Indigenously Developed LiF : Mg, Cu, P Thermoluminescent Phosphor for Radiation Dosimetric Applications

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Abstract

A highly sensitive and tissue equivalent LiF: Mg, Cu, P Thermoluminescent (TL) phosphor in powder form has been developed. The TL sensitivity of this phosphor is about 1.5 times that of Harshaw-Bicron LiF: Mg, Cu, P (TLD-100 H) by peak height measurements. It gives TL emission band around 370 nm. Its dose vs-TL response is linear up to 10 Gy. Reusability study shows that its sensitivity does not decrease even after 10 cycles of reuse. Annealing temperature was found to affect the glow curve shape and sensitivity.

Introduction

Nakajima et al (1978) reported for the first time in 1978, the preparation of LiF: Mg, Cu, P, a highly sensitive and nearly tissue equivalent TL phosphor. Thereafter many workers (Wu et al 1984, Wang Shoushan 1988, Azarin et al 1989, Horowitz et al 1990, Kolotilin et al 1993, Zha et al 1993) prepared this phosphor in their laboratories following different procedures and studied in detail its characteristics. It is worth noting that unlike CaSO₄:Dy (Yamashita et al 1968, 1971, Ayyangar et al 1974, Azarin 1984), none of the laboratories reported to have used the same preparation procedure. By manipulation of dopant concentration Horowitz and Horowitz (1992) could achieve the TL sensitivity about 35 times as compared to that of TLD-100. Wang Shoushan (1988) has also studied extensively the effect of concentrations of Mg, Cu, P on the sensitivity and glow curve structure of LiF: Mg, Cu, P and concluded that Mg and P concentration influences the height and width of 220 °C glow peak whereas concentration of Cu influences not only 220 °C and 250 °C peak but also the intensity of 110 °C peak. As per their investigation, the optimum concentration was found to be 0.2 mol % MgF₂, 0.0046 mol % CuF₂ and 1.90 mol % (NH₄)H₂PO₄. Patil and Moharil (1995) showed that LiF: Mg, Cu, P could be made using simple procedure which did not involve a use of nitrogen atmosphere.

In the present paper, the preparation procedure and characteristics of LiF: Mg, Cu, P TL phosphor prepared indigenously in BARC are described and compared with that of TLD100-H.

Materials and Methods

Commercially available LR grade LiF was purified by vacuum distillation method (Muralidhar Rao 1974). Appropriate quantities of purified LiF and dopants Mg, Cu and P in the form of MgF₂, CuCl₂·2H₂O and (NH₄)H₂PO₄ respectively were mixed thoroughly. The mixture was melted in a platinum crucible at 960 °C in a furnace for fifteen minutes and then cooled rapidly to room temperature. The polycrystalline phosphor thus obtained was ground to powder (74-210 microns). Several such batches were prepared by varying the dopant concentrations. The batch having highest TL output was chosen to study its sensitivity and other TL characteristics in comparison with Harshaw TLD-100H.

A locally made TL reader having EMI 95248 photomultiplier (S-11 response) as a detector was used for taking the TL measurements. Glow curves were recorded...
using linear heating rate of 10°C/s. For optimisation of annealing temperature, virgin phosphor samples were annealed at various temperatures in the range 240°C-320°C for 10 minutes. Peak height of 210°C glow peak was recorded after a test dose of 0.1 Gy. For gamma dose - vs - TL response, phosphor samples from the same batch were irradiated with Co - 60 gamma rays from 0.01 to 10^6 Gy.

Reusability studies were carried out for 10 cycles of reuse by adopting two different procedures:

**Procedure #1**
All the 10 samples (30 mg each) were first annealed at 280°C for 10 minutes, irradiated to a test gamma dose (0.01 Gy) and then readout by holding the temperature at 280°C for 10 seconds. After reading all the samples, one of the samples was removed from the process and marked as "cycle 1". This was repeated for ten cycles.

**Procedure #2**
The above process was repeated except that instead of pre-annealing at 280°C for 10 minutes, pre-annealing was done at 240°C for 10 minutes and the samples were also readout holding the temperature at 240°C for 10 seconds.

TL emission spectra were recorded on an indigenously made TL emission spectrometer using a locally made monochromator (CEL India). 1 nm slit was used for recording the TL emission spectra.

**Results**
During preparation of LiF:Mg,Cu, P, only freshly distilled LiF powder was used as it was observed that it gave better reproducibility.

**Glow curve**
Figure 1 shows the glow curves of virgin LiF:Mg,Cu,P (BARC) phosphor prepared in this laboratory and Harshaw TLD 100-H after a test gamma dose of 0.1 Gy. Both the phosphors have similar glow curves with main dosimetric peak at about 210°C. Out of various batches prepared by varying concentrations of Mg, Cu and P, the batch of LiF prepared by doping 0.4 mol % Mg, 0.002 mol % Cu and 0.85 mol % P was found to give highest TL sensitivity which was about 1.5 times (peak height) as compared to TLD 100-H.

**Effect of annealing treatment**
Figure 2 shows the glow curves of LiF:Mg,Cu,P (BARC) taken after various pre-irradiation annealing treatments. In general four glow peaks at about 120, 165, 210 and 275°C are seen. It can be seen that, as the annealing temperature is increased from 230 to 320°C, 165°C glow peak decreases whereas 210°C glow peak height increases up to pre-annealing temperature of 280°C and beyond this temperature, it again decreases. The effect of annealing treatment on the TL sensitive (210°C peak height) of LiF:Mg,Cu,P (BARC) and TLD 100H is shown in Figure 3. It can be seen that 280°C for 10 min annealing treatment increases the TL sensitivity of LiF: Mg, Cu, P (BARC) phosphor by about 1.25 times as compared to 240°C, 10 min annealing treatment, whereas in the
case of TLD-100H, annealing treatment 240°C, 10 min gives maximum TL sensitivity.

Gamma Dose vs. TL Response

Figure 5. shows the gamma dose -vs-TL response of LiF:Mg,Cu,P (BARC) and TLD-100H. Both phosphors show linear response up to 10 Gy. Beyond this, the dose response becomes sub-linear and saturates above $10^3$ Gy.

Reusability

No loss in sensitivity was observed after 10 cycles of reuse if reusability procedure #2 is adopted. However, 25% loss of sensitivity was observed in case of reusability procedure #1. It was observed that, although, 280°C, 10 minutes annealing treatment gave maximum TL sensitivity, it was not very useful for reuse of the phosphor. Pre-irradiation annealing treatment at 240°C for 10 min give better reusability.

Effect of phosphorus doping

Figure 4 shows the variation of TL sensitivity of LiF:(Mg 0.4 mol % , Cu 0.002 mol %, P) with various phosphorus concentration. The TL sensitivity increases with phosphorus concentration. It was observed that the TL sensitivity is a step function of P concentration. This result agrees with the observation made by Bilski et al 1996.

Emission spectrum

The figure 5 shows an emission spectrum of LiF: Mg,Cu,P (BARC) taken at 200°C temperature. The spectrum shows a broad TL emission band around 370 nm which corresponds to Cu$^+$ emission as reported by Patil and Moharil (1995).
Discussion

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. For example, McKeever (1991) states that 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 can be assumed that the TL is emitted from Mg / P phases. Mahajna et al (1995) claimed that P takes role of Ti in LiF:Mg,Cu,P. Bos et al (1996) 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 (1996) 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 doesn’t involve directly in the TL process. On the contrary, the work of Patil and Moharil (1995) 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 phosphorus.

As the gamma vs. TL dose response curve (fig. 5) is linear up to 10 Gy, this phosphor can be used for personnel monitoring and radiation dosimetry up to a dose level of 10 Gy.

Conclusions

1. TL sensitivity of LiF:Mg,Cu,P phosphor is highly dependent on the preparation procedure and specially on age and purity of LiF powder.
2. Although the best annealing treatment of 280°C, 10 minutes to LiF:Mg,Cu,P phosphor prepared in this laboratory was found to give highest sensitivity as against 240°C, 10 minutes, for TLD-100 H and GR-200, however, pre-annealing treatment at 240°C, 10 min was found to best suited for reusability of the phosphor.
3. Presence of phosphorus helps in incorporation of more copper into the lattice which has been found to be responsible for increasing the sensitivity of LiF:Mg,Cu,P phosphor.
4. Indigenously developed nearly tissue equivalent LiF:Mg,Cu,P phosphor can be
used for personnel and environmental monitoring and in medical physics applications.

References
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