CHAPTER 2

THERMOLUMINESCENCE

Thermoluminescence (TL) is the phenomenon of emission of light from an insulator or semiconductor when it is heated [1]. This is not same as the light spontaneously emitted from a substance when it is heated to incandescence. Thermoluminescence is the thermally stimulated emission of light following the absorption of energy from radiation. There are three factors necessary for the production of thermoluminescence. Firstly, the material must be an insulator or a semiconductor as metals do not exhibit luminescent properties. Secondly, the material must have previously absorbed energy during exposure to radiation. Thirdly, the luminescence emission is triggered by heating the material. In addition to this, there is an important property of thermoluminescence that cannot be inferred from the above statement. It is the peculiar characteristic of thermoluminescence that, once heated to excite the light emission, the material cannot be made to emit thermoluminescence again by simply cooling and reheating the specimen. In order to re-exhibit the luminescence the material has to be re-exposed to radiation, whereupon raising the temperature will once again produce light emission.

When radiation is incident on a material, some of its energy may be absorbed and reemitted as light of a longer wavelength. This phenomenon known as Stoke's Law is the process involved in luminescence. The wavelength of the emitted light is a characteristic of the luminescent substance and not the incident radiation. Luminescence emission occurs by the transfer of energy from radiation to the electrons of the substance, thus exciting the electrons from a ground state 'g' to an excited state 'e'. When the excited electron returns to the ground state the absorbed energy is released as luminescence emission. When the delay between the transitions is less than 10^{-8}s, the emission is called fluorescence and it is independent of temperature. When an electron excited from ground gets trapped in a level 'm' below the excitation level and remains there till additional energy is given to go to level 'e' and then return to ground 'g' releasing light, the emission is known as phosphorescence. It is characterized by the delay between radiation absorption and the time to reach full luminescence intensity. Phosphorescence itself can be subdivided into two types called short period ($t < 10^{-4}$ s) and long period ($t > 10^{-4}$ s) based on the time delay [2,3]. The time delay observed in phosphorescence corresponds to the time the electron spends in the trap. Thermodynamically it can be shown that the mean time electrons spent in the trap at temperature T is given by

$$t = So^{-1} \exp (E/K_bT) \quad \text{..............................(2.1)}$$

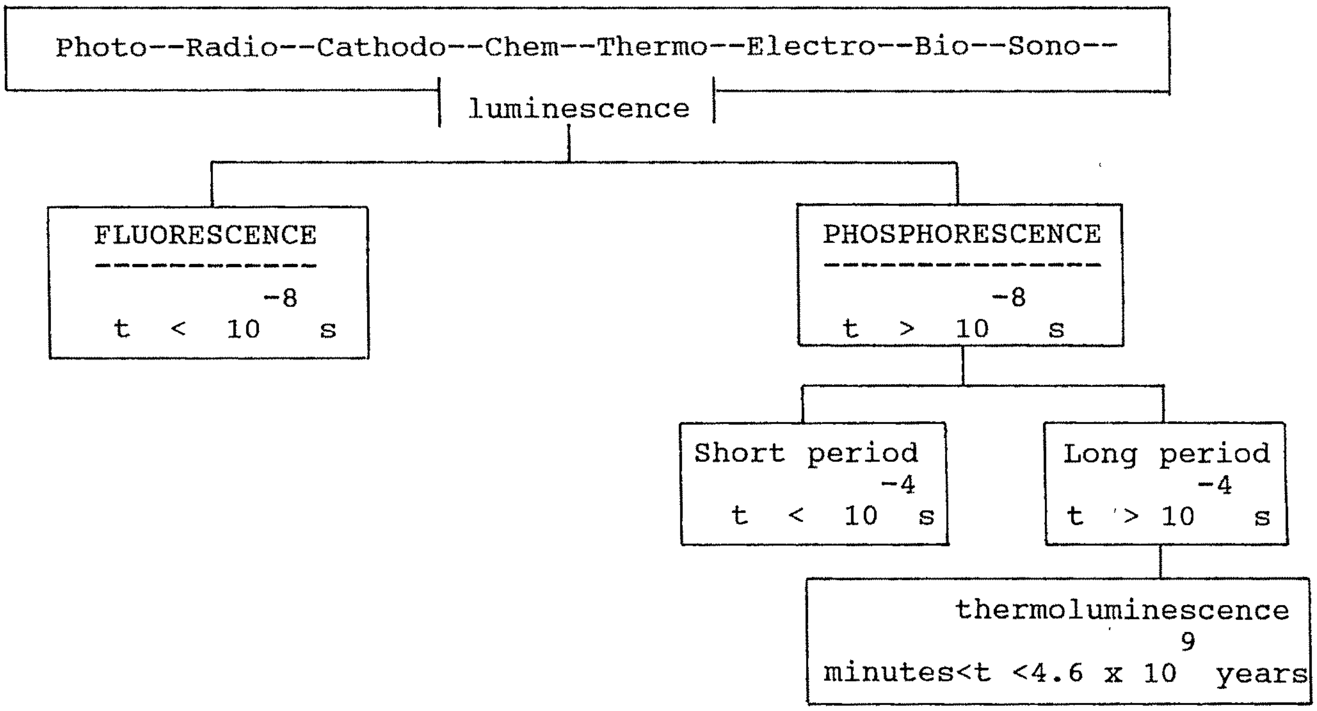
where So is a constant

E1 the energy difference between stages or trap depth

K_b Boltzman's constant

This clearly shows that phosphorescence is exponentially dependent upon time. In phosphorescence the combined value of E and T are such that t is very small and luminescence is observed easily at the temperature To, at which irradiation takes place. In case the trap is deep enough, then the values of E and To are such that $E >> K_bTo$ and thus 't' is very large. In reality, this means that the electron will remain trapped in level 'm' indefinitely or till the temperature To is below 298 K. However, luminescence emission can be induced by raising temperature. As 'T' rises, 't' decreases and consequently the intensity increases as the electrons become free from the trap and recombination takes place. As the luminescence has been stimulated by heating, it is called thermoluminescence.

The family tree of luminescence phenomena is as follows.



The luminescence peaks in fluoresence, phosphoresence and thermoluminescence are graphically shown against time in Fig. 2.1. For a suitably deep trap the thermoluminescence can be

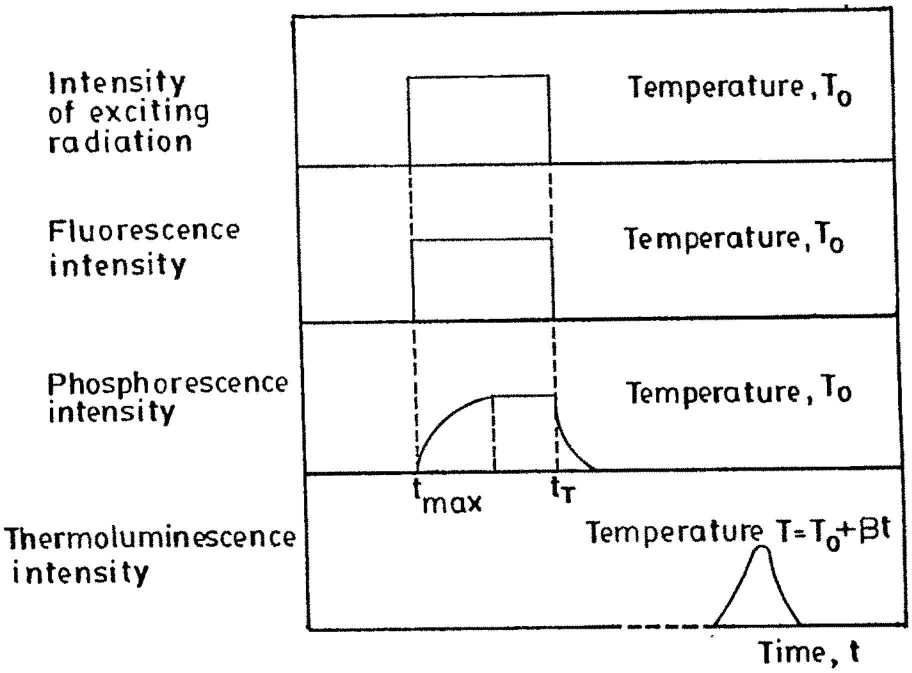


Fig. 2.1 Relationships between radiation absorption and the emissions of fluorescence, phosphorescence and thermoluminescence. T_0 is the temperature at which irradiation takes place: β is the heating rate: t_T is the time at which the irradiation ends and the decay of phosphorescence begins.

triggered an indefinite time after the irradiation ceases. This time may range from minutes to years. A practical limit on the time between irradiation and thermoluminescence readout is set only by the age of the solar system at 4.6×10^9 years.

The various luminescence phenomena are given names which reflect the type of radiation used to excite the emission. Thus there is photoluminescence (excitation by optical or ultraviolet light), radiophotoluminescence (nuclear radiations, i.e. γ -rays, β - particles, etc.) and Cathodoluminescence (electron beam). In addition to excitation by radiation, luminescence can also be generated by chemical energy, mechanical energy, biochemical energy and even sound waves.

The thermoluminesence curves or glow curves are graphs of luminescence intensity versus temperature, obtained by heating the sample at a constant rate after irradiation at room temperature. When the sample is excited at low temperatures, the excitation energy is stored in various traps within the sample. These traps may be due to metastable levels within the impurity or due to other crystalline imperfections in the host lattice. The energy required for an electron to escape from the trap is known as the thermal activation energy or the trap depth.

The traps empty as the sample is heated above the temperature of excitation. If there is only one trap, the TL will be weak at the initial temperature (T = Ti) but then increases with temperature, reaches maximum at glow temperature (Tg) and then drops down to zero as the traps are emptied. If the trap distribution consists of separate groups of trap depths then these groups are observed as thermoluminesence maximas. By knowing the glow peak temperature Tg, it is possible to find out the activation energy or the trap depth.

A typical glow curve for LiF, one of the most studied thermoluminescent phosphors is shown in Fig. 2.2 In the figure, four peaks are shown indicating that four different species of trap are being activated within this particular temperature range, each with its own value of E and So. The area under each peak is related to the number of filled traps, which, in turn is related to the amount of radiation initially imported to the specimen.

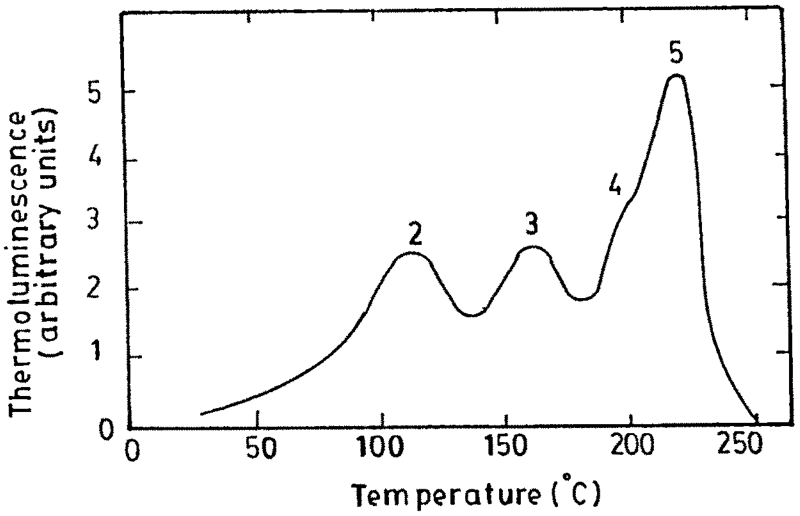


Fig. 2·2 A thermoluminescence 'glow-curve' from LiF doped with Mg and Ti following irradiation.

2.1 EARLY OBSERVATIONS

The first scientifically recorded observation of thermoluminescence was made in 1663 by Robert Boyel who noted a glimmering light from a diamond. Boyel also stimulated the luminescence emission by more conventional means by using the heat from a hot iron, from friction and from a candle. In 1676 Elsholtz observed a similar effect from a mineral fluorspar[4]. It is difficult to pinpoint exactly when the word thermoluminescence was first used in the published literature, but it was used in 1895 by Widemann and Schmidt[5] in what Becker[6] described as probably the first careful experimental investigation of radiation induced TL under presently used name. However the first theoretical models for TL phenomenon appeared only in the 1940s which was three hundred years after the first recorded observation. Randall and Wilkins[7,8] suggested the "first order kinetics" model, while Garlick and Gibson[9] developed another model, more suitable for some TL curves, known as the "second order kinetics", model. Besides thermoluminescence the other thermally stimulated processes are 1) Thermally Stimulated Conductivity (TSC) 2) Thermally Stimulated Electron Emission (TSEE) 3) Thermally Stimulated Depolarization (TSD) 4) Thermogravimetry (TG) 5) Differential Thermal Analysis (DTA). Other methods though less extensively used are Evolved Gas Analysis (EGA). Thermal Disorption, Thermal Annealing, Partial Thermoremagnet Magnetisation (TRM) and Dilatometry[10]. In all these processes the sample is heated in a controlled manner and a certain physical property is continuously monitored.

2.2 APPLICATIONS OF THERMOLUMINESCENCE

2.2.1 Radiation Dosimetry :

The increased use of TL which became evident in the late 1940s and early 1950s was partly due to the work of Randall and Wilkins and of Garlick and Gibson. The prime motivators for the emergence of TL as a practical research tool in several different fields of application were Farrington Daniels and his research group at the University of Wisconsin, USA, during the 1950s. The absorption of radiation increases the level of TL observed from a specimen by filling the localised energy levels with trapped electrons. The absorption of heat from the environment, on the other hand, tends to reduce the number of trapped electrons by thermally releasing them. Thus, the intensity of TL from a specimen is the result of competition between trap filling by radiation and trap emptying by thermal excitation. At given temperature of irradiation, many materials display an intensity of TL which is proportional to the amount of radiation absorbed, and this led Daniels and his colleagues[11] to propose that TL may be used as a means of radiation dosimetry. The first proper application of TL to dosimetry was in 1953 when LiF was used to measure the radiation following an atomic weapon test. LiF did not re-emerge as a first class dosimeter until the work of Cameron and his colleagues in 1960s[12]. It was also realised that the unpredictable behaviour of LiF could be offset by various pre and post-irradiation annealing procedures[13]. The commercial dosimeter TLD-100 consists of LiF doped with approximately 170 mole ppm Mg and 10 mole ppm Ti. This material remains the most popular TL dosimeter in use today.

2.2.2 Age Determination :

The discovery of natural thermoluminescence (NTL) was made from samples of ancient pottery[14,15]. This observation led to its immediate development as a means of archaeological dating. The basic premise is that the ingredients of the pottery lose their accumulated geological doses when the pot is fired during its manufacture. Because of high temperature experienced during the firing the thermoluminescence level is re-set to zero. The newly made pot is subjected to natural radiation from the radioactive elements naturally present in the clay and surroundings. Thus the pottery now accumulates an absorbed dose which is proportional to its archaeological age i.e. the time since firing. The basic age relation is as follows.

AGE = ABSORBED DOSE / DOSE RATE

ABSORBED DOSE = ARCHAEOLOGICALLY ACQUIRED THERMOLUMINESCENCE

DOSE RATE = THERMOLUMINESCENE PER UNIT DOSE OF RADIATION / ANNUAL DOSE FROM RADIOACTIVE IMPURITIES

The method of TL dating progressed through the 1960's and 1970's via the development of improved methods of extracting the thermoluminescent grains from pottery in order to facilitate the calculation of the natural dose rate. Thus, the quartz-inclusion[16], fine-grain[17], and pre-dose technique[18] methods were introduced. Recently, Sunta and David[19] proposed firing temperature technique. The result is that TL dating is now considered by archaeologists as a dependable method of age determination.

2.2.3 TL Applications to Geology :

The occurrence of Natural Thermoluminescence (NTL) from rocks has long been known from the study of TL in fluorites by Trowbridge & Burbank[20]. Calcite too was known to be a good phosphor. Daniels et al[11] stated that of over 3000 natural minerals studied (granates, limestones etc.), approximately 75% were found to exhibit NTL of such an intensity that it was easily measured. Some of the recorded NTL was bright enough to be sufficient for reading a newspaper. Daniels and his colleagues were instrumental in providing the relationship between the natural radioactivity and NTL although this connection had already been suggested[20]. It was this relationship which led directly to the use of TL as a means of arriving at the geological age of the specimen. However age determination is not the only way that TL is utilized in geology. In some instances TL is more sensitive for detecting the traces of radioactivity than Geiger counter or a Scintillation counter. This technique has found widespread application in radioactive mineral prospecting. One aspect of geology in which TL is proving to be particularly useful is the study of meteorites and lunar material. Herscrel's[22] observation of TL from the Middlebrough meteorite remained unexploited until the potential usefulness of the technique in meteorite research was recognized by Houtermans and his colleagues in the late 1950s[23]. More recently, the balance between radiation filling of traps and their thermal emptying in meteorites has been used to provide information relevant to the nearness of the sun whilst in space (i.e. in the orbit) and to the time the meteorites have spent on earth. A number of useful reviews were given by McKeever &

Sears[24]. Early speculation on the TL from lunar materials [25,26] was concerned primarily with a possible explanation for Transient Lunar Phenomena (anomalous brightness from specific regions of the moon's surface), the possibility of using TL to establish the heat flow characteristics beneath the lunar surface, and to measure the solar flare particle spectra averaged over last 10 years. More recently TL on natural zeolites have been reported[27,28,29].

2.2.3 Defects in Solids :

In a solid where each atom is subject to periodic array of potential wells, the allowed energies of electrons be only in 'allowed zones' and the other possible energy values constitute 'forbidden zones' or 'band gaps'.

The occupancy of each zone or band is described by the density of states function,

$$N(E) = Z(E)\, f(E) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

Where, f(E) is the Fermi-Dirac distribution function given by

$$f(E) = 1 / (\exp[(E-E_f)/KT] + 1) \qquad \ldots\ldots\ldots\ldots\ldots (2.3)$$

where, $N(E)$ - density of occupied energy levels

$Z(E)$ - density of available energy levels

E_f - Fermi level

At absolute zero temperature those energy levels below Ef are completely full while those above Ef are completely empty as shown in Fig. 2.3. For semi conductors and insulators Ef is above the uppermost valence energy with the result that the valence band is entirely full and the materials are non-conductors. Electronic conduction will only occur when the valance electrons are given enough energy to surmount the energy gap Eg in order to reach the next highest empty band usually called the conduction band. The situation is shown in Fig. 2.4.

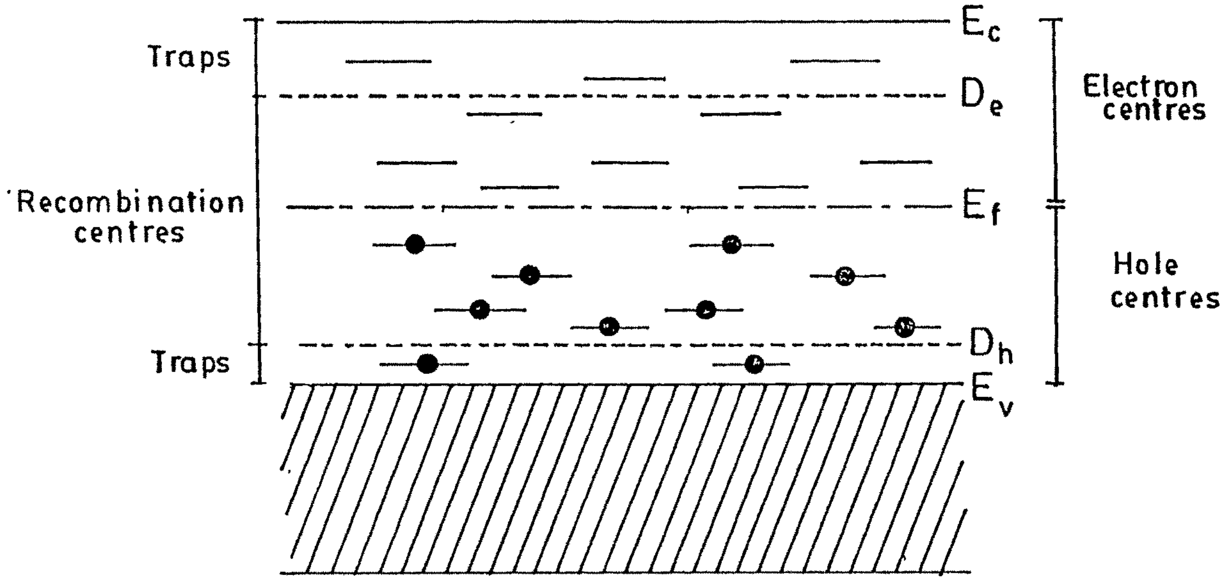


Fig. 2.3 Energy level at absolute zero temperature

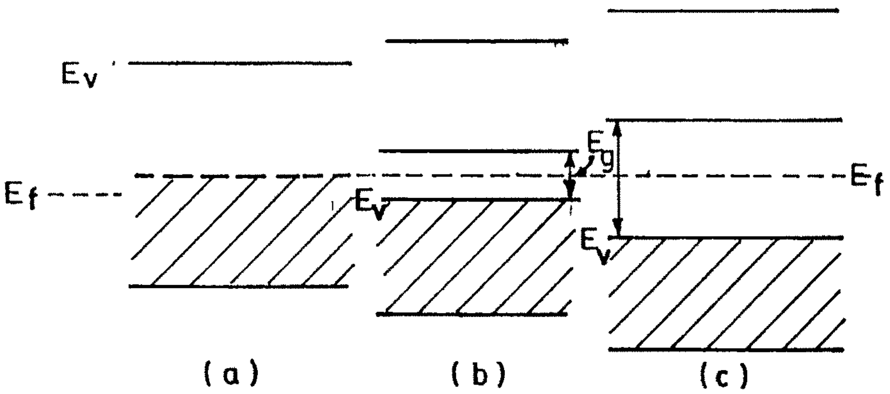


Fig. 2.4 (a) The partially filled valence band for a metal at absolute zero. The shaded area represents the fully occupied states. This is compared with the completely filled valence bands for (b) a semiconductor and (c) an insulator. Here the filled bands are separated from the next highest empty band by a socalled "forbidden' gap E_g. E_f is the position of the Fermi level and E_v is the top of the valence band.

For an ideal crystalline semi conductor or insulator, $Z(E) = o$ when $Ec > E > Ev$. Here Ec is the bottom of the conduction band and Ev is the top of the valance band. Wherever structural defects occur in a crystal, or if there are impurities within the lattice, there is a break down in the periodicity of the crystalline structure and it becomes possible for electrons to have energies forbidden in the perfect crystal.

Experiments on TL can be expected to yield useful information on the properties of various types of defects present within an insulator or a semiconductor.

Thermoluminescence is particularly sensitive to traces of impurities in specimen. Though the exact role of impurities is unknown, in most cases their presence is considered essential for TL to occur. It is believed that the impurities give rise to the localised energy levels within the forbidden energy gap and that these are crucial to the TL process. As a means of detecting the presence of defect levels, the sensitivity of TL is unrivalled. TL provides, in principle at least, a unique tool in the determination of the distribution of the defect energies. However, sensitivity of this method makes interpretation of the results difficult and prevents its use in say chemical analysis where even the purest of materials are 'impure' from the point of view of thermoluminescence.

In addition to defect levels caused by extrinsic defects there are also those due to intrinsic defects, such as lattice vacancy and interstitials. Defects produced by the radiation itself may also be important. Recent studies have shown that in some samples the production of one TL photon may involve several defect levels in a kind of cooperative effort[30]. Investigations which attempt to describe the defect state of a material by using TL alone are limited.

2.2.4 Other Applications :

In biology TL technique is finding increasing usage. Tatake[31] summarize the pre-1975 literature where as more recently[32] TL from DNA-base analogues has been observed.

These materials act as tumour inhibitors by a mechanism of radical conversion and it is hoped that TL will help to understand the charge transfer process involved. The technique also has been used to identify the dust particles responsible for lung diseases in miners[33] and the volcanic soil responsible for non filarial elephantiasis[34]. A full list of applications of TL would also include the use of suitable phosphors for image storing devices, a test for fire damage in building materials, a quality control tool for ceramics and an aid in forensic science. Becker[35] even notes that there have been attempts to identify the cause of ball lightning by examining the TL from bricks, where the phenomenon occurred.

REFERENCES

1. McKeever, S.W.S. (1985), Thermoluminescence of Solids Cambridge University, Cambridge.
2. Garlick, G.F.J. (1949) Luminescence materials, Oxford Uni. Press, London.
3. Curi, D. (1960) Luminescence in Crystals, Methen, London.
4. Seely, M.A. (1975) J. Archaeological Sci. 2, 17.
5. Wiedemann, E. & Schmidt. G.C. (1895) Amm. Phys. Chem. New Folge, 54, 604.
6. Becker, K. (1974) Health Physics, 27, 32.
7. Randall, J.T. & Wilkins, M.H.F. (1945a) Proc. of Royal Soc. London, 184, 366.
8. Randoll, J.T. & Wilkins, M.H.F. (1945b) Proc. of Royal Soc. London, 184, 390.

9. Garlick, H.J. & Gibson, A.F. (1948) Proc. Phy. Soc. 60, 574.

10. Chen, R. & Krish, Y (1981) Analysis od Thremally Stimulated Process; Regaman Press, Oxford.

11. Daniels, F., Boyed, C.A. & Saunders, D.F., (1953) Science, 117, 343.

12. Cameron, J.R., Suntharalingam, N. & Kenney, G.N., (1968) TL Dosimetry, Univ. Wisconsin Press, Madison.

13. Zimmermen, D.W. Rhyner, C.R. & Cameron., (1966) Health Physics, 12, 526.

14. Kennedy, G.C. & Knopff, L. (1960) Archaeology, 13, 147.

15. Grogler, S.J. Hwtermans, F.G. & Staffer, H. Health Physics, Acta., 33, 595.

16. Fleming, S.J., (1966) Archaeometry, 9, 170.

17. Zimmermen, D.W., (1967) Archaemotry, 10, 26.

18. Zimmermen, J., (1971a) J. Phys. C., Sol. St. Phys., 4, 326.

19, David, M. & Sunta, C.M. (1981a) Ind. J. Pure & Appl. Physics 19, 1041.

20. Trowbridge, J. & Burbank, J.E., (1898), Am. J. Sci. Ser. 4, 5, 55.

21. Ellsworth, H.V., (1932) Can. Dept. Mines, Geol. Surv. Geol. Ser., 11, 55.

22. Herscrel, A.S., (1889) Nature, 60, 29.

23. Houtermans, F.G. & Liner, A., (1966) J. Geophys. Res., 71, 3387.

24. McKeever, S.W.S. & Sears, D.., (1979) Meteorities. 14, 29.

25. Sun, K.H. & Gonyales, J.L., (1966) Nature 212, 23.

26. Sidran, M., (1968) J. Geophys. Res., 73, 5196.

27. Murthy, K.V.R. & Joshi, T.R. (1989) J.M.S. University, 45-56.

28. Manmohan, R. et al, (1992) Thermoluminescence and its applications, Tata McGrow Hill, 133-36.

29. Gandhi, Y. et al (1992), Thermoluminescence and its applications, Tata McGrow Hill, 145-49.

30. Mayhugh, M.R. (1970) J. Appl. Phys. 41, 4776.

31. Tatake, V.G. (1975) Proc. Natel. Symp. on TL (Madras), 202.

32. Cooke, D.W., Rhodes, J.F., Samti, R.S. & Aexander, C. (1980) J. Chem. Phys., 73, 3573.

33. Kriegsers, W. & Scharmann, A. (1980) Nucl. Instrum. Meth., 175, 239.

34. Towesend, P.D., Blanke, J.H., Price, E.W. & Rendell, H.M. (1983a), Radiat. Eff., 72, 103.

35. Becker, K., (1973) Solid State Dosimetry, CRC Press, Cleveland.