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Radiophotoluminescence and thermoluminescence characteristics of undoped and Mg doped LiF phosphor in the high dose region

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ABSTRACT

Radiophotoluminescence (RPL) and thermoluminescence (TL) from undoped and Mg-doped LiF powder samples were investigated for high dose dosimetric applications. F-aggregate centres in LiF are created by radiolysis. The RPL emission at 530 nm and 650 nm from F_3^+ and F_2 centres respectively (on excitation at 450 nm) in undoped commercial LiF powder enhanced with increasing sintering temperature. Its TL glow curve showed peaks at 145, 290 and 365 °C. The RPL-TL correlation studies carried out for the first time showed that the thermal annihilation of F_3^+ and F_2 centes following F_i^0 - V_a (interstitial-vacancy) recombination cause 290 °C and 365° TL peaks respectively. This showed that F_2 centres are thermally more stable than F_3^+ centres. Its integrated TL response kept increasing nearly linearly up to 14 kGy, in contrast to the response of the TL peaks in dosimetry grade LiF:Mg, Ti (TLD-100). However, the TL from LiF suffers from fading problems. A 100 °C, 15 min pre-read annealing treatment erased most of the 145 °C TL peak without disturbing the other high temperature peaks. A 750° C, 22 h sintering treatment in carbon atmosphere shifted the major TL glow peak of undoped LiF to 200 °C but reduced its TL sensitivity by more than a factor of 10. Mg-doped LiF samples exhibit a TL glow curve peaking at ~240 °C with satellite peaks typical of Mg doped LiF whose shape did not change significantly with gamma dose. However it showed lower TL and RPL sensitivities as compared to those of undoped LiF. All LiF except LiF alfa (750 °C, 1 h, CB) showed sublinear increase in TL with dose and therefore will cause inaccuracy in dose measurements especially at high doses due to reduced sensitivity. LiF alfa 750 °C, 22 h and 1000 °C, 6 min sintered powder samples are better than others because their RPL sensitivity increases nearly linearly with dose. However, a low fading observed in the latter sample supports its application. The bright yellow RPL emission seen through a 550 nm cut on filter illuminated with a 450 nm blue LED or He-Cd laser light could quickly confirm an irradiated consignment on which LiF samples are affixed. The increase in green to red emission ratio with dose and post-irradiation storage period might be related to slow migration of anion vacancies created by one secondary electron track to F centres created by another track and consequent conversion of $F_2 \rightarrow F_3^+$ centres.

1. Introduction

Colored LiF salt has always been considered as a singular optical material among alkali halides and other dielectric crystals for its peculiar characteristics, which in due time have been applied with success in thermoluminescence (TL) and laser technology. The application of LiF in laser technology has been reviewed by Baldacchini (2002). In practice, miniaturized photoluminescent (PL) patterns can be produced rather easily by using low-energy electron beams and soft X-rays. So, LiF salt is becoming a new interesting photonic material with promising developments in basic research and applications in lasers and other fields as well. High level gamma irradiation (30–10^5 Gy) is employed for several applications including food processing, sterilization of medical products, polymerization, polymer degradation etc (IAEA, 1998). For food irradiations 1–10 kGy is the dose region of interest. Department of atomic energy recognized irradiation facilities operate at several places in India. It is necessary to confirm if a product is irradiated or not and also the exact irradiation dose. Presently, no simple radiation dosimeter system exhibiting linear and stable response exists in this dose region. Electron spin resonance of alanine dosimeter recommended by IAEA requires expensive detective equipment. Color change of chemical dosimeter is highly qualitative. There is a need to develop simple, stable and precise radiation dosimeters for this purpose. Especially in food irradiation of perishable commodities,

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radiation is delivered in sub-ambient temperatures such as chilled (0 ± 4° C), frozen (−20 ± 2° C) atmosphere and radiation doses are required to be measured at these low temperatures (Sanyal et al., 2010). Available chemical dosimeters in liquid state are not suitable for sub-ambient dosimetry. In order to address these problems solid state dosimeters could be the most suitable option after necessary studies. Passive radiation monitors such as TL or radiophotoluminescent (RPL) dosimeters are simple to operate. However, presently used TLDs exhibit multiple glow peak structure, change in glow peak structure with dose and saturation/sublinear or supralinear response in the high dose region due to saturation of filled traps and/or trap competition/trap damage leading to nonlinear response with dose (Lakshmanan and Bhatt, 1979; 1981; Bhuwan Chandra et al., 1982a, 1982b). In the present work it is intended to develop new RPL/TL phosphors which overcome these drawbacks. At high gamma doses, F-centres created by different electron tracks in LiF aggregate to form F_2 and F_3^+ centres which give intense RPL in the high dose region (0.1–10^2 kGy) (Lakshmanan et al., 1996). A commercial system known as Sunna dosimeter based on this technique is being used for high level radiation dosimetry using pure LiF phosphor (Kovacs et al., 2002, 2004; Murphy et al., 2002). The RPL characteristics of TL grade LiF:Mg, Ti and LiF:Mg,Cu,P stimulated by blue light (460 nm) and measured in a pulsed mode within a spectral window around 530 nm were investigated recently to ultrahigh electron doses ranging upto 1 MGy. The RPL dose response of both detectors was found to be linear up to 50 kGy and sublinear in the range of 50 kGy to 1 MGy (Mrozik et al., 2014). The effect of dopants' concentration on high dose high temperature TL of LiF:Mg,Cu,P detectors were also studied (Obryk et al. 2017). While the defect centres giving rise to RPL in undoped LiF have been well identified (Lakshmanan et al., 1996), those giving rise to various TL peaks in undoped LiF have not yet been identified. No study on RPL -TL correlation has been carried out so far. While all members of the alkali halide family are candidates for F-aggregate-centre luminescence dosimetry, LiF was chosen for a number of reasons. First, the LiF is stable against humidity. Secondly LiF crystal is commercially available in large quantities through its use as optical window material. Thirdly, LiF is nearly tissue equivalent in its energy response to photons, making it a suitable material for mixed field dosimetry applications. Finally, LiF can be excited by a low cost, commercially available 450 nm He-Cd blue-light laser and its F-aggregate centre luminescence occurs significantly within the visible spectrum. This feature simplifies light detection since phototubes that are sensitive to the visible light spectrum are readily available. Due to these special features of LiF, the RPL from thin reactive LiF films have been used as nuclear sensors (Cosset et al., 1997). It was possible to record the transversal proton beam intensity profile by acquiring the RPL image of the irradiated spots on LiF films by a standard optical microscope (Piccinini et al., 2014).

Unlike undoped LiF, Mg-doped LiF does not exhibit low temperature TL peak which would eliminate post-irradiation fading. Therefore apart from undoped LiF, Mg-doped LiF powder was also synthesized and studied. The present study compares the TL and RPL characteristics of a commercial grade LiF powder in undoped as well as Mg doped form in the high gamma dose region after suitable sintering/melting treatments.

2. Material and methods

Commercial grade LiF powder made by Alfa Aesar, England was used in this study after 750 °C, 1 h (sample A) sintering in alumina crucible under reducing atmosphere since firing in air did not result in reproducible results due to the incorporation of atmospheric oxygen in LiF crystal lattice. The carbon reducing atmosphere was achieved by keeping the powder samples in a covered alumina crucible which was placed in another covered crucible containing carbon powder (N33 grade). The burning of carbon in an enclosed manner releases carbon monoxide which acts as reducing atmosphere. This procedure is much simpler and cost effective when compared to the conventional method of flushing with high pure H_2 + N_2 gas mixture to achieve reducing condition. The sintered LiF cake was crushed using an agate mortar and pestle into a powder form of about 74 μm size. In addition the effects of prolonged annealing at 750 °C in carbon atmosphere (sample C) as well as melt quenching in air at 1000 °C (sample B) in a platinum crucible on the RPL and TL characteristics of LiF (alfa) powder were studied (the melting temperature of LiF = 845 °C). Mg-doping was carried out by sintering the physical mixture of LiF and MgF_2 (1% by weight) at 750 °C for 22 h (sample D) in carbon atmosphere in an alumina crucible as well as by melt quenching the mixture at 1000 °C for 6 min (sample E) in air in a platinum crucible. In the latter case, the red molten LiF in the platinum crucible was withdrawn from the furnace and poured onto a copper plate kept at room temperature for swift cooling. The hard solid obtained was then crushed into a powder form (74–210 μm). Fast cooling of melted LiF material resulted in higher TL sensitivity as a result of defect centre stabilization when compared to slow cooled samples. All ground LiF powders were milk white in color. Table 1 shows the classification of LiF powder samples used in this study. Gamma irradiations were performed in a ^{60}Co gamma cell having a dose rate of 3.73 kGy/h. Dose range covered was 0.05–100 kGy with a focus at 1–10 kGy as the latter dose region is often used for food preservation. All LiF samples showed a slight brownish color after high gamma dose irradiations as a result of intense color centre production. RPL measurements were carried out in a continuous mode in a Jobin Yvon spectrofluorimeter. The powder sample (~150 mg) was completely filled in a cavity in the solid sample holder in the fluorimeter during RPL measurements. The average of 10 such measurements (1σ = ± 5%) was recorded. The band width used was 2 nm. Optical photographs of the unirradiated and irradiated (300 kGy) LiF (alfa) sintered pellet after 750 °C, 1 h CB treatment were taken with a Sony DSC-S730 camera and Canon Power Shot SD 770 IS still camera *in situ* in the fluorimeter under 450 nm excitation with a 5 nm band width. TL measurements were mostly carried out with a Nucleonix make reader at a linear heating rate of 8 °C/s. The effect of heating rate variation on the TL response was not studied. The maximum readout temperature was 400 °C. At ultra high doses, in order to record the contribution of TL peaks appearing beyond 400 °C, an isothermal heating with 400 °C clamping temperature was used. About 10 mg of the phosphor powder was spread uniformly on the heater planchet during each TL measurement. Five TL measurements (1σ = ± 5%) were carried out at each dose. The average of these readings (TL/mg) was taken for sensitivity comparisons. For materials with high TL efficiencies, a neutral density filter was inserted in between the heating planchet and the photomultiplier so that the photo current does not saturate. In order to study the correlation between TL and RPL, partial thermal bleaching of the TL peaks was carried out by heating sufficient quantity of the irradiated powder on the heater planchet of the TLD reader and the RPL measurements were carried out from the powder collected from the planchet subsequent to thermal cleaning of each TL peak. RPL and TL fading studies were carried out by storing at RT the powder samples in white paper wrapper as well as in black paper wrapper following irradiations. Optical fading of 530 nm RPL green emission was carried out by keeping the irradiated sample in the fluorimeter and shining it

Table 1
Classification of LiF powder samples used in this study.

Sample	Description	Sintering Treatment
A	LiF Alfa	750 °C, 1 h, CB[a]
B	LiF Alfa	1000 °C, 6 min, air
C	LiF Alfa	750 °C, 22 h, CB
D	LiF Alfa + MgF_2 (1%)	750 °C, 22 h, CB
E	LiF Alfa + MgF_2 (1%)	1000 °C, 6min, air

[a] CB – carbon black.