EFFECT OF ANNEALING AND RADIATION EXPOSURES ON LiF (TLD -100) PHOSPHORS

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Abstract

This paper presents the results of an investigation on the characteristics of LiF (TLD - 100). Two sets of LiF badges, the first consisting of 10 pairs of badges and the second consisting of 6 pairs were examined. The badges were pre-annealed and exposed to x ray source. The pattern of the curves obtained from the first set which was annealed with an external oven for one hour at 300°C shows an appreciable response, while the second set annealed for 1 minute shows no significant response; suggesting that annealing sensitized the response of the phosphor. It was found that proper annealing at higher temperatures for longer length of time appears to improve the sensitivity of the phosphor, thus, enhancing its usefulness for radiation dosimetry. In addition, we observed that saturation sets in at higher dose. Saturation was found to set in at 4 units of exposure corresponding to 13.87mSv in the first set, while in the second set, it occurred at 5 units of exposure corresponding to 14.86mSv. The range of the dose for which LiF could be effectively used before saturation sets in lies between 13.87mSv and 14.86mSv.

Keywords: *Annealing, radiation exposure, LiF (TLD-100) thermoluminescence*

1. Introduction

Thermoluminescent dosimeter (TLD) is a thermally activated phosphor in which ionizing radiation causes trapping of freed electrons or (holes) at lattice defects in the crystal structure. Thermoluminescent (TL) is the emission of light that occurs when electrons escapes from the traps and return to stable state. The escape probability could be greatly increased by raising phosphor temperature. If the TL emission is obtained and plotted against time during which the temperature is varied, a glow curve is obtained with several peaks which correspond to various energies of the emptied traps. Thermoluminescent (TL) dosimeters are widely used for radiation detection in environmental, industrial and personal applications (Attix, 1986).

The main advantages of TL dosimeters over other detectors are: wide useful dose range, small physical size, re-usability, and therefore economy, no need for high voltage or cables, and tissue equivalence (LiF) for most radiation types (Aschan, 1999). These properties make TL detectors very useful tools for clinical dosimetry. Since its first use for *invivo* dosimetry for radiotherapy (Daniels et al., 1953), the use of TL detectors has become an important technique for clinical and environmental dosimetry (Kron, 1995).

Different groups of investigators have tried to develop, improve and study characteristics of TL phosphors. Lakshamanan et al. (1981) have proposed a new model for explaining the non-linearity in the response characteristics of three common thermoluminescent phosphors ($CaSO_4$: Dy, CaF_2: Dy and Mg_2SiO4: Tb). In addition, Takenaga et al. (1983) worked on lithium borate ($Li_2B_4O_7$: Cu) activated with copper. They reported that the TL output is linear with exposure to about 10^5R and become sublinear above this;

while $Li_2B_4O_7$: Mn shows supralinearity from 150R to $3x10^5$R. Joshi et al. (1983) examined the thermoluminescent characteristics of NaCl: Ca and reported that it was sublinear at low dose; supralinear at higher dose and eventually saturates. They concluded that NaCl: Ca phosphors satisfy most of the desirable characteristics of a TLD material and can be of use in gamma ray dosimetry. However, a drawback due to atmospheric contamination of the phosphor was observed.

Recently, Chen et al. (2002) have reported a new high sensitivity lithium material doped with magnesium, copper and phosphorus (LiF: Mg, Cu, P.). It has been demonstrated that LiF: Mg, Cu, P is highly efficient as Thermoluminescence dosimeter (Mckeever et al., 1995). However, Wu et al. (1984) and DeWerd et al. (1984) earlier noted that this material loses its sensitivity upon high temperature annealing, a fact that has kept it from commercial development for a number of years. Moreover, recent work has shown, however that it is possible to avoid the annealing treatment and thus maintain the sensitivity of the material over many uses for low dose dosimetry.

Several attempts have been made to understand the structure of certain defects present in the TLD-100 responsible for the complex behaviours of the Thermoluminescence glow peak of the material (Fairchild *et al.*1978; Toshiyuki, 1979; Tekenaga *et al,* 1983; Bos *et al.*, 1993; Joshi *et al.*, 1982; Fairchild *et al.,* 1982a). Very, recently, Yazici et al., (2001) investigated the Thermoluminescence emission band of LiF: Mg, Ti by a simple developed model and they reported that two emission bands were observed for all glow peaks with peak energies at around 3.0eV and 2.75eV. The unique characteristics of LiF (TLD-100) phosphor, which include, tissue equivalence, chemical stability to acid, alkali, organic solvent and water vapour have made it necessary for us to examine the influence of annealing and radiation exposures on it.

In this present work, certain characteristic of LiF: Mg, Ti otherwise called LiF (TLD-100) phosphor is examined

2. Theoretical Consideration

Several band models of TL emission have been developed by different investigators using a number of theoretical calculations based on the shape of emission bands(Huang et al.,1950; Pekar, 1950; Pekar, 1952) . However, the shape of TL emission spectra of some TL material (i.e. LiF: Mg, Ti) is not successfully explained with the developed models (Piters, 1991).

In a recent study, Yazici *et al.* (2001) developed a new simple model based on classical treatment of the lattice vibration and Frank- Condon principle to describe the shape of TL emission band of crystalline solid. According to this model, there are at least two distinct localized energy levels, one of which acts as a trap (T) and the other as a recombination (luminescent) centre (R) (Mckeever, 1985). After the electrons have been raised to excited states they may be re-trapped or, alternatively, emit a photon by returning to the ground state of the centre. The electrons in the traps must be excited to the conduction band (CB) that is, transition of A and B for TL to take place. These electrons then undergo migration in the conduction band and recombine with holes in the luminescent centre by the emission of photons (transition from D and C). The creation of recombination can be through multi-phonon emission and transition of electrons from the excited state to the ground state of luminescent centre via emitting photons as in the Figure 1. The allowed transition includes, (A) and (B) thermal release, (C) migration, (D) non-radiative recombination and (E) radiative recombination.

The number of trapped electrons and, hence, the intensity off thermoluminescence is determined by the amount of radiation energy absorbed and the time for which the phosphor is stored before heating. The probability per unit time that the electron will escape from the trap is given by (Matveev, 1981).

$$P = Se^{-E/kT} \qquad (1)$$

where E is the trap depth, k is the Boltzmann constant, T is the temperature and S is defined as

$$S = N_B V \sigma_t \qquad (2)$$

is the density of states of the band into which the electrons escape, V is the thermal velocity and , is the capture cross section. *P* can still be written as

$$P = \frac{1}{\tau} \qquad (3)$$

where, the time spent in the trap is given by

$$\tau = \frac{e^{E/kT}}{S} \qquad (4)$$

Equation (4) shows the dependence of the time spent in the trap on the depth E of the trap and on the storage temperature. The number of trapped electrons at time *t* can be expressed as

$$n_t = n_{t_0} e^{-pt} \qquad (5)$$

Where is the number of initial electrons trapped. The number of photon *I* emitted per unit time due to the release of trapped electrons is

$$I(t) = \alpha P_{n_{t0}} e^{-pt} \qquad (6)$$

is constant defined as the ratio between the number of light emitting recombination and the total number of recombination.

When the temperature increases at constant time rate, $dT/dt = c$

the expression for emission as a function of temperature *T* becomes

$$I = \alpha n_{t_0} P(T) e^{\frac{1}{c}\int_0^T P(T)\,dt} \qquad (7)$$

Therefore the technique for measuring thermoluminescence consists of raising the temperature of the phosphor at a constant rate. The shallow depth are first emptied and when only one trap is present, the TL goes through one peak and decreases as the trap will contribute a peak at different temperatures.

3. Materials and Methods

LiF: Mg, Ti (TLD- 100) samples used in this study were single crystalline chips obtained from Federal Radiation protection service (FRPS) of the Department of Physics, University of Ibadan. Other materials include: Solaro TLD reader, electrically operated external oven from FRPS. The X Ray Source is a picker machine model DGO 1010 obtained from University college Hospital, Ibadan and operated at 10mAs, 60kVp and source to sample distance (SSD) of 90cm for routine chest X-Ray examinations.

The LiF (TLD 100) Phosphor used consist of two batches, the first batch is made of ten pair and second six pairs. Each of the TLD badges was labeled for easy identification. And to limit the error due to residual information (electron), each of the badges was pre-annealed before the subsequent irradiation (Yazici *et al.*, 2001) and the base line value documented for reference in the subsequent reading.

The Samples were irradiated with x-ray source at room temperature after quenching. The irradiation period was fixed to 0.05s throughout the experiments. For the first batch after the exposure of the pairs only a pair was read and annealed with an external oven at a temperature of 300°C for 1hour, while the remaining nine pairs were kept neither read nor annealed. Thereafter, the ten pairs were exposed again; but the first and an additional pair were read and annealed under the same temperature condition. The process continued for each exposure, each time an additional pair was added to read and annealed group until ten exposures were carried out. Moreover, the same process was used for the six pairs except that six exposures were carried out and the annealing was at 300°C for 1 minute (Ayyangar *et al.*, 1968). Solaro TLD reader was used for reading the light emitted from the phosphors and for annealing of the six pairs.

Each of the phosphors is made of two stations denoted by 2 and 4. The calculation of the absorbed dose was obtained using the following equation (Model 680 Dual Channel TLD Reader Manual)

$$Dose\ (mSv) = \left[\frac{\left(\frac{m_1 + m_2}{2}\right) \times \beta}{100}\right] \qquad (8)$$

Here, m_1 = reading of light output from station 2, m_2 = reading of light output from station 4 and β = calibration factor = 2.75.

4. Results and Discussion

Figure 2 shows the variation of the absorbed dose with number of annealing for the two batches. With regard to the first batch, the minimum absorbed dose recorded was 14.57mSv and this was obtained from the badge annealed once. The absorbed dose increased steadily at the left arm of the curve with increase in the number of annealing. The peak of the curve is centred on 7units of annealing and the absorbed dose equivalent to 48.38mSv. This declined gradually to 32.07mSv at the annealing unit of 10.

In the second batch annealed for 1minute with an inbuilt oven at temperature of 300^{0}C, the results obtained indicate that the lowest value of the absorbed dose is 15.19mSv while the peak dose was 19.49mSv, corresponding to a unit and 6units of annealing respectively.

Figure 3 describes the variation of the accumulated dose with the number of exposure. The curve with the first batch shows that the lowest dose was 3.03mSv. This increases linearly to 5.71mSv, above which the dose increases supralinearity to about 13.87mSv. Beyond 4units of exposure the accumulated dose rose steadily as it approaches the peak value of 14.81mSv corresponding to 2units of exposure and further increases sharply to 13.68mSv. The accumulated dose after the exposure of 4unit increases steadily to 14.86mSv and finally rested on exposure of 6units corresponding to an accumulated dose of 15.19mSv.

The result obtained in the first batch of the badges shows that the highest dose was found to be 48.38mSv at annealing value of 7units. However, the lowest to dose was 14.57mSv for the pair of badges annealed once. The result slows that there is an appreciable and significant difference between the lowest absorbed and the highest dose recorded, about 33.81mSv which represent 70% variation.

This result implies that an increase could probably be attributed to the creation of more trapping centres in the phosphor crystal due to repeated annealing at temperature of 300^{0}C for 1 hour after each read out. Gibson (1948) had reported that the schottky defects in crystal lattices increases exponentially with temperature and could be frozen in subsequent cooling. Additionally, it is commonly reported that the TL response characteristics of the high temperature could be due to the variation in trace impurities present in the host crystal or due to critical dependence of the defect structure formation on the heating and cooling rates of the phosphor. According to Carlsson (1969) and Toivonen (1993), the shortened annealing procedure with a lower annealing temperature (approximately 300^{0}C) reproduces relative detector sensitivities better than the procedure where the TL detectors are heated up to 400^{0}C in free air. Hence, the rise in the absorbed dose at that annealing temperature (300^{0}C) could have contributed to creation of more trapping centres, and could have led to the sensitivity at the left arm of the curve.

On the other hand, the down turn noticed at the 7units of annealing could have stemmed from the declines in the trapping efficiency of the trap centres at high annealing units and thermal quenching of the deep traps. Aschan (1999) has reported possible damages to the detector resulting from a long- term treatment at high temperature.

Moreover, no significant variation was observed in the second batch which was annealed at the same temperature but for a short period (1 minute). The dose annealing curve shows that the highest dose was 19.62mSv and the lowest 15.19mSv representing a percentage variation of 23%. This low variation could be attributed to annealing for a short time.

Furthermore, as regard the variation of accumulated dose with the number of exposures, the result obtained in both batches seem to follow a pattern, only that a striking feature has been identified in the second bath.

In the first batch, the highest value of dose was recorded as 14.76mSv at 9units of exposure. The pattern shows supralinearity (linearity above normal) above 6units of exposure. The second batch also shows supralinearity at high dose. Lakshamanan et al. (1981) have identified supralinearity and attributed it to increased trapping of charge carrier in the dosimetry traps during irradiation due to a reduction in trapping efficiency of deep traps caused by the radiation damage. The lower limit of exposure for LiF is set by spurious effects caused either by oxidation in air or tribothermoluminescence (signal induced by mechanical or grinding of phosphor) (Cameron, 1968).

The saturation or overloading that set in at high dose is said to result from placing the detector in radiation field above the intended range. This can be explained in terms of change in trapping efficiency of traps (having the same depth) with radiation dose. The TL response saturates and the number of charge carrier trapped remains the same beyond particular dose.

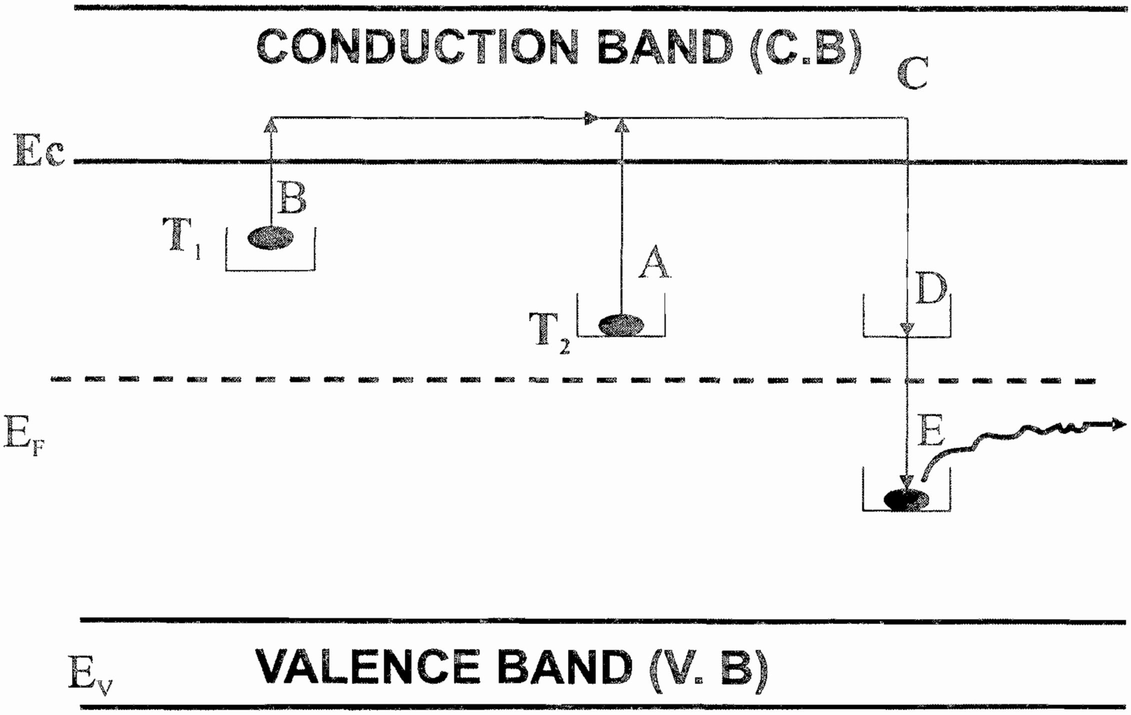

Fig. 1: Simple band model for TL emission

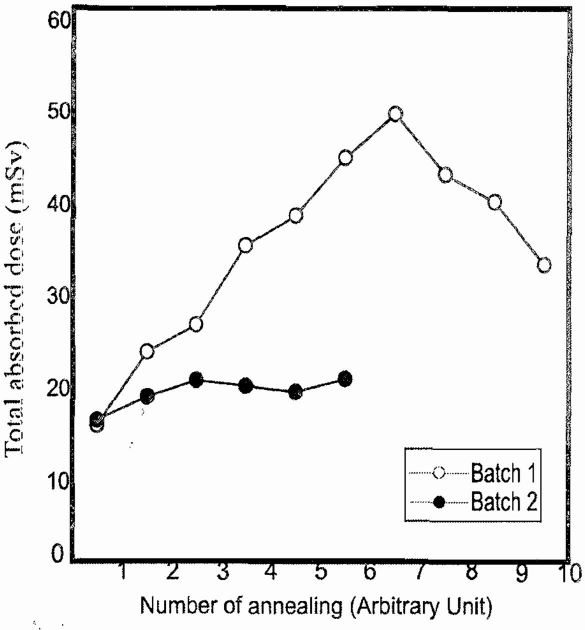

Fig. 2: Variation of total absorbed dose with number of annealing

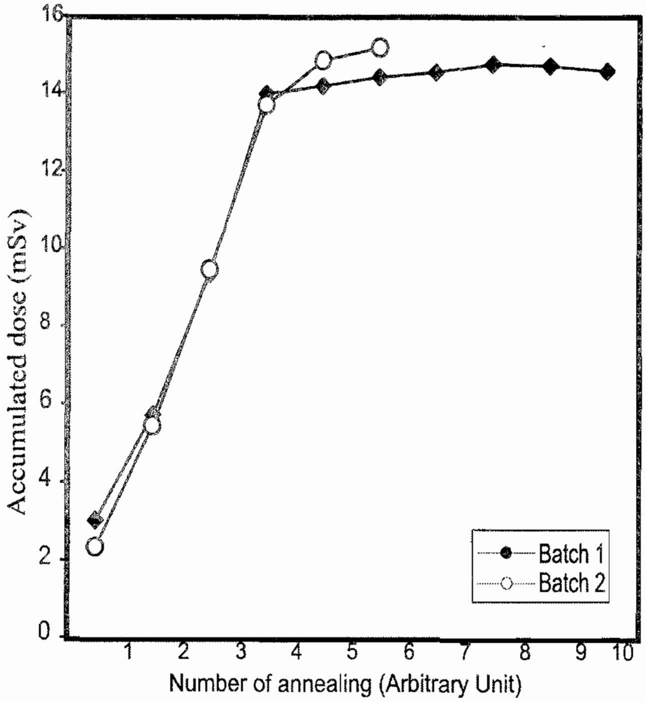

Fig. 3: Variation of accumulated dose with number of exposure

5. Conclusion

The variation of the absorbed dose with the annealing for LiF (TLD - 100) badges annealed with an external oven operated at 300°C for 1hour was investigated. Significant variation in the response to annealing was observed. The peak value of the dose annealing curve is at 7units of annealing, thereafter, there was a gradual decline in the value of the dose. From the pattern of the dose annealing curve, it is necessary to employ shortened annealing procedure with lower annealing temperature (300°C) for a length of time, about 1hour; this improves reproducibility and sensitivity of the detector (Bilski et al., 1997; Toivonen et al., 1999). Repeated heat treatment at high temperature (400°C) could lead to radiation damage of the LiF. Heat treatment for a short period off time could also reduce the sensitivity of the detector. Consequently, appropriate annealing temperatures and time of detector should be obtained from the manufacturer to enhance optimum performance of the detector and to ensure that its life span is not reduced.

The pattern of the variation of the accumulated dose with the number of exposure for both batches show supralinearity at high dose. In addition, saturation sets in at high dose. However, the striking disparity between the two curves is that saturation sets in the first batch at 4units of exposure corresponding to 13.87mSv and that of the second batch at 5units of exposure corresponding to 14.86mSv which is higher than the first batch.

As a final note, the result obtained from the two batches show that LiF (TLD-100) Phosphor can be effectively used in the neighbourhood of 14.36 0.5mSv before saturation sets in.

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