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Thermoluminescent Phosphors for Radiation Dosimetry

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Abstract. The use of thermoluminescence (TL) as a method for radiation dosimetry of ionizing radiation has been established for many decades and has found many useful applications in various fields, such as personnel and environmental monitoring, retrospective dosimetry, medical dosimetry, space dosimetry, high-dose dosimetry. Method of preparation, studies and applications of thermoluminescence (TL) dosimetric materials are reviewed. Several high sensitivity thermoluminescent dosimeters (TLDs) are now commercially available in different physical forms. These commercial TL dosimeters comply with a set of stringent requirements stipulated by the International Electrotechnical Commission (IEC). Specific features of TL phosphors for thermal neutron, fast neutron and high-energy charged particle (HCP) dosimetry are also considered. Some of the recent developments in the field of optically stimulated luminescence (OSL) and radiophotoluminescence (RPL) are also summarized. Comparative advantages of TL, OSL and RPL dosimeters are given. Results of recent studies of TL in nanosized materials are briefly presented. Future challenges in this field are also discussed.

Contents of Paper

1. Introduction
2. Basic Thermoluminescence Process
3. Thermoluminescence Dosimetry
4. Preparation of TLD materials and their Characterization
    - 4.1 Lithium Fluoride
        - 4.1.1 LiF:Mg,Ti
        - 4.1.2 LiF: Mg,Cu,P
    - 4.2 Lithium Tetraborate
    - 4.3 Magnesium Borate
    - 4.4 Other Lithium-, Sodium- and Potassium-based Compounds
    - 4.5 Magnesium Orthosilicate-based TL Phosphors
    - 4.6 $CaSO_4$:Dy/Tm TL Phosphors
    - 4.7 Calcium Fluoride (CaF_2)
    - 4.8 Al_2O_3 - based TL Phosphors
    - 4.9 BeO-based TL Phosphor
    - 4.10 $BaSO_4$:Eu TL Phosphor
    - 4.11 TL of Nanophosphors
    - 4.12 Phosphors based on Other Luminescence Techniques

5. Important Areas of Radiation Dosimetry
  5.1 Personnel Monitoring
  5.2 Environmental Dosimetry
  5.3 Neutron Dosimetry
  5.4 Dosimetry in Medical Applications of Radiation
  5.5 Retrospective Dosimetry
  5.6 High Dose Dosimetry
  5.7 Space Dosimetry
6. Summary
References

1. Introduction

The phenomenon of thermoluminescence (TL) has been known for a long time. In 1663 Robert Boyle reported to the Royal Society on the observation of the glow from a diamond when warmed in dark. In 1904, Marie Curie reported the ability of the mineral fluorite to exhibit TL after being exposed to a radium source. Further experimental and theoretical work was carried out by Urbach [1] in 1930, Randall and Wilkins [2] and Garlick and Gibson [3] developed TL models in 1945 and 1948, respectively, which allowed quantitative calculations of thermoluminescence kinetic parameters. Initially, the dosimetry measurements were dominated by ionization chamber measurements and photographic film until resurgence of techniques based on luminescence and other solid state techniques [4]. It is now about 60 years since Farrington Daniels and his research group at the University of Wisconsin (USA) first suggested the use of thermoluminescence (TL) as a technique in radiation dosimetry [5] through studies of LiF as a TL material and it became evident that the desirable properties of the material were the result of the interplay between the complex defects present within the material resulting from the presence of Mg and Ti. This realisation emerged from the work of Cameron and colleagues [6, 7] and this work led eventually to the patenting of TLD-100 by the Harshaw Chemical Company in 1963. Daniels and co-workers also investigated TL properties of Al_2O_3 for its possible use in radiation dosimetry [8]. A TL peak at 236 ^{o}C depends on sodium impurity and the TL area increases in an approximately linear manner with concentration of sodium ion present as an impurity. All these developments in the field of thermoluminescence dosimetry, in the initial years, till mid 1970s, were also influenced by the pioneering work of Leverenz [9], Curie [10], Aitken [11, 12] and others, and International Conferences on Thermoluminescence and Luminescence Dosimetry held in 1965 [13], 1968 [14, 15], 1971 [16], and 1974 [17].

2. Basic Thermoluminescence Process

When ionizing radiation is incident on an insulating crystal some of the deposited energy is stored in the lattice at defect sites, colour centres, etc. Upon heating the crystal, this stored energy is released and a fraction of it may be emitted as visible light (prior to onset of black-body radiation at higher temperatures, i.e. > 250 ^{o}C). This is called thermoluminescence. Within certain limitations, the amount of light emitted is proportional to the radiation dose previously absorbed by the TL material.

Figure 1 gives schematic representation of thermally stimulated luminescence phenomena in an insulating or semiconducting material assuming one trap-one recombination centre model. The absorption of energy from an ionizing radiation source by an insulating or semiconducting material causes the excitation of free electrons and holes and subsequent trapping of these electronic species at defects (trapping states) or metastable states within the material. The subsequent absorption of thermal energy by the metastable trapped charge, say, electron, results in the stimulated relaxation of the system back to its equilibrium condition. During the relaxation process recombination of the electronic charge with the trapped hole (recombination centre) occurs, and if the recombination is radiative, luminescence is emitted.

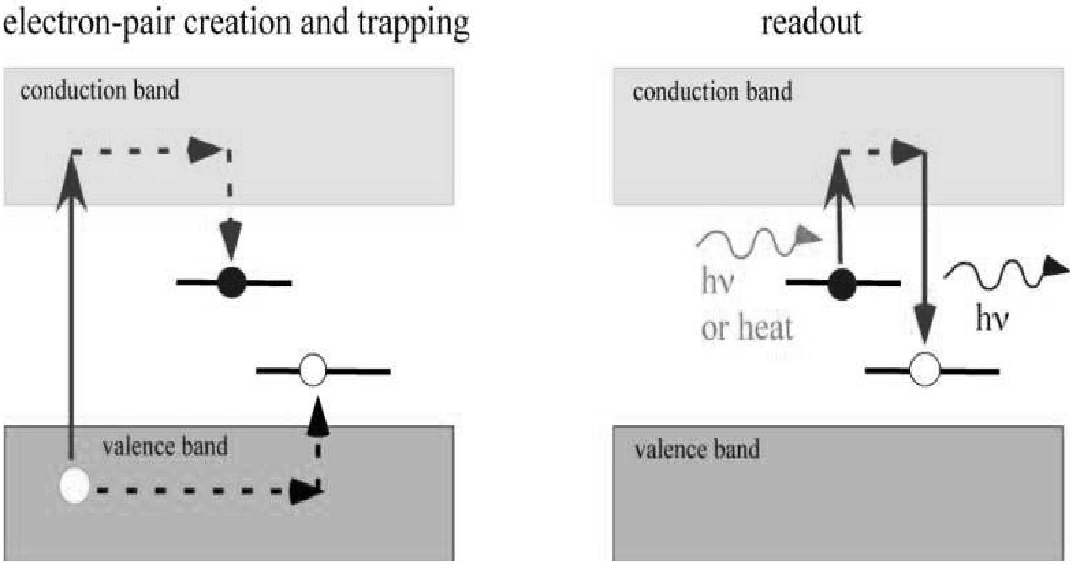

Fig. 1 A simple model of the thermoluminescence process: (a) Irradiation with ionization radiation leads to generation of electrons and holes, and trapping of free electrons and holes; (b) Release of electrons from the traps upon heating or optical stimulation of the phosphor material and recombination at the luminescence centre leading to emission of light.

3. Thermoluminescence Dosimetry

In thermoluminescence dosimetry the relationship between the signal and the absorbed dose to be measured must be determined by an appropriate calibration.

Thermoluminescent Dosimeters (TLDs) have found increasing application with the progress made in the development of solid thermoluminescent dosimeters and instrumentation for reading them. Many TLD based systems are now commercially available, and are widely used in routine personal dosimetry, environmental monitoring and clinical radiation dosimetry. The extreme sensitivity of TL for detecting the presence of defects, as few as 10^7 within a specimen, is beneficial for detecting low radiation levels which are encountered in personal and environmental monitoring.

Thermoluminescent Dosimeters (TLDs) are increasingly accepted for radiation dosimetry for the following reasons:

(a) The existence of nearly tissue equivalent thermoluminescent materials;
(b) Sufficiently high sensitivity and accuracy for both personal and environmental monitoring;
(c) Commercial availability as small sized solid detectors adaptable for both manual and automatic processing;
(d) Suitability for beta skin and extremity dosimetry;
(e) Availability of materials with excellent long term stability under varying environmental conditions;
(f) Ease of processing;
(g) Reusability;
(h) Linearity of response with dose and dose rate over a wide range.

Some general characteristics of the most common thermoluminescent materials used for radiation protection dosimetry are listed in Table 1.

The effective atomic number Z_{eff} (see Table 1) is an indication of the material's energy response. Table 2 shows the photon energy response at 30 keV relative to that at 1.25 MeV for the TL phosphors The effective atomic number of LiF (8.14) is close enough to the value for tissue (Z_{eff} = 7.42) to make it tissue equivalent. Out of the materials given in Table 2, only beryllium oxide and lithium borate have lower values of Z_{eff} than tissue. However, unlike LiF:Mg,Ti, LiF:Mg,Cu,P has relative TL response less than 1 in the photon energy range 30 to 200 keV.

Table 1 General characteristics of some commercially available thermoluminescent dosimeters [18-26]

TLD type	Effective atomic number Z_{eff}	Main peak (^oC)	Emission maximum (nm)	Relative sensitivity	Fading (at 25 °C, samples kept in dark)	Useful dose range
LiF:Mg,Ti	8.14	200	400	1	5%/year	20 µGy-10Gy
LiF:Mg,Cu,P	8.14	210	368	40	5%/year	0.2 µGy-10 Gy
LiF:Mg,Cu,Si	8.14	240	384	55	Negligible	1 µGy-20 Gy
$Li_2B_4O_7$:Mn	7.3	220	605	0.40	4%/month	0.1mGy-3Gy
$Li_2B_4O_7$:Cu	7.3	205	368	8	10%/2 months	10 µGy-10^3 Gy
MgB_4O_7:Dy/Tm	8.4	190	490	6-7	4%/month	5 µGy-50 Gy
BeO	7.1	190	330	~ 1.00	8%/2 months	0.1 mGy-0.5 Gy
Mg_2SiO_4:Tb	11	200	380-400	40-53	very slight	10 µGy-1 Gy
$CaSO_4$:Dy	15.3	220	480-570	30	1%/2 months	2 µGy-10 Gy
$CaSO_4$:Tm	15.3	220	452	30	1-2%/2 months	2 µGy-10 Gy
CaF_2:Mn	16.3	260	500	5	16%/2 weeks	10 µGy-10 Gy
CaF_2 (natural)	16.3	260	380	23	very slight	10 µGy-50 Gy
CaF_2:Dy	16.3	215	480-570	15	8%/2 months	10 µGy-10 Gy
Al_2O_3:C	10.2	190	420	60	5%/year	0.1 µGy-10 Gy

Table 2 Photon energy response at 30 keV relative to that at 1.25 MeV for phosphors with different Z_{eff}

TL Phosphor	Z_{eff}	Relative response	Reference
LiF: Mg, Ti	8.14	1.35	[27]
LiF: Mg, Cu, P	8.14	1.06 (Min. resp. of ~0.85 in the energy range 80-130 keV)	[22,27]
$Li_2B_4O_7$:Mn	7.3	1.05	[21]
$Li_2B_4O_7$:Cu	7.3	0.84	[20,21]
BeO	7.1	~ 1.00	[18,19]
MgB_4O_7:Dy/Tm/Mn	8.4	1.7	[23,28]
Mg_2SiO_4:Tb	11.0	4.5	[29,30]
$CaSO_4$:Dy/Tm	15.3	10-12	[18,27]
CaF_2:Dy/Tm/Mn	16.3	13-15	[18]
Al_2O_3:C	10.2	2.9	[26]
$BaSO_4$:Eu	45-47	40-50 (at ~ 50 keV)	[31,32]

4. Preparation of TLD materials and their Characterization

There is a vast literature on the methods of preparation and characterization of TL phosphors [18, 19, 33-43]. In this section, some of these methods are discussed in brief.

TLD materials are prepared by adopting one of the following methods: (i) co-precipitation technique, (ii) solid-state diffusion method, (iii) recrystallization from solution, (iv) growing single crystals from melt, (v) Solution Combustion Synthesis (SCS) method, and (vi) sol-gel method.

In the co-precipitation technique, required amounts of chemical compounds along with trace amount of activator are added to form desired compound. The precipitated compound (after appropriate washing, drying of the product) is sintered at higher temperature to facilitate diffusion of activator and formation of appropriate number of defects in the crystallite material.

In the solid-state diffusion method, the desired materials are intimately mixed and the mixture so formed is sintered at higher temperature for the formation of compound as well as uniform dispersal of the activators in the lattice. Sometimes flux is used to lower the melting point of the compound thereby facilitating better incorporation of the activator.

In the re-crystallization from solution, appropriate amount of chemical compound along with the desired amount of activator are dissolved in a solvent and the solution thus formed is slowly evaporated to dryness to form the required TLD phosphor. $CaSO_4$:Dy and $CaSO_4$:Tm are prepared by this method [44].

Crystal growth from melt is the most popular method for growing single crystals of semiconductors, metals, oxides, halogenides and chalcogenides at large scale. It is classified further under four headings:

(i) Czochralski technique: This is one of the major melt-growth techniques. It is widely used for growing large-size single crystals for a wide range of commercial and technological applications. One of the main advantages of Czochralski method is the relatively high growth rate.

(ii) Bridgman technique: In this technique the crucible containing the molten material is translated along the axis of a temperature gradient in a furnace.

(iii) Verneuil Method: Verneuil method (also called flame fusion technique) is used to grow large quantity of crystals with high melting temperature. It was originally developed for producing synthetic gemstones. Now-a -days the technique is used to grow a variety of high-quality crystals such as corundum, spinel, rutile and strontium titanate, which are widely applied in laser devices and precision instruments, as well as in thin film technologies as substrates.

(iv) Kyropoulos Method: The Kyropoulos method was initially developed for growth of large alkali halide crystals by the German scientist Spyro Kyropoulos. Later large sapphire crystals were also grown by using this method. The main distinction between Kyropoulos and Czochralski is the different crystal shapes and the solid-liquid interface curvature.

Combustion synthesis has been proposed to prepare oxide-based phosphors of smaller size particles. This method involves a highly exothermic reaction between an organic fuel and metal salts (oxidizers) in an aqueous solution. The reaction is initiated at low temperatures (around 500 ^{o}C) and proceeds to completion in a few minutes. The peak reaction temperature depends on the fuel and oxidizer molar ratio.

Sol-gel technique: Sol-gel method is a chemical technique that uses metal alkoxides (a kind of metal-organic compounds) for synthesis and production of powder or ceramic samples through a series of chemical processes, including hydrolysis, gelation, drying, and thermal treatment.

4.1 Lithium Fluoride. Farrington Daniels and his research group at the University of Wisconsin (USA) first suggested the use of thermoluminescence (TL) as a technique in radiation dosimetry [5] through studies of LiF as a TL material and it became evident that the desirable properties of the material were the result of the interplay between the complex defects present within the material resulting from the presence of Mg and Ti. This realization emerged from the work of Cameron and co-workers [6, 7] and this work led eventually to the patenting of TLD-100 by the Harshaw Chemical Company in 1963. Since then it has been the most widely used TLD material for various applications, particularly for personnel and medical dosimetry. LiF:Mg,Ti dosimeters known as TLD-100, TLD-600, and TLD-700 depending on their preparation from natural lithium or lithium enriched with ^{6}Li or ^{7}Li, respectively.TLD-100 consists of Li in its natural abundance (7.5% ^{6}Li and 92.5% ^{7}Li), TLD-600 are prepared from pure lithium chemical compound enriched in

^{6}Li (95.6% ^{6}Li and 4.4% ^{7}Li)), while TLD-700 are prepared by enriching the starting Li-compound in ^{7}Li (99.93% ^{7}Li and 0.07% ^{6}Li). The book of McKeever et al. [19] and many other books and review articles describe preparation and properties of LiF dosimeters.

4.1.1 LiF:Mg,Ti. LiF:Mg,Ti dosimeters come in a variety of physical forms, including powder, hot pressed chips, extruded rods, powder embedded Teflon discs or single crystals. Among these the most popular form is probably the hot pressed chips available in the size 3.2 x 3.2 x 0.9 mm^3. These chips have been used for personnel monitoring as the TLD badge marketed by Harshaw Chemical company (presently known as Thermo Fisher Scientific) as well as by other commercial manufacturers of TLD personnel monitoring badges. These hot pressed chips are also widely used for medical physics applications.

Harshaw's patent [45] describes two preparation methods for LiF:Mg,Ti TL phosphor powders: the solidification method, and the single crystal method.

In the solidification method, lithium fluoride (10^6 parts by weight), magnesium fluoride **(**400 parts by weight), lithium cryolite (200 parts by weight), and lithium titanium fluoride (55 parts by weight) are mixed in a graphite crucible. The mixture is homogeneously fused in vacuum and the product slowly cooled, then crushed and sieved between 60 and 200 μm.

The single crystal method consists of growth from the melt using either the Czochralski or Stockbarger-Bridgman methods and graphite crucibles using furnace having vacuum or inert-atmosphere to grow single crystals. Powders may also be prepared from single crystals by pulverising and sieving between 60 and 200 μm.

Harshaw's patent also describes the preparation of extruded LiF dosimeters. To obtain them, the LiF powder mixture is placed in a neutral atmosphere and pressed at 3.5 x 10^8 Pa at a temperature of 700 °C**,** pushing the mixture with a piston through a hole which acts as a die. The bar, obtained in this way, is cut in sections to prepare pellets/chips of uniform thickness and finally the faces of the pellets are polished. The extruded dosimeters have identical TL characteristics as the TL phosphor powder (also described in the paper of Azorin et al. [41]). McKeever et al. [19] state that the most sensitive LiF:Mg,Ti material is obtained with approximately 180 ppm Mg^{2+} and 10 ppm Ti^{4+}.

Phosphor embedded PTFE (polytetrafluoroethylene) discs are prepared by mixing fine grains of phosphor (having grain size comparable to or less than that of PTFE powder) with PTFE powder, generally in the weight ratio of 1:3, followed by cold compaction and sintering at about a temperature of 390 °C for about 1hour. Alternatively, phosphor emddeded tape may be obtained from a sintered phosphor-PTFE billet from which TL detectors of suitable size and thickness could be obtained.

Another method is described by Portal [46] to prepare sodium stabilized LiF TL dosimeters by using 200 ppm of magnesium fluoride and 1-2 wt% of sodium fluoride.

Sources of LiF:Mg,Ti TLDs include Thermo Fisher Scientific (Harshaw), USA (powder, chips (3.2 x 3.2 x 0.9 mm^3; 3.2 x 3.2 x 0.38 mm^3), disk (dia. 4.5 mm x 0.8 mm) and rods (dia.1 mm x 6 mm), sold as TLD-100, TLD-600 or TLD-700, Rexon TLD Systems, Inc., USA (www.rexon.com) (in their website it is stated that Rexon is committed to ongoing suppy of TLD products and services pioneered by Teledyne and Victoreen, such as LiF:Mg,Ti (TLD-100, TLD-600 and TLD-700) powder, chips, disks and rods, PTFE/TLD products: disks, ultra thin (50 μm), low energy disks, rods (long, mini and micro), LiF:Mg, Ti (DTG-4, as sintered chips and in ^{6}Li and ^{7}Li versions) from Russia, LiF:Mg,Ti from Poland, Krakow: marketed as MTS-N, MTS-6 or MTS-7, depending upon the isotopic content of Li), having dia. 4.5 and 0.9 thickness. These dosimeters are also available as thin layer circular pellets (active layer 0.05 mm), micro cubes (1x1x1 mm^3), rods or powder. Solid Dosimetric Detector & Method Laboratory (DML), Beijing, P.R. China offers a broad spectrum of products: GR-100 series LiF:Mg,Ti with natural, Li-6 or Li-7 composition (www. chinadml.com); Mirion Technologies markets RADOS TLD dosimeters as well as those of Panasonic (TLD 802) and Harshaw TL dosimeters, including dosimetry systems (www.mirion.com); RadPro International GmbH, Germany (www.radpro-int.com) is a distributor of RADOS TLD systems and TLD material of Mirion Technologies and RADCARD (www.radcard.pl) (former TLD Poland). Table 3 gives details of LiF:Mg,Ti from different manufacturers.

Table 3 Details of LiF:Mg,Ti from different manufacturers.

Manufacturer/ Physical form of TLD	Method of preparation	Dose range	Remarks
Thermo Fisher Scientific (Harshaw); Powder, Chips, single crystals [45,92].	(i)Homogeneous fusion of LiF and activators in vacuum; (ii) By the method of extrusion; (iii) Growth of single crystals by the Czochralski method.	30 µGy-1 Gy (linear); 1 Gy -20 Gy (supralinear)	For photons, electrons and neutrons.
RADCARD (former TLD Poland), Powder, chips and micro-cubes [47, 48]	Reproducible doping method and sintering.	10 µGy-3 Gy	TL Sensitivity comparable to LiF:TLD-100.
DML, P.R. China, available as sintered chips [49]	LiF:Mg, Ti (GR-100).	Dose threshold = 14 µGy [49]	TL sensitivity is 1.3 times LiF:TLD-100. LiF:Mg, Ti sensitized chips (GR-100M)
Russia, Sintered chips [50]	DTG-4	Used in personnel monitoring [51]	Sensitivity comparable to that of LiF:TLD-100.
Vinten Instruments Ltd., Sintered pellets[52]	LiF-7	Dose threshold = 14 µGy	TL sensitivity comparable to that of LiF:TLD-100.
SEDOS GKD TLD-System, Hot-pressed Thin Layer LiF:Mg,Ti TLD [53, 54]	The radiation-sensitive TL material is welded onto an aluminium substrate serving as a carrier.	Designed to measure whole body values of $H_P(10)$ and H_P (0.07).	The TLD system is planned to become a legal dosimeter for German radiation monitoring.

Sensitization is a technique involving pre-irradiation and annealing which produces increased sensitivity in some thermoluminecent materials, such as LiF:Mg,Ti and $CaSO_4$:Dy. Additional benefits associated with sensitization such as extended linearity in the dose response curve, reduction in photon energy dependence and reduction in the dose threshold have been reported [55]. LiF:TLD-100 is observed to be up to six times more sensitive after exposure to 10^3 Gy gamma radiation followed by an annealing treatment at 280-300 ^oC for 60 min. This increased sensitivity is eliminated if the material is subsequently annealed for an hour at 400 ^oC. However, exposing sensitized LiF:Mg,Ti to ultraviolet (254 nm) radiation during annealing at 280-300 ^oC is reported to reduce background effects while maintaining increased sensitivity [55-57, 89]. Charles et al. [56] have indicated that by optimizing this procedure, reductions in dose thresholds of a factor of 2 to 3 can be achieved. Driscoll et al. [22] report to have obtained a sensitization factor of 4 by following simultaneous UV (254 nm) and thermal treatment (270-290 ^oC), however, no overall reduction in dose threshold was observed due to larger variation in the background signal of the samples.

However, they report that dose thresholds of about 10 μGy for GR-100M samples (having sensitization factor between 3 and 5) quoted by the manufacturer (Baoli Science and Technology Ltd, China) were confirmed by them. These results confirmed the trend of reduction in dose threshold following sensitization reported by Charles et al. [56]. Jones [58] investigated the comparative performance of sensitized and non-sensitized TLDs when mounted on identifiable plaques for automatic reading. Bhuwan Chandra et al. [59] reported that the PTTL (using 254 nm UV light) in the gamma irradiated (10^3 Gy) sample after subjecting to simultaneous UV and thermal treatment (UV/thermal annealed) persisted even after 4 h of bleaching and remained constant at the level equivalent to 0.53 Gy of ^{60}Co gamma ray dose. They also observed that the response of peak 5 as a function of UV exposure in UV/thermal sensitized and dark-sensitized LiF (TLD-100) samples were different. The difference in the nature of the two PTTL curves appeared to show that the centres responsible for the PTTL in UV/thermal bleached samples were different from those related to peak 10. Thus, these results cast some doubts on the re-estimation capability of UV/thermal sensitized LiF:Mg,Ti dosimeters. There is no published report on the use of sensitized LiF:Mg,Ti dosimeters for routine personnel or environmental monitoring.

4.1.2 LiF: Mg,Cu,P. The preparation of LiF:Mg,Cu,P phosphor was first reported by Nakajima et al. [60, 61]. Lithium fluoride of special grade was used as the material. This material was mixed in water with activators CuF_2 (0.05 mol%), $MgCl_2$ (0.2 mol%), and ammonium phosphate. The wet mixture in a platinum crucible was heated at 1050 ^oC for 30 min (melting point of LiF is 847 ^oC) in nitrogen gas atmosphere after being dried at about 80 ^oC for 4 h. The melted LiF material in the crucible was rapidly cooled to 400 ^oC during 30 min and the polycrystalline LiF:Mg,Cu,P is obtained. The phosphor was reported to have promising characteristics for use as a dosimeter. It was reported that the phosphor had TL sensitivity about 23 times that of LiF (TLD-600), a linear TL dose response in the range 50 μGy to 10 Gy, a TL emission spectrum in the range 340-410 nm and 5% TL fading in 30 days when stored at 40 ^oC. Wu et al. [62] prepared LiF:Mg,Cu,P phosphor powder by thermal treatment at 900 ^oC for 1h in N_2 atmosphere. Its TL sensitivity was reported to be about 23 times higher than that of LiF (TLD-100). Its TL response was linear from 0.3 mR to 1000 R. Its energy dependence is reported to be similar to that of LiF (TLD-100). The phosphor was reported to be stable and reusable without significant loss of sensitivity. Niwa et al. [63] prepared single crystals of LiF:Mg,Cu,P. It is reported that the TL emitted from a single crystal with 0.25 mole percent phosphorus was one order higher than that emitted from LiF powder sample with the same mole percent phosphorus and the same weight. They report that single crystals could not be grown with phosphorus content more than 0.25 mole percent in the starting/base material.

Wang et al. [64, 65] reported the development of special technology to prepare LiF:Mg,Cu,P TLD in the form of solid chips with high signal to noise ratio, which made it possible to apply these detectors in personnel, clinical and environmental monitoring. LiF:Mg,Cu,P was developed in powder as well as chip form. A special grade of LiF powder was mixed in water with different quantities of MgF_2, CuF_2, and $NH_4H_2PO_4$. The wet mixture was placed in a platinum crucible. After being dried at about 200 °C for 2 h, it was melted under a nitrogen stream in an electric furnace at 1050 °C for 30 min. The melted material in the crucible was rapidly cooled down to room temperature. The poly-crystallized LiF(Mg,Cu,P) material was powdered and washed with about 1N hydrochloric acid, then washed with distilled water until no chloride ions could be detected. Finally, it was dried at 100 °C for 1 h and was then sieved. Two methods have been used to produce LiF:Mg,Cu,P chips, i.e. hot pressed square chips and sintered circular chips. The dosimetric performances of sintered LiF:Mg,Cu,P chips (circular) are reported to be the same as those of hot pressed square chips, but the production cost of the former is much lower than that of the latter. It is reported [66] that solid chips of ^{6}LiF/^{7}LiF:Mg,Cu,P have been prepared in the same way. Thin films of LiF:Mg,Cu,P are also produced in Solid Dosimetric Detector & Method Laboratory (DML). All these developments and different methods used by several groups for the preparation of LiF:Mg,Cu,P have been summarized by Zha et al. [24]. Subsequently, Shen et al. [67] reported that the main features of GR-200A have been improved dramatically by adding a chemical additive and adopting a particular preparation technology. It is reported that the sensitivity of GR-200A has been increased to 65 times as high as TLD-100 from the original 29 times. The residual signal has been decreased to less than 1% from the original of about 2.5% following the 240 ^{o}C readout. This led to decrease in detection threshold and increase in the signal-to-noise ratio. Horowitz and Horowitz [68] used high-purity optical-grade LiF and other necessary salts as dopant and co-dopants to prepare a high sensitivity LiF:Mg,Cu,P TLD phosphor powder. The phosphor was prepared by melting in a nitrogen atmosphere at 1000 ^{o}C. Incorporation of oxygen in the molten stage was stated to be absolutely necessary for obtaining high sensitivity phosphor in a reproducible manner.

Niewiadomski [47] reported the development of LiF:Mg,Cu,P (also known as MCP) phosphor powder and sintered pellets. It is also reported that the sintering procedure for the development of MCP pellets was different than that adopted for the development of sintered LiF:Mg,Ti (also known as MTS) pellets. These sintered pellets (circular) were named as MCP-N, MCP-6 or MCP-7, depending upon the isotopic content of Li. These MCP-type ultra-sensitive thermoluminescent dosimeters, available as solid detectors or powder, are 30 times more sensitive to gamma ray doses than MTS-N dosimeters (www.radcard.pl). Formerly known as TLD Poland, presently, these dosimeters are marketed as RADCARD dosimeters. Azorin et al. [41, 69] reported development of LiF:Mg,Cu,P TLD phosphor powder in ININ Mexico. In freshly precipitated pure LiF, aqueous solution of $MgCl_2$, CuF_2 and $(NH_4)_2HPO_4$ activators, in required concentrations, were added. The dried material was placed in platinum crucible and subjected to thermal treatment at 573 K for 15 min. The temperature was then raised to 973 K and maintained at this temperature for 1h., resulting in the formation of crystalline mass of LiF:Mg,Cu,P. The crystalline material was crushed and sieved to select phosphor powder with grain sizes between 100 and 300 µm. Its TL sensitivity is reported to be about 25 times than that of LiF:TLD-100. Its detection threshold was reported as 65 nGy and linearity in dose response in the range 100 µGy to 100 Gy. Kolotilin et al. [50] used a method similar to that reported by Nakajima et al. [60, 61] for the preparation of LiF:Mg,Cu,P phosphor powder. However, LiF:Mg,Cu,P solid dosimeters were prepared by compaction of powder and sintering, resulting in disks each of dia. 5 mm and 1 mm thickness. Table 4 gives a comparison of TL characteristics of various LiF phosphors prepared by different methods.

Table 4 Comparison of TL characteristics of LiF phosphors prepared by different methods.

Phosphor and physical form	Method of preparation	TL intensity relative to LiF:TLD-100	TL emission peak (nm)	Dose range (region of linearity)
LiF:Mg,Cu,P phosphor powder(Japan)[60,61]	Melting the raw materials at 1050 ^{o}C for 30 min in N_2 atmosphere.	23 (as compared to LiF:TLD-600)	340-410	50 µGy to 10 Gy (5 % fading in 30 d)
LiF:Mg,Cu,P phosphor powder (China)[62]	Thermal treatment at 900 oC for 1h in N_2 atmosphere.	23	380 nm	0.3 mR to 1000R (The phosphor was reported to be stable and reusable without significant loss of sensitivity)
LiF:Mg,Cu,P single crystals (Japan)[63]	Single crystals using dopant conc.: Mg(0.2 mol%), Cu (0.05 mol%), P(0.25 mol%)	----	-----	----
LiF:Mg,Cu,P phosphor powder and chips (DML, China)[64, 65]	(i) Melting the raw materials at 1050 ^{o}C for 30 min in N_2 atmosphere.	29-44	----	Linear up to12 Gy.

	(ii)Special technology for sintered chips.			
LiF:Mg,Cu,P chips (GR-200A) (DML, China) [67]	By adding a chemical additive and adopting a particular preparation technology.	65	----	Linear up to 12Gy. (The residual signal has been decreased to less than 1% from the original of about 2.5% following 240 ^{o}C readout.)
LiF:Mg,Cu,P phosphor powder [68]	Melting in a nitrogen atmosphere at 1000 ^{o}C; incorporation of O_2 in molten stage..	----	----	----
LiF:Mg,Cu,P (MCP) phosphor powder and sintered chips (TLD, Poland) [47, 89, 90]	Sintering procedure for the development of MCP pellets was different than that adopted for the development of sintered LiF:Mg,Ti (MTS) pellets.	30	-----	Linear response from 1 µGy to 1 Gy.
LiF:Mg,Cu,P TLD phosphor powder (ININ, Mexico) [41, 69]	Thermal treatment at 973 K for 1h.	25	-----	Linear dose response: 100 µGy to 100 Gy.
LiF:Mg,Cu,P phosphor powder and sintered chips [50]	(i)Method similar to that reported by Nakajima et al. for the preparation of LiF:Mg,Cu,P phosphor powder. (ii) Solid dosimeters were prepared by compaction of powder and sintering.	20	-----	Linear response up to 4.38 Gy. (Detection threshold= 1.23 µGy.)
LiF:Mg,Cu,P phosphor powder [70]	Melted in a platinum crucible at 960 ^{o}C and quenched to room temperature.	1.5 times TLD-100H (Harshaw)	370	Linear dose response up to 10 Gy.
LiF:Mg,Cu,P (TLD-100H) phosphor powder and sintered chips (Thermo Fisher Scientific (Harshaw), USA) [93-95]	High sensitivity pressed pellets of 3.6 mm dia. and in different thicknesses are manufactured.	25	-----	Linear dose range: 2.5 µGy to 10 Gy.
LiF:Mg,Cu, Na,Si (Korea) [72, 73]		Twice that of LiF:Mg,Cu,P	366	Linear from 10^{-4} to 100 Gy. (A lower residual signal than LiF:Mg,Cu,P.)
LiF:Mg,Cu, Na,Si (China) phosphor powder [75]	-----	30		Linear from 5 mGy to 18 Gy. (A residual signal 0.2% following 260^{o}C readout.) Discontinued due to thermal susceptibility of LiF:Mg,Cu,Na,Si , which appeared to be associated with the Na conc.
LiF: Mg,Cu,Si sintered discs (Korea) [77- 80]	The preparation procedure comprises six steps: mixing raw chemicals, activation,	55	385	1 µGy to 20 Gy

	pulverising, pressing, sintering and annealing. The activation was carried out using the granulation method.			
LiF: Mg,Cu,Si phosphor powder and sintered pellets (China) [82, 83]	(i)Phosphor powder by heating the mixture at 1050 ^{o}C for 30 min. in N_2 atmosphere in a platinum crucible. (ii) The pressed pellets (4.5 mm dia and 0.8 mm thickness) were sintered at 830 ^{o}C under nitrogen gas atmosphere.	35	300 to 550 nm range, with peak emission at ~380 nm. Also, weak emission around 610 nm for Cu conc. ≤ 0.01 mol%.	Dose range not given. The residual signal for LiF:Mg,Cu,Si is about 0.4% following readout at 260 ^{o}C for 12 s , which is approximately half of that observed for GR-200A following readout at 240 ^{o}C for 12 s. The temperature between 260 ^{o}C and 290 ^{o}C can be used to treat LiF:Mg,Cu,Si.

TL sensitivity of these LiF: Mg,Cu,P dosimeters was about 20 times higher than that of LiF:Mg,Ti (DTG-4). Its detection threshold was 0.14 mR (1.23 µGy) and showed linear response up to 500 R (4.38 Gy). Shinde et al. [70] purified the commercially available LR grade LiF by vacuum distillation method. The purified LiF and dopants Mg, Cu and P in the form of MgF_2, $CuCl_2.2H_2O$ and $NH_4H_2PO_4$, respectively, were mixed thoroughly. The mixture was melted in a platinum crucible at 960 ^{o}C and quenched to room temperature. The polycrystalline phosphor was thus obtained. The following dopants concentrations were found to be optimum: Mg 0.4 mol%, Cu 0.02 mol%, P 0.85 mol%. Patil and Moharil [71] showed that LiF:Mg,Cu,P could be made using a simple procedure which did not involve use of nitrogen atmosphere and platinum crucible. They used the reactive atmosphere processing (RAP) for doping Cu^+ successfully in LiF. It may be noted that unlike rare earth (RE) doped $CaSO_4$ TL phosphors, none of the laboratories reported to have used the same preparation procedure to develop LiF:Mg,Cu,P phosphor.

LiF:Mg,Cu,Na,Si with high TL sensitivity was first developed by Nam et al. [72]. The optimum composition of dopants was found to be Mg 0.6 mol%, Cu 0.8 mol%, and 1.8 mol% each of Na and Si. The new phosphor was reported to have TL sensitivity about two times higher than that of LiF:Mg,Cu,P. For a constant heating rate of $5^{o}C.s^{-1}$, the main dosimetric peak of the glow curve appeared at 234 ^{o}C. The TL dose response of the peak was reported to be linear from 10^{-4} to 100 Gy, with no observed supralinearity or saturation. It was reported [73] that a personnel TL dosimeter using sintered LiF:Mg,Cu,Na,Si TL detector was designed and based on the experimental results of the new dosimeter, it was found appropriate to estimate personnel dose equivalent for wide range energy of photon fields. The results of Lee et al. [74] showed that Mg plays a role in the trapping of the charge carriers and Cu plays a role in the luminescence recombination process; however, the effect of Na and Si on the glow curve structure and the TL emission spectra is much less than that of Mg and Cu. It was considered that Na and Si each play a role in the improvement of the luminescence efficiency.

Tang et al. [75] (China) also reported development of a new high sensitivity LiF:Mg,Cu,Na,Si thermoluminescent phosphor with low residual signal and good stability to heat treatment. The main dosimetric peak of this phosphor occurs at 197 ^{o}C at a heating rate of 1 $^{o}C\ s^{-1}$. It is reported that its TL response at both 260 ^{o}C and 280 ^{o}C were reproducible within a coefficient of variation of 2% over ten re-use cycles without systematic decrease. It retained the main advantages of LiF:Mg,Cu,P phosphor, and had a lower residual signal and a better stability to heat treatment. However, subsequently, Tang reported [76] that the height of the main peak depends strongly on the annealing temperature. He reported that the thermal susceptibility of LiF:Mg,Cu,Na,Si appeared to be associated with the Na concentration. The lower the Na concentration, the less sensitive the TL was to annealing temperature. The optimum Na dopant concentration was found to be 0%. Thus the phosphor was discarded for its use in routine dosimetric applications.

Subsequently, Lee et al. [77-79] reported dosimetric characteristics of a new LiF:Mg,Cu,Si thermoluminescent (TL) material developed at KAERI, Korea and compared with those of commercially available LiF:Mg,Cu,P (GR-200A)(China). It is reported that LiF:Mg,Cu,Si thermoluminescence dosimeter (TLD) can be heated up to 573 K without any loss of TL sensitivity or any change in the glow curve structure. High-temperature glow peak in LiF:Mg,Cu,Si was significantly lower than that in GR-200A, consequently the residual signal was only 0.025%, which is about 35 times less than that of GR-200A. The residual signals of LiF:Mg,Cu,P (GR-200A), LiF:Mg,Cu,Na,Si, and LiF:Mg,Cu,Si were reported to be 0.92, 0.15 and 0.025%, respectively. The TL sensitivity of the LiF:Mg,Cu,Si TLD was reported to be about 55 and 1.1 times higher than those of the LiF:Mg,Ti (TLD-100) and GR-200A, respectively [77]. It was concluded that the replacement of dopant P by Si resulted in LiF:Mg,Cu,Si with improved TL properties in which the dual-step annealing method (537 K for 10 min followed by 533 K for 10 min) enabled to overcome the two major disadvantages of LiF:Mg,Cu,P (i.e., (i) a thermal loss in the TL sensitivity when it is annealed at a temperature above 513 K (240 ^{o}C), and (ii) a relatively high residual signal). Therefore, the authors strongly believed that LiF:Mg,Cu,P could be replaced by LiF:Mg,Cu,Si in the field of radiation dosimetry. Lee et al. [77] and Kim et al. [80] reported that for the reader annealing using a maximum readout temperature and clamping at 260 ^{0}C, no significant change in the TL sensitivity and glow curve structure was observed for more than 100 reuse cycles of exposures (5.5 mGy) and readout. However, requirement of dual-step annealing method, for restoration of sensitivities of peaks 1- 4, is indicative of complex nature of defects in this triply-doped phosphor. TL emission spectrum of LiF:Mg,Cu,Si was found to have three emission bands peaking at 355, 385 and 440 nm similar to that of LiF:Mg,Cu,P but differing in the relative intensities [78]. Negligible fading, insensitivity to room light and absence of the effect of pre- or post-storage annealing on the response and the glow curve structure was observed. The dose response for this TL material (LiF:Mg,Cu,Si) was reported to be linear in the range 1 μGy to 20 Gy and a sub-linear response was observed for higher doses. The minimum measurable dose value of 0.3 μGy as 3σ of the background readout of unirradiated samples was reported [25]. The reusability of this newly developed TL detector sufficiently satisfied IEC standards [80]. It is also reported [81] that indigenously developed ^{6}LiF:Mg,Cu,Si and ^{7}LiF:Mg,Cu,Si TLDs provided a better alternative to TLD-600 and TLD-700 for the dosimetry of mixed fields of neutrons and gamma rays.

Recently, Tang et al. [82, 83] have reported development of highly sensitive LiF:Mg,Cu,Si TL discs with good stability to heat treatment, which they report are less sensitive to annealing at a certain temperature than LiF:Mg,Cu,Si developed in Korea [77]. The shape of the glow curve for the new LiF:Mg,Cu,Si disc is similar to that for standard LiF:Mg,Cu,P (GR-200A), and shows minimal differences when annealed in the range from 260 ^{o}C to 290 ^{o}C for 10 min. The TL sensitivity for LiF:Mg,Cu,Si is much lower than that for GR-200A, but is 35 times larger than that for TLD-100. The residual signal for LiF:Mg,Cu,Si is about 0.4% following readout at 260 ^{o}C for 12 s at a heating rate of 15^{o}C s^{-1}, which is approximately half for GR-200A following readout at 240^{o}C for 12 s. Thus, the temperature between 260 ^{o}C and 290 ^{o}C can be used to treat LiF:Mg,Cu,Si. These results indicated that the new LiF:Mg,Cu,Si disc has a good stability to thermal treatments and a lower residual TL signal. On the basis of TL spectral measurements it is concluded that Mg dopant mainly plays a role in the formation of trapping centres, both Cu and Si play a role in the main emission process and Cu also plays a role in reducing the emission around 610 nm. Table 4 gives characteristics of LiF:Mg,Cu,P, LiF:Mg,Cu,Na,Si and LiF:Mg,Cu,Si TL phosphors prepared using different methods. It also gives comparison of dosimetric characteristics of LiF doped with various combinations of the dopants: Mg, Cu, P, Si and Na.

It is worth mentioning here that LiF:Mg,Cu,Si and LiF:Mg,Cu,B materials were first developed and reported by Nakajima et al. in 1978-79 [60, 61]; but, they were not attractive in comparison to LiF:Mg,Cu,P because of their low TL sensitivity. TL sensitivities of LiF:Mg,Cu,Si and LiF:Mg,Cu,B were about 4.4 and 4.3 times, respectively, than that of LiF:TLD-600.

Although the role of Mg in LiF:Mg,Cu,P to provide trapping centres for electrons is well established, there is no consensus about the roles of Cu and P. As per McKeever [84], neither Cu nor Mg are directly involved in the emission process since in the material doped with only Cu, the wavelength of emission is very different from those samples which contain P. He also argued that since it is necessary to have large quantities of P in order to obtain the brightest material, it could be assumed that the TL is emitted from Mg/P phases. Thus P was assigned the role of a luminescent activator. Mahajna et al. [85] claimed that P takes role of Ti in LiF:Mg,Cu,P. Bos et al. [86] proposed the dual role of P, which is involved in the trapping of charge carriers (although the role of Mg is more dominant). It also acts as luminescent centre. Bilski et al. [87] proposed that P is luminescent centre while Cu induces some competitive processes, which reduce the formation of higher order complexes of Mg related defects. According to them, Cu is not involved directly in the TL process. On the contrary, the work of Patil and Moharil [71] shows that Cu^+ is acting as a luminescent centre. They proposed that radiation creates excess electron colour centres and defects associated with trapped interstitial halogen atoms. During heating, the halogen atoms are released from interstitial position and they recombine with electrons. The energy of recombination is efficiently transferred to nearby Cu^+ ion, which acts as luminescent centre. But the above-proposed model doesn't discuss the role of P. Chen and Stoebe [88] concluded that Cu^+ plays a role in the luminescence recombination process in the LiF:Mg,Cu,P material using the extended X-ray absorption fine structure (EXAFS) measurements. According to Shinde et al. [70] phosphorus seems to play a dual role: it acts as a hole trap and also increases the TL sensitivity by assisting the incorporation of Cu ions into the LiF lattice. They also proposed that Cu^+ plays a role in the luminescence recombination process.

Lee et al. [74, 78], Kim et al. [25] and Tang et al. [82, 83] studied the emission spectra of LiF doped with various combinations of the dopants: Mg, Cu, P, Si and Na. The measurements and analysis of the three-dimensional TL spectra of Lee et al. [74] showed that in LiF:Mg,Cu,Na,Si sample, a 385 nm peak wavelength is observed in the low-temperature range (30–160°C) and the value of the peak wavelength at the main peak at 210°C is observed to be ~366 nm, while a 355 nm luminescence is emitted at the high-temperature range (~250°C). They also report that the emission of LiF:Mg,P is totally different from that observed for LiF:Mg,Cu,P, exhibiting a maximum at ~405 nm. While the TL spectra of the LiF:Mg,Cu,Na,Si sample and the LiF:Mg,Cu sample, which had no Na and Si dopants, have almost the same luminescent behaviour. The main emission peak at 385 nm was observed in the TL emission spectra of the samples which contain Cu, but the 385 nm emission was not observed in that of the LiF:Mg,Na,Si sample, which did not contain Cu. They also report that the glow curves of the samples that contain the Mg dopant are very similar, since they have the same number of peaks and their temperatures are the same. These curves are very different from those obtained for the LiF:Cu,Na,Si (CNS) sample, which does not contain Mg. Thus, they proposed that Mg plays a role in the trapping of the charge carriers and Cu plays a role in the luminescence recombination process; however, the effect of Na and Si on the glow curve structure and the TL emission spectra is much less than that of Mg and Cu. It was considered that Na and Si each played a role in the improvement of the luminescence efficiency. They reported [74] that the TL intensity of the LiF doped with Mg,Cu was ~30% of that of the sample doped with Mg, Cu, Na, and Si, but that doped with Mg,Na and Si was only 3%. From their results they [74] inferred that the emission of LiF:Mg,P is totally different from that observed for LiF:Mg,Cu,P, exhibiting a maximum at ~405 nm. From these results, they proposed that the Cu acts as a luminescent centre and that the Na and Si are not luminescent dopants, because the peak wavelength of the TL emission is not influenced by the Na and Si dopants. They also commented that the thermoluminescence characteristics of LiF:Mg,Cu,Na,Si TL material are very similar to those of the LiF:Mg,Cu,P material. In the LiF:Mg,Cu,Na,Si material, Na and Si dopants correspond to the P dopant in the LiF:Mg,Cu,P material. They stated that measurement results in their study agreed well with those of Patil and Moharil [71]. Thus, they concluded that the Cu dopant is directly involved in the process of the 385 nm emission. Lee et al. [78] and Kim et al. [25] reported emission spectral measurements for LiF:Mg,Cu,P samples. TL emission spectrum of LiF:Mg,Cu,Si was found to have three emission bands peaking at 355, 385 and 440 nm similar to that of LiF:Mg,Cu,P but differing in the relative intensities. They report that the peak temperature and the TL emission spectra of dosimetric glow peak in all samples having Mg, Cu were always found to be the same irrespective of the third dopant which influenced only the intensity of TL emission spectrum. The emission band peaking at 385 nm was assigned to Cu.

Tang et al. [82] investigated the effect of heat treatments on LiF:Mg,Cu,Si. The shape of the glow curve for LiF:Mg,Cu,Si was reported to be similar to that for standard LiF:Mg,Cu,P (GR-200A), and showed minimal differences when annealed in the range from 260 °C to 290 °C for 10 min. The TL sensitivity for LiF:Mg,Cu,Si was found to be much lower than that for GR-200A, but is 35 times larger than that for TLD-100. The glow curve shape of LiF:Mg,Cu,Si annealed at 260 °C for different times shows minimal differences and TL response remains stable. These results indicate that the new LiF:Mg,Cu,Si disc has a good stability to thermal treatments and a lower residual TL signal. The residual signal for LiF:Mg,Cu,Si is about 0.4% following readout at 260 ^{o}C for 12 s, which is approximately half of that observed for GR-200A following readout at 240 ^{o}C for 12 s.

Tang et al. [83], on the basis of their results on the 3D TL spectra and glow curves of LiF:Mg,Cu,Si with various Mg, Cu and Si concentrations, reported that the shapes of glow curves in LiF:Mg,Cu,Si, LiF:Mg,Cu and LiF:Mg,Si were similar and the glow curves had peaks at approximately the same temperatures but with significantly different intensities. In the case of LiF:Cu,Si sample, which had no Mg dopant, the glow curve shape was totally different from the others. Thus, they concluded that Mg dopant plays mainly a role in the formation of trapping centres in LiF:Mg,Cu,Si TL material. Tang et al. [83] report that the spectra of LiF:Mg,Cu,Si, LiF:Mg,Cu and LiF:Mg,Si are similar in the range of 300–550 nm. Neither the temperature of the glow peak nor the wavelength of the emission maximum changes with variation of dopants concentrations when Cu is more than 0.01 mol % in LiF:Mg,Cu,Si. The emission in LiF:Mg,Cu,Si with Cu concentration 0.01 mol % is similar to that in LiF:Mg,Si, which also shows some weak emission around 610 nm, and is different from that in LiF:Mg,Cu,Si with Cu concentration higher than 0.01 mol %. Thus, they concluded that both Cu and Si play a role in the main emission process and Cu also plays a role in reducing the emission around 610 nm. However, full characterization in terms of minimum detectable dose, region of linear dose range, etc., is not reported for LiF:Mg,Cu,Si (China).

LiF:Mg,Cu,P phosphors have been thoroughly characterized by Nakajima et al. [60, 61], Wu et al. [62], DeWerd et al. [95], Bhatt et al. [27, 96], Wang et al. [63, 64], Driscoll et al.[52], Prokic and Botter-Jensen [23], Zha et al. [24], Pradhan and Bhatt [97], Mahajna et al. [85], Bilski et al. [87, 89], etc.. LiF:Mg,Cu,Na,Si and LiF:Mg,Cu,Si TL phosphors have been characterised by Nam et al. [72], Jung et al. [73], Lee et al. [74], Tang et al. [75, 76], Lee et al.[78, 79], Kim et al. [25], Rahman et al. [80] and Tang et al. [82, 83].

It was reported by Jung et al. [73] that “a personnel TL dosimeter using sintered LiF:Mg,Cu,Na,Si TL detector was designed and based on the experimental results of the new dosimeter; it was found appropriate to estimate personnel dose equivalent for wide range energy of photon fields”. But, there is no published report on use of either LiF:Mg,Cu,Na,Si or LiF:Mg,Cu,Si for routine dosimetric applications. A published report in 2002 by Kim et al. [98] states that $CaSO_4$:Dy dosimeter based Teledyne 300 automatic TLD reading system and a C-300 badge is being used for routine personnel monitoring service in Korea.

It is also pertinent here to mention that of all the LiF:Mg,Cu,P-based phosphors, the one manufactured by Thermo Fisher Scientific (Harshaw, USA) has been tested thoroughly in the configuration of personnel monitoring TLD badge over a large number of cycles of re-use [92-94]. It is reported that the personnel monitoring TLD cards, made from LiF:Mg,Cu,P (Harshaw) TLD chips (the detector element having encapsulation of Teflon), heating up to 260 °C during TL readout resulted in about 0.01% sensitivity loss per use over 1000 reads (resulting in 10 % total loss in sensitivity) which is reported to be comparable to the loss of sensitivity in LiF:Mg,Ti (Harshaw) based TLD cards. Moscovitch [92] states that the advantages of LiF:Mg,Cu,P include high sensitivity as compared to LiF:Mg,Ti, almost flat photon energy response, low fading rate and linear dose response. The lack of supra-linearity at higher dose levels is particularly useful for accident dosimetry, and eliminates the source of error usually associated with the application of supra-linearity corrections. The main drawbacks are still the relatively high residual signal and the loss of sensitivity for high readout temperatures. However, this does not limit the usefulness of LiF:Mg,Cu,P for low dose levels typical to personnel or environmental dosimetry, but may be a limiting factor for high dose applications such as clinical dosimetry.

4.2 Lithium Tetraborate. Lithium tetraborate ($Li_2B_4O_7$) doped with manganese (Mn) was first proposed by Schulman et al. in 1967 [99] for TL dosimetry applications as a tissue equivalent material. This material was prepared by melting the raw materials to a temperature higher than the melting point of lithium tetraborate and then rapidly cooling to room temperature. The glassy material thus obtained is fired at a sufficient temperature to crystallize it. The major drawbacks of this material are its poor sensitivity, hygroscopic nature, and relatively large fading. The low TL sensitivity was caused partly by the emission in the 600 nm region of the spectra, which is far from the response region of most photomultipliers.

Recently, Annalakshmi et al. [101] synthesized manganese (Mn) doped $Li_2B_4O_7$ using solid state reaction technique by sintering at 750 °C for 3 h in an alumina crucible. It is reported that the glow curve shows a high temperature peak at 250 °C, which is highest among all other lithium borate phosphors studied in the literature. Linear dose response is observed up to 10 Gy. TL intensity was maximum for Mn concentration around 0.32 wt.%. The solid state synthesis route was found to result in non-hygroscopic and low-fading phosphor as compared to other preparation techniques. $Li_2B_4O_7$:Cu was prepared by Takenaga et al. [20] by sintering technique. To raw lithium borate ($Li_2B_4O_7$) powder was added a solution of $CuCl_2$ in acetone or alcohol, and the mixture was then stirred and dried. The $Li_2B_4O_7$ powder containing the activator compound was heat-treated in air in a platinum boat for about 1 h at a temperature of 900-913 °C, which is just below the melting point (917 °C) of $Li_2B_4O_7$. Because of the heat treatment, clear crystals having an almost spherical form were produced from the raw $Li_2B_4O_7$ powder, which was porous and opaque. The heat treatment causes diffusion of the activator into $Li_2B_4O_7$ crystal interiors, as well as re-crystallization and sintering due to diffusion, vaporization and deposition. The use of copper activator instead of manganese in lithium borate [20, 21] overcame the drawback of poor TL sensitivity and red TL emission spectra to an emission spectrum of copper activator, at about 360 nm (see Table 3). However, commercially available $Li_2B_4O_7$:Cu thermoluminescent material from Panasonic Inc. is produced in powder form which is inconvenient for routine dosimetric use.

Prokic and co-workers have developed and characterized sintered pellets (4.5 mm dia and 0.95 mm thickness) of $Li_2B_4O_7$ doped with copper and other co-dopants/co-activators, such as Ag, In, P [48-50]. Generally, sintered forms are preferred due to ease of their handling during routine use. Also, for low dose measurements they give better signal to noise ratio. Prokic [104] reported that the relative photon energy response factors for $Li_2B_4O_7$: Cu,In and $Li_2B_4O_7$: Cu,In,Ag were 0.94 and 0.97, respectively at 33 keV compared to that at 1.25 MeV. Thus, they offer flatter photon energy response compared to $Li_2B_4O_7$:Cu due to their better tissue equivalence. Table 5 gives comparison of characteristics of doped $Li_2B_4O_7$ TL phosphors prepared using different methods.

Recently, Patra et al. [112] have reported that luminescence studies, in single crystals of $Li_2B_4O_7$ (LTB) doped with Cu and Ag and Cu, Ag co-doped, revealed a sensitizer role of Ag in the LTB:Cu,Ag crystal. They further report that, despite an energy transfer from Ag^+ to Cu^+ centers, emission from both the centers participates in the thermally stimulated luminescence (TSL) of co-doped crystal. They propose that the LTB:Cu,Ag crystal will be a better and efficient material for TSL dosimeters compared to singly doped LTB crystals. Therefore, to exploit the full potential of the co-doped LTB, a suitable TSL readout system consisting of a PMT having a peak response in the range of 200–600 nm will be necessary. However, no comparative measurements have been provided in this connection. Takenaga et al. [47], Lakshmanan et al. [113-114], Wall et al. [21], Prokic [104], Furetta et al. [105] and others had studied extensively various characteristics of these phosphors for their projected application in radiation dosimetry. Singh et al. [111] have reported synthesis and characterization of $Li_2B_4O_7$:Cu nanophosphor using solution combustion synthesis method. However, its TL sensitivity is very low and dose response in the range 1mGy-5kGy, with linearity over a limited range.

Table 5 Comparison of TL characteristics of $Li_2B_4O_7$ phosphors prepared by different methods.

Phosphor and physical form	Method of preparation	TL intensity relative to LiF:TLD-100	TL emission peak (nm)	Dose range
$Li_2B_4O_7$:Mn(0.1 wt.%); Powder [99]	Melting the raw materials	0.4	600	0.1 mGy-3 kGy (Linear up to 3 Gy)
$Li_2B_4O_7$:Mn(0.1 wt.%) sintered pellets [100]	0.2% SiO_2 was added. Sintering at 880 °C for 1h in air.	8 times that of TLD-800 (Harshaw).	----	Linear up to 10^4 Gy.
$Li_2B_4O_7$:Mn (0.32 wt.%), Powder [101]	Solid state reaction technique by sintering at 750 °C for 3 h	1.0	580	1 mGy- 1 kGy (Linear up to 3 Gy)
$Li_2B_4O_7$:Cu; Powder, Japan[20,102]	By sintering technique.	8.0	368	10 µGy-1 kGy
$Li_2B_4O_7$:Cu; Powder[103]	Sintering temp. 913-915 °C for 1h.	0.64 of $Li_2B_4O_7$:Cu (Japan) [47]	-----	------
$Li_2B_4O_7$:Cu; Sintered pellets[104, 105]	Sintering at 850 °C. SiO_2 was added for preventing effects of humidity.	0.5	360	20 µGy-1 kGy
$Li_2B_4O_7$:Cu,In; Sintered pellets [104, 105]	Sintering at 850 °C. SiO_2 was added for preventing effects of humidity.	1.0	360	10 µGy-1 kGy
$Li_2B_4O_7$:Cu,In,Ag; Sintered pellets [104]	Sintering at 850 °C.. SiO_2 was added for preventing effects of humidity.	2.0	360	10 µGy-1 kGy
$Li_2B_4O_7$:Cu,Ag,P; Sintered pellets [106]	Sintering technique. SiO_2 was added for preventing effects of humidity.	5.0	360	10 µGy-1 kGy
$Li_2B_4O_7$:Cu Single crystals [107]	Grown using the Czochralski method.	3.3	352	1 mGy to 1 kGy
$Li_2B_4O_7$:Cu,Ag Single crystals [108]	Using the Czochralski method.	5.0	370	1 mGy to 1 kGy
$Li_2B_4O_7$:Cu Single crystals [109]	Grown using the Czochralski method.	Higher than the powder samples	366	0.2 mGy-20 Gy
$Li_2B_4O_7$:Tm; Glassy state [110]	By melting the raw materials. 0.25 wt.% SiO_2 was added to reduce hygroscopicity.	---	455	mGy-1 kGy

4.3 Magnesium Borate. Due to its near tissue equivalence ($Z_{eff.} = 8.4$), rare earth-doped MgB_4O_7 TL phosphors have been investigated by many researchers [115-118] for their possible use in personnel monitoring and other applications. Kazanskaya et al. [115] prepared MgB4O7: Dy (0.1

mol%) sintered pellets. These detectors showed good sensitivity and linear dose response in the dose range 10 µGy to 10 Gy, but these detectors showed 25% fading in 40 days, whereas the MgB_4O_7: Dy (0.5 mol%) phosphor powder developed by Lakshmanan et al. [116] showed 40% fading in 17 days. Thus, they were not suitable for dosimetric use. Prokic reported development of highly sensitive MgB_4O_7: Dy/Tm sintered thermoluminescent dosimeters [117, 118]. She also developed MgB_4O_7: Dy*/Tm* sintered discs (with a co-dopant as sensitizer). These, MgB_4O_7: RE* sensitized, detectors were more sensitive than the non-sensitized magnesium borate thermoluminescent material [118, 119].

Prokic also developed highly sensitive MgB_4O_7:Mn sintered pellets having linear dose response in the range 10 µGy to 45 Gy and negligible fading in 4 months [120]. Prokic and Furetta et al. [121, 122] report the development and dosimetric characterisation of a new production of MgB_4O_7:Dy,Na thermoluminescent material. The detectors showed wide dynamic dose range (90 µGy to 40 Gy), minimum detectable dose of 6 µGy and a fading of 8 % in 3 months. It is reported that though previously prepared sensitized magnesium borate TL materials activated with Dy^{3+} or Tm^{3+}, were highly sensitive phosphors, they showed high fading, multiple peak structure of the main peak and slight chemical instability. It is reported that these shortcomings of the magnesium borate phosphors have been entirely overcome by improvement over the original preparative procedure and the development of MgB_4O_7: Dy,Na TL material with optimum characteristics, maintaining a sensitivity of 6-7 times higher than TLD-100 obtained using a Harshaw 2000A reader [23, 121, 122]. (It is reported that a sensitivity of about 15 was obtained using Alnor Dosacus TLD reader.) These dosimetric characteristics make this TL material very useful for multiple dosimetry applications, particularly in individual monitoring and in various medical dosimetry purposes. MgB_4O_7:Dy,Na TL dosimeters are successfully used on a large scale for legal personnel dosimetry control in Yugoslavia [121, 122]. The efforts towards development MgB_4O_7-based detectors by various groups are summarized in Table 6.

Fukuda et al. [126] reported TL characteristics and emission spectra of CaB_4O_7 doped with Dy^{3+}, Eu^{2+}, Pb^{2+} and Cu^{+}. These phosphors were developed as sintered pellets. For a heating rate of 20 °C min^{-1}, the TL glow peaks can be roughly grouped into three temperature regions: (I) 75~110 °C, (II) 170~190 °C, and (III) 255~275 °C. Their emission spectra depend on the activator and its valence. The activators release to the luminescence in the following way: Eu^{2+} to 440 nm, Dy^{3+} to 480 and 580 nm, Pb^{2+} to 275 nm, and Cu^{+} to 540 nm, respectively. All the TL glow peaks showed no supra-linearity before they saturated at an exposure of about 2.58 $C.kg^{-1}$ (10^4 R). Peaks appearing at the temperature regions II and III retained memories of irradiation for a storage period of 6 months in the dark at room temperature. However, TL sensitivities of individual phosphors were not reported. Tekin et al. [127] developed sintered pellets of CaB_4O_7:Dy. CaB_4O_7:Dy showed three glow peaks at about 50 °C, 240 °C and 380 °C, the intensity of the 240 °C glow peak being the maximum; TL sensivity of 240 °C TL peak was 8 times higher than that of LiF (TLD-100). There are no other detailed reports on the development and characterization of this phosphor.

Table 6 Comparison of TL characteristics of MgB_4O_7 phosphors prepared by different methods

Phosphor and physical form	Method of preparation	TL intensity relative to LiF:TLD-100	TL emission peak (nm)	Dose response (Region of linearity)
MgB_4O_7:Dy (0.1 mol%) sintered pellets[115]	By sintering at 960 °C. (TL peak at 190-200 °C.)	10-20 (as compared to LiF sintered pellets)	470 & 556	10 µGy to 10 Gy. (25 % fading in 40 d.)
MgB_4O_7:Dy (0.5 mol%) phosphor powder [116]	By sintering at 950 °C for 2h. (Main TL peak at ~ 200 °C.)	1.5	----	1 mGy to 40 Gy for 200 °C TL peak (40 % fading in 17 d.)
MgB_4O_7:Dy/Tm sintered discs [117,118]	Prepared by sintering technique. (TL peak ~210 °C.)	2	i).480 &570 nm for Dy –doped. ii).450 nm for Tm-doped.	~ 10 µGy to 100 Gy. (10 % fading in 60 d.)

MgB_4O_7:Dy*/Tm* sintered discs (with a co-dopant as sensitizer). [118-119]	Prepared by sintering technique. (TL peak ~ 210 °C.)	6-7	i). 480 &570 nm for Dy -doped ii). 450 nm for Tm-doped.	~ 10 μGy to 100 Gy. (10 % fading in 60 d.)
MgB_4O_7:Mn sintered pellets [120]	Prepared by sintering technique. (TL peak ~ 270 °C.)	6	480 & 530	10 μGy to 45 Gy. (Negligible fading in 4 months.)
MgB_4O_7:Dy,Na sintered pellets [121, 122]	Sintered pellets each of size: 4.6 mm dia. and 0.95 mm thickness.	6-7	480 &570	90 μGy to 40 Gy. Minimum detectable dose= 6 μGy. (Fading 8 % in 3 months.)
MgB_4O_7:Dy pellets (Phosphor-impregnated Teflon pellets [123]	Phosphor and Teflon in the wt. ratio 1:2. Pellets of 6 mm dia. and thickness 0.8mm. Sintered at 400 °C for 1.5h.	----	----	2.58x10^{-7}C.kg^{-1} to 1.25x10^{-3} C.kg^{-1} (1mR to 5x10^{3} R)
MgB_4O_7:Cu(0.5%) phosphor powder [124]	Mixture fired at 1200 °C for 4h in an alumina crucible.	1.5 times than that of MgB_4O_7:Mn(0.5%)	-----	1-60 Gy. (Fading 15% in 50 d.)
MgB_4O_7:Gd,Li phosphor powder [125]	Solid state sintering technique.	5 times than that of TLD-100.	550 (Emission is characteristic of the host lattice.)	1 mGy to 10^{3} Gy. (Dosimetric peak at 250 °C.)

4.4 Other Lithium-, Sodium- and Potassium-based Compounds. It has been reported [128-130] that the perovskites (ABX_3, where “A” and “B” are cations and “X” is an anion. The “A” and “B” cations can have a variety of charges) are very interesting hosts for their thermoluminescent properties. Eu- or Ce-doped crystals of $KMgF_3$ (a compound which belongs to the perovskite group) were investigated for their possible application as thermoluminescent dosimeters (TLDs) by Furetta et al. [128]. $KMgF_3$:Eu^{3+} single crystals prepared by Kyropoulos technique showed main TL peak at ~ 613 K. TL sensitivity of these detectors was reported to be 4.4 times than that of LiF:Mg,Ti. TL dose response of these detectors was linear in the range 4 mSv to 1 Sv. Moharil et al. [129] reported that $KMgF_3$:Eu^{3+} phosphor powder, prepared by solid state diffusion at 1075 K, showed main TL peak at 530 K, which had TL sensitivity 0.20 times than that of $CaSO_4$:Dy. The phosphor showed characteristic Eu^{3+} emission at 577, 595 and 617 nm. The phosphor showed linear dose response in the range 0.01 C/kg to 0.2 C/kg. Bacci et al. [130] reported that optical absorption and emission measurements clearly show that, despite doping of the material with Eu^{3+} ions, only Eu^{2+} ions are incorporated in the crystalline samples. Systematic thermoluminescence experiments indicated that the intensity of the glow peak of the Eu-doped phosphor was linearly dependent on the dopant concentration and on the radiation dose. Kitis et al. [131] reported that TL sensitivity of Pb-doped samples is about 10 times higher than that of Ag-doped.

Kitis et al. [132] reported that the TL response of $KMgF_3$:Ce (660 mol%) was 167 times higher than that of LiF:Mg,Ti. Its main glow peak was centred at about 160°C, with TL emission at ~ 360 nm [133]. The material was reported to have very good thermal stability, no fading and had a linear TL response at very low doses. It may be pointed out here that dopant concentrations much higher than 10 mol% would lead to formation of a separate phase in the doped material, thereby distorting the basic characteristic of the host material., as well as leading to concentration quenching of luminescence. Other authors have reported that 660 mol% of Ce^{3+} in the host resulted in the highest TL sensitivity in the phosphor material. However, doping of 660 mol% in $KMgF_3$ would require ~ 1300 g of CeF_3 as against ~120 g for molar wt. of $KMgF_3$ as the host material. Therefore, in such a compound luminescence properties will be dominated by CeF_3 host. Also, Z_{eff} of such a compound will be very high as against 13 of $KMgF_3$. In this context, it may be noted that in another publication [134] by the same group, it was reported that $KMgF_3$:Ce (1.5 mol%) single crystals showed TL sensitivity ~ 90 times than that of LiF:Mg,Ti. These detectors showed linear dose response in range 100 µGy to 10 Gy and 3-4 % fading at the end of a storage period of about 100 h. It is commented that the high sensitivity of $KMgF_3$:Ce made it very useful for medical and environmental radiation dosimetry. The presence of ^{40}K in any sample of $KMgF_3$ produces a β self-irradiation. A possible contribution of self-dose to the external dose can be accurately estimated in specific cases, e.g., during short monitoring periods in environmental dosimetry. The self-dose irradiation should not be a serious problem in other dosimetric applications where high doses have to be monitored as in the case of clinical dosimetry.

Kitis et al. [136] reported that $LiMgF_3$:Ce (2.97 mol%) phosphor powder was about 3 times more sensitive than LiF:Mg,Ti. The phosphor showed linear dose response in the range 2 mGy to 10 Gy and no post-irradiation fading in 20 days. Bernal et al. [137] reported the synthesis of $LiMgF_3$:DyF_3 sintered pellets. Li_3PO_4:Mg,Cu [138] and $NaLi_2PO_{4:}Eu^{3+}$ [139] phosphor powders showed TL sensitivities 1.2 times that of $CaSO_4$:Dy and ~ 0.5 times that of TLD-700H, respectively, whereas $LiCaAlF_6$:Eu^{2+} [140] phosphor powder showed nearly twice that of $CaSO_4$:Dy.

Table 7 Other lithium-, sodium- and potassium-based compounds giving TL

Phosphor and physical form	Method of preparation	TL intensity relative to LiF:TLD-100	TL emission peak (nm)	Linear dose range
$KMgF_3$:Eu^{3+} single crystals [128]	Single crystals by Kyropoulos technique. TL peak at ~ 613 K.	4.4 times that of LiF:Mg,Ti	----	4 mSv to 1 Sv ($Z_{eff.}$ = 13.0)
$KMgF_3$:Eu^{3+} phosphor powder [129]	Solid state diffusion at 1075 K. Main TL peak at 530 K.	20% of $CaSO_4$:Dy.	577, 595 and 617 nm	0.01 to 0.2 C/kg
$KMgF_3$:Pb single crystals [131]	Single crystals by Kyropoulos technique. Main TL peak at ~ 170 °C.	Sensitivity of Pb-doped samples is about 10 times higher than that of Ag-doped.	------	0.2 to 100 Gy.
$KMgF_3$:Ce (660 mol%) phosphor powder [132]	Obtained by the melt of KF and MgF2, in stoichiometric ratio, and the dopant, using Czochralski method in an argon atmosphere.	167 times that of LiF:Mg,Ti	~ 360 nm [133]	MDD = 2.1 µGy. No detectable post-irradiation fading in 15 days.
$KMgF_3$:Ce single crystals [134]	Using the Czochralski method in an argon atmosphere	92 times that of LiF:Mg,Ti (for Ce conc. of 1.5 mol%).	360 nm	100 µGy to 10 Gy. 3-4 % fading at the end of a storage period of about 100 h.
$KMgF_3$:Eu,Ag phosphor powder [135]	Fired at 800 °C for 1h in argon atmosphere. (TL peak around 260 °C)	3	356 nm	-----
$LiMgF_3$:Ce (2.97 mol%) phosphor powder [136]	Melting of the component salts.	3.18 times that of LiF:Mg,Ti		2 mGy to 10 Gy. No post-irradiation fading in 20 d.
$LiMgF_3$:DyF_3 sintered pellets [137]	Thermal treatment at 973 K for 5 h in air.	------	------	Up to doses of 20 Gy.
Li_3PO_4:Mg,Cu phosphor powder [138]	Precipitation method and use of 2 wt.% NH_4Cl flux. Treated at 860 °C	1.2 times that of $CaSO_4$:Dy	370 nm	0.13 mGy to 100 Gy.

	for 1h in air.			
$NaLi_2PO_4$:Eu^{3+} phosphor powder [139]	Solid state diffusion method.	~ 0.5 times that of TLD-700H	-----	Sub-linear up to 10 Gy; linear in the range 10 – 1000 Gy. $Z_{eff.}$ ≈ 10.8. Main TL peak ~ 458 K.
$LiCaAlF_6$:Eu phosphor powder [140]	Co-precipitation and melting the mass in a graphite crucible in air.	Nearly twice that of $CaSO_4$:Dy	375 nm	2.58x10^{-3} to 0.126 C/kg (10 - 488 R).
Li_2BPO_5:Cu$^+$ phosphor powder [141,142]	Wet chemical method and use of NH_4Cl as flux.	7.8 times that of LiF:Mg,Ti	368 nm	1 to 16 Gy. TL peak at ~143 ^{o}C. $Z_{eff.}$ = 10.29.
$LiMgPO_4$:Tb,B phosphor powder [143]	Solid-state diffusion method.	26% of $CaSO_4$:Dy	380, 417,440, 490, 545 and 585 nm.	Recommended as a highly sensitive OSL phosphor having OSL sensitivity 1.3 times than that of Al_2O_3:C.
$LiCaBO_3$:Tm phosphor powder [144]	Solid-state diffusion method.	Sensitivity of 230 and 430 ^{o}C TL peaks is 2.9 and 8.3, resp., than that of TLD-100.	460 nm	230 ^{o}C peak is linear from 20 mGy to 100 Gy. 15% fading per month for 230 ^{o}C peak and 5-10% for 430 ^{o}C peak.
$LiMgBO_3$:Tb phosphor powder [145]	Solid-state diffusion method.	4 times than that of TLD-100.	544 nm	20 mGy to 1 kGy. Main TL peak at 240 ^{o}C. Negligible fading in 2 months.
$NaCaPO_4$:Dy (0.3 mol%) phosphor powder [146]	Combustion synthesis.	1.15 times than that of $CaSO_4$:Dy	482, 576 nm	0.01 Gy to 10 kGy. Main TL peak at 230 ^{o}C. No fading in 5 weeks.
$LiCaPO_4$:Eu^{2+} phosphor powder [147]	Solid-state reaction	4 times than that of TLD-100.	-------	-----------

Recently, Dhoble et al. [141] have published a chapter on “Li-based phosphors for thermoluminescence dosimetry”. A number of Li-based TL phosphors, such as $LiNaSO_4$:Cu, $LiNaSO_4$:Cu, Mg, $LiNaF_2$:Cu, $LiNaF_2$:Cu, Mg, Li_2BPO_5:Cu$^+$ [142], have been synthesized and studied for their possible application in radiation dosimetry. Most of these have been reported to have linear dose response in the range 1-15 Gy. Also, minimum detectable dose (MDD) has not been investigated for these phosphors. Thus, due to very narrow/limited range of study of dose response, it is difficult to comment on the applicability of these phosphors in radiation dosimetry.

$LiCaBO_3$:Tm and $LiMgBO_3$:Tb (Z_{eff} ~ 8) phosphor powders have been prepared by Solid-state diffusion method and their TL sensitivities were reported to be 8 and 4 times, respectively, than that of LiF:TLD-100. Both the phosphors have linear dose response up to 10^3 Gy, negligible storage fading and a simple annealing procedure for reuse [144, 145]. Shinde and Dhoble [146] have reported the preparation and characterization of $NaCaPO_4$:Dy (0.3 mol%) phosphor powder using combustion synthesis method. Its TL sensitivity was reported to be 1.15 times than that of $CaSO_4$:Dy and linear dose response in the dose range 0.01 Gy to 10 kGy. Its main TL peak occurred at ~ 230 ^{o}C and no fading was observed in 5 weeks. More et al. [147] have reported synthesis of $NaCaPO_4$:Eu^{2+} phosphor powder using Solid-state reaction. Its TL sensitivity is reported to be about 4 times than that of TLD-100. The efforts towards development of different Li-based TL phosphors by various groups are summarized in Table 7.

4.5 Orthosilicate-based TL Phosphors. Mg_2SiO_4:Tb is an attractive thermoluminescent material because of its high sensitivity to gamma-rays and chemical stability (Hashizume et al. [29], Prokic and Yukihara [30], Ayyengar et al. [148]). It was first introduced by a Japanese group [29, 149]. The phosphor was subsequently produced on commercial scale and marketed by Kasei Optonix Ltd., Japan. Toryu et al. [149] reported that the gamma radiation sensitivity as well as the gamma: UV response ratio increase with increasing preparation temperature. Samples sintered at 1700 ^oC gave highest TL sensitivity for X- and γ - rays. Lakshmanan and co-workers [150-152] have done detailed characterization of Mg_2SiO_4:Tb TL phosphor powder marketed by Kasei Optonix Ltd., Japan. The phosphor was reported to give very high intrinsic TL sensitivity to ultraviolet (UV) (wavelength 253.7 nm) radiation. The intrinsic TL sensitivity of Mg_2SiO_4:Tb TL phosphor powder to ultraviolet (UV) (wavelength 253.7 nm) radiation was reported [151] to be about 1100 times higher than that of $CaSO_4$:Dy TLD phosphor. Jun and Becker [153] have reported the preparation procedure for Mg_2SiO_4:Tb followed by them. Appropriate amount of MgO, SiO_2 and the dopant was dried and this dried mixture was treated at ~1700 ^oC in alumina or platinum crucible followed by powdering and sieving in a grain size fraction 0.1 – 0.2 mm. TL sensitivity of the phosphor was reported to be 40 times than that of LiF:Mg,Ti (TLD-100). Bhasin et al. [154] reported development of a sensitive Mg_2SiO_4:Tb phosphor powder. Their method involved intimate mixing of MgO and silica gel (in the molar ratio of 2:1), 10 mg atoms Tb per mol. of Mg_2SiO_4. The dried mass was melted in a silica crucible by directly blowing the Burshane-oxygen flame over it (temp. of flame ~ 2750 ^oC). Phosphor powder was separated between 80 and 200 tylor mesh. TL sensitivity of the phosphor was reported to be 79 times than that of LiF:Mg,Ti (TLD-100). Bhasin et al. [154] also reported that the phosphor gave very high intrinsic TL sensitivity to UV (wavelength 253.7 nm) radiation. A freshly prepared Mg_2SiO_4:Tb sample, after annealing at 500^oC, when exposed to a 10 W germicidal Hg lamp at 5 cm induced as much TL as induced by 2000 R of ^{60}Co gamma rays.

Recently, Prokic and Yukihara [30] have reported development of ultra-high TL sensitive Mg_2SiO_4:Tb. Mg_2SiO_4:Tb has been synthesized by sintering technique under the reaction between the stoichiometric amounts of MgO and SiO_2 with the addition of optimal Tb_4O_7 activator concentration of about 12 mg atoms Tb per mole of Mg_2SiO_4. It was sintered for 1h at 1660 °C in air under extremely slow heating rate in an electric furnace. Finally, the polycrystalline phosphor was crushed and sieved in the grain sizes between 75 and 200 μm. After cold pressing of polycrystalline material into pellets of 4mm diameter and 0.8mm or 0.4 mm thickness, they were sintered under the same conditions like during the preparation of the crystalline phosphor. The sintered TLD pellets are opaque and very hard. The phosphor has a simple glow curve with main TL peak at about 210 °C and very low fading. Its TL sensitivity is reported to be 110 times than that of LiF:Mg,Ti (TLD-100), with a detection threshold of 0.5 μGy. Table 8 gives comparison of TL characteristics of Mg_2SiO_4:Tb phosphors prepared by different methods. Nakajima [155] has published a review dealing with different methods of preparation and study of various characteristics of silicate-based TL phosphors.

Table 8 Comparison of TL characteristics of Mg_2SiO_4:Tb phosphors prepared by different methods.

Sr. No	Physical form and method of preparation	Main TL peak (^oC)	TL sensitivity	Dose response (Region of linearity)
1.	Mg_2SiO_4:Tb encapsulated in glass tubes of 2 mm dia. and 10 mm length. Optimum Tb concentration was 10^{-3} g-atom per mol. of Mg_2SiO_4 [29].	~ 200 ^oC	100 times than that of LiF:Mg,Ti.	Linear in the range 0.3 mR to 300 R (Beyond this slight supralinearity up to 10^4 R. Fading less than 3% in 60 d.)
2.	Mg_2SiO_4:Tb phosphor powder. Mixing 6.01 g of finely powdered, analytical grade SiO_2 with 8.06 g MgO and forming paste with a	~180 ^oC	40 times than that of LiF:Mg,Ti.	Linear in the range 2 mrad to 400 rad (Supra-linearity at higher doses, saturation at ≥ 10^6 rad). MDD = 2 mrad and 0.1 mrad with

	solution of 18.3 mg Tb_2O_3 in about 10 cm^3 of a diluted mixture of HCl and HNO_3. The dried mixture was treated at ~1700 ^oC in alumina or platinum crucible followed by powdering and sieving in a grain size fraction 0.1 – 0.2 mm [155].			photon counters. No fading during storage of gamma – irradiated phosphor for 3 months at either room temperature or 30 ^oC.)
3.	Mg_2SiO_4:Tb phosphor powder. MgO and silica gel (in the molar ratio of 2:1), 10 mg atoms Tb per mol. of Mg_2SiO_4. The dried mass was melted in a silica crucible by directly blowing the burshane-oxygen flame over it (temp. of flame ~ 2750 ^oC). Phosphor powder separated between 80 and 200 tylor mesh.	~ 300 ^oC (Other low intensity TL peaks at 50, 90, 170 and 420 ^oC)	79 times than that of LiF:Mg,Ti.	Linear in the range 20 mR to 300 R (Supralinear, about 25%, in the range 300 to $2x10^4$ R. Sublinear after 50,000 R before approaching saturation.
4.	Mg_2SiO_4:Tb sintered pellets of 4 mm dia. and 0.8 or 0.4 mm thickness. By the reaction between the stoichiometric amounts of MgO and SiO_2, with appropriate amount of Tb (12 mg atom Tb per g-mol. of Mg_2SiO_4) and sintering at 1660 ^oC for 1h. For preparing pellets, phosphor grains in the range 75 and 200 µm, were compacted into pellets of dia. 4 mm. They were sintered under the same conditions like during the preparation of polycrystalline phosphor [30].	210 ^oC (Minor TL peaks at 285 and 330 ^oC)	110 times than that of LiF:Mg,Ti.	Linear up to 10 Gy (Supra-linearity, about 20%, at higher doses, saturation at about $5x10^2$ Gy. Minimum detectable dose (MDD)= 0.5 µGy. Fading less than 3% in 3 months.)

4.6 $CaSO_4$:Dy/Tm TL Phosphors. Yamashita et al. [44, 156] reported a simple and an excellent method for preparation of highly sensitive $CaSO_4$:Dy and $CaSO_4$:Tm TL phosphors in 1968. Analytical-reagent-grade $CaSO_4.2H_2O$ and reagent-grade activator material were mixed in a proper ratio and dissolved in sulfuric acid to form saturated solution of $CaSO_4$. The mixed solution was kept at about 300 ^oC by heating so that crystalline samples appeared as the acid evaporated. Samples thus prepared usually consist of shining crystals 1-3 mm long [156]. In order to reduce the variability of phosphor characteristics, from batch to batch, and to increase stability for repeated uses by post-annealing, the virgin crystals were subjected to pre-irradiation annealing treatment at 700 ^oC for 2h. The crystalline sample, mesh size from 100 to 200, was used for studying the dosimetric characteristics of the phosphors. Yamashita et al. [156] reported that of all the 14 rare earths (REs) used for preparation of RE–doped $CaSO_4$ phosphors, $CaSO_4$:Dy and $CaSO_4$:Tm showed the highest sensitivity with essentially a single peak at about 220 ^oC. Emission spectrum of $CaSO_4$:Tm consists of a main sharp peak at 450 nm with minor ones at 360, 470 and 520 nm, and $CaSO_4$:Dy has two main peaks at 480 and 570 nm. It was reported [44, 156] that the dosimetric characteristics of these two phosphors were excellent except for their non-tissue equivalence ($Z_{eff.}$ = 15.3). Minimum detectable exposure was reported to be lower than 200 µR (5.16 10^{-8} C/kg). Dose response was reported to be linear up to 3000 R and supralinear above this exposure level, whereas $CaSO_4$:Tm was linear up to 300 R and supralinear above this exposure level. These two phosphors showed 1-2% fading per month. Subsequently, Ayyangar et al. [148] reported that the TL sensitivities of $CaSO_4$:Dy and $CaSO_4$:Tm prepared by them, following the method suggested by Yamashita et al. [156], were about 38 and 32 times, respectively, than that of LiF:TLD-100.

Several researchers have spent a great amount of efforts improving the TL properties of $CaSO_4$:Dy and $CaSO_4$:Tm phosphors by studying the influence of starting material, particle size, grinding and activator concentration on the shape of the glow curve [157-162].

Lakshmanan et al. [163] have developed a simplified co-precipitation technique for the synthesis of $CaSO_4$:Dy phosphor, which circumvent the cumbersome procedure, used so far, namely, evaporation of (highly corrosive) concentrated H_2SO_4. High TL sensitivity (20% more than the present material), uniform microcrystalline morphology, lower grain size suitable for manufacturing dosemeters in solid form, better glow curve structure, lesser glow peak shift and better linearity and simplified preparation technique make the new phosphor a better alternative. The new recipe of $CaSO_4$:Dy based on co-precipitation technique is not only economical but also compatible for large scale production. This novel method of synthesis of $CaSO_4$:Dy TLD powder is suggested to be suitable for manufacturing teflon discs used in personnel monitoring. Recently, Rivera et al. [164] have also suggested preparation of $CaSO_4$:Dy by precipitation method for gamma radiation dosimetry. Although the method of Yamashita et al. [156] for preparation of Dy - or Tm - doped $CaSO_4$ phosphors is simple, it is not ideal for preparing the phosphor in bulk quanties. The problem basically is of handling and evaporating large quantities of conc. H_2SO_4 which have attendant problems of corrosion and pollution. Also, it was observed that this procedure of open air evaporation of acid gives rise to batch- to- batch variation in TL sensitivity due to contamination by external impurities [165]. Rao et al. [165] devised and standardized a new method which employs distillation of saturated solution, containing required amount of $CaSO_4$ and the dopant, by gradient heating (275-300 ^{o}C) using air as the carrier gas. Nearly 98% of the H_2SO_4 is recovered, of which more than 90% is 35-36 N. It is recycled for manufacturing subsequent batches. The resulting crystalline product is heated and annealed at 700 ^{o}C for 2h to remove any residual traces of H_2SO_4, as well as to stabilize its TL characteristics for repeated uses [166]. The method of Rao et al.[165] is used for commercial production of the $CaSO_4$:Dy phosphor (600 g per batch) by Renentech Laboratories Pvt. Ltd., Mumbai, India.

Azorin and Gutierrez [167] also used a somewhat similar method for laboratory scale preparation of $CaSO_4$:Dy/Tm TL phosphors. Required amounts of $Ca(NO_3)_2.4H_2O$ and the dopant were dissolved in conc. H_2SO_4 in a flask which is connected to a sealed condenser system with constant air flow as carrier for the acid vapour. A beaker containing a NaOH solution captures and neutralizes the condensed acid. A hot plate is used to provide the heat required to drive the reaction, while the temperature is monitored by chromel-alumel thermocouple. Crystallization can be controlled by varying the temperature and air flow rate. After an evaporation period of about 12 h, single crystals of $CaSO_4$ are obtained whose dimensions depend on the starting materials and on the type and concentration of dopants. M. Prokic [28, 117] has developed new sintered thermoluminescent dosimeters for personnel and environmental dosimetry. Efforts to develop highly sensitive sulphate-based TL phosphors by various researchers have been summarized in Table 9. However, they have not been fully characterized to assess their performance for personnel and environmental dosimetry.

Table 9 Comparison of sensitivities of sulphate-based TL phosphors for radiation dosimetry.

Sr. No.	Phosphor	TL sensitivity relative to $CaSO_4$:Dy
1.	$CaSO_4$:Tm, Mo	2.5 [168]
2.	$CaSO_4$:Dy, P	1.5 [169]
3.	$CaSO_4$:Dy, Ag	1.2 [170]
3.	$CaSO_4$:Dy,Zn	1.47 [171]
4.	$K_3Na(SO_4)_2$:Eu	3.0 [172]
5.	$K_2Ca_2(SO_4)_3$:Eu	5.0 [173]
6.	$NaMgSO_4F$:Ce	1.0 [174]
7.	$NaMgSO_4Cl$: Cu	5.59 [175]
8.	$NaMgSO_4Cl$: Ce	6.18 [175]
9.	$NaMgSO_4F:Eu^{3+}$	4.79 [176]
10.	$Na_3SO_4F:Eu^{3+}$	17.5 [176]

4.7 Calcium Fluoride (CaF_2). Calcium fluoride exists in nature as fluorite mineral. Its TL properties were studied by many investigators (McKeever, [18], McKeever et al., [19], Portal [177]). TL glow curve of natural CaF_2 exhibits several peaks with a predominant and stable peak at ~ 250 °C; the lower temperature peaks are rather unstable. Although the use of this material for radiation dosimetry has been largely discontinued in many countries, in the past, increasing interest in the fluorite had been due to its high sensitivity, abundance in nature and low production cost. Synthetic CaF_2 activated with manganese (CaF_2:Mn) was developed and studied by Ginther and co-workers in 1950s. CaF_2:Mn (3 mol%) is prepared by co-precipitation of CaF_2 and MnF_2 from the solution of $CaCl_2$ and $MnCl_2$ in ammonium fluoride. The precipitate is dried and heated in a neutral atmosphere oven at 1200 °C, ground and sieved in the grain size range 80 to 200 mesh. It is marketed by Harshaw under the trade name TLD-400. It is about 5 times more sensitive than LiF:TLD-100 and has wide dynamic linear dose response – 1 mrad to $2x10^5$ rads, saturation occurs at 10^6 rads. One of the largest users of CaF_2:Mn-based dosimeter (bulb type design based on a single CaF_2:Mn element) has been US Navy since 1975. Recently, it has been reported that CaF_2:Mn-based dosimeter has been replaced by LiF:Mg,Cu,P-based four element Harshaw TLD badge due to better dosimetric characteristics of LiF:Mg,Cu,P [94]. Dy-activated calcium fluoride (CaF_2:Dy) is more sensitive than CaF_2:Mn. Its TL characteristics were studied by Binder and Cameron [178]. It is marketed by Harshaw under the trade name TLD-200. The TL glow curve consists of six peaks which are difficult to separate. Among these peaks, those at 120 and 140 °C exhibit high fading, whereas the peaks at 200 and 250 °C are stable and dosimetrically relevant. The phosphor shows 25% fading per month. A post-irradiation treatment at 115 °C for 10 min removes the fading effect considerably. CaF_2:Dy serves mostly for measurement of low doses for environmental monitoring applications. Tm-doped calcium fluoride (CaF_2:Tm) has been developed and characterized by Lucas and Capser [179]. 0.35 mol% of Tm gives optimum response and desirable characteristics. Its glow curve shows two prominent peaks at 150 (peak 3) and 250 °C (peak 5), the latter peak has supralinear response, whereas the former does not show supralinearity. This material is marketed by Harshaw under the trade name TLS-300. It has been reported [180, 181] that the high temperature (250 °C) glow peak in CaF_2:Tm (TLD-300) gives higher relative TL efficiency for HCP irradiations as compared to the low temperature (150 °C) glow peak. This difference in LET dependence of the two peaks (using ratio method) has been used to obtain from one single TLD detector, exposed to HCPs, dose and the radiation quality (Hoffmann et al. [182], Pradhan et al. [183], Lakshmanan et al. [184]). Prokert and Sommer [185] studied the dosimetric chacteristics of a new hypersensitive TL phosphor, CaF_2:Cu, prepared at the Moscow State University. However, studies by the authors indicated that Ho was the dominant impurity in the phosphor and that copper may be present as a co-dopant. The dose characteristic showed a linear dose response in the range between 10^{-6} and 10 Gy and the TL sensitivity was found to be 160 times higher than that of LiF-TLD-100. This high sensitivity was projected for potential phosphor to permit precise low dose measurements after short irradiation periods. Furthermore, the high thermal, chemical and mechanical stability were expected to enable multiple uses of the detectors.

4.8 Al_2O_3 - based TL Phosphors. The history of aluminium oxide (Al_2O_3) as a radiation dosimeter dates back to the 1950s, when a large number of materials, incuding Al_2O_3, were investigated to determine their TL properties. Aluminium oxide (alumina) is found in natural mineral form as sapphire and ruby. It may be synthetically produced as either γ- alumina or α-alumina (also known as corundum). Several research groups have tried to synthesize Al_2O_3 doped with different types of dopants, and tested their suitability in radiation dosimetry. However, the development of C-doped introduction of Al_2O_3 TL and optically stimulated luminescence (OSL) phosphor was an important landmark in the field of luminescence dosimetry. Table 10 gives Comparison of TL characteristics of Al_2O_3 - based phosphors prepared by different methods.

Al_2O_3:C crystals are grown from the melt (at 2050 °C). The grown samples are usually in the form of long, single crystal rods, which are then cut to size, normally 5 mm diameter single crystal discs, 1mm thick. Corundum grown by the Verneuil method is used as the raw material. After growth, the material is given a one-time anneal at 950 °C for 30 minutes to remove any charge from deep traps. The crystal growth is performed in a highly reducing atmosphere in the presence of graphite. The end result is a high quality, single crystal of α-Al_2O_3 doped with 100-5000 ppm of carbon. The purpose of the highly reducing atmosphere when growing TLD quality material is to induce into the samples large concentrations of oxygen vacancies (F and F^+ centres) by a process known as subtractive coloration. These centres play an integral part in the TL and OSL process. The OSL of this phosphor is also utilized for personnel dosimetry. The α-Al_2O_3:C single crystals (5mm diameter, 1 mm thick) may be obtained from the Urals Polytechnical Institute, Russia, Thermo Fisher Scientific (Harshaw), USA (sold as TLD-500K), Rexon TLD Systems, Inc., USA, and some other commercial suppliers. The α-Al_2O_3:C phosphor powder and single crystals, both being OSL grade materials, are available from Landauer Inc., USA.

Table 10 Comparison of TL characteristics of Al_2O_3 - based phosphors prepared by different methods.

Sr. No.	Physical form and method of preparation	Main TL peak (°C)	TL sensitivity	TL emission (nm)	Dose response (Region of linearity)
1.	Al_2O_3:Si,Ti (300, 100 ppm) phosphor powder. Prepard by sintering in air by flame treatment (To about 2000 °C).[186]	250 °C (Main TL peak).	5 times that of LiF:TLD-100	420 nm	250 °C peak saturates at $3x10^2$ Gy. Minimum detectable dose = a few tens of μGy.
2.	Al_2O_3:Mg,Y sintered pellets (8 mm diameter x 1 mm thickness). Cold pressed pellets containing appropriate amounts of Mg and Y were sintered at 1600 °C in air. [187]	An intense dosimetric peak at ~ 280 °C, with a low intensity shoulder at ~ 190 °C at a heating rate of $10^oC.s^{-1}$.	-------	440 nm, weak emission at 695 nm.	0.1 mGy to kGy.
3.	Al_2O_3: Na, Ti (0.7, 4.0 mol%).[177,188]	265 °C (Main TL peak), 435, 635 °C.	Comparable to LiF:TLD-100.	550, 390 nm.	5x 10^{-2} to 10 Gy. Saturation at 10^3 Gy.
4.	$A1_2O_3$:Cr, Ni single crystals (10 **x** 10 **x** 1 mm^3). Grown by the Verneuil method. [189]	330 °C.	150 times higher than TLD-100.	695 nm.	TL sensitivity comparison was done at an X-ray dose > 10 Gy.
5.	α-Al_2O_3:C single crystals (5 mm dia. x 1 mm thickness). Using subtractive colouration technique.[26]	A single glow peak at 460 K	50 times higher than that of LiF:Mg,Ti.	420 nm	Negligible fading
6.	Al_2O_3 single crystals. Grown by Czochralski method. [190].	Five TL peaks in the range 90 to 400°C.	-----	-------	350 °C TL peak in Al_2O_3:Si, had been shown to exhibit a useful response from 0.1 kGy to at least 10 kGy.

Two typical TL glow curves for Al_2O_3:C and $CaSO_4$:Dy phosphors are given in Figs. 2 and 3.

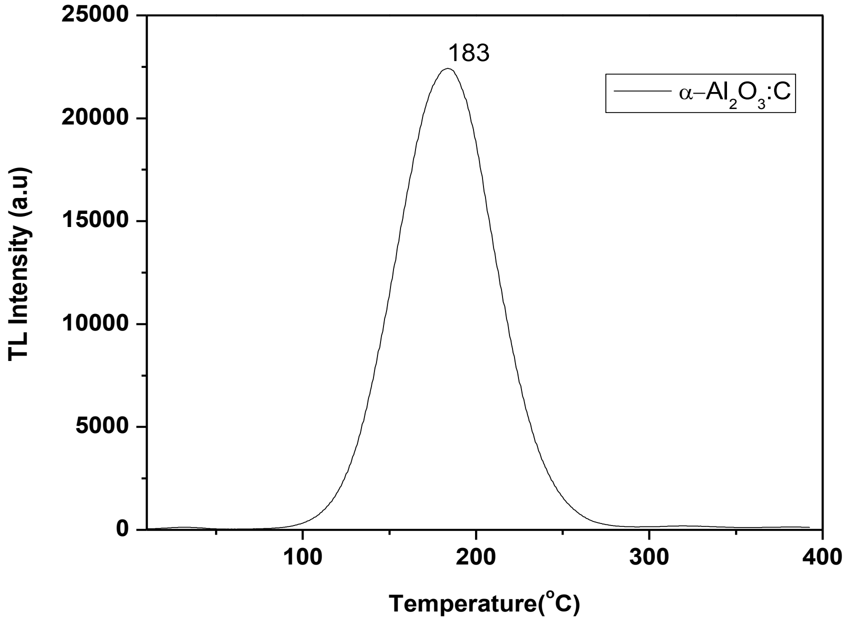

Fig. 2 Typical TL glow curve of Al_2O_3:C phosphor

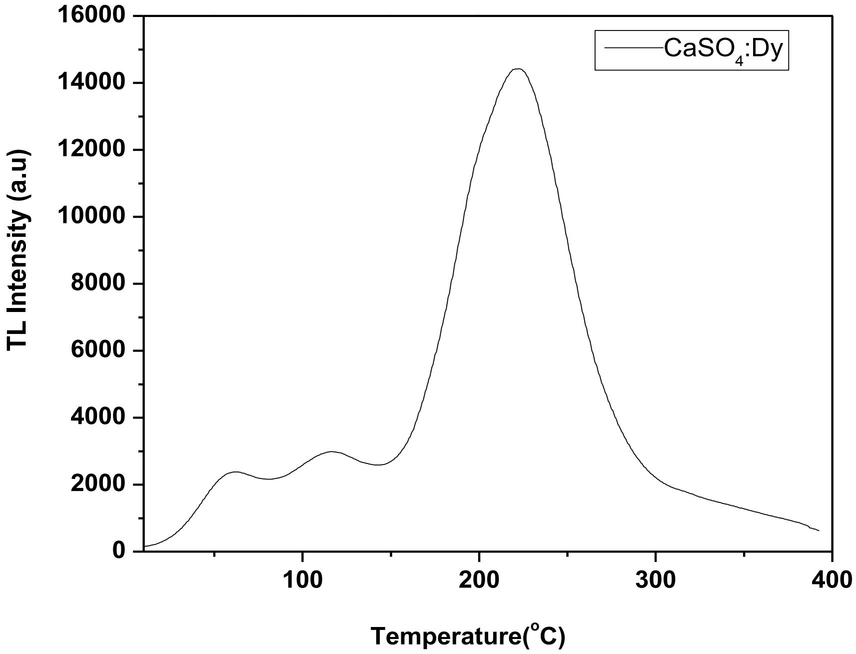

Fig. 3 Typical TL glow curve of $CaSO_4$:Dy phosphor

4.9 BeO-based TL Phosphor. Beryllium oxide (BeO) is a material with a long history in TL dosimetry. Special interest in BeO as a potential material for personnel dosimetry is determined by its low effective atomic number (Z_{eff} =7.13), which is very close to that of the biological tissue (Z_{eff} =7.42). Some of the TL properties of BeO have been reported in literature [19, 177, 191-193]. BeO in powder form is extremely toxic, leading to a condition known as *berylliosis*. Therefore, only specially equipped laboratories can use/handle it in powder form. Sintered pellets (prepared by sintering at a temperature ~ 1500 °C) are also available which are used as transistor bases in the electronic industry. In this ceramic form, material presents no danger as long as abrasion of the surfaces and therefore production of powder and dust is avoided [19, 177]. Out of all the BeO ceramics manufactured, Crase and Gammage [192] identified BeO Thermalox^{TM} 995 as the most suitable for TL dosimetry. Dose response curve of the main dosimetric peak (220 °C) of BeO (Thermalox^{TM} 995) is linear-supralinear-sublinear. The linear region extends from approximately 10 mR up to 100 R where it becomes supralinear. The curve starts to saturate at exposure levels of ~ 10^4 R. Sensitivity of BeO is comparable to that of LiF:Mg,Ti [177]. TL emission spectrum of BeO Thermalox^{TM} 995 consists of a main emission at ~ 335 nm. As per Busuoli et al. [194], a two-element dosimeter using BeO (Thermalox 995) discs, 4 mm in diameter, had been developed and the dosimetric characteristics of the TL dosimeter were reported. Investigations carried out during the last decade [195] have shown that in the optically stimulated luminescence (OSL) mode, BeO has higher sensitivity than in the TL mode.

4.10 $BaSO_4$:Eu TL Phosphor. Eu^{2+} - doped phosphors have been investigated for their TL and OSL response. This is possibly due to the allowed nature of $4f^6 5d \rightarrow 4f^7$ transition on Eu^{2+} ion. Also, the emission spectra of Eu^{2+} doped phosphors lie in the peaking region of the response of commonly available photomultiplier tubes (PMTs). Therefore, Eu^{2+}-doped phosphors yield good PL and TL. Okamoto et al. [196] reported the development of $BaSO_4:Eu^{2+}$ TL phosphor and phosphor embedded Teflon TL sheets for study of hadronic and electromagnetic cascade showers in ultrahigh energy interactions. The $BaSO_4:Eu^{2+}$ (Japan) Teflon TL sheet was reported as an effective detector because of its high sensitivity for detection of cascade showers (around 1 TeV), high position resolution of about 50 µm, wide dynamic dose range and little thermal fading of stored TL signal. TL sensitivity of $BaSO_4$:Eu embedded Teflon disc was reported to be ~ 4-6 times that of $CaSO_4$:Dy embedded Teflon discs [197,198]. Annalakshmi et al. [199] reported the preparation of $BaSO_4$:Eu by solid-state reaction in different reducing atmospheres. The TL glow curve of $BaSO_4:Eu^{2+}$ showed only a single peak at 513 K unlike other phosphors and the TL intensity is about three to four times higher than that of $CaSO_4$:Dy. The TL dose response of the phosphor was found to be linear up to the dose range of 10^3 Gy beyond which saturation sets in. Although $BaSO_4$:Eu is not a tissue equivalent material, due to its good TL and OSL sensitivity and wide dynamic range, it can be used for relative dose measurements for applications in radiation dosimetry. Also, its high sensitivity can be used for imaging applications similar to that of $CaSO_4$:Dy and LiF:Mg,Cu,P in TL mode, and of BaFBr:Eu in PSL/OSL mode.

4.11 TL of Nanophosphors. Thermoluminescence (TL) of phosphor materials is successfully used for personnel and environmental monitoring, retrospective dosimetry, as well as for medical physics applications. Commercial TL dosimetry systems providing high sensitivity and low fading have been designed on the basis of these materials and put to successful operation. However, the dose range of these traditional phosphors is normally not over 100 Gy, while higher doses need to be measured in technological and medical applications (e.g. sterilization of medical products, irradiation of food products, etc.). In this connection, various nanophosphors have been synthesized and studied for their possible application in radiation dosimetry. Nanophosphors present a type of phosphors consisting of particles 10-100 nm in size, which include nanopowders, pressed compacts, nanoceramics, thin films on substrates, nanopowder coatings of different thickness, etc. [200].

Nanophosphors, such as $CaSO_4$:Dy and $BaSO_4$:Eu, were prepared by Salah and Sahare coworkers [201-205] who studied their TL characteristics with the objective of their application in radiation dosimetry. TL sensitivity of nanocrystalline phosphors, at low doses, was found to be much less than that of their bulk analogues. But the dose vs. TL response of these nanophosphors did not saturate up to the studied dose of 5 – 20 kGy. Most of these nanophosphors were prepared by chemical co-precipitation method. It is reported that TL glow curves of the nanophosphors show multiple peaks compared to their bulk analogues, and TL maxima of the dosimetry peak appear shifted relative to the main dosimetric peak in polycrystalline phosphors. Nanophosphors of LiF:Mg,Cu,P and $Ba_{0.97}Ca_{0.03}SO_4$:Eu may be useful for dosimetry of high LET beams [204, 205].

For nanoparticles, increase in surface to volume ratio would lead to formation of high concentration of surface defects, including F-type surface centres. The appearance of multiple peaks in nanophosphors has also been related to high concentration of surface trapping centres/defects. Specific causes of low luminescence efficiency are not known. For nanophosphors, after gamma or beta irradiation, spontaneous recombination losses may occur, which result in less storage in terms of trapping in metastable states. This could be one of the reasons for observing less intense TL peak in nanophosphors than in their bulk analogues at relatively low doses. Increase in surface defects may lead to increase in non-luminescent relaxation processes. Kortov [200] explained the higher radiation resistance of nanophosphors (which is also the reason for extended dose response) as due to efficient sinking and annihilation of defects at nano-grain boundaries; as a result, accumulation of defects in nanomaterial is retarded. Jacobsohn et al. [206] showed that degree of crystallinity and the presence of impurities, including OH^- groups, are detrimental to luminescence efficiency in nanophosphors. In this context, it is interesting to note that nanosheets of $CaSO_4$:Mn and $CaSO_4$:Ce, having an average thickness of 35 nm, synthesized by hydrothermal method [207, 208], gave TL sensitivity 8-10 times higher than that of LiF:Mg,Cu,P(GR-200) commercial phosphor hot-pressed chips (about 200 times that of LiF:Mg,Ti(TLD-100)). $CaSO_4$:Mn nanocrystalline phosphor gave three TL peaks at 485, 504 and 526 K, compared to a prominent TL peak at about 373K in polycrystalline phosphor. Its dose response was linear up to 7 Gy, before leading to saturation at higher doses. This indicates that the method of synthesis used plays an important role in determining the characteristics of nanophosphor. The authors have recommended these two highly sensitive phosphors for environmental monitoring. In this context, it may be mentioned here that LiF:Mg,Cu,P(GR-200) gives wide dynamic dose response in the range 1 μGy to 10 Gy, its minimum detectable dose was reported to be 60 nGy to 1 μGy. Unfortunately, the dose response of the new $CaSO_4$:Mn nanocrystalline phosphor was given in Gy level. Also, minimum detectable dose was not reported for the developed phosphors. Thus, it is difficult to assess applicability of these highly sensitive phosphors for environmental monitoring.

Soft tissue equivalence (Z_{eff} =7.4) of diamond (Z=6) and its chemical stability make it an attractive material for dosimetry, particularly for medical applications. Chemical vapour deposited (CVD) polycrystalline diamond films exhibited a prominent TL peak at about 280 ^{o}C with linear dose response up to 20 Gy [209]. However, the synthesis process and growth conditions can strongly influence the TL signal in CVD diamond. Recently, nano-diamond films grown from Tequila using pulsed-liquid injection chemical vapour deposition (PLICVD) technique has been reported to be promising for the high-dose dosimetry [210]. Nano-diamond thin films show TL glow curve with peaks at 170 and 350 ^{o}C. The dose response of these films was reported to be linear in the dose range 100 to 1600 Gy. However, direct comparison of TL sensitivities of CVD polycrystalline diamond and nano-diamond films is not readily available in the published literature. Thus, nanophosphors could find many potential applications in the field of radiation dosimetry, such as low-energy beta dosimetry, high-LET dosimetry, and high-dose dosimetry for technological applications.

4.12 Phosphors based on Other Luminescence Techniques. In the last two decades an alternative technique, optically stimulated luminescence (OSL), has been developed, as the optical nature of the readout process does not involve problems of blackbody radiation and thermal quenching. Due to this and some other advantages, OSL is also being used for various applications in radiation dosimetry, such as personnel and environmental dosimetry, retrospective/accident dosimetry and medical dosimetry. The development of Al_2O_3:C TL/OSL phosphor by Akselrod et al. [26] and later investigation of its suitability for personnel dosimetry using pulsed OSL (POSL) technique of stimulation by Akselrod and McKeever [211], resulted in the development of a personnel dosimetry system based on Al_2O_3:C OSL phosphor. Applications of OSL phosphors in different fields have been highlighted in a number of publications [212-214]. Although radio-photoluminescence (RPL) dosimeters were developed in parallel with TLD systems during 1960s, but high pre-dose and photon energy dependent detector material prevented major breakthrough of the glass dosimetry. However, in mid 1980s, introduction of readout systems using a pulsed UV stimulation, in place of conventional mercury UV lamps, helped in reducing pre-dose by a factor of 100 (from mSv to a few µSv) [215]. This development resulted in the manufacture of improved RPL glass dosimeters and fully automatic RPL reader systems capable of measuring doses in the range 10µSv to 10Sv. Applications of RPL glass dosimeters have been highlighted in a number of publications [216, 217]. Advantages and disadvantages of TL and OSL techniques have been given by McKeever and Moscovitch [218], and Olko [219]. Recently, Bhatt [220] has given comparative advantages of TL, OSL and RPL dosimeters.

5. Important Areas of Radiation Dosimetry

- Personnel monitoring
- Environmental dosimetry
- Neutron dosimetry
- Dosimetry in medical applications of radiation
- Retrospective dosimetry
- High dose dosimetry
- Space dosimetry

5.1 Personnel Monitoring. The primary objective of personnel monitoring/individual monitoring is the measurement or assessment of radiation dose delivered to personnel during their occupational exposure (ICRP-60, 1991) [221]. Examples include workers in nuclear industry, hospital radiotherapy technicians, workers in industrial radiography and high intensity gamma irradiators, etc. In addition, the objectives of personnel monitoring for external exposures include the following objectives [221, 222]:

1. It is intended to provide information on the external radiation exposure of individuals working with radioactive materials and/or radiation producing devices;
2. Personnel monitoring results provide information on routine exposures, assist in work planning, allow control of the workplace, and provide exposure information in accident situations;
3. By means of such monitoring it is hoped to limit the exposure of such personnel to within prescribed limits, which are based on recommendation of international and national bodies;
4. Assessment of effective dose and, if appropriate, equivalent doses for compliance purposes;
5. In addition, these results assist those responsible for radiation safety in keeping exposures as low as reasonably achievable (ALARA).

As per UNSCEAR 2008 Report [223, 224], about 10 million workers are exposed to radiation from artificial sources, which include medical uses sector, nuclear fuel cycle, industrial uses, miscellaneous uses and military activities. External monitoring of these radiation workers is carried out using personnel dosimetry badges, which include thermoluminescent dosimeters (TLDs), optically stimulated luminescent dosimeters (OSLDs), radiophotoluminescent dosimeters (RPLDs), and film badges [225]. These personnel dosimeters should comply with IEC requirements for "passive integrating dosimetry systems for personal and environmental monitoring" [226, 227]. Due to non-reliability of photographic film for long-term stability of stored information, particularly in tropical climates, this method of personnel dosimetry has nearly phased out and being replaced by TL, OSL and RPL methods of personnel dosimetry.

5.2 Environmental Dosimetry. In the last two decades regulatory authorities in many countries have become more acutely aware of the increasing concern demonstrated by the public with regard to the potential environmental impact of "man-made" radiation exposure such as: (i) controlled releases of gaseous radionuclides from nuclear power stations during day-to-day operations, (ii) low-level waste disposal, (iii) nuclear fuels reprocessing, (iv) incidents of nuclear power station accidents, and (v) activities connected with nuclear power industry. In many countries, TLD systems are in place near nuclear installations for the purpose of monitoring pre-operational levels (background levels) as well as levels above the natural background, which can be linked with the operation of these facilities. Important requirements of TLD materials are: (i) Tissue equivalence is not an issue, (ii) since exposure levels are low, long exposure times are required, and long-term stability becomes vitally important, along with high sensitivity, and (iii) gamma emitters are the main radiation sources of interest. Detection threshold or minimum detectable dose of ~ 10 μGy is expected for environmental monitoring [226, 227].

A number of phosphors, such as $CaSO_4$:Dy, $CaSO_4$:Tm, CaF_2:Dy (TLD-200), and LiF:Mg,Cu,P are quite suitable for this purpose. In India, natural CaF_2 filled in 1.5 mm thick brass capsules are used for environmental monitoring for determining pre-operational levels in and around the site of nuclear power stations and subsequently, periodically, after commissioning of the power stations. Performance of these dosimeters for their use in environmental monitoring has been assessed during a series of inter-comparison experiments for environmental dosimetry; their performance was very good [228, 229]. Recently, BARC developed an automated PC based TLD reader system by modifying the existing personnel monitoring card dosimeter from three-element to two-element $CaSO_4$:Dy embedded Teflon TLD disc (each disc covered with 1 mm thick copper filter) for the environmental gamma monitoring [230].

5.3 Neutron Dosimetry. Fast neutrons are of great interest and importance to radiobiologists and medical and health physicists as they have much larger biological effectiveness as compared to X- and gamma rays; and personnel are more often exposed to significant doses from fast neutrons than they are from thermal neutrons. TL dosimeters are being used for the detection of X-, gamma and beta radiations, and these methods are well established, reliable and quite accurate. However, direct fast-neutron response of TL and other luminescent materials is very small because of poor cross-section of the constituent elements to most of the nuclear reactions at high neutron energies. Al_2O_3:C has neutron sensitivity lower than ^{7}LiF:Mg,Ti (TLD-700) [231]. Thus measurement of dose due to fast neutrons remains one of the challenging tasks in luminescence radiation dosimetry. TL phosphors have been tried for fast neutron dose measurements by:

i) Irradiating them in contact with hydrogen-rich organic materials used as proton radiators [232];
ii) Activation of some of the constituent elements of the material using threshold nuclear reactions;
iii) Use of high LET sensitive TL peaks (e.g. 250 °C TL peak in CaF_2: Tm) [183]; and
iv) Use of Albedo technique.

The most commonly used TLD technique for personnel monitoring in neutron fields, however, is *albedo* dosimetry. Fast neutrons are moderated and backscattered from the body. These scattered thermal neutrons are detected by thermal neutron sensitive TL detectors. By using a pair of TLDs, one having sensitivity to both thermal neutron and gamma rays (e.g., ^{6}LiF) and other having sensitivity only to gamma rays (e.g., ^{7}LiF), the net dose due to neutrons (thermal, intermediate and fast) can be estimated together with gamma ray component. Highly sensitive TL or OSL materials could be made neutron sensitive (by mixing with enriched ^{6}LiF powder) and other component neutron insensitive (i.e. without mixing with ^{6}LiF powder). Yukihara et al. [233] demonstrated the possibility of producing neutron sensitive OSL dosimeters using a mixture of Al_2O_3:C and ^{6}LiF or $^6Li_2CO_3$ neutron converters.

5.4 Dosimetry in Medical Applications of Radiation. One of the important applications of TL and OSL dosimetry has been in the field of medical physics for their application in radio-diagnosis, nuclear medicine and radiotherapy. Thermoluminescent dosimeters (TLDs) have become popular in these fields due to their high sensitivity, miniature size, tissue equivalence, high stability to environmental conditions, low TL fading, reusability, linear dose response and sufficient precision and accuracy. Integrating mode of TL phosphors, such as LiF:Mg,Ti, LiF:Mg,Cu,P, Al_2O_3:C, has been widely used for clinical dosimetric measurements, e.g., central axis depth-dose curves, in-phantom measurements, in-vivo dosimetry, surface doses, quality assuarance, etc., of high energy photon and electron beams [234]). Applications of OSL phosphors in medical dosimetry are described by Akselrod and McKeever [212], Pradhan [235], and Yukihara and McKeever [214].

5.5 Retrospective Dosimetry. In situations where no direct radiation monitoring data are available, luminescence dose reconstruction obtained using material from the immediate environment of population or from the persons in the vicinity of the incident/accident can be used to validate values obtained from computational techniques. TL technique has been successfully employed in dose evaluation in Hiroshima and Nagasaki Atomic bomb explosion sites in Japan, radioactive fallout of nuclear tests at Nevada test sites in USA, and radioactive fallout from the Chernobyl nuclear reactor accident. The OSL technique has also been applied to retrospective dosimetry using environmental materials from the Chernobyl accident area [236].

OSL properties of memory chip modules (from telephone, ID and credit cards), ceramic resistors from mobile phones and other electronic components from personal electronic devices have shown interesting and promising results for their use in accident dosimetry [237-239]. Recently, the European Radiation Dosimetry Group10 on Retrospective Dosimetry has published a “Review of Retrospective Dosimetry Techniques for External Ionizing Radiation Exposures” [240].

5.6 High Dose Dosimetry. Since, dose vs TL response of all commonly known TL phosphors saturates at about 10^3 Gy, dose response of high temperature TL peak (400°C) as well as photo-transferred TL (PTTL) response of the dosimetry peak (230°C) in $CaSO_4$:Dy and $CaSO_4$:Tm has been investigated [241, 242] for high dose dosimetry in the range $10^2 – 10^6$ Gy. Fig. 4(a) shows the dose response of dosimetry (250 °C) and RTL peaks occurring at 400 and 485 °C, as well as PTTL response at the dosimetry peak in $CaSO_4$:Dy [243]. The dose response of high temperature peak (~400°C) saturates above a gamma ray dose of 1.2×10^6 Gy, whereas PTTL response of 230°C peak saturates at a γ-dose of 5×10^5 Gy. Fig. 4(b) shows relative intensity of PTTL peak (250 °C) as function of UV (254 nm) exposure duration.

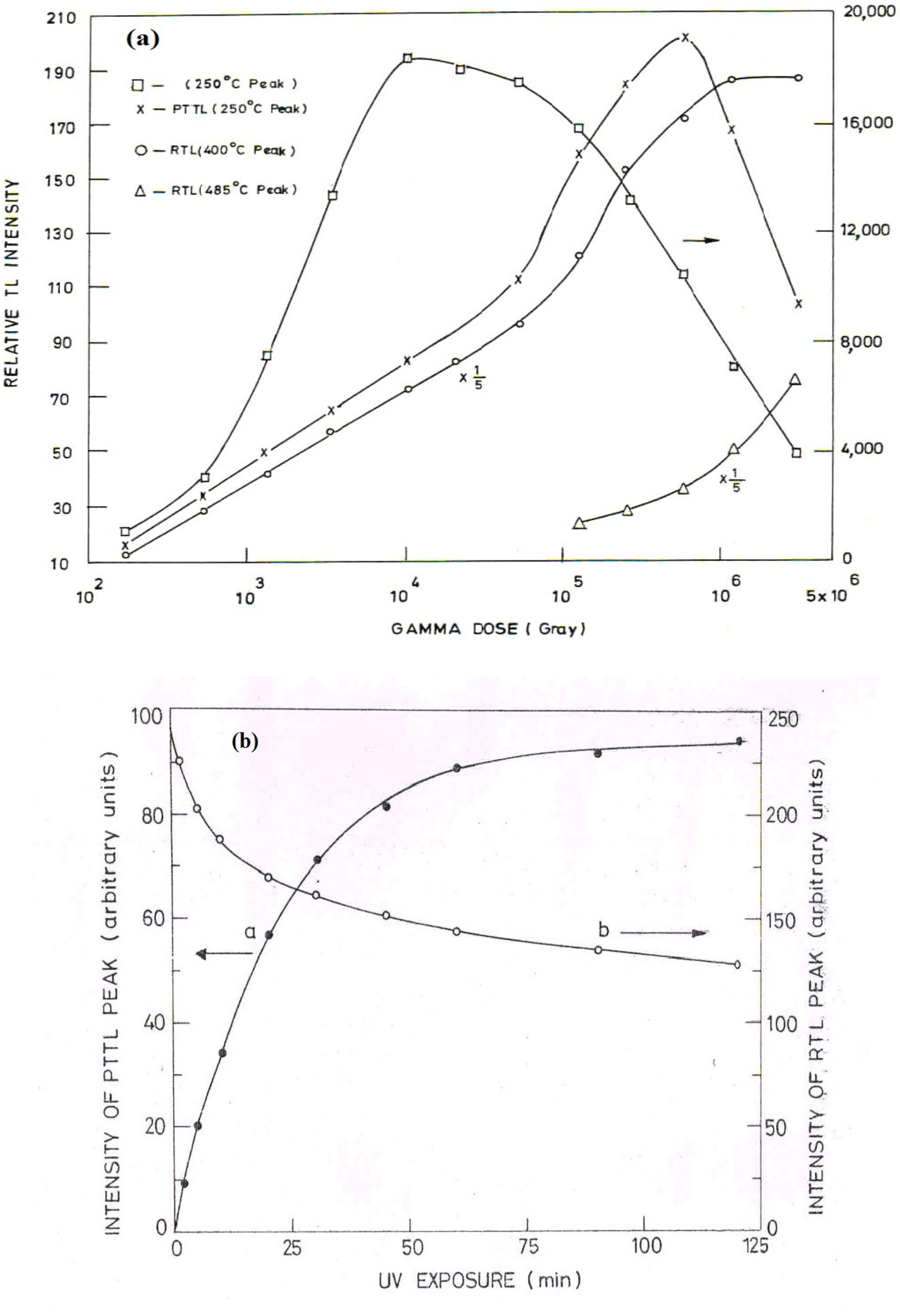

Fig. 4 (a) Dose versus TL response of dosimerty (250 °C) and RTL peaks occurring at 400 and 485 °C, as well as PTTL response at the dosimetry peak in $CaSO_4$:Dy. (b) Relative intensity of PTTL peak (250 °C) as function of UV (254 nm) exposure duration (adopted from Ref. [243]).

Obryk et al. [244] report that on the basis of the newly discovered behaviour of LiF:Mg,Cu,P detectors at high and ultra-high doses, a new method of thermoluminescence (TL) measurement of radiation doses ranging from micro-Grays up to a mega-Grays has been recently developed at the Institute of Nuclear Physics, Warsaw (Poland). The method is based on the relationship between the TL signal, integrated in the given temperature range and dose. It is quantified by a parameter called the 'ultra-high temperature ratio'. It has been demonstrated that this new method can measure radiation doses in the range of about 1 μGy to 1 MGy, using a single LiF:Mg,Cu,P detector. This method was recently successfully blindly tested for 10 MeV electrons up to doses of 200 kGy. It can be used for dosimetry in high-energy accelerators, especially in the Large Hadron Collider at CERN, and has great potential for accident dosimetry in particular.

Recently, Kortov et al. [245] have described advantages and challenges of high-dose thermoluminescent detectors. High-dose luminescent dosimetry is high-temperature one in the majority of cases. It employs TL peaks from deep traps present in the detector material or brought about by high-dose irradiation. Using TL deep traps in Al_2O_3:C, it is possible to measure the absorbed dose up to 100 kGy. Heating (900 ^{o}C, 1 h) of highly irradiated TLD-500 detectors restore their initial properties. Kortov et al. [240] have commented that the thermally assisted- OSL (TA-OSL) method, recently suggested by Soni et al. [246] in Al_2O_3:C, is an excellent advancement of high-dose luminescent dosimetry with involvement of deep traps.

5.7 Space Dosimetry. The radiation environment in space is a complex mix of charged particles: medium and high-energy protons, electrons, alpha particles and high-energy heavy ions, over wide energy ranges and with varying fluxes [247]. Astronauts working in Low Earth Orbit (LEO) are exposed to a radiation level, which is about 100 times higher than the natural radiation level on Earth and will be further increased for travels to Mars. Due to the variety of routine space crew activities on the International Space Station (ISS) and the Space Shuttle, there is a need to monitor the individual radiation exposures of the crew members for reliable estimation of radiation risk to them. TL and OSL detectors have good efficiency for LET of radiation < 10 keV/μm, with decreasing efficiency, although non-zero, for higher LET (> 10 keV/μm) radiation [214, 248, 249]. Therefore, no single dosimeter will provide absorbed dose estimates across the full LET spectrum of space radiation. Thus, combinations of dosimeters are required to estimate the dose equivalent due to space radiation. Currently, this is performed using passive detectors such as thermoluminescent detectors (TLDs) or optically stimulated luminescence dosimeters (OSLDs) and plastic nuclear track detectors (PNTDs). However, suitable correction needs to be applied for the response of TLDs or OSLDs for LET > 10 keV/μm.

6. Summary

This review discusses in detail the role of ‘Thermoluminescent Phosphors’ in the field of Radiation Dosimetry. Synthesis of TLD materials, to be used as phosphors, for example, Lithium Fluoride (LiF:Mg,Ti, and LiF: Mg,Cu,P), Lithium Tetraborate, Magnesium Borate, Calcium Fluoride (CaF_2), $CaSO_4$:Dy/Tm, $BaSO_4$:Eu, Magnesium Orthosilicate-based, Al_2O_3 – based, BeO-based TL Phosphors, and their characterization constitutes the core of this review. A good number of highly sensitive and near-tissue equivalent TL phosphor materials have been developed, characterized and recommended for dosimetric use by various researchers. However, these developed phosphors should comply with IEC requirements for “passive integrating dosimetry systems for personal and environmental monitoring”. Only then they could be useful for their practical application in radiation dosimetry. As per the present international scenario, LiF:Mg,Cu,P (in TL mode) and Al_2O_3:C (in OSL mode) are the vanguards of the luminescence dosimetry programmes. These two phosphors comply with all the IEC requirements of passive integrating dosimetry systems. With the present interest in TL and OSL materials development, it is hoped that new and more sensitive luminescent materials will be available in the coming years for use in field of radiation dosimetry.

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Luminescence Related Phenomena and their Applications

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Thermoluminescent Phosphors for Radiation Dosimetry

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