

Recent Advances and Opportunities in TLD Materials: A Review

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Abstract. Thermoluminescence (TL) is the thermally stimulated emission of light from an insulator or a semiconductor following the previous absorption of energy from ionizing radiation. TL dosimetry is used in many scientific and applied fields such as radiation protection, radiotherapy, industry, and environmental and space research, using many different materials. The basic demands of a thermoluminescent dosimeter (TLD) are good reproducibility, low hygroscopicity, and high sensitivity for very low dose measurements and good response at high doses in radiotherapy and in mixed radiation fields. In this review, we have discussed the past developments and the future opportunities in TLD materials and our efforts to make better future use of low cost materials in TLD applications. For this we have studied and discussed two efficient TLD phosphors with low cost and simple method of preparation on large scale for TLD materials. One of the phosphors is LiF:Mg,Cu,P (LiF: MCP), and another one is LiCaAlF₆:Eu, which has the potential to replace conventionally used CaSO₄:Dy TL dosimeter. LiF: MCP and LiCaAlF₆: Eu phosphors are potential candidates for TL dosimetry and could be good replacement for commercially available phosphors. Apart from this, we have also studied thermoluminescence in Aluminate and Borate materials. We have discussed in detail all three types of TLD materials. First, our study includes complete detail of material properties, methods and dosimetric characterizations of LiF: MCP Phosphor; second, it includes a new TL Dosimeter, LiCaAlF₆: Eu and its dosimetric characterizations; and lastly on some TL properties of Li₅AlO₄: Mn and MgB₄O₇: Dy,Na. In this review, we discuss some recent developments in radiation dosimetry with regards to the measurement techniques and material preparations. Although many materials have been and are currently being studied for TLD, still there is a scope for the improvement in the material properties useful for the TLD, and the synthesis of new, more suitable materials.

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1. Introduction

Radioactive radiations are commonly used in the medical and nuclear fields. Persons working in such fields always have a danger to be exposed to hazardous nuclear radiations and need monitoring of radiation doses. Although there are number of other methods to detect the radiations such as ionization chamber, GM counter, etc., TLD phosphors have many advantages over these such as smaller size, easiness of handling, faster readouts, lower costs, etc. TLDs are increasingly accepted for radiation dosimetry for several reasons such as existence of tissue (human) equivalent thermoluminescence materials, sufficiently high sensitivity and accuracy for both personnel and environmental monitoring, availability of small size solid detector adaptable for both manual and automatic processing, existence of materials with excellent long-term stability under varying environmental conditions and good reusability.

Thermoluminescence (TL) or Thermally Stimulated Luminescence (TSL) is stimulated thermally after initial irradiation given to a phosphor by α - rays, γ -rays, β - rays, UV- rays and X-rays. Thermally stimulated luminescence is the phenomenon of emission of light from a material, which has been exposed before to ionizing radiation, by increasing its temperature [1].

Thermoluminescence dosimetry is widely used for dosimetric measurements, especially for personnel dose monitoring. Thermoluminescence dosimetry materials offer long-term information storage and versatile applications in different types of radiations including X-rays, gamma (γ) and beta (β) rays, and neutrons [2-5].

During 1950s more and more thermoluminescent materials were examined for their usefulness as dosimetric phosphors. Single crystals activated with metal ions were mostly examined, beginning with manganese-activated calcium sulphate which was occasionally used for radiation and UV dosimetry. Since 1957 special interest has been shown in natural fluorite, manganese-activated lithium borate, and beryllium oxide as an alternative to lithium fluoride for energy-independent photon measurements, as well as in dysprosium-activated calcium fluorite and calcium sulphate and terbium-activated magnesium orthosilicate. A second generation of materials including greatly improved RPL glasses and TL phosphors and a wide variety of commercial systems became available during the 1960s [6]. Our available knowledge on solid-state dosimeters now doubles every few years which makes it increasingly difficult for individual scientists, particularly in small institutions or developing countries, to keep their knowledge up to date.

1.1 CaSO₄: Dy Phosphor. CaSO₄ is one of the most sensitive TLD products used in dosimetry. CaSO₄: Mn has been used for detection of doses as low as 20 μ rad but exhibits very strong fading as its TL peak occurs at 90°C. CaSO₄: Dy and CaSO₄: Tm are the most interesting phosphors in CaSO₄ series, since their response is considerably stable. The CaSO₄: Dy phosphor has been used as a dosimeter in radiation dosimetry particularly for low-dose measurements. The intrinsic TL sensitivity of CaSO₄: Dy to ionizing radiation has been found to increase with the temperature of thermal treatment [7]. Traditionally, CaSO₄:Dy TLD materials are used extensively for the radiation dosimetry purpose due to low cost, high sensitivity, and very high storage stability in ambient climatic conditions [8]. Considerable work has been done on CaSO₄ singly doped phosphors in the last few decades, and Dy or Tm doped CaSO₄ thermoluminescent phosphors are highly attractive due to their desired dosimetric properties [9-13]. Yamashita et al. [14] first prepared CaSO₄: Dy for thermoluminescence dosimetry (TLD) of ionizing radiations. Prockic et al. [15] studied the impurity which would sensitize the thermoluminescence of CaSO₄: Dy, and made a phosphor which is 20% more sensitive than CaSO₄: Dy. Recently, Muke et al. [16] have reported solid state synthesis of Eu²⁺- doped CaSO₄:Eu²⁺ phosphor. M. Prokic [17] studied the effect of lithium co-dopant on the thermoluminescence response of some phosphors. The results show that lithium co-dopant when present in CaSO₄:Dy, CaSO₄:Tm, CaF₂:Mn, MgB₄O₇:Dy, MgB₄O₇:Tm, MgB₄O₇:Tb, MgB₄O₇:Mn, CaB₄O₇:Dy and CaB₄O₇:Tm thermoluminescent phosphors induces higher luminescence efficiency. Co-doping with Li of the above given phosphors resulted in increasing the TL sensitivity from 1.2 to 3.4 times. The high TL output of these TL phosphors could be used in dosimetric practice for special short-term measurements.

1.2 LiF: MCP Phosphor. LiF: MCP material is being considered to be a standard detector in TL dosimetry. The LiF: MCP detectors were used during measurements of cosmic radiation on Earth's orbit at the International Space Station [18]. LiF: MCP is highly sensitive thermoluminescence detector, as it is able to measure doses over a wide range (generally from μ Gy to kGy) [19]. Thermoluminescence of LiF: MCP has been studied extensively for more than five decades. Efforts of Cameron et al. [20] saw the development of a LiF based phosphor. LiF:Mg,Ti was one of the sensitive LiF based phosphor used in personnel dosimetry. It was made commercially available by Harshaw chemical company in 1967 (US Patent) [21]. Various laboratories developed LiF: MCP phosphor with different dopants. A highly sensitive dosimeter LiF:Mg,Cu,Si was developed by Lee et al. [22] which has been investigated at Korean Atomic Energy Research Institute (KAERI) and compared with those of commercially available LiF:Mg,Cu,P (GR-200A). LiF:Mg,Cu,Si thermoluminescence dosimeter (TLD) can be heated up to 300°C without any loss of TL sensitivity or any change in the glow curve structure. After this, some of the laboratories in the world are successful in developing LiF: MCP phosphor [23-25]. These are as much as 40 times more sensitive

than LiF-TLD 100 (approximately 1.3 mGy) and show better linearity. However, the response is extremely sensitive to thermal history, the glow curve is complicated and the sensitivity is permanently damaged if read out temperature exceeds 240°C. Another LiF dosimeter with four dopants LiF:Mg,Cu,Na,Si was developed by the researchers in Korean Atomic Energy [26]. All these LiF based dosimeters show sensitivity approximately 40 times higher or more than conventional TLD-100. LiF:Mg, LiF:Cu, LiF:P and LiF:Mg,Cu,P materials were synthesized by the chemical co-precipitation method. LiF:Mg, LiF:Cu, LiF:P and LiF:MCP nanocrystalline samples were synthesized with different dopant concentrations.

Mandowska et al. [27] found that TL emission of highly irradiated LiF:Mg,Cu,P (MCP-N) detectors is very complex especially in the region of very high doses (>1 kGy). The number of peaks increases with dose in the long wavelength region indicating new types of recombination centres (RCs). Recent theoretical models [28, 29] for LiF:Mg,Cu,P and LiF:Mg,Ti assume simultaneous localized and delocalized recombination. It seems that in the case of localized recombination, with increasing dose the average distance between traps and RCs decreases. It may result in the decrease of the energy levels separation, and the red-shift of emitted photons.

MCP-N TL detectors were studied after exposures with dose of γ -rays up to 100 kGy and TL glow curves were measured up to temperature of 550°C. TL emission spectra integrated over a temperature range of 47-470°C were analyzed. The recombination centers were observed above 4 kGy. The long wavelength emission was visible at the doses of 4 kGy and higher, indicating that such an amount of energy deposited in the detector volume makes additional recombination centers active [30]. LiF:Mg, LiF:Cu, LiF:P and LiF:MCP materials were synthesized through the chemical co-precipitation route. Samples were annealed in the range of 100–573 °C. TL glow curves of these nano-crystalline samples show two main peaks, one at around 131 °C and another broad peak centered at around 217 °C. However, further studies of LiF based phosphors with different activators (Mg, Cu, P, Ti, Si, Na, etc.) still attract researchers, as the problem of loss of sensitivity and reusability is yet to be completely understood, especially, the role of Cu in the LiF:Mg,Cu,P phosphor material. The comparison of the nano-phosphor under investigation with commercial LiF: MCP (TLD-700H) TLD chips and CaSO₄: Dy (TLD-900) was also done in order to find its suitability for TL dosimetry [31].

1.3 LiCaAlF₆ Phosphor. LiCaAlF₆ doped with Ce³⁺ was studied by Faulstich et al. [32] and investigated for use in photonic devices. Liu et al. [33] investigated Ce:LiCAF solid state laser source for tunability in the UV wavelength region. The laser-induced fluorescence spectrum of LiLuF₄:Pr³⁺ single crystals, pumped by an F2 pulsed-discharge molecular laser at 157 nm, were obtained in the VUV and UV regions of the spectrum at room temperature. A number of new fluorescence peaks were observed for the first time to our knowledge. They were assigned to the dipole-allowed transitions 4f5d → 4f2 of Pr³⁺ ion [34]. LiCaAlF₆:Pr³⁺ exhibits photon cascade emission that can be useful for obtaining phosphors with quantum efficiency exceeding 100% [35].

LiCaAlF₆ doped with Ce³⁺ was studied using thermoluminescence and scintillation by many workers. Nikl et al. [36] reported TL peak at 230°C and the emission is a characteristic of Ce³⁺. Gektin et al. [37] suggested LiCaAlF₆:Ce³⁺ has good potential for neutron dosimetry. They studied TL of both doped as well as un-doped LiCaAlF₆ [38] and observed only one peak in doped crystals at 350°C which they have attributed to Ce³⁺ while in undoped crystals, they did not get 350°C peak, instead they witnessed peaks at 190°C and 260°C. Specifically, they successfully demonstrated that shallow and ultra deep traps (found in LiCaAlF₆:Ce³⁺ scintillators) lead to the energy storage, which results in afterglow appearance in LiCaAlF₆:Ce irradiated at room temperature. On the other hand, Kawaguchi et al. [39] had observed the two glow peaks around 180°C and 250°C in Ce³⁺ doped LiCaAlF₆ but not witnessed a high temperature (350°C) peak, and hence they concluded that the emission was not related to Ce³⁺. Recently, Amaral et al. [40] made a very important prediction that Eu³⁺ and Nd³⁺ could be more effective activators as compared to Ce³⁺ and Yb³⁺ for stronger optical

activity. There are few reported studies on photoluminescence [41] and thermoluminescence [42] in $\text{LiCaAlF}_6\text{:Yb}^{2+}$ also. LiCaAlF_6 doped with Ce^{3+} was used for laser application. The attractive properties of LiCaAlF_6 are low effective atomic number of 14 and low density of 2.98 g/cm^3 because low sensitivity for background gamma-rays can be expected. $\text{LiCaAlF}_6\text{:Ce}$ showed good performance as a solid state ultra violet laser material. The scintillation properties of $\text{LiCaAlF}_6\text{:Eu}$ scintillator and its capability for thermal neutron imaging application has been investigated [43]. LiCaAlF_6 rare-earth-ion-doped scintillators of neutron detectors with high efficiency have been developed for the neutron gamma discrimination by using the pulse shape discrimination in the $\text{LiCAF}\text{:Ce}$ scintillator, which is frequently used in organic liquid scintillators, to selectively detect neutrons with the $\text{LiCAF}\text{:Ce}$ scintillator under an intense high-energy gamma-ray field [44]. Theoretically, it is predicted that compensation of Li^+ vacancy is preferred for substitution of Ca^{2+} by La^{3+} whereas Ca^{2+} vacancy is favored for substitution of Li^+ by Ce^{3+} [45]. Shiran et al. [46] further investigated that LiCaAlF_6 doped with activators like Eu could be the system for investigation with reference to exploration of suitable material for TL dosimetry. They observed glow peaks around 340, 420 and 490 K that are the same as those in the undoped material. However, TL intensities were found to be much higher in Eu^{2+} -doped material.

1.4 Lithium Aluminates and Magnesium Borate Phosphors. For use in personal monitoring, the response of the phosphor should be similar to that of tissue, which has the equivalent atomic number close to 7.4. A low Z phosphor is thus better suited for use in personal monitoring, provided it has other necessary dosimetric properties. Kirk et al. [47] prepared and studied lithium borate, which is a low Z material, for dosimetry but its sensitivity is rather poor. A more sensitive and much-improved $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ phosphor that can be prepared from commercially available raw materials was developed in 1980 by Takanaga et al. [48]. Phosphors, doped with Cu, Dy or Tb, were also later studied by Lorrain et al. [49]. In view of the above, an attempt has been made to study the thermoluminescence of some lithium aluminates and magnesium borate. The lithium ceramics [50] such as LiAlO_2 , LiAl_5O_8 , $\text{Li}_2\text{Al}_4\text{O}_7$, $\text{Li}_4\text{Al}_2\text{O}_5$ and Li_5AlO_4 doped with Cu and Mn, and magnesium borate TLD phosphor, $\text{MgB}_4\text{O}_7\text{:Dy}$ co-doped with Na, were tried for dosimetric applications by Furetta et al. [51]. The compound LiAlO_2 has industrial applications, which include tritium-breeding material in fusion reactors and electrolyte matrix for the molten carbonate fuel cells, where in $\gamma\text{-LiAlO}_2$ is used as the non-conducting inert matrix to contain carbonate electrolyte between the anode and the cathode. The low-temperature form, $\alpha\text{-LiAlO}_2$, is used as a catalyst support and for the preparation of de-lithiated alumina compounds. The synthetic mineral is extensively studied because of its complex phase transition and interesting magnetic and fluorescent properties when doped with Fe^{3+} . The compound has two forms; a low temperature primitive cube and a high temperature spinel form.

The preparation of polycrystalline magnesium borate activated by dysprosium, $\text{MgB}_4\text{O}_7\text{:Dy}$, has been reported at first in 1974 [52]. This phosphor is a near tissue equivalent material with an effective atomic number for photoelectron absorption equal to 8.4. Prockic presented a more detailed report on application of such phosphors in Yugoslavia [53-55]. Mg-borate powder is now commercially available and rare earth doping can be achieved easily [56]. Several researchers investigated the use of magnesium borate as TL material [57- 60]. This phosphor has near tissue equivalence with an effective atomic number for photoelectric absorption equal to 8.4, compared to 7.4 for water and soft biological tissue. $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ is a newly prepared TL material with attractive features for dosimetric applications, such as near tissue equivalence, simple glow curve, high sensitivity and low fading [61].

2. Synthesis Methods

2.1 Precipitation Method used for the Synthesis of CaSO_4 . Ingle et al. [10] have described the simplest method for preparing $\text{CaSO}_4\text{:Dy}$ phosphor by precipitation from aqueous solution of CaCl_2 with dilute sulphuric acid. For incorporating Dy, appropriate amount of aqueous solution of

DyCl₃ was added prior to precipitation. Ratio of Ca²⁺:Dy³⁺ in solution was 1000:1. The precipitate was repeatedly washed by distilled water to remove the traces of acid, dried and then annealed at 975 K for 1 h followed by quenching to room temperature (RT). This sample will be designated as CaSO₄: Dy-P. The phosphor shows poor sensitivity, and the glow peak temperature is also around 400 K instead of 500 K. Typical glow curve of a sample exposed to 2.58×10^{-2} C/kg (2.58×10^{-2} C/kg = 86.96 Gy) is shown in Fig. 1 (curve a). The possible reasons for such results are the presence of background impurities, especially monovalent impurities like sodium and/or improper incorporation of Dy³⁺. Dysprosium sulphate is soluble in water to some extent and this may prevent co-precipitation. For testing this hypothesis, sample P was dissolved in sulphuric acid and then recrystallized, washed with distilled water, dried, annealed at 975K for 1 h and quenched to room temperature. This sample will be designated as CaSO₄: Dy-PD. Glow curve and sensitivity of the resulting phosphor was similar to the phosphor used in the dosimetry (Fig.1, curves b, c). This shows that dysprosium is co-precipitated in sample CaSO₄: Dy-P. The supportive evidence was obtained from the PL measurements. Dy³⁺ exhibits weak PL in the form of sharp lines around 482 and 573 nm corresponding to transitions $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$, respectively, as shown in Fig. 2.

Nomenclature for various CaSO₄ samples prepared by the precipitation route by Ingle et al. [10] is described in the box below:

CaSO₄:Dy-P: CaCl₂ (aq.solution)+DyCl₃ (0.1 mol %) precipitated by dil. H₂SO₄.

Precipitate washed with distilled water, dried, annealed at 975K for 1 h and quenched to RT

CaSO₄:Dy-PD: Sample P dissolved in dil. H₂SO₄, recrystallized, washed with distilled water, dried, annealed at 975K for 1 h. and quenched to RT

CaSO₄:Dy-SD: CaSO₄ · 2H₂O and Dy₂O₃ dissolved in dil. H₂SO₄. Recrystallized and annealed as above

CaSO₄:Dy-CD: CaCO₃ and Dy₂O₃ dissolved in dil. H₂SO₄. Recrystallized and annealed as above

CaSO₄:Dy-CND: CaCO₃ and Dy₂O₃ dissolved in dil. HNO₃. Solution added to dil. H₂SO₄. Recrystallized and annealed as above

CaSO₄:Dy-ND: Ca(NO₃)₂ · 4H₂O and Dy₂O₃ dissolved in dil. H₂SO₄. Recrystallized and annealed as above

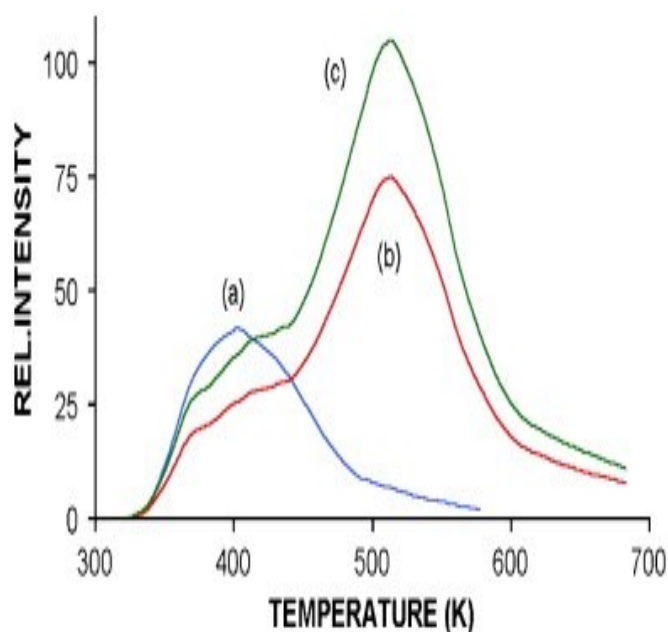


Fig. 1 Thermoluminescence glow curves of $\text{CaSO}_4\text{:Dy}$ (0.1 mol %) phosphors exposed to 2.58×10^{-2} C/kg. (a) Sample P, (b) samples PD and SD, and (c) sample ND

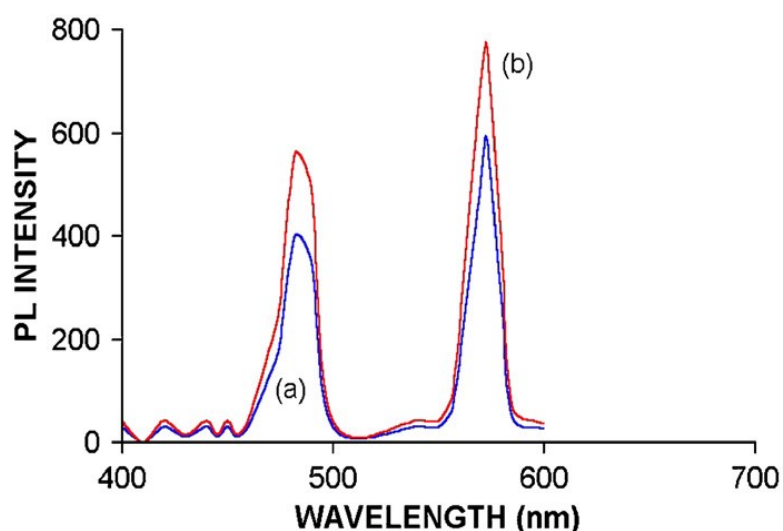


Fig. 2 Typical PL of Dy^{3+} in $\text{CaSO}_4\text{:Dy}$. Emission spectra were obtained for 354 nm excitation. (a) Samples PD, CD, SD, and (b) Sample ND

2.2 LiF: MCP Synthesis. The thermoluminescent dosimeters used were manufactured by Bicorn Company, LiF: Mg, Ti (TLD-100) and LiF: MCP (TLD-100H). Kolotilin et al. [62] have used costly and bulky ways for the preparation of LiF: MCP material such as passing hot HF vapors over the LiF material, using the inert atmosphere and high vacuums at higher temperature ($> 700^\circ\text{C}$). Horowitz and Horowitz [63] started with the optical grade LiF and other necessary salts. Phosphor was prepared by melting in nitrogen–oxygen atmospheres at 1000°C . Clearly such type of sophisticated preparation technique will be useful only for laboratory scale and if one has to develop the phosphor at large scale then one should go with much simpler way. We have developed this phosphor with a very simple method of preparation called as ‘Reactive Atmospheric Processing Technique’ (RAPT).

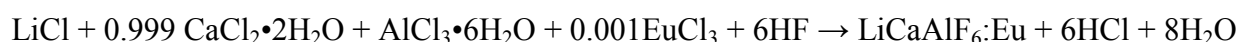
When phosphors are prepared by conventional solid state route by heating in air, usually un-wanted impurities like OH^- , O^{2-} , etc. get incorporated. Such impurities can be quite harmful to the

luminescence processes. Especially, fluorides are highly susceptible to hydrolysis. To get over this difficulty, phosphors are prepared in inert atmosphere of N₂, Ar, etc. Scavengers like PbF₂ have also been used to get rid of OH⁻ ions. Even such phosphors may show inefficient luminescence possible due to deviation from stoichiometry. The stoichiometry can be preserved by preparing the crystals in 'Reactive' atmosphere instead of the inert atmosphere, e.g., preparation of fluoride crystals in fluorine atmosphere will prohibit the substitution of F⁻ by other impurity ions. The reactive atmosphere processing (RAP) [64] was successfully used by Pastor and co-workers for preparation of optical/laser quality crystals [65-67]. We have adopted and modified this technique for the preparation of LiF: MCP phosphor. In the simplified, modified RAP, the phosphor/ingredients are heated with an appropriate RAP agent like Teflon, NH₄F.HF, NH₄Cl, etc. in a closed glass tube at about 450°C for 1 hour. It is then transferred to a graphite crucible pre-heated to a suitable temperature. The molten phosphor/reacted ingredients are then quickly quenched to room temperature. The procedure eliminates the need for vacuum and yet produces suitable phosphors which are as good as those produced by more sophisticated techniques.

5ml of Hydrofluoric acid (HF) was taken in a Teflon beaker. Lithium carbonate was added smoothly to it to form LiF. The precipitate so formed has been dried under blowing air. To the dried precipitate, CuCl₂ solution was sprinkled and dried again. This precipitate was then heated in a test tube at 500°C with NH₄Cl to remove OH⁻ ion traces in LiF. Reactive Atmosphere Process was used in which powder was then poured in graphite crucible containing MgF₂ and NH₄H₂PO₄. MgF₂ is prepared freshly by adding the MgCO₃ in the HF. Crucible was heated at 870°C to melt LiF powder. Finally melted LiF: MCP is rapidly quenched to room temperature.

2.3 LiCaAlF₆: Eu(0.1%) Synthesis. Preparation of complex aluminum fluorides is not simple. Fluorides are susceptible to continuous hydrolysis. At high temperatures they are known to incorporate oxygen and hydroxyl for fluorine ion causing distortion in the lattice. Hydrolysis in fluoride has great impact on their luminescence properties and is responsible for their inefficient luminescence. In order to prevent hydrolysis these materials were often prepared in a reactive atmosphere of argon or nitrogen at high (>600°C) temperature, which requires costly and bulky arrangements. Further these materials were prepared by solid state diffusion of constituent fluorides having vastly different melting points leading to non-stoichiometry and unreacted products in the final product. To overcome this, excess of volatile component in the starting mixture is attempted. The excess quantity has to be optimized depending on the conditions of the crystal growth. Sometimes a risky method for the preparation of these fluorides such as flow of hot HF vapors over the initial compounds was found to be necessary for preparation of these fluorides in order to prevent hydrolysis.

Use of chlorides as starting materials helps in preventing the hydrolysis in fluoride materials. Hence complex fluorides were prepared by dissolving the analytical reagent grade chlorides of the constituent metals with stoichiometric ratios in double distilled water in a PTFE container. For activation, EuCl₃ was added during the synthesis. Temperature of the solution was raised to 80°C and stoichiometric amount of HF was added drop wise. A simple reaction for the preparation of LiCaAlF₆: Eu(0.1%) is given below:



Solvent was evaporated off at 80°C. The precipitate was washed several times with distilled water and dried. Sample was then melted at 800°C in a graphite crucible and quenched on the graphite plate. It is noteworthy that Europium does not show efficient luminescence in the sample prepared only by wet chemical method but a melting and heating of the sample is necessary.

All the samples were prepared by solid-state diffusion method. For the synthesis of Li₅AlO₄: Cu (100ppm), fine particle size Al₂O₃ was first prepared by urea combustion of Al (NO₃)₃.9H₂O (s.d.fine chem., extra pure). The combustion was carried out at 500°C. The precursors were

weighed as per the stoichiometric calculations. $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ (24.7g Loba chem., GR grade) was decomposed in an alumina crucible in resistive furnace at 590°C for 1 hour to get Li_2O (3.0g), which was then mixed thoroughly with Al_2O_3 (2.047g) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.00048g, Loba chem., GR grade). The mixture was annealed at 650°C for 12 hours with intermittent mixing and grinding. A white powder sample of $\text{Li}_5\text{AlO}_4\text{:Cu}$ was thus obtained. The same method was followed for the synthesis of $\text{Li}_5\text{AlO}_4\text{:Mn}$ (100ppm), where $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.00034g, Loba chem., GR grade) was used for Mn doping.

2.4 $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ Synthesis. $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ was synthesized by ceramic method. MgCO_3 (3.926g, Loba chem., GR grade), H_3BO_3 (4.95g, Qualigens chem., AR grade), Dy_2O_3 (0.00373g, Indian Rare Earths Ltd.) and Na_2CO_3 (0.0011g, s.d.fine chem., AR grade) were taken in stoichiometric proportion. The precursors were first mixed and ground thoroughly and annealed in a resistive furnace at 500°C for 6 hours. The powder was again crushed and annealed at 900°C for 12 hours. The white powder sample of $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ was thus prepared.

3. Irradiation of Materials

3.1 γ -ray Exposure. A Theratron 780E therapy machine employing a ^{60}Co source at Regional Cancer Hospital, Nagpur was used for γ -ray exposures to various samples. The exposure rate was calculated for the field size of irradiation of $10\text{cm} \times 10\text{cm}$ at 80 cm distance. It was 909.2 mGy/minute on 09/06/2006. The rate was calculated each time, when the samples were irradiated. Accordingly the time required for various doses was calculated. The phosphors were given an exposure from 0.1 Joule/Kg to 10 Joules/Kg (1 Joules/Kg = 1 Gy).

3.2 β -ray Exposure. Exposure of β ray was obtained from $^{90}\text{Sr} \rightarrow ^{90}\text{Y}$ source at Radiation Safety System Division, BARC, Mumbai. The exposure rate was 20 mGy/minute. The time required for various doses was calculated and accordingly the exposure was given to the phosphors from 0.01 Joule/Kg to 1 Joule/Kg (1 Joules/Kg = 1 Gy).

3.3 X-ray Exposure. Different energy photons of effective energies 17.6 KeV, 22.7 KeV, 24.85 KeV, 65.90 KeV, 83.10 KeV, 117.6 KeV, 125 KeV and 223.9 KeV of X-rays were obtained from YXLON International X-ray machine at BARC, Mumbai. The source was first calibrated by using ionization chamber for each time by putting it at a distance of 2 metres in air. The samples were put at the same distance. The time required for 0.01 Joule/Kg of dose was calculated for various energy photons and accordingly the exposure was given to the phosphors.

4. TLD Properties

4.1 $\text{CaSO}_4\text{:Dy}$ Phosphor

4.1.1 Thermoluminescence Glow Curve. $\text{CaSO}_4\text{:Dy}$ remains one of the most useful and sensitive thermoluminescence dosimeter (TLD) for radiation dosimetry. The possibility of using $\text{CaSO}_4\text{:Dy}$ as a dosimeter for high doses of gamma radiation has been explored in recent years [68-70].

The TL study of $\text{CaSO}_4\text{:Dy}$ phosphor exposed to an absorbed dose of 10 Gy of ^{60}Co gamma radiation and the evolution of the TL glow curve shape is shown in Fig. 3. This TL glow curve exhibits two main peaks centered at 150 and 300°C , respectively. The variation of the TL intensity of the $\text{CaSO}_4\text{:Dy}$ as a function of gamma absorbed dose is shown in Fig. 4. It is observed that the TL response is linear in the range from 1 to 30 Gy. The shape of the glow curve remains almost the same for exposures between 1 to 300 Gy but the relative heights of the two peaks change as a function of gamma radiation. The TL intensity of the peaks increases as the gamma dose increases without change in the glow curve shape, as shown in Fig. 4.

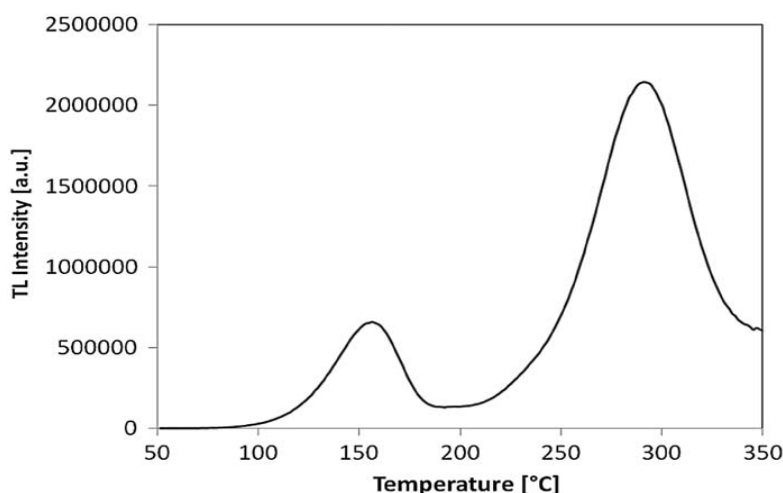


Fig. 3 Typical TL glow curve of gamma irradiated $\text{CaSO}_4:\text{Dy}$ (adopted from Ref. 68).

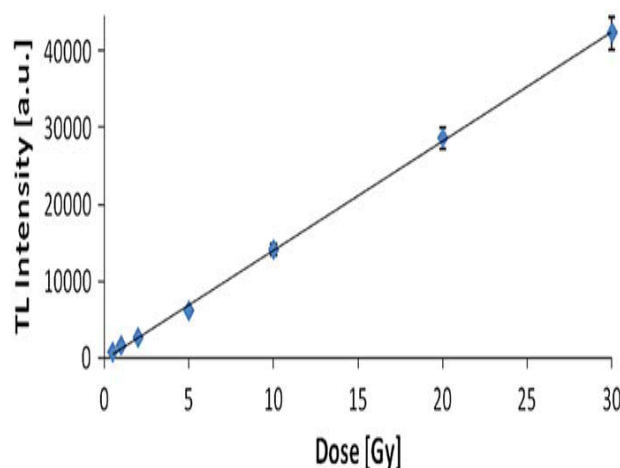


Fig. 4 Dose response of $\text{CaSO}_4:\text{Dy}$ as a function of gamma absorbed dose (adopted from Ref. 68).

4.1.2 Effect of Dopant Concentrations. The study of glow curve structure on the basis of concentration of impurities is one of the main parameters to develop requisite dosimeter with various activators. TL emission spectra of $\text{CaSO}_4:\text{Dy}^{3+}$ and the photoluminescence emission of $\text{CaSO}_4:\text{Dy}^{3+}$ are shown in Figs. 1 and 2, respectively.

4.1.3 Heating Rate Effect. $\text{CaSO}_4:\text{Dy}$ phosphor obtained was annealed at different temperatures in the range of 773 to 1173 K for 1 h. The samples remained 24 h in the oven and then switched off in order to reach the room temperature. The glow curve (Fig. 5) of sensitized $\text{CaSO}_4:\text{Dy}$ samples by giving different heat treatments, in the temperature range (773–1173 K), and irradiated at the gamma dose (0.1 Gy), is recorded. It is observed that the intensity of TL glow curve increases with temperature. In all cases, the glow curves exhibited three glow peaks at about 363, 398 and 493 K [7]. When $\text{CaSO}_4:\text{Dy}$ was heated at 1073 and 1173 K, the TL intensities were 31.75 and 32 units, respectively, considering the sensitivity of the TLD-100 as the unit. However, the peak 3 of the glow curves remains unchanged. Other authors [14, 70] have reported that the maximum TL response of peak 3 (503K) is reached at 973K of sensitivity of thermal treatment (STT). They also have observed that at $\text{STT} \geq 1073$ K the TL intensity of peak 3 begins to decrease.

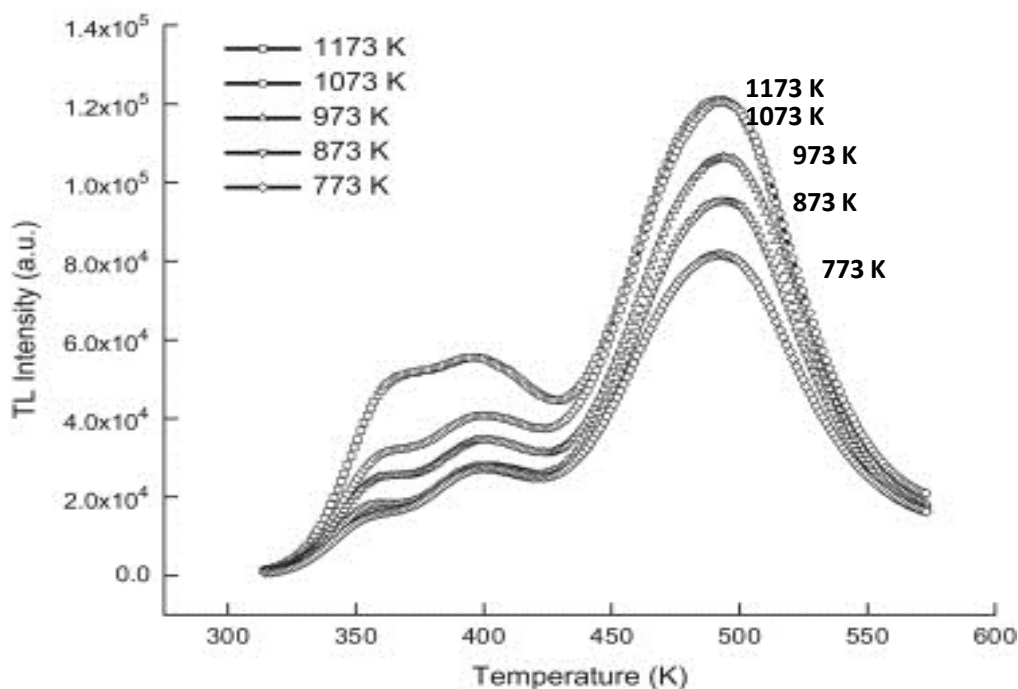


Fig. 5 TL intensity of $\text{CaSO}_4\text{:Dy}$ as a function of thermal treatment temperature. TL intensities for 1073 and 1173 K almost overlap (adopted from Ref. 7).

4.2 $\text{CaSO}_4\text{:Eu}^{3+}$ sample for Radio Photoluminescence (RPL) Dosimetry. CaSO_4 phosphors activated with Dy or Eu were prepared by various methods like precipitation or acid distillation [10]. The RPL of $\text{CaSO}_4\text{:Eu}^{3+}$ is used for dosimetry. Emission and excitation spectra of Eu^{3+} and Eu^{2+} photoluminescence are shown in Fig. 6. Eu^{3+} emission is weak arising from forbidden transitions $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (around 590 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (around 611 nm), whereas efficient Eu^{2+} emission corresponding to transition from levels $4\text{f}^5\text{d}_1$ configuration to the ground state $^8\text{S}_{7/2}$ configuration peaks at 385 nm in CaSO_4 . Phosphors prepared by precipitation and solid state methods are not suitable for preparing $\text{CaSO}_4\text{:Dy}$ TL dosimetry phosphor, therefore, it required several options for the starting calcium compounds. Hence these are not suitable for RPL dosimetry and exhibited the emission and excitation characteristics of RPL as shown in Fig 6.

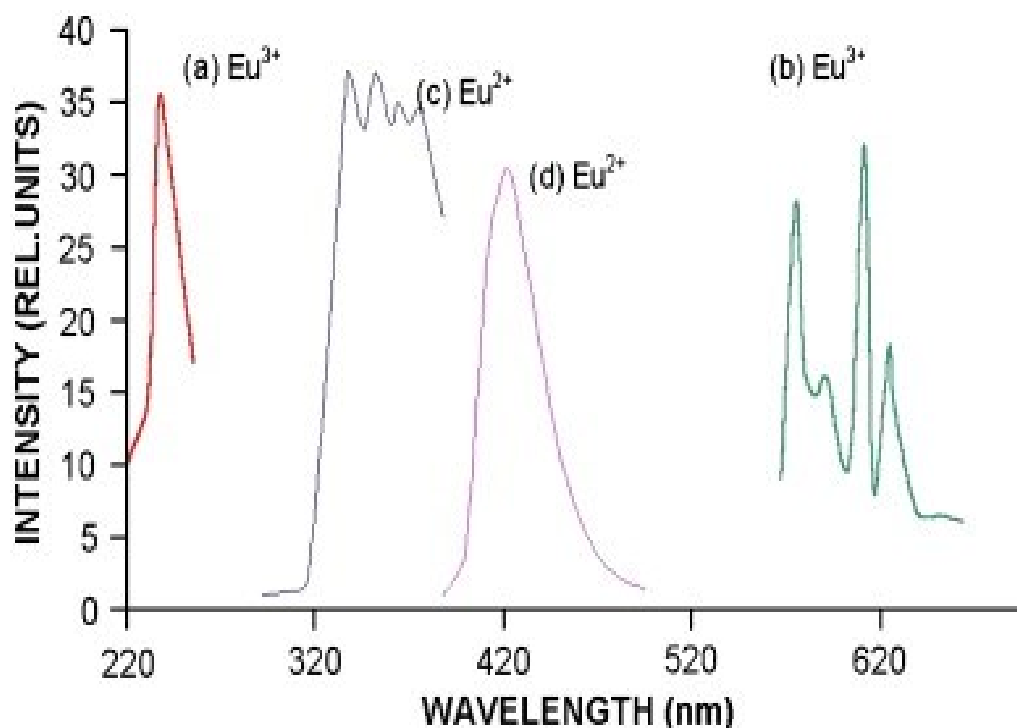


Fig. 6 Typical PL spectra of Eu^{3+} and Eu^{2+} in CaSO_4 : (a) Excitation spectrum for 611 nm Eu^{3+} emission, (b) Eu^{3+} emission spectrum for 254 nm excitation, (c) excitation spectrum for 385 nm Eu^{2+} emission, and (d) Eu^{2+} emission spectrum for 320 nm excitation (adopted from Ref. [10]).

4.3 LiF: MCP Phosphor

4.3.1 Thermoluminescence Glow Curve. LiF-based dosimeters are very sensitive not only to its impurity content but also to other treatments as well, such as thermal, mechanical and radiation treatments [71]. After exposure to ^{60}Co irradiations, LiF-based dosimeters are the most widely used thermoluminescence phosphors in personal radiation monitoring [72]. In a previous study, the glow curve of LiF:Mg,Ti (TLD-100) was investigated under different thermal treatments. Activation energy and frequency factor of the trapping centers are to be strongly influenced by the thermal treatment. The LiF (TLD-100) has its extremely complicated glow curve structure which had led to great difficulty in the arriving of universally accepted characterization of its fading properties [73]. A glow curve of LiF: MCP is intense near 220°C as shown in Fig. 7. The difficulty stems from the loss of sensitivity if the material is heated above $240 \pm 5^\circ\text{C}$ [74]. However, some experiments indicate that short duration (approximately 12s) heating above 240°C , as in the case during TL readout, can significantly reduce the residual signal without affecting the sensitivity [75].

Thermoluminescence glow curve of newly developed LiF: Mg(0.22),Cu(50 ppm),P(1%) was compared with the LiF TLD-100H powder obtained from the Harshaw company and Chinese LiF GR-200P powder. LiF: MgCuP developed by us has 25% intensity compared to Chinese LiF and about 30% to that of LiF TLD-100H. The glow curves shown (Fig. 7) were recorded for a dose of 1 Joule/Kg under identical conditions. Glow curve structure of the sample prepared by us was similar to that of TLD-100H and GR-200P.

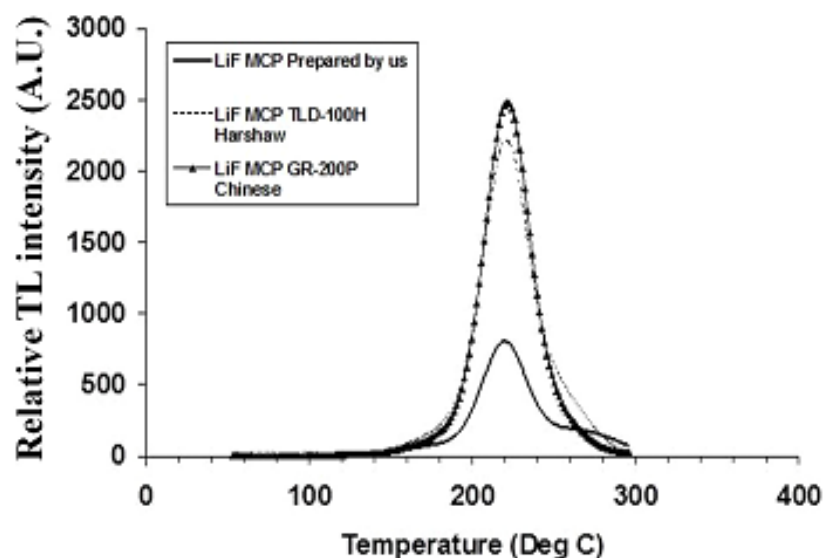


Fig. 7 TL glow curve of LiF: MCP compared with commercially available phosphors.

4.3.2 Effect of Dopant Concentration. The glow curve structure and TL intensity of LiF: MCP is mainly dependent on the impurities doped in the host. Therefore, the investigation of dependency of the glow curve structure on the concentration of impurities is one of the main parameters to develop requisite dosimeter. There is lot of literature available on the preparation of LiF dosimeters with different concentration. The reported value of impurities in LiF are in between (0.8% to 1.92%) for P, (0.15% to 0.25%) for Mg and (20ppm to 500ppm) for Cu. In order to obtain maximum TL output from LiF: MCP, concentration of Mg, Cu and P must be properly adjusted. Slight variation in this can alter the dosimetric properties of the phosphor. We varied the concentration of these dopants as follows: Mg from (0.15% to 0.3%), Cu from (20 ppm to 500ppm) and P from (0.6% to 2%). The concentrations mentioned here are the concentrations of MgF_2 , CuCl_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ added to LiF powder.

4.3.3 Effect of Mg Concentration

With increasing concentration of Mg, TL intensity of main glow peak, i.e. 220°C increases. Maximum TL intensity was observed for concentration in between 0.225% to 0.25% of Mg. Above 0.25% loss in sensitivity was observed. There was no change in the glow curve shape upto the concentration of 0.3%. Fig 8 shows the variation of TL intensity with Mg concentration.

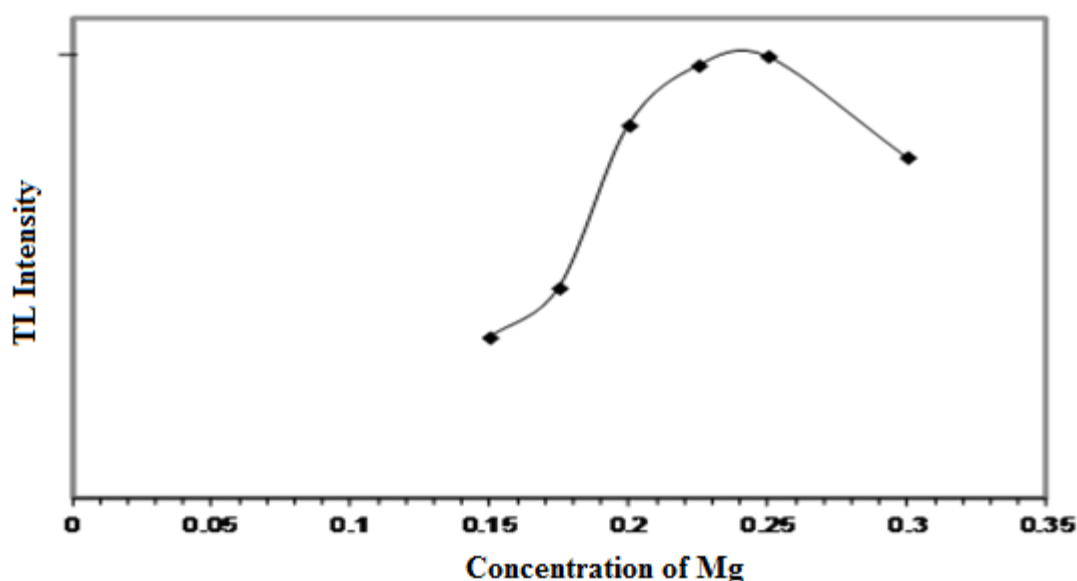


Fig. 8 Effect of Mg concentration on TL intensity of LiF:Mg,Cu,P Phosphor

4.3.4 Effect of P Concentration

Concentration of P was varied from 0.6% to 2%. TL intensity was found to increase with increasing concentration of P upto 1%, but above 1% it reduces. A significant loss in TL sensitivity and changes in the shape of TL glow curve was observed for concentration of P over 1%. With increasing concentration of P further, an undesired peak at 270°C was also found to increase. Fig 9 shows variation in TL intensity with P concentration. Relative TL intensity of LiF: MCP phosphor shows a sharp peak at 1% concentration, which gets distorted for higher concentrations.

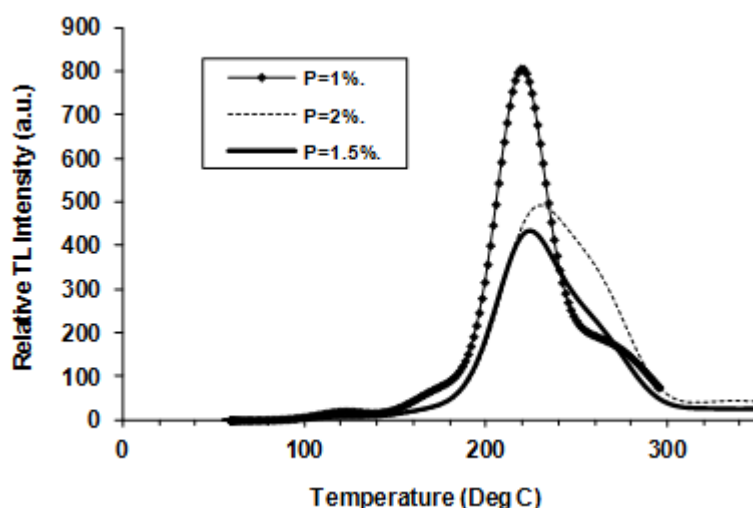


Fig. 9 Effect of P concentration on the TL intensity of LiF:MCP phosphor.

4.3.5 TL Emission Spectra. The emission spectrum matches with the reported values in the literature. It is noteworthy that TL emission falls in the region where most of the photomultiplier tubes have a maximum response. TL emission spectra of the sample was recorded, after the sample was irradiated with a dose of 10 KGy obtained from ^{60}Co gamma source and then heated at constant temperatures of 150°C and 175°C, respectively. The TL emission spectra obtained consists of a single peak with a maximum at 370 nm. The TL emission spectra of LiF: MCP is shown in Fig. 10.

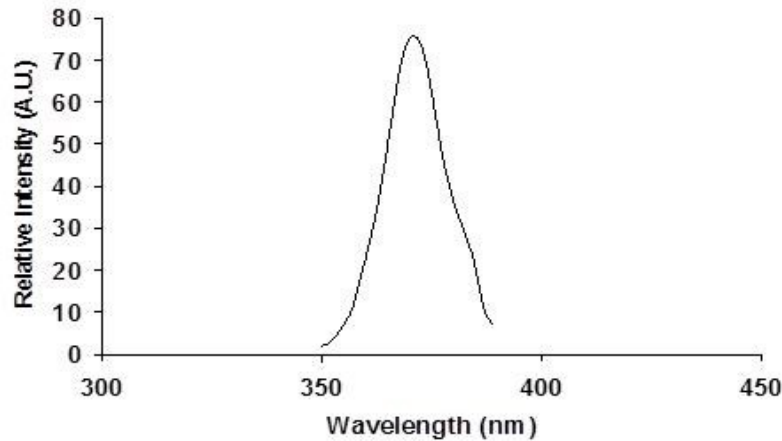


Fig. 10 TL emission spectra of LiF: MCP phosphor prepared by RAP technique

4.3.6 Grain Size Effect. Several researchers have studied grain size effect on the TL of LiF:Mg,Ti and LiF:Mg,Cu,P phosphors [76, 77]. LiF: MCP powder of different grain sizes were obtained by using different mesh size of sieves. Maximum TL is obtained when the mesh size of sieve is 125 μm to 180 μm . All the dosimetric characterizations were carried out with the particles in this range. Grain size effect on the TL of LiF: MCP phosphor is shown in Fig. 11.

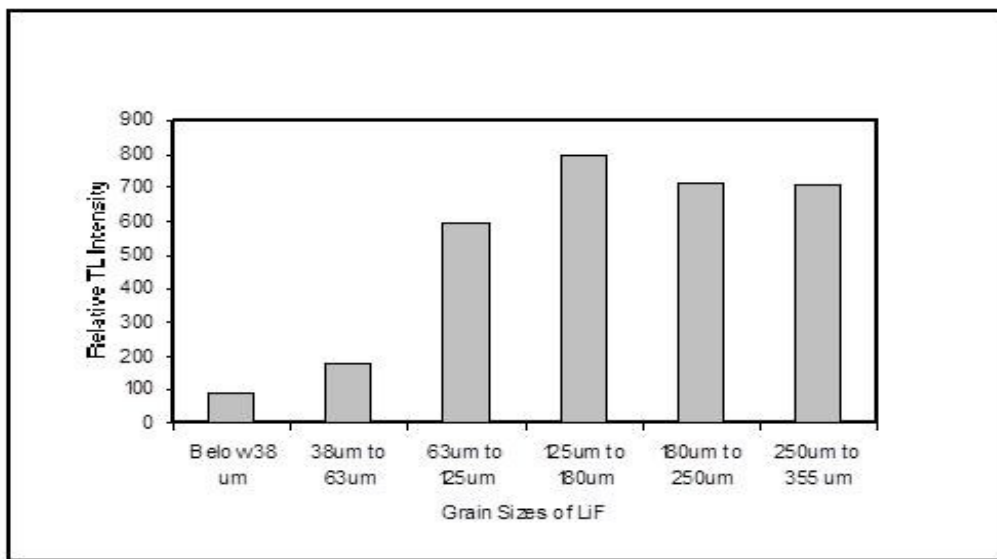


Fig. 11 Grain size effect on the TL of LiF: MCP phosphor.

4.3.7 Effect of Annealing Procedure. One of the parameters to be investigated was the annealing temperature in order to get the highest TL sensitivity and to eliminate the effects of the previous irradiations. It is also very much useful to avoid temperatures that may result into permanent loss of TL sensitivity of the phosphor. Hence the experiment was carried out using different annealing temperatures. Two type of annealing processes were used. In the first case, samples were annealed at 240°C, 250°C, 280°C and 300°C in a temperature controlled oven. Annealing period was 5 minutes for each temperature. In the second case, sample was heated on a *kanthal* heating plate of TL reader for 5 minutes at the above temperatures. It was found that annealing at 240°C on the *kanthal* heating plate for 5 minutes of TL reader was sufficient to restore the original TL sensitivity of the LiF: MCP TL dosimeter and to remove the previous dose. Heating in the oven at any of the above temperatures reduces the TL output of the phosphor. Effect of annealing temperature on the TL of LiF: MCP phosphor is shown in Fig. 12.

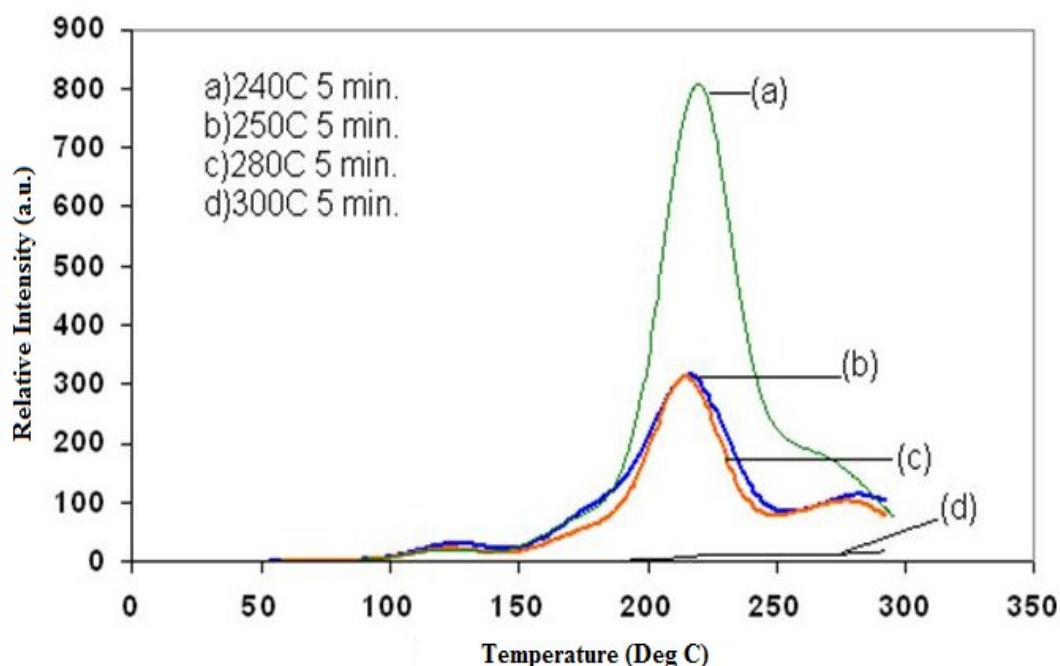


Fig. 12 Effect of annealing temperature on the TL of LiF: MCP phosphor.

4.3.8 Linearity of Dose Response. To test the linearity, the sample was irradiated with different doses of 0.01 to 5 Joule/Kg (Joule/Kg=Gy) and the glow curves were recorded on TL reader. It is evident that the thermo-luminescence intensity increases with the increase in the radiation doses. The linearity is well observed in the full range of radiation doses used (Fig. 13). For LiF: MCP phosphor, a good sensitivity was found for a lowest dose of 0.01 Joule/Kg (Joule/Kg = Gy).

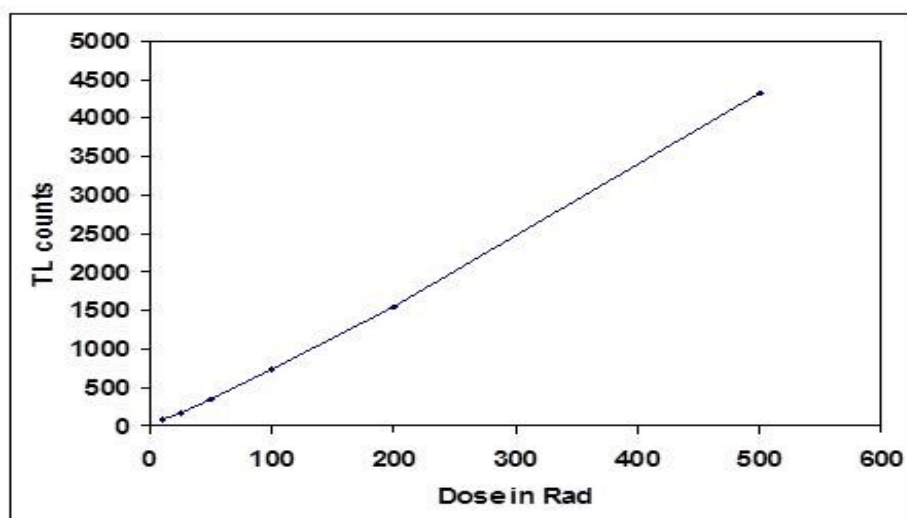


Fig. 13 Dose response of LiF: MCP Phosphor.

4.3.9 Energy Dependence. The relative photon energy response for LiF: MCP is 1.42 at 24 keV as shown in Fig. 14. TL material has an effective atomic number for photoelectric absorption (Z_{eff}) of 8.2, compared with 7.4 for tissue and for most applications; it is considered quasi-tissue equivalent. The samples were exposed in free air, under equilibrium conditions, to heavily filtered X-rays of narrow spectra. X-ray spectra with mean energies in the range 17 to 225 keV were used and the responses were normalized to that measured with ^{60}Co gamma rays.

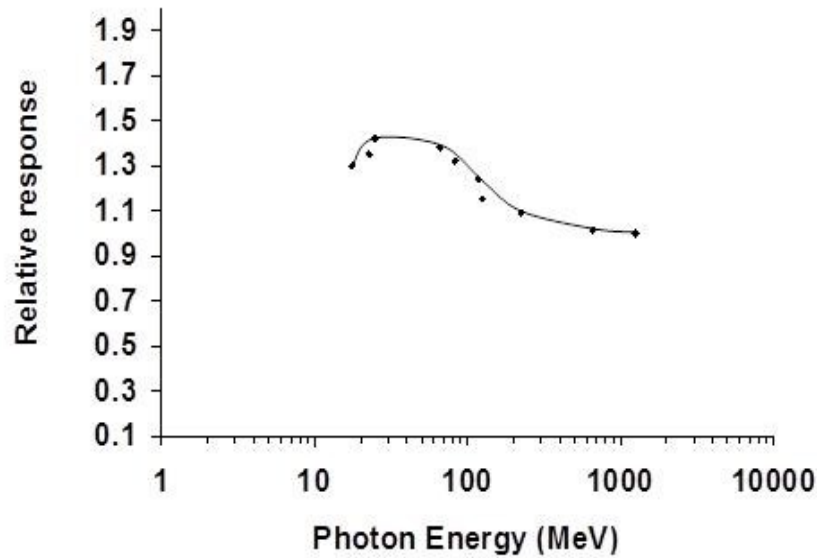


Fig. 14 Photon energy response of LiF: MCP Phosphor.

4.3.10 Fading Effect. For studying the fading effect samples were irradiated to a dose of 500 rad and TL readouts were taken at regular intervals of time. No fading was observed in the LiF: MCP sample prepared by us over a period of 15 days.

4.3.11 Heating Rate Effect. The effect of heating rate on the sample has been studied by heating the sample at different heating rates, from 2°C to 20°C/s. Not much loss in TL intensity was observed at different heating rates. However, the main glow peak shifts from 220°C to 232°C gradually with the increase in the heating rate (Fig. 15).

4.3.12 Repeatability of Results. In order to study the repeatability of TL output of LiF: MCP, the sample was irradiated first, readout up to 240°C taken and then heated at 240°C for 5 minutes on the *kanthal* heating plate of TL reader. Then again the sample was irradiated and similar procedure was followed. The TL readout values at this temperature are reproducible within a variation of 2% over ten cycles without systematic decrease.

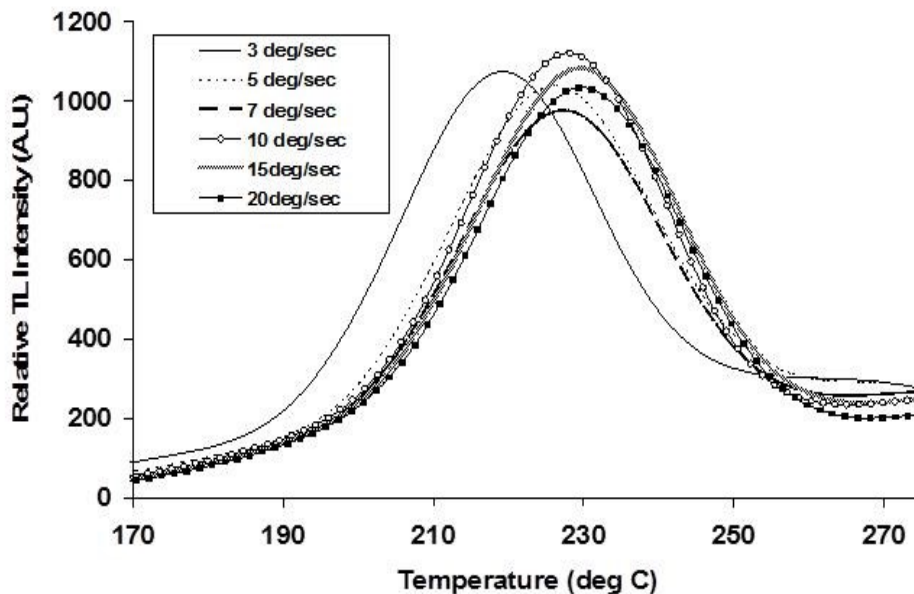


Fig. 15 The heating rate effect on LiF: MCP phosphor

4.3.13 Reproducibility of Samples. In order to check the reproducibility of samples with same sensitivity, a batch of 10 samples each of 10g weight was prepared. Variation in the TL intensity of sample in the batch was found to be around + 5% to – 5%. Fig. 16 shows the TL intensity of batch of 10 samples. The TL intensity of each of the sample is around 30 % of LiF: MCP TLD-100H obtained from Harshaw chemical company.

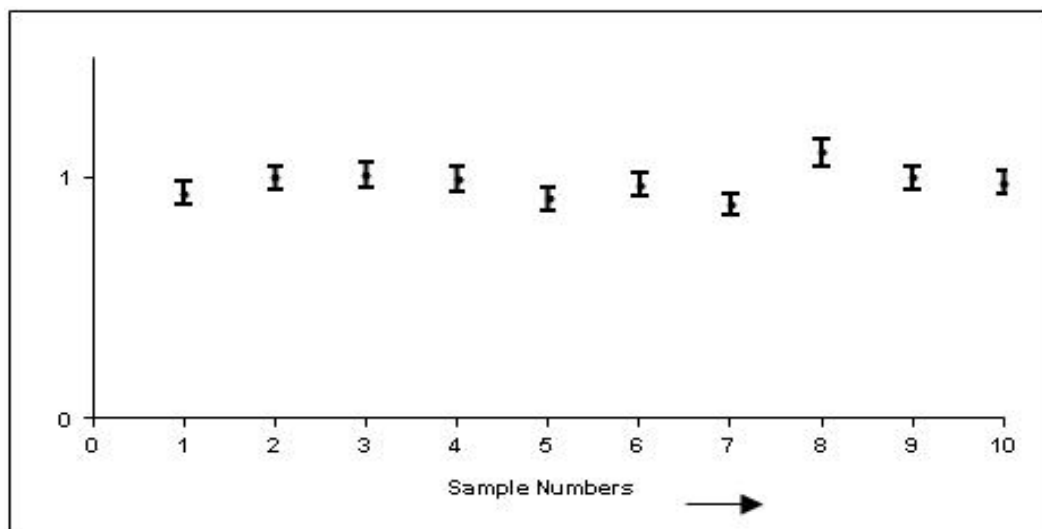


Fig. 16 Reproducibility of LiF: MCP

4.4 LiCaAlF₆:Eu Phosphor

4.4.1 Annealing Procedure. In LiCaAlF₆: Eu (0.1%), it is found that the melted and quenched sample gives small amount of thermoluminescence even without any exposure to radiation. This may put error in readings for low radiation doses. Annealing procedure is necessary in order to reduce any previously absorbed dose. Hence it is necessary to remove this unwanted TL. An experiment was carried out to optimize the sample TL for range of temperature between 250°C to 400°C. Sample was heated in steps of 30°C from 260°C to 400°C. An annealing at 330°C for ½ hour is found sufficient to erase the small TL observed without irradiation and also to retain the TL sensitivity of sample. Fig. 17 shows that the TL response of LiCaAlF₆: Eu(0.1%) from irradiated samples annealed at different temperatures (shown in Fig 12). The best annealing was observed for 330°C. At higher temperatures a rapid decrease in TL was observed. For each TL measurement, a sample annealed at 330°C is used.

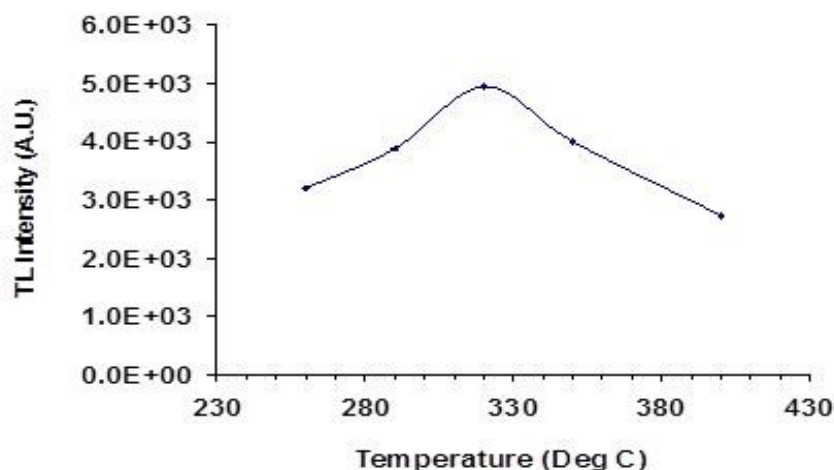


Fig. 17 TL emission vs. temperature of annealing for LiCaAlF₆:Eu (0.1%)

4.4.2 Glow curve of LiCaAlF₆:Eu(0.1%). The TL emission spectrum of LiCaAlF₆:Eu has a maximum at 370 nm, while it is at 540 nm in case of CaSO₄:Dy, where the PMT response is poor. However, if at all a PMT with a flat response over 350-600 nm is available then in that case TL in LiCaAlF₆:Eu is expected to be equivalent to CaSO₄:Dy. Fig. 18 shows the glow curves of LiCaAlF₆:Eu (0.1%), LiF: MCP (Harshaw TLD-100H), LiF: MCP (GR-200P China), CaSO₄:Dy (Renentech TT-88 India) for a gamma dose of 1.0 Joule/Kg at a heating rate of 2°C/s. The measured glow peak temperatures and TL peak intensity and relative intensities in terms of % are shown in Table 1. The glow curve of LiCaAlF₆:Eu²⁺ consists of two peaks; the main dosimetric peak at 185°C and a shoulder at 250°C. For purpose of comparison, sample is compared with commercially available phosphors such as CaSO₄:Dy (Renentech TT88 India), LiF: MCP TLD-100H obtained from Harshaw chemical company and GR-200P obtained from China. It was found that LiCaAlF₆:Eu was as much intense as GR-200P sample while it is nearly 3 times of CaSO₄:Dy and 1.5 times of Harshaw TLD-100H. It has to be noted that the comparison is only indicative. The relative heights of glow peaks for LiCaAlF₆:Eu and CaSO₄:Dy will depend on the PMT response used and TL emission of phosphor. In the present study, we used a Hamamatsu R6095 PMT which has maximum response over 380 to 500 nm.

Table 1 Comparison of LiCaAlF₆:Eu with commercially available phosphors

S.N.	Phosphor	Effective Z	Peak Temp.	TL Peak Intensity (A.U.)	% TL with respect to CaSO ₄ :Dy
1	LiCaAlF ₆ :Eu (0.1%)	13.6	185°C	5080	340.03%
2	CaSO ₄ :Dy (Renentech TT-88 India)	15.3	230°C	1494	100.00%
3	LiF:MCP (Harshaw TLD-100H)	8.2	220°C	3135	209.83%
4	LiF: MCP (GR-200P China)	8.2	220°C	4138	276.97%

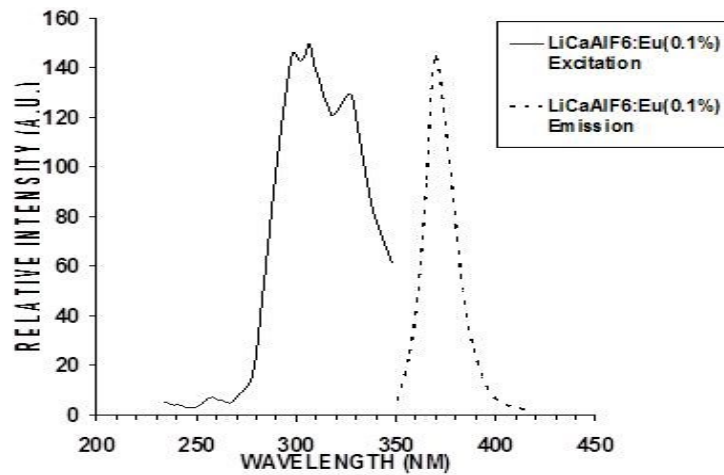


Fig. 18(a) TL excitation and emission peaks of $\text{LiCaAlF}_6:\text{Eu}(0.1\%)$

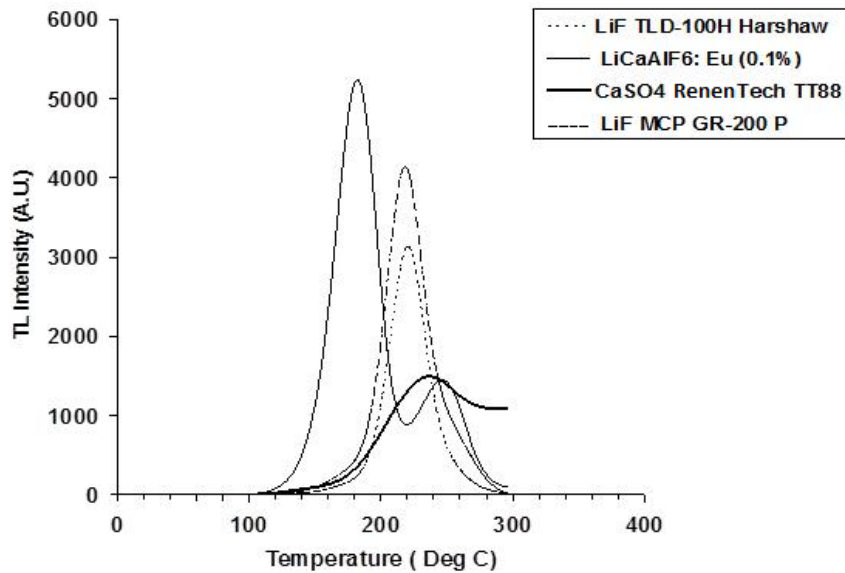


Fig. 18(b) Thermoluminescence Glow Curves of LiF:MCP TLD-100H (Harshaw); $\text{LiCaAlF}_6:\text{Eu}(0.1\%)$; $\text{CaSO}_4:\text{Dy}$ (Renentech TT88 India) and LiF: MCP GR-200P (China).

4.4.3 Effect of Eu concentration on PL and TL of LiCaAlF_6 : Eu Phosphor

Fig. 19 shows photoluminescence (PL) of LiCaAlF_6 with different concentrations of Eu^{2+} [(a) 100, (b) 500, (c) 1000, (d) 1500, and (e) 2000 ppm]. From the figure, it is found that the PL intensity of $\text{LiCaAlF}_6:\text{Eu}^{2+}$ increases monotonously with Eu concentration. On the other hand, the TL intensity of same phosphor shows a different behavior (shown in the same figure) on the right hand curve passing through a maximum that corresponds to Eu concentration of 1000 ppm and the intensity falls for higher concentrations. The difference can be understood on the basis of a suggestion of Shiran et al. [46]. Eu is assumed to play a dual role. It stabilizes the traps and it also acts as a luminescence center. Thus, beyond a certain concentration further increase does not result in an increase in TL yield. On the contrary the process is hampered possibly due to pair formation.

We did not observe any Eu^{3+} emission in our samples or a deep trap high temperature peak in thermoluminescence. Alternatively, the results might be explained also by postulating an independently driven concentration of electron traps (F centers most probably). As the intensity of the TSL glow curve is determined by the smaller concentration from those of the hole and electron traps and Eu^{2+} must act as the hole trap, it is easy to understand the increase of TSL intensity with

increasing Eu concentration and its later saturation (due to constant concentration of electron traps, which becomes smaller with respect to the Eu one). Though we have not recorded the detailed TL emission spectrum at this stage, it could be verified using filters that the TL emission is in the same region as the Eu^{2+} emission [78].

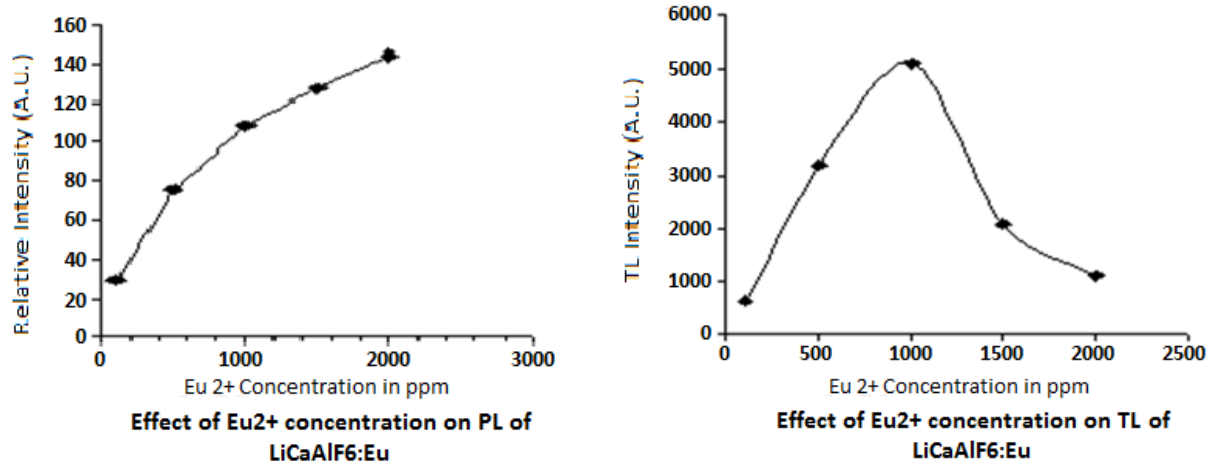


Fig. 19 Eu^{2+} concentration effect on PL and TL of LiCaAlF_6 : Eu Phosphor

4.4.4 Quenching Temperature of LiCaAlF_6 : Eu for TL

The study of effect of quenching temperature on TL output is necessary to decide the perfect quenching temperature for which optimum TL can be obtained. These studies are shown in Fig. 20. We used quenching temperatures from 150 to 700°C. The response is exponential indicating that the preferable quenching temperatures should be more than 700°C, may be nearer to the melting point of the phosphor, i.e., 825°C.

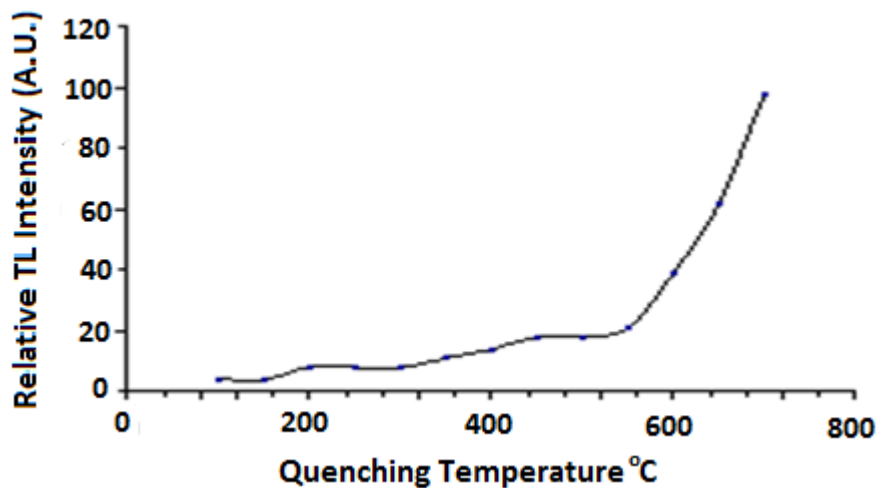


Fig. 20 Variation in TL intensity of LiCaAlF_6 : Eu with quenching temperature.

4.4.5 Thermoluminescence Emission Spectra. The narrow band of spectrum has major emission at 369 nm at temperatures 117°C, 130°C, 160°C, and 200°C. It has a very small peak at 512 nm for the temperatures 110°C and 205°C. It is important to note that the TL emission is in the region of 350-400nm where most of the commonly available PMT have maximum response. We found that LiCaAlF_6 : Eu is suitable TLD phosphor for further systematic dosimetric studies as shown in Fig. 21.

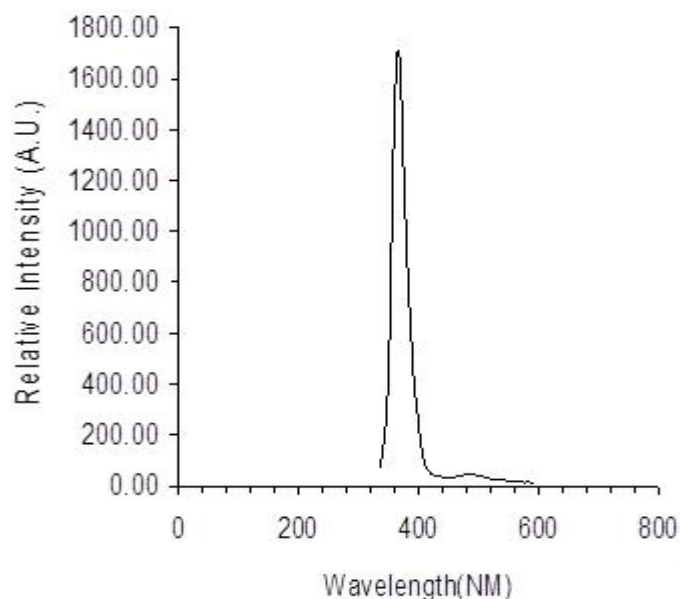


Fig. 21 Thermoluminescence emission spectra of the $\text{LiCaAlF}_6:\text{Eu}$.

4.4.6 Dose Response and Linearity. TL response of a phosphor is required to be linear over a considerable range of doses. The linearity of the TL response of the phosphor to radiation dose is one of the important properties for a dosimeter. To obtain the curve of TLD responses as a function of the radiation dose, $\text{LiCaAlF}_6:\text{Eu}(0.1\%)$ and $\text{CaSO}_4:\text{Dy}$ is irradiated to 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.00 Joule/Kg with ^{90}Sr beta source at room temperature. The response curves for $\text{LiCaAlF}_6:\text{Eu}$ and the standard $\text{CaSO}_4:\text{Dy}$ are shown in Fig. 22, using logarithmic scales. It is observed that the two curves are almost linear and parallel indicating that $\text{LiCaAlF}_6:\text{Eu}$ responds in the same manner as the standard $\text{CaSO}_4:\text{Dy}$ phosphor.

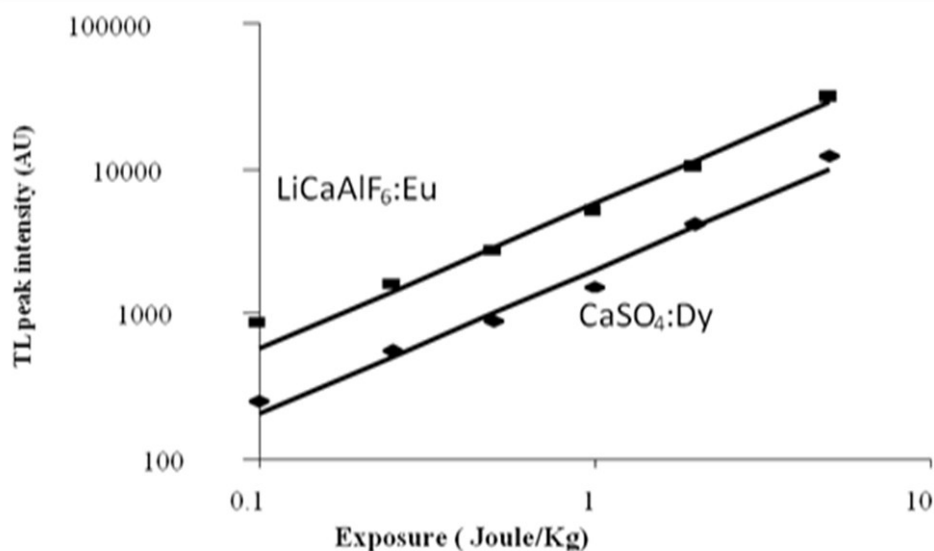


Fig. 22 TL response curves for $\text{LiCaAlF}_6:\text{Eu}$ and $\text{CaSO}_4:\text{Dy}$ in various dose ranges [Ref. 78]

4.4.7 Minimum Detectable Dose of β rays. A minimum detectable dose of $\text{LiCaAlF}_6:\text{Eu}(0.1\%)$ is estimated by adopting a standard deviation method. Experimentally determined minimum detectable dose is defined as that dose which gives three times the standard deviation of the zero dose reading of the dosimeters. For this purpose, seven different glow curve readings were taken. After this, the readings for residual counts were also taken. From this data, the minimum detectable dose is estimated to be 93.66×10^{-6} Joule/Kg.

4.4.8 Energy Response for X-rays. $\text{LiCaAlF}_6\text{:Eu}(0.1\%)$ has an effective atomic number for photoelectric absorption (Z_{eff}) of 13.6 compared to 7.4 of human tissue. Phosphors containing significant quantities of high Z elements over-respond to low energy photons compared to tissue because of the very high Z dependence of the photoelectric absorption coefficient which dominates the gamma ray attenuation coefficients at low energies. Samples were exposed in free air to the pre-defined constant dose (0.01 J/Kg) of X-rays of energies 17.6 KeV, 22.7 KeV, 24.85 KeV, 65.90 KeV, 83.10 KeV, 117.6 KeV, 125 KeV, and 223.9 KeV. The responses were normalized to that measured with ^{60}Co gamma rays. For 24.85 KeV X ray, the $\text{LiCaAlF}_6\text{:Eu}(0.1\%)$ phosphor is found to have an over response of about 5.5 times, with same dose from γ -radiations of 1250 keV of ^{60}Co γ -rays, as shown in Fig. 23.

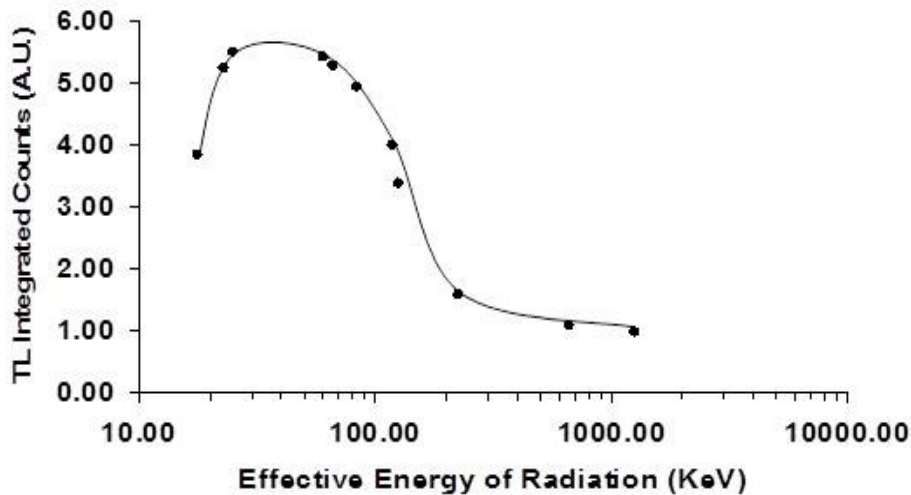


Fig. 23 Energy dependence of $\text{LiCaAlF}_6\text{:Eu}(0.1\%)$ material

4.4.9 Fading Effect due to Storage. $\text{LiCaAlF}_6\text{:Eu}$ sample after annealing at 330°C for $\frac{1}{2}$ hour is irradiated with 0.05 Joule/Kg dose of β -rays and then stored in the dark for about 20 days in order to test the fading properties of main TL peak. The integrated counts of TL glow versus storage period are shown in Fig. 24. Except the early fading within 98 hours the phosphor has only $< 6\%$ loss after 20 days of storage.

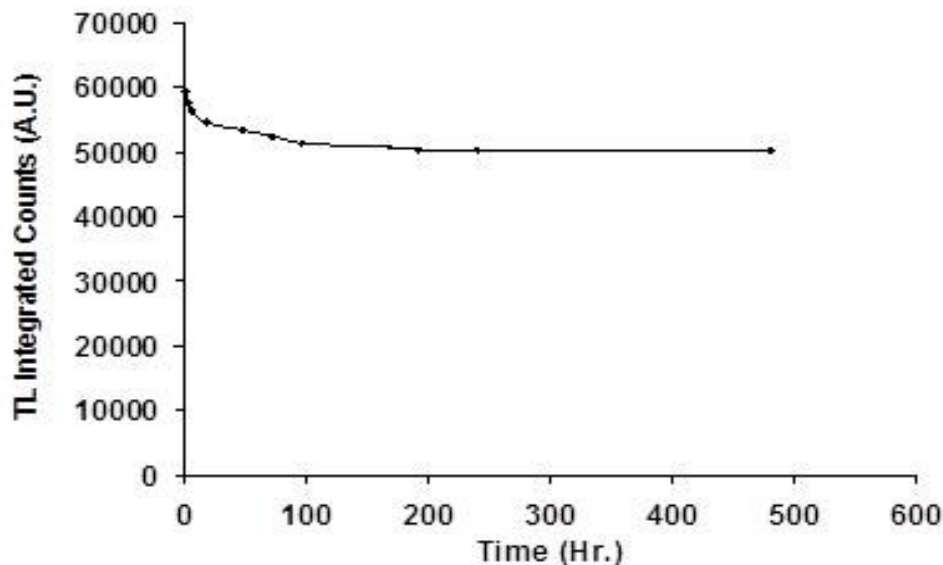


Fig. 24 Effect of storage on the TL of $\text{LiCaAlF}_6\text{:Eu}(0.1\%)$

4.4.10 Reusability. LiCaAlF_6 : Eu (0.1%) powder is first annealed at 320°C for $\frac{1}{2}$ hr before irradiation to 0.05 J/kg and subjected to ten readout–exposure cycles. Fig. 25 shows about TL response of LiCaAlF_6 : Eu phosphor for ten cycles of reuse. The result shows that the dosimeter can measure gamma dose of 0.05 J/Kg with less than 4% variation for 10 sequential measurements.

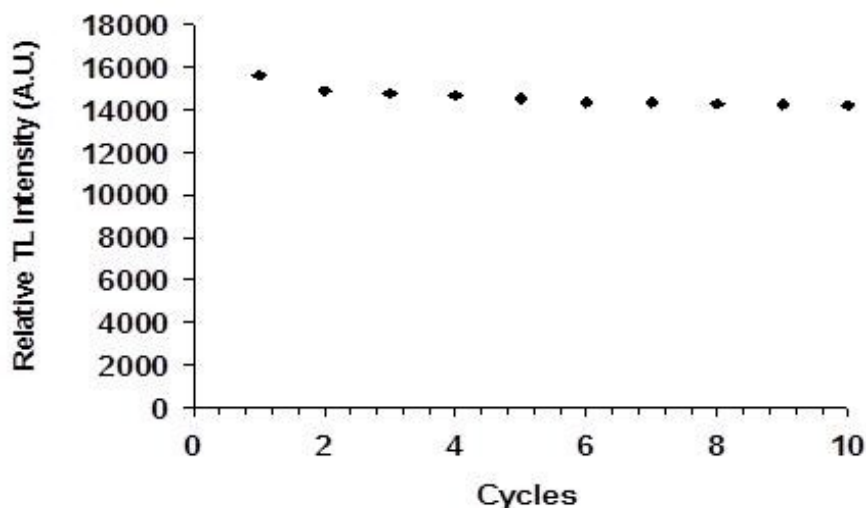


Fig. 25 Reusability of the TL response of LiCaAlF_6 : Eu for 10 cycles.

4.5 TL in Lithium Aluminates and Magnesium Borate

In Lithium-Aluminium mixed oxide system, besides Li_5AlO_4 , other various different phases like LiAlO_2 , LiAl_5O_8 , and $\text{Li}_4\text{Al}_2\text{O}_5$ are also possible. Li_5AlO_4 : Cu (100 ppm) was able to show the TL emission. Other samples were discarded at the first phase because of no or feable TL emission. The sample Li_5AlO_4 : Cu (100 ppm) was then characterized for its structure.

4.5.1 Thermoluminescence of Li_5AlO_4 :Cu

Li_5AlO_4 has Z_{eff} very close to tissue equivalence, and hence this promising material was further tested for rest of the dosimetric parameters. We have taken thermoluminescence measurements of Li_5AlO_4 : Cu, Li_5AlO_4 : Mn and MgB_4O_7 : Dy, Na and compared them with that of LiF : TLD-100 which is widely accepted and commercially used TLD material for fixed exposure of 100 R (0.8696 Gy) and a sample amount of 5mg.

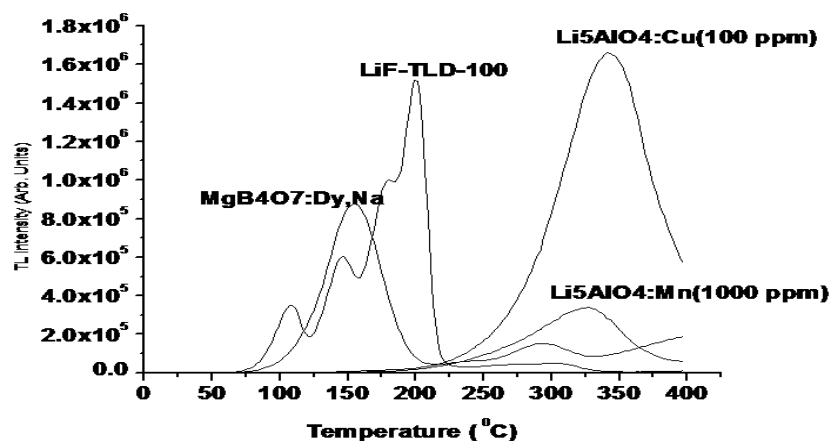


Fig. 26 Glow curves of Lithium Aluminates and Magnesium Borate

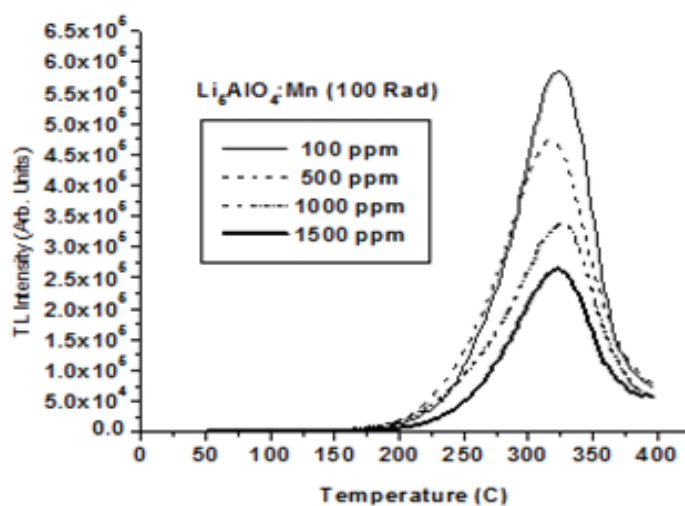
The results are properly scaled and shown in Fig. 26. A glow curve for LiF:Mg,Ti (TLD-100) is also shown for comparison. The intensity scale was reduced to 50%. The TL intensity of $\text{Li}_5\text{AlO}_4\text{:Cu}$ is about 62% of that for TLD-100, whereas the TL Intensity for $\text{Li}_5\text{AlO}_4\text{:Mn}$ was very much less, about 20% of that for TLD-100. The glow curve for $\text{Li}_5\text{AlO}_4\text{:Cu}$ consists of a single glow peak mostly symmetrical at about 341°C. Its shape is very simple and relatively at much higher temperature as compared to TLD-100. Its full width at half maximum is relatively higher than that of TLD-100.

In case of $\text{Li}_5\text{AlO}_4\text{:Mn}$ also the similar TL behavior was noticed. It has a very low intensity and the peak is very wide. The peak temperature in this case is about 327°C. At the first step it may be noted that Cu doping is more effective than Mn in Li_5AlO_4 . However, the $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ has shown promising results as expected. The glow curves for the $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ phosphor were in agreement with those of Furetta et al. [51].

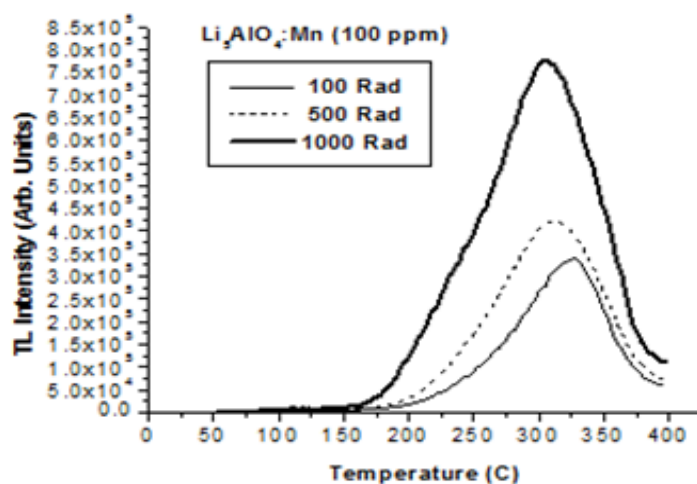
4.5.2 Thermoluminescence of $\text{MgB}_4\text{O}_7\text{:Dy,Na}$

$\text{MgB}_4\text{O}_7\text{:Dy,Na}$ is one of the known promising materials suggested for TL Dosimetry [79]. It has a simple glow curve consisting of well defined main peak at around 163°C using heating rate of 2°C/s and a small high temperature peak at around 300°C. Shahare et al. [57] have investigated the possibility of this material as a promising TL dosimeter. They observed TL peak at 193°C. It was pointed out that the material may consist of two phases after complete synthesis, namely B_2O_5 (30 %) and B_4O_7 (70%) phases; 30% phase (B_2O_5) is relatively unstable [57]. Addition of Na may stabilize the formation of a single and pure phase, i.e. B_4O_7 . Therefore the samples with different doping levels (equal contribution of Dy and Na making total of 500 ppm, 1000 ppm, 1500 ppm, and 2000 ppm) were prepared and investigated under identical exposures. Fig. 27 shows the variation in TL intensity with Dy doping concentration in $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ for the fixed exposure. It is noticed that the TL intensity at the peak 163°C increases with doping concentration. Comparison of TL glow curves of $\text{Li}_6\text{AlO}_4\text{:Mn}$ and $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ shows some interesting results (Fig. 27).

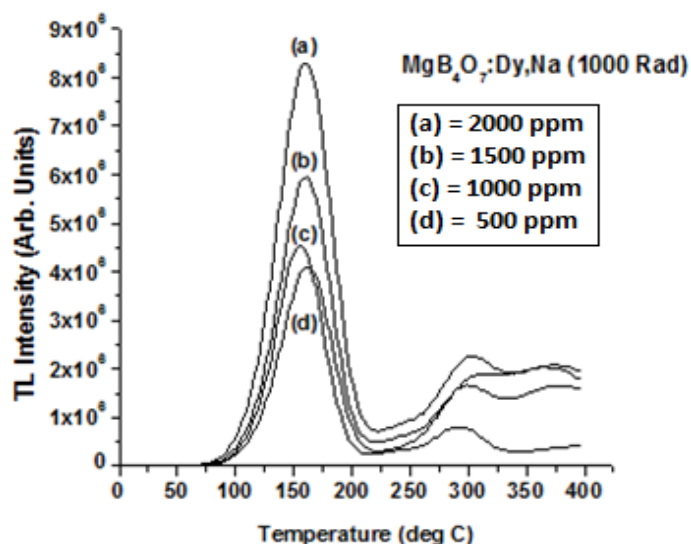
The dose dependence for 1000 ppm sample was also investigated and the results are shown in Fig. 27. It is observed that the TL intensity increases with the increasing exposure. The peak temperature seems to remain constant for all the doses delivered. We have further studied the effect of heating rates on the glow curve of $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ and the results are tabulated in Table 2. There is no change in the shape of the glow curves. Our findings are very well in agreement with that of Furetta et al. [80]. The increase in heating rate shifts the TL peak towards high temperatures with the decrease in TL intensity (peak height) and a little broadening of the glow peak. In this study, a uniform heating rate of 2°C/s was used for all the samples under study. The increase in heating rate increases FWHM, which means widening of glow curve occurs at higher heating rates.



(a)



(b)



(c)

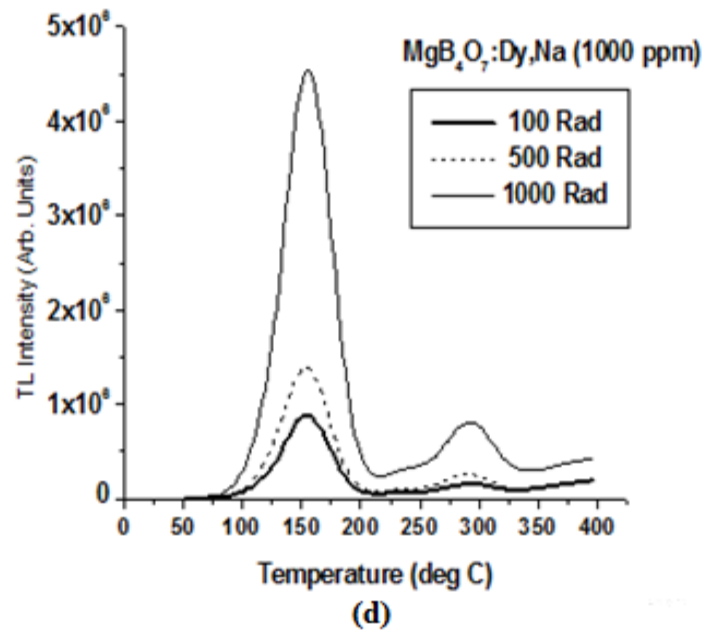


Fig. 27 (a) TL glow curves of $\text{Li}_5\text{AlO}_4\text{:Mn}$ at different conc. of Mn, (b) TL glow curves of $\text{Li}_5\text{AlO}_4\text{:Mn}$ at different dose rates, (c) TL glow curves of Mn $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ at different conc. of Dy, Na, (d) TL glow curves of Mn $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ at different dose rates.

4.5.3 TL Response curves

The relationship between TL response and dose for $\text{Li}_5\text{AlO}_4\text{:Cu}$, $\text{Li}_5\text{AlO}_4\text{:Mn}$, and $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ is reported in Fig. 28, where the glow curve peak height is plotted against the exposure. The irradiations were performed using a ^{60}Co gamma ray source. For each level of dose, five dosimeters were irradiated simultaneously under build up conditions. Each data point corresponds to the mean of the five readings. The perfect linearity is observed in $\text{Li}_5\text{AlO}_4\text{:Cu}$ and $\text{MgB}_4\text{O}_7\text{:Dy,Na}$ for the full range of doses used, i.e. 10 Rad to 10000 Rad. It is observed that the $\text{Li}_5\text{AlO}_4\text{:Cu}$ (100 ppm) is more sensitive than $\text{MgB}_4\text{O}_7\text{:Dy,Na}$. The intrinsic TL sensitivity of a thermoluminescent material is expressed as the TL yield per unit mass and unit of ionizing radiation exposure. In this study, the TL sensitivity is expressed as peak height per unit mass of dosimeter and per unit of dose of gamma rays ($\text{TL mg}^{-1}\cdot\text{Gy}^{-1}$), and the data are given in Tables 2 and 3, relative to TL sensitivity of LiF:Mg,Ti (TLD-100).

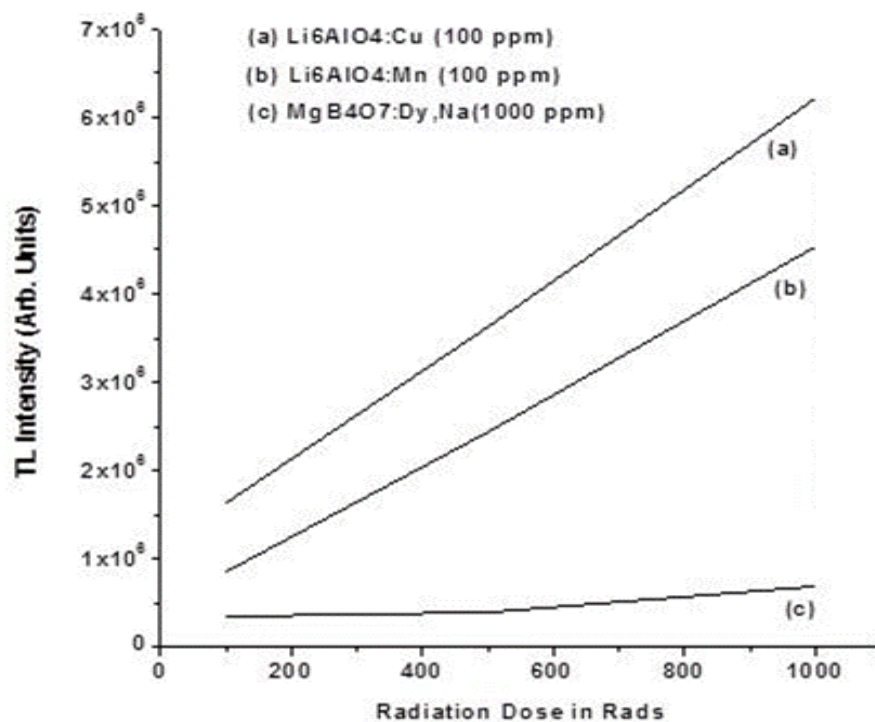


Fig. 28 (a) Response curves for all three phosphors

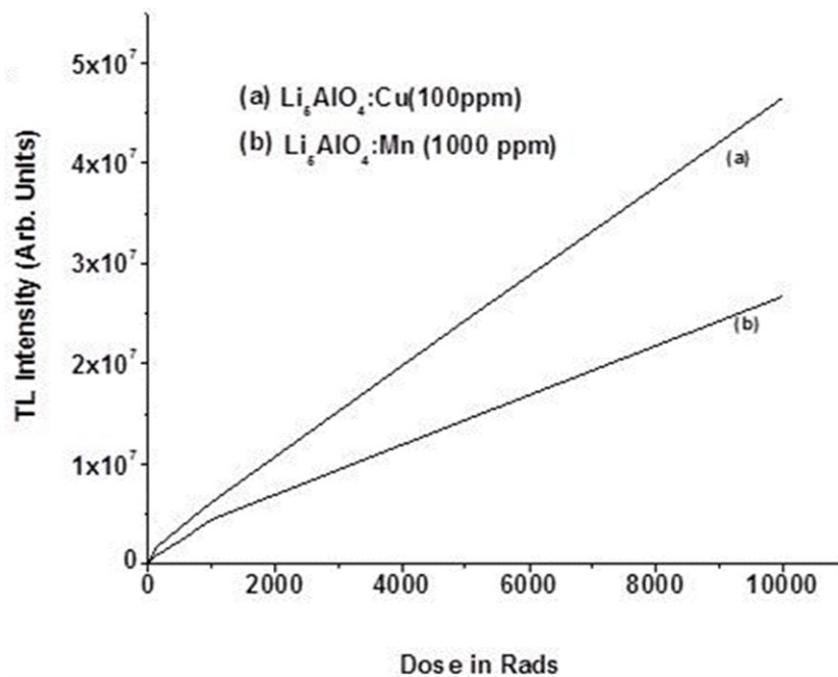


Fig. 28 (b) Response curves for $\text{Li}_5\text{AlO}_4:\text{Cu}$ and $\text{MgB}_4\text{O}_7:\text{Dy,Na}$ at very high exposures

Table 2 Dependence of TL peak temperature of $\text{MgB}_4\text{O}_7: \text{Dy,Na}$ on heating rate

Heating Rate	TL Peak Temperature	FWHM	TL Intensity (normalized)
2 °C/s	163	58	13530
4 °C/s	183	62	12941
6 °C/s	193	64	12353
9 °C/s	203	68	10882
20 °C/s	210	71	10588
30 °C/s	220	71.5	10294

Table 3 Thermoluminescence characteristics of investigated TLD Materials

Detector	Z_{eff}	Main TL peak °C	Reuse annealing	Maximum dose in linear range (Gy)	Fading (3 months) 25 – 27°C (Approx.)	Relative TL sensitivity (TL $\text{mg}^{-1} \text{Gy}^{-1}$)
LiF: Mg, Ti (TLD –100)	8.2	190 –195	1 hr x 400 °C	1-5	5.0%	1.000
$\text{MgB}_4\text{O}_7: \text{Dy, Na}$	8.55	163	1 hr x 400 °C	75	8.0%	0.193
$\text{Li}_5\text{AlO}_4: \text{Cu}$	8.2	341	1 hr x 450 °C	100	1.5 %	0.360
$\text{Li}_5\text{AlO}_4: \text{Mn}$	8.2	327	1 hr x 450 °C	100	15 %	0.0745

4.5.4 Reusability Test. Reusability and thermal stability were checked for all the promising samples. Lithium aluminates and magnesium borate samples were exposed to a dose of 100 Rads, their TL glow curves were recorded and the samples were heated up to 400°C. Several such exposure readout cycles were performed. No change in TL intensity/sensitivity was found.

4.5.5 Fading Test. In order to determine the fading characteristics, the selected phosphors were annealed at 400°C and then suddenly quenched to room temperature. These samples were irradiated to a dose of 1 Gy to 100 Gy. TLD samples were stored in dark conditions of room temperature between 25-27°C. In order to minimize the effect of a possible reader drift, the samples were exposed at different periods of time prior to readout, from 2 months to 1 day. Readout was performed for all the irradiated samples at the same time. Fig. 29 shows the fading effect of all three phosphors.

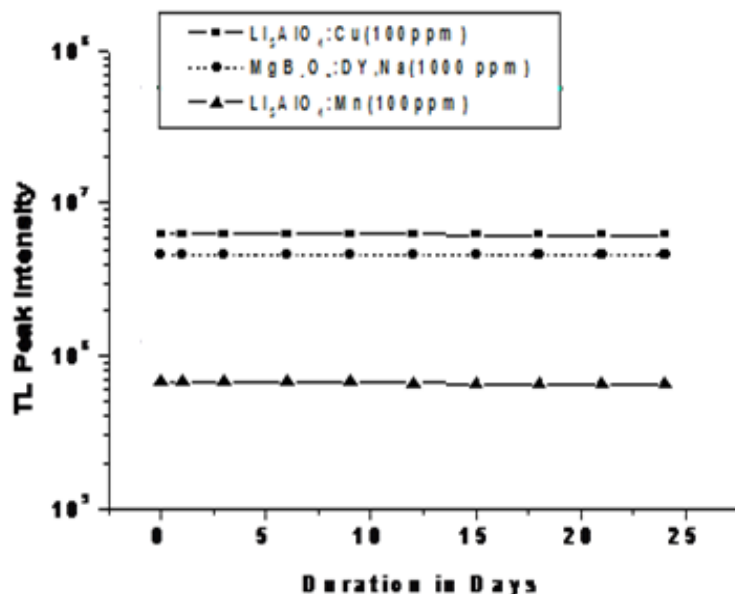


Fig. 29 TL intensity recorded on different days

These investigations are yet preliminary. The tailoring of the material, with the choice and control over the co-dopant, to yield high TL intensity and the peak of the glow curve at appropriate temperature is to be carried out. The further study of these systems with respect to dose linearity, fading characteristics, reuse treatment, and batch processing will decide their usefulness in the TL dosimetry.

5. Summary

In the last three decades, consecutive studies on CaSO_4 and LiF standard materials gives a special attendance to their use in TL and TL related phenomena. Because of good chemical stability and applications, above said phosphors are prominently and consistently used in research as well as applied sciences. In this review, we are successful in making a path for researchers to study efficient TLD phosphors through simple and low cost method for large scale preparation. The review also explores the TL studies on $\text{LiF}:\text{MCP}$, $\text{LiCaAlF}_6:\text{Eu}$, $\text{Li}_5\text{AlO}_4:\text{Cu}$, and $\text{MgB}_4\text{O}_7:\text{Dy, Na}$ for radiation dosimetry. In the present review, we discussed only for radiation dosimetry and have come to the conclusion that $\text{LiF}:\text{MCP}$ and $\text{LiCaAlF}_6:\text{Eu}$ may replace $\text{CaSO}_4:\text{Dy}$ in TL dosimetry. We also conclude that $\text{Li}_5\text{AlO}_4:\text{Mn}$ and $\text{MgB}_4\text{O}_7:\text{Dy,Na}$ compare with $\text{LiF}:\text{TLD-100}$ which is widely accepted and commercially used TLD material for fixed exposure of 100R (0.8696 Gy).

The $\text{LiF}:\text{MCP}$ and $\text{LiCaAlF}_6:\text{Eu}$ samples developed by our group show a comparable TL intensity with $\text{LiF}:\text{MCP TLD-100H}$ obtained from Harshaw chemical company. The glow curve of $\text{Li}_5\text{AlO}_4:\text{Cu}$ consists of a single glow peak symmetrical at about 341°C and MgB_4O_7 glow curve consisting of main peak at around 163°C using heating rate of 2°C/s . A comparison of TL study of $\text{Li}_5\text{AlO}_4:\text{Mn}$ with $\text{MgB}_4\text{O}_7:\text{Dy,Na}$ has been made. The perfect linearity is observed in $\text{Li}_5\text{AlO}_4:\text{Cu}$ and $\text{MgB}_4\text{O}_7:\text{Dy,Na}$ for the full range of doses used, i.e. 10 Rad to 10000 Rad. It is observed that the $\text{Li}_5\text{AlO}_4:\text{Cu}$ (100 ppm) is more sensitive than $\text{MgB}_4\text{O}_7:\text{Dy,Na}$.

Our investigations reveal that these materials are not only sensitive but also satisfy all the basic requirements for TLD materials, such as low Z, symmetrical glow curve in required temperature range ($< 200^\circ\text{C}$), low fading, linearity over considerable dose range, with an excellent reproducibility and reusability. This strongly supports the use of prepared materials in environmental, radiation as well as personal dosimetry.

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