a suitable combination of the temperature of irradiation and dose rate; the age estimation is done from

$$t_1 e^{-\frac{E}{KT_1}} = t_a e^{-\frac{E}{KT_\mu}}$$

where T_1 & t_1 are the temperature and duration of the laboratory irradiation and T_μ & t_a are the average temperature and age of the archaeological storage.

v) Dating by UV transfer TL technique(179), in which the sensitivity for UV induced transfer TL from the archaeological TL is measured and from this the archaeological dose estimated (§ sec.VI.5). This method has the same advantages as the predose dating method.

The TL method applied to the study of archaeological objects of ceramic character has been holding out better promises in recent times especially in rapid and reliable forgery detection(66); there is also a possibility of being able to do a "finger printing" of the ancient potteries by cataloguing the natural TL glow curves of the "whole" sample(178).

X.2 – Biology & Biochemistry

Application of TL techniques in the study of biological and biochemical systems is increasingly favoured in recent times and necessarily all the measurements are done in the LNT-RT range. The attempts have been successful in the study of hydroxy and aminobenzoic acids, urea, nucleic acids, proteins, plant leaves, algae and bacteria: the TL results could indicate the poorer stability of the orthoform of the benzoic acids(7); the inter and intra molecular transfer of radiation damage in nuclei acids, proteins and their constituents could be correlated with their TL behaviour(204); the photosynthetic electron transport routes in the Z diagramme could be correlated with TL and additional routes delineated(176) and the interaction between salts and proteins could be understood from the TL patterns(3).

X.3 – Forensic Sciences

The major study in Forensic Sciences is to evolve and standardise methods to compare evidentiary materials with similar materials of known origin which are invariably available only in minute quantities and are required to be analysed non destructively for evidence purposes. Thermoluminescence can offer an attractive technique in selected materials that are commonly encountered in criminal cases viz: glass, soil, safe insulation materials, etc(39,90). This can be used as an exclusionary evidence ie. when the TL characteristics do not match, it can be said with certainity that a particular sample has not come from a known source. To reduce the probability of any coincidental matching and improve the confidence on the TL measurements whose signal to noise ratio may be bad, examinations may be made of the TL glow curves from the virgin samples as well as after a heavy artificial gamma or X-ray irradiation and also of the TL emission spectra.

The application of TL methods to detect art forgeries, which strictly is part of Forensic Sciences, has already been discussed.

X.4 – Geology

Geology is one of the earliest disciplines to accept the TL technique into its fold in a variety of applications such as identification of minerals, classification of mineral deposits, age determination, thermal histories of mineral deposits, radioactive trace estimation in rocks, stratigraphy etc(129).

In a large limestone quarry, TL characteristics of various samples collected from the same stratum over a half mile face were identical but differed greatly even for a few feet displacement on either side of the stratum(175). Thus, this could provide a means of determining whether two samples of sedimentary rocks were laid down at the same time in the same environment, although they are widely separated geographically. TL could also be used as a means of correlating limestones(15).

A correlation has been successfully arrived at(187) between the stages of diagenesis of sedimentary dolomites and the relative intensities of their various TL glow peaks after artificial gamma irradiation. The degree of dolomitisation of calcite and limestone samples could be inferred by the extent to which a new peak appears at about 330°C in the natural TL glow curve which is otherwise peaking around 280°C(115,149)

TL dating method has been successfully employed in estimating the age of radioactive mineralisation of a deposit in India by measuring the TL of smoky quartz crystals collected from a non-radioactive intrusive layer in between two radioactive veins in the deposit(102) Useful correlations have been obtained between TL and Tectonic/magmatic events in the orogenesis of limestone deposits in Malaya(88). The potential of TL as a means of dating young siliceous ocean sediments has also been explored recently(87). TL techniques has been suggested in paleothermometry to determine magma temperatures; it essentially consists of a numerical integration of the TL decay equation over the time-temperature conditions realised during cooling of the magma and this has been successfully employed for various limestone-basalt zones in northern Arizona(96).

TL measurements on granite samples have been used to obtain radial temperature profiles from the centre of a nuclear explosion in Algeria(61).

The attempts to use TL as a prospecting tool for selected minerals has so far been unsuccessful(121) but hopes are still being voiced and efforts are continuing in this regard(154).

X.5 – Quality Control in Industry

Even as early as 1938, the application of TL in the control of feldspars in ceramic products has been described(55). The amount of TL given out by a ceramic after artificial irradiation is directly indicative of its feldspar content at trace levels where any other type of quantitative analysis is time consuming. Thus in ceramic industry where a particular process is repeated many number of times to produce batches of the same material, any uncontrollable variations in the feldspar contents can be checked quickly and efficiently.

The efficiency of certain surface catalysts like Al_2O_3, can be quickly and efficiently evaluated by their TL sensitivities(25). The lattice defects which permit the adsorption reactions might also play a role in the TL emitted by these substances and the nature and intensity of TL emitted may be gainfully correlated with the catalytic activity. The TL glow curve in such cases could be used as a criterion in controlling the preparative parameter of a desired catalyst.

In principle, TL methods could be employed in the quality control of many of the glass, ceramic and semiconductor products; recently it has even be shown in the case of textile fibres that the low temperature TL glow curve changes can be correlated with structure differences and/or chemical tracer impurities(6). However these have not yet received the attention of the industries.

X.6 -- Radiation Dosimetry

Most of the developments in the understanding and applications of the TL owe their origin singularly to the efforts made in the use of this phenomenon in the field of Radiation Dosimetry and in the research for more sensitive dosimetric phosphors. The main basis in Thermoluminescence Dosimetry (TLD) is that TL output is directly proportional to the radiation dose received by the phosphor and hence provides a means of estimating unknown irradiations. Also, TL can provide a perfect passive measurement ie. integrated irradiation levels over extended periods of the order of even years. Thus it finds immense use in the monitoring of doses received by radiation workers on a routine basis: weekly/monthly/yearly depending upon whatever a situation may warrant. It should however be borne in mind that most of the TL phosphors are not tissue equivalent (in terms of energy absoption by irradiation) and hence the relevant dose which is medically significant to a radiation worker from protection point of view, is not readily obtained. Some of the phosphors like LiF, $Li_2B_4O_7$, BeO etc which are nearly tissue equivalent score a definite point over others like $CaSO_4$, CaF_2, Mg_2SiO_4 etc which are however more sensitive.

Some of the obvious advantages and limitations of TLD compared to other available options like Photographic Film dosimetry and Photoluminescent glass dosimetry are given below:

X.6.1.a – Advantages of TLD

i) highly economical (mostly because the phosphors can be easily prepared in the laboratory and are reusable);

ii) very sensitive, reasonably accurate and linearly response over a wide range of the dose;

iii) flexibility of dosimeter design-extremely small sizes approximating to point detectors, flexible chord types, circular, rectangular shapes, capillaries etc are all possible suited to the particular application;

iv) quick, on the spot dose evaluation possible;

v) perfect passive measurements over long periods without interference from weather changes, intrinsic fading etc possible;

vi) large scale automatic processing in routine applications feasible; and

vii) approximate energy spectrometry of an unknown gamma field possible by the use of a high Z TL phosphor and a combination of "energy filters"

X.6.1.b – Limitations

i) repeat reading not feasible – this can be partly circumvented by having a back-up dosimeter to have a confirmatory reading; a UV transfer-induced repeat reading also possible in the high dose ranges;

ii) evidence value for later verification almost nil compared to the photographic method;

iii) spatial resolution and information on type of radiation not possible;

iv) neutron dosimetry is still in an infant stage for routine applications;

v) directional dependance quite severe but can be minimized by proper design; and

vi) spurious reading rate relatively high but can be kept within tolerable limits.

The present state of art of TLD in beta, X, gamma and neutron monitoring is briefly described below:

X.6.2 – A TLD for Beta, X and Gamma Monitoring

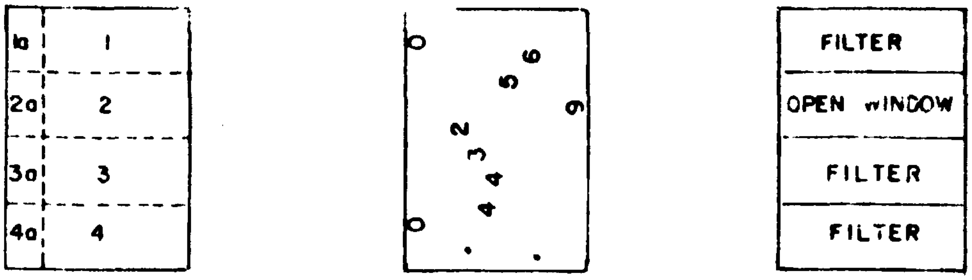
It can be stated in general that a TL phosphor exhibits the same sensitivity to beta, X and gamma – radiations on equal rad (absorbed energy) basis. Depending upon the energy dependence curve of a particular phosphor, suitable filters can be used for applications in unknown fields. In the case of beta dosimetry however such filters will reduce the sensitivity appreciably and the problem can only be faced by having separate calibrations for beta (and X, gamma) exposures.

One of the best models for a TLD badge for beta, X and gamma personnel monitoring is commercially available(53) and consists of the TL phosphor (either LiF or $CaSO_4$:Dy) impregnated in a rectangular piece of teflon (44.45 x 31.75 x 0.4 mm^3) which has eight invisible segments and punch holes for identifications (Figure 58). It is kept in a casette which is divided into four compartments providing different energy filtrations. While segments 1 to 4 provide the main exposure evaluation, the corresponding smaller segments marked "a" can be read as a "back-up" dosimeter. The system is satisfactorily energy independant and fully automatic with a process (identification, preheat, read out and anneal of each of the four main segments) capacity of about 500 dosimeters in an eight hour shift.

X.6.3 – Techniques in Neutron Dosimetry Using TLD's

X.6.3.a – Prompt Response Method

Neutron detection by any TL phosphor is possible only if there is sufficient reaction cross section for the neutrons in question. Hence the general technique is either to use a phosphor whose constituents present a significant cross section for the neutrons or to mix an otherwise gamma sensitive phosphor with a material whose elements provide a sufficient reaction cross section: ^{6}Li isotope (with its very high (n, α) cross section for thermal neutrons) in LiF phosphor; ^{32}S isotope (with its significant cross section for (n, p) reaction for fast neutrons) in $CaSO_4$ phosphors; any phosphor mixed with Dy_2O_3, B_2O_3, Li_2SO_4 etc (with their high activation cross sections) for thermal neutron detection and phosphor mixed with hydrogenous materials like sugar, alcohol, polyethylene etc (with their high p-scattering cross sections) for fast neutron detection.



Multi area dosimeter. 4 main readout areas (1, 2, 3, 4) and 4 backup areas (1a, 2a, 3a, 4a).

Rear view of dosimeter with identification numbers. 2 dots insure dosimeter is properly insered in reader.

Standard personnel badge filter array.

Figure 58 – Multi-area TL dosimeter badge of Teledyne Isotopes (Dauch, J. E., 1974 – ref. /53/).

By properly adjusting the weight ratios of the neutron sensitive material and the TL sensitive phosphor, it is also possible to have a rem response dosimeter which can read directly doses in neutron gamma mixed fields where the gamma/neutron ratios are within ressonable limits$^{(9)}$. There are two important factors which need special care in neutron dosimetry of personnel exposures:

i) effect of self shielding when using TL phosphors with very high cross sections (hence only very thin detectiors should be used) and

ii) effect of body albedos which generate moderated thermal neutrons from incident epithermal neutrons besides reflecting incident thermal neutrons on the body.

If the TL phosphor is not "adjusted" to give a rem response in a neutron-gamma field, it is obvious that measurements have to be made with a pair of TLDs (one sensitive only to gammas and the other to both) so that the neutron and gamma components of the exposures could be individually estimated. Table VI illustrates this point well.

With a phosphor having an appreciable (n, γ) cross section, the TL sensitivity can be increased by providing a high Z back-scatterer for the escaping high energy capture gamma rays. Even a phosphor having no appreciable thermal cross section can be used as a thermal neutron detector with a cadmium filter and lead backscatterer$^{(140)}$.

In some phosphors there are significant LET-dependant glow-curve changes which can be advantegeously used for neutron detection purposes. A typical example is TLD-700 whose gamma induced TL peak is around 200°C but gives also a peak at 260°C for fast neutron irradiation due to the high LET recoils of the elastic scattering. One can have individual gamma calibrations for these two peaks and relate the difference between the two readings as proportional to the fast n dose$^{(59)}$.

An important technique in fast neutron measurements using TLD is to use a proton recoil irradiator surrounding the phosphor so that the recoil protons will deposit energy in the phosphor(198). Various irradiation geometries have been tried and the comparative efficiencies reported are given in Table VII.

Yet another important technique is to thermalize the fast neutrons and detect the thermal neutrons with a thermal neutron-sensitive TL detector, eg. ^{6}LiF at the centre of a Bonner sphere(56). In fact this has been combined with the body albedo effect and a sophisticated but useful and compact TLD badge has been successfully developed for personnel neutron monitoring purposes(85).

Table VI

Comparison of Relative Thermal Neutron and Gamma Sensitivities of the often used TLD Phosphors and Recomended Mixtures of Phosphors(9)

Phosphor/mixture	n_{th} response in ^{60}Co equivalent R per 10^{10} n . cm^{-2}	Relative γ sensitivity compared to TLD-100
CaSO$_4$ (0.05% Dy)	0.38	29
CaSO$_4$ (0.2% Dy)	0.75	35
CaSO$_4$ (3.0% Dy)	4.65	10
CaSO$_4$ (Dy, 0.8%^{6}Li) (Dy, 9.1%Li$_2$SO$_4$)	3.60 (rem response for thermal neutrons)	26
CaSO$_4$ (Dy, 4%^{6}LiSO$_4$) (Dy, 1.5% TLD-100)	18.6 (rem response for Th & int energy neutrons)	27
Li$_2$B$_4$O$_7$: 0.1% Mn	165.0	0.34
TLD-600	1520	1

Table VII

Relative Performances of Various TLD Proton Recoil Irradiator Systems studied in fast Neutron Detection

System	Neutron energy studied	Response ratio with & without proton irradiator
CaF$_2$ + Polyethylene (sandwitch)	14 MeV	10
CaSO$_4$ (Dy) + Polyethylene (sandwich)	14 MeV	13
CaF$_2$ + Polyethylene (powder mix)	Am - Be n	16
CaF$_2$ + Sugar (powder mix)	Am - Be n	33
CaSO$_4$ (Dy) & alcohol (suspension)	Pu - Be n	1.3
LiF & alcohol (suspension)	14 MeV	4.0

X.6.3.b – Activation Induced TL Method

Here advantage is taken of the activation induced radioactive product (preferably short-lived) whose induced TL during decay is separately measured by erasing the "prompt TL signal" immediately after the end of the neutron irradiation; this way the interfering gamma exposure if any during the neutron irradiation is completely eliminated(160). The method is efficient only if the activation product is beta active and a method has been suggested recently to mix rareearth oxides (having very high thermal and in some cases intermediate energy neutron cross sections and leading to beta decay with a convenient half life) with the usual TL phosphors and relate the activation induced TL with the fluence of neutron irradiation(150). The same principle is applicable for detecting fast neutrons in the range of 2.7 MeV by making use of ^{32}S (n, p) ^{32}P reaction in $CaSO_4$ phosphors(128)

X.6.4 – UV Dosimetry Using TLDs

TLDs offer the easiest yet sensitive means of measuring UV exposure on a routine basis which was until recently considered a sophisticated measurement to make. As discussed earlier (§ sec.VI.5), UV measurements can be made by either of the two methods: (i) intrinsic reponse of the TL phosphor or (ii) UV induced transfer TL from pre gamma-irradiated and partially erased phosphor. In fact with $CaSO_4$ (Dy) phosphor, both the methods have been found to complement each other in the exposure ranges covered: the former can be used in the exposure range of 4×10^4 erg mm^{-2} down to about 400 erg mm^{-2} and the latter for exposures less than 400 erg mm^{-2} for 253.6 nm UV photons which are used for bactericidal action in medical industries(38,148).

X.6.5 – The TL method of radiation monitoring is one of the most economical, easy to achieve and readily adaptable, radiation measuring technique for any laboratory and stands out at the moment as the most widely used dosimetric system.

X.7 – Miscellaneous Applications of TL

TL methods have been attempted on lunar materials to understand the thermal histories and recent surface activities(51); the annual average lunar surface temperature could also be estimated from the TL measurements(86,143). The variation in the TL output of various regions of the meteorite sample could be extrapolated to get an idea of "pre-entry" shape of meteorites(183).

In radiation physics, TL detectors offer excellent possibilities to obtain data partaining to reactor shielding studies(214). There have been suggestions to use TLD for measurements of microwave and laser outputs(20,58).

There has been interesting applications of TLD in diagnostic or therapeutic medical procedures by making in vivo dose measurements(33). The TL measured from the roof tiles nearly twenty years after the atomic bombing of Hiroshima and Nagasaki cities, have given valuable information on radiation dose distributions around "ground zero"(89).

The method of TL photography (auto-luminography, in fact) is gaining importance at least among mineralogists to record directly the distribution pattern of TL sensitive mineral inclusion in a TL insensitive mattrix like clay. Some of the interesting photographs can be seen in reference(129). The technique(48) has been advocated as a tool for the environmental analysis of sedimentary core samples in identifying silt and clay layers, $CaCO_3$ and FeO nodules and some diagenetic and sedimentary features(171). In a more or less similar approach, image screens containing TL phosphors have been used, for the storage of X-ray or thermal neutron radiographs(99).

Radioluminescence which is nothing but TL emission at room temperature is becoming increasingly useful in the spectrochemical analysis of elements like lanthanides, Mn, Ag, etc in certain mattrices at even ppb levels(111). If the TL glow pattern is known, the temperature or radioluminescence measurements can be judiciously chosen to improve detection limits even further.

XI – SCOPE OF TL STUDIES IN FUTURE

It may perhaps be said now that a kind of stale feeling has set in the minds of TL workers who are more or less convinced that as for as basic research is concerned every thing possible has been beaten out and the TL phenomenon remains as complicated as ever. If the TL process is considered to consist of the three phases of energy absorption, storage and stimulated emission, it is the trapping parameters (which dictates the storage phase) that has remained impregnable to analysis. If the number of these parameters are kept limited and a model is assumed, then kinetic equation and vigorous solutions are possible(105); but actually the unknowns involved can be imagined to be very many and even if one can assume certain values and solve the problem mathematically, it will serve little purpose as long as no experimental measurements of these quantities are possible. Isolated experiments and explanations of the results in terms of individual mathematical models are all equally probable and their sum total are not really informative from the point of view of a generalised understanding. A realistic model will depend upon abstract parameters such as band and defect structures and quantities such as mobility and luminous efficiency as a function of temperature which are never known with any reasonable accuracy. In this respect, phosphors with one kind of trapping centres – eg. F centres in alkali halides offer better understanding of the TL process in them. But the cases of the more sensitive and hence useful TL phosphors – eg. LiF, CaF$_2$, CaSO$_4$ etc – having innumerable kinds of traps are difficult to solve in that no analysis can take all of them into account simultaneously and offer a satisfactory model for the TL process. In this connection it may be said that attempts to fit numerically the experimental TL glow curves "in toto" will be a welcome progress in the right direction.

Hence, the trend of future research in the field of TL should be to get more and more insight into the trapping parameters with an ultimate desire to be able to predict the TL characteristics of a phosphor from a knowledge of some of its critical physico-chemical properties. That the situation is not so hopeless is borne out of some scattered results which are not well publicised: one is the linear relationship obtained between the alpha induced TL sensitivities of various phosphors and their saturation limits which is essentially the number of available trapping sites in the respective phosphors (Figure 25, ref.(217)); the second is the linear relationship obtained between the TL ages of various dolomitic-limestone samples and their natural TL outputs expressed in percentage of their saturation limits (Figure 59, ref.(149)). In the former case different phosphors with widely varying TL characteristics are involved and in the latter, same compound but with different geological histories are involved; in both the cases the trapping parameters should have widely varying basic considerations but it is interesting to see some "orderliness" as hinted by the simple linear relationships obtained in the graphs.

In case of TL phosphors where the trapping centres are considered to belong to the host lattice and which are paramagnetic CaSO$_4$ (RE) for example(144), – careful quantitative estimates should be possible and the influence on addition of the activator reasonably evaluated. Study of TL as well as ESR behaviour of more and more pure samples will also help to understand the trapping parameters in these cases.

Position induced annihilation of electron trapping centres could offer a new possibility to understand more about the trapping parameters. This has never been attempted and in some preliminary experiments conducted by the author interesting observations have been made on TLD 700 extruded chips. The source used was ^{22}Na which emit both positrons and 1.3 MeV gamma photons. TL outputs were measured for virgin as well as pre-and post-gamma irradiation of the sample with ^{60}Co source. The results (Figure 60) hint that positron annihilation leads to an increase in the TL output of a pre-gamma irradiated sample while it decreases the gamma efficiency for TL generation if it precedes the gamma irradiation. The former may be imagined to be the result of a greater cross section presented by the previously trapped electrons for positron annihilation and subsequent refilling of traps by the 0.51 MeV annihilation photons irradiating the crystal; the latter may be thought in terms of a pseudo positive charge space created in the positron irradiated crystal which causes increased decay of the trapped electrons generated by the subsequent gamma irradiation. The study is still in an infant state and there are serious reproducibility problems. But the potential still remains unquestioned and studies can be formulated to see the behaviour of each kind of trap to the positron annihilation and detailed annihilation life time measurements could be performed to get more knowledge about the trapping states.

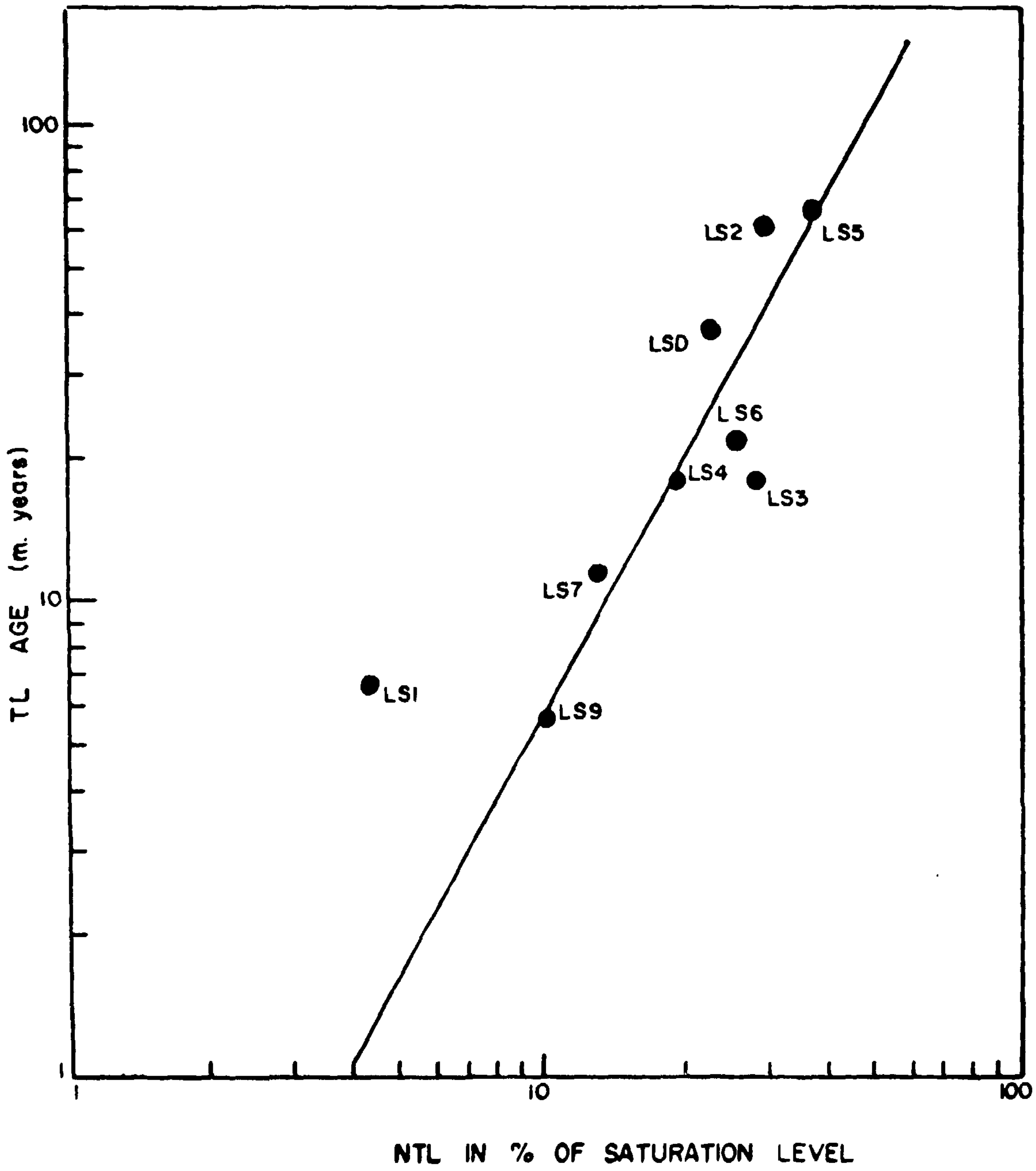


Figure 59 – Relation between TL age and the NTL (expressed in % of dose required to reach saturation) in various dolomitic limestone samples (Nambi, K. S. V., 1977 – ref. /149/).

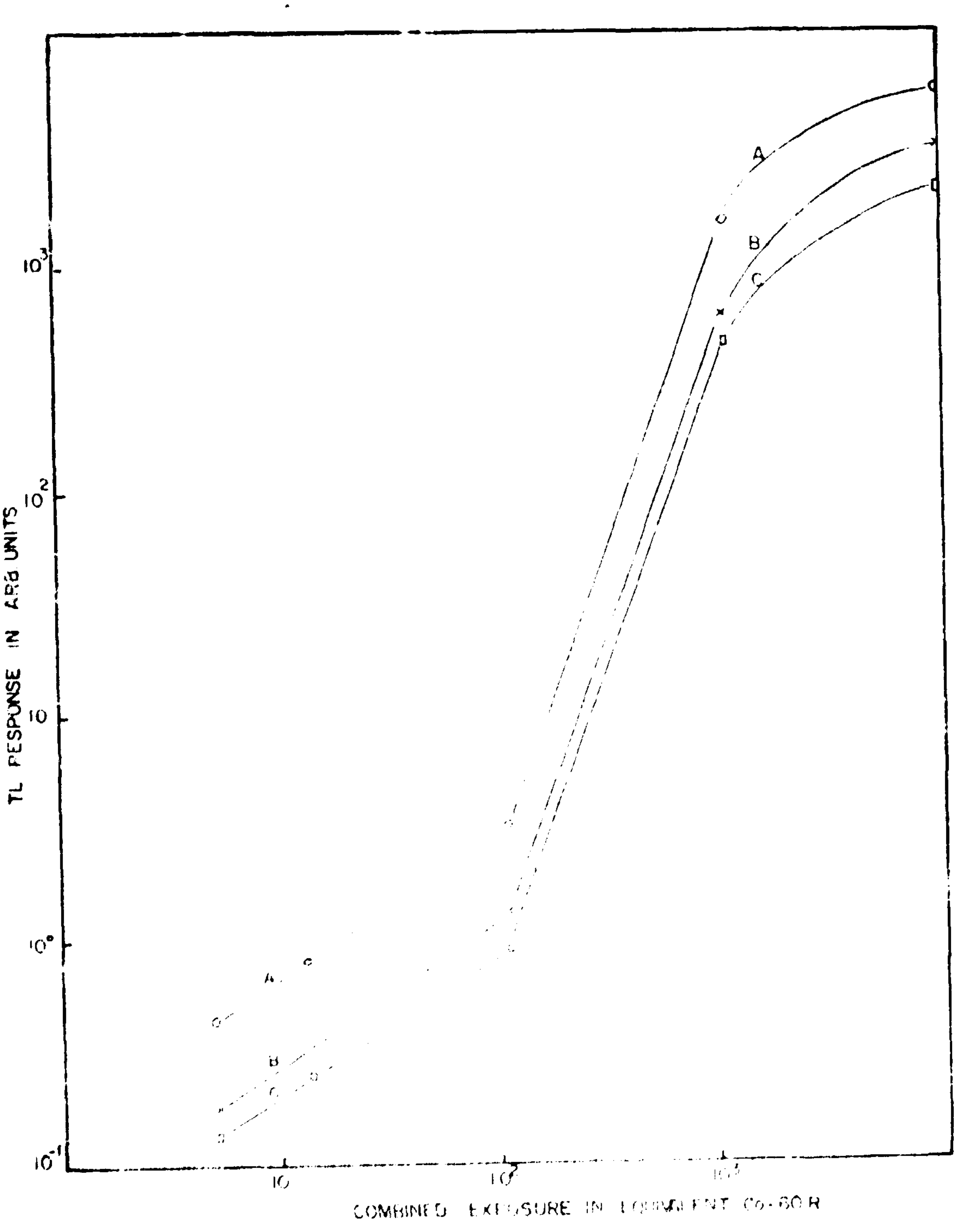


Figure 60 – TL response of LiF TLD-700 chip dosimeters for combined gamma and positron irradiations. A) a fixed positron exposure (4 R gamma equiv.) succeding various gamma exposures B) sum of individual gamma responses with that due to the fixed positron exposure C) the positron exposure preceding the various gamma exposures. (Nambi, K. S. V., 1977 – ref./146/).

In the area of TL phosphor development, efforts are being continously made in the area of neutron dosimetry and currently there have been suggestions such as use of F centre formation in MgO(170), use of hydrogen-diffused TL phosphors(136), use of nonlinear dependance of light on volume density of excitation of certain materials like CaS(109) and use of certain hydrogen-rich compounds mixed with TL phosphors(60). All these need further careful examination to establish their provenness in dosimetric field applications. In gamma dosimetry efforts are being made to obtain a low Z TL material which could be easily made and having as high a sensitivity as $CaSO_4$ (RE) phosphors and promising results have recently been reported in the case of $Li_2B_4O_7$ phosphors(173,202).

The study of human bone for its TL characteristics (obviously only low temperature measurements may be fruitful) is warranted as this holds out a good promise in Forensic Science applications. If sufficient knowledge is developed, it may even prove to be a good dosimeter in criticality accidents.

Thus, not withstanding the progress which may or may not be made in the understanding of TL, the well established applications of it will continue to gain popularity in times to come and there is already sufficient ground for the industries to start using this as a quick and inexpensive analytical tool in the quality control of certain selected products.

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