

# The effect of optical bleaching at selected photon energies on the thermoluminescence of LiF:Mg,Ti

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Keywords: Optical absorption, Thermoluminescence, photon bleaching, TLD-100, composite glow peak 5

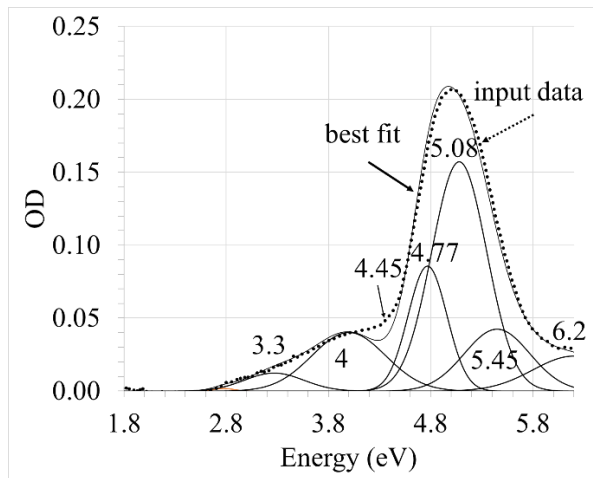
**Abstract.** A new interpretation of the optical absorption energy spectrum of LiF:Mg,Ti (TLD-100) is presented in which the 4.0 eV band is composed of two-sub-bands at 3.8 eV and 4.3 eV. The new interpretation is of central importance in the understanding of the geminate recombination mechanisms giving rise to composite glow peak 5 in the thermoluminescence (TL) of TLD-100. Photon bleaches at energies of 3.6 eV and 4.3 eV on samples of gamma irradiated TLD-100 were carried out in order to investigate the correlation of the 4.3 eV absorption band with the electron-hole configuration giving rise to glow peak 5a and the 3.8 eV absorption band with the e-only configuration giving rise to glow peak 5. The 4.3 eV bleach decreases peak 5a dramatically and increases peak 4 (a hole-only configuration). No such effect is observed following the 3.6 eV bleach. The results strongly support the suggested structures giving rise to the 4.3 eV and 3.8 eV bands observed in the optical absorption energy spectrum.

## 1. Introduction

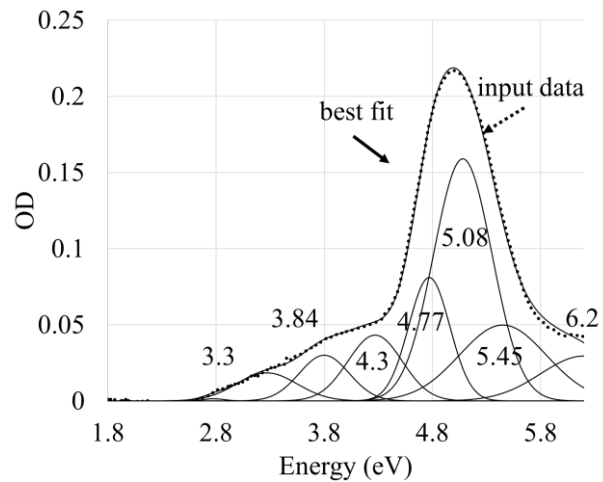
Recent investigations [1] have suggested that the 4.0 eV optical absorption (OA) band in LiF:Mg,Ti (TLD-100) is actually a composite structure consisting of two bands at 3.84 eV and 4.3 eV. In this new interpretation, the 3.84 eV and 4.3 eV bands replace the broad 4.0 eV band and the 4.45 eV band. The poor fit to the experimental spectrum at ~ 4.45 eV was the reason that prompted various authors [2-3] to include an additional band of unknown origin at this energy as shown in Figure 1. A typical OA spectrum with the new interpretation is shown in Figure 2.

The 5.45 eV band is believed to arise from a trapping center (TC) which acts as the competitor to the 4 eV TC when the sample is heated to produce the TL of composite peak 5. The 5.08 eV band arises from F center absorption and the 4.77 eV band may be F center –related but its exact structure is unknown. The 3.3 eV band is believed to be arise from Mg based dipoles and is correlated with glow peak 2. Both the 3.3 eV band and the 4 eV band are absent in the OA spectrum of 4N single crystal LiF (Figure 3) which establishes their association with the Mg and Ti dopants in TLD-100. The extremely low relative intensity of both glow peaks 5a and 5 in the 4N sample, approximately 0.1% per mgm compared to TLD-100 which lends additional credence to the reasoning that the 4.3 eV entity observed in 4N material do not origin from the same impurities.

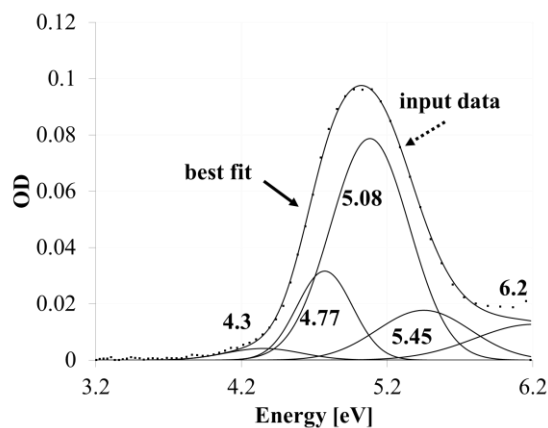




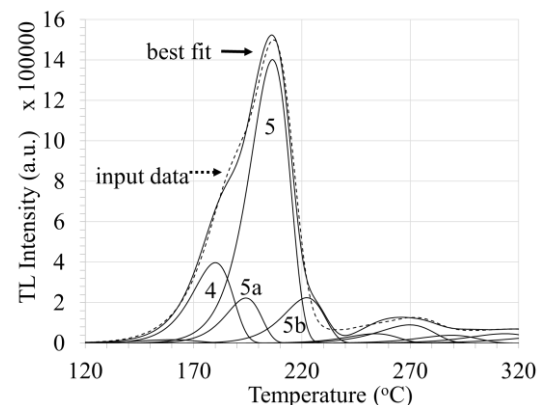
**Figure 1.** OA spectrum with conventional analysis – 4.0 eV and 4.45 eV OA bands of sample with 0.4mm sample, irradiated to 2500 Gy. Input data (dotted line), fit (solid line). Reproduced from [1].



**Figure 2.** OA spectrum with new analysis – 3.84 eV and 4.3 eV bands of 0.4mm samples, irradiated to 2500 Gy. Input data (dotted line), fit (solid line). Reproduced from [1].



**Figure 3.** OA spectrum of 0.9 mm 4N single crystal LiF irradiated to 1000Gy.



**Figure 4.** Typical TL glow curve TLD-100 following irradiation and PIA.

The 4.0 eV band has been associated with a trimer trapping center (TC) based on Mg-Livac dipoles and coupled to Ti-OH molecules [2,3]. The 4.45 eV band was considered controversial in nature and could not be associated with any specific defect [4]. The 4.0 eV OA band has been associated with glow peak 5 in the glow curve of LiF:Mg,Ti (TLD-100) which is also believed to be a composite structure consisting of glow peak 5a (arising from an electron-hole configuration) and the major peak 5 (arising from an e-only configuration) in a spatially correlated trapping center/luminescent center (TC/LC) [5]. It is also believed that the hole-only configuration gives rise to peak 4 in the thermoluminescence (TL) glow curve [6,7]. This TC/LC model has been used to explain many of the ionization density dependent characteristics of these glow peaks [8] but distinct OA bands supporting the interpretation of glow peaks 5a and 5 have not been

observed prior to this work. A typical glow curve of TLD-100, following gamma irradiation to 1 Gy and post irradiation anneal (PIA) to 160°C for 6 s, is shown in Figure 4.

## 2. Materials and Methods

Four samples of TLD-100 (3 x 3 x 0.89 mm<sup>3</sup>) were irradiated to 1Gy with <sup>137</sup>Cs gamma rays. The samples were pre-irradiation annealed at 400°C for 1 hr followed by slow cooling (50 °C hr<sup>-1</sup>) to room temperature. Glow curve readout was carried out at a heating rate of 1°C s<sup>-1</sup> following a post-irradiation anneal (PIA) of 160°C for 6 s which removes the low temperature glow peaks and simplifies the analysis of the effects of the photon bleach on the glow curve. Glow curve deconvolution was carried out with first order peak shapes based on ancillary thermal and optical excitation which isolate peaks 4 and 5 and allow estimates of the peak parameters relatively free of deconvolution uncertainties [9]. The starting parameters of the deconvolution analysis are shown in **Table 1**. The 160°C PIA removes peaks 2 and 3 from the glow curve.

**Table 1.** Glow peak starting parameters used in the deconvolution analysis.

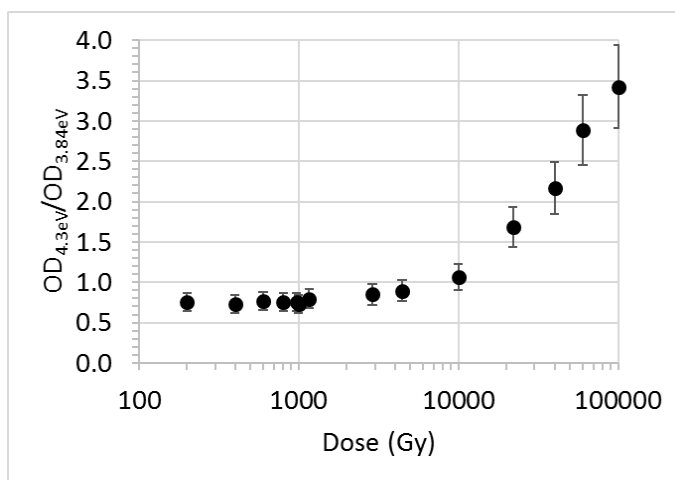
Peak	Peak Temperature [°C]	Activation Energy [eV]
2	119	1.1
3	162	1.15
4	182	1.9
5a	196	2.3
5	208	2.15
5b	224	2.25
6	241	2.1
7a	256	2
7	271.5	2
8	291	2
9	315.5	2
10	338	1.8
11	366.5	1.8

For the optical bleach experiments the light source employed was a 300 W xenon lamp attached to an Oriel 1/8 m monochromator with 1200 lines·mm<sup>-1</sup> grating and 0.76 mm entrance and exit slits allowing a bandwidth of 5 nm. The output intensity at 310 nm was 0.3 mW·cm<sup>-2</sup>. The optical absorption spectra were measured with a Genesis-5 UV/Visible wavelength spectrophotometer (Milton Roy Inc.) equipped with an IBM-PC. The OA spectra were deconvoluted using a commercial “Peak-Fit” non-linear curve fitting program from Jandel Scientific with Gaussian peak shapes. In addition background subtraction of the OA spectra from irradiated material was also carried out. OA measurements of samples before irradiation were used as background data.

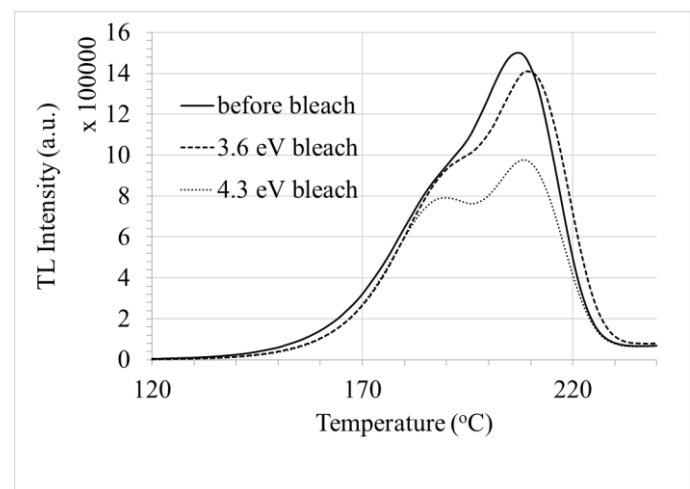
## 3. Results and Discussion

The preferential population of the 4.3 eV OA band at high levels of dose is shown in **Figure 5** and suggests on statistical grounds that it may be associated with the e-h configuration and glow peak 5a and the 3.84 eV OA band with the e-only configuration and glow peak 5. The motivation for this work, therefore, was to observe the effect of 3.6 eV and 4.3 eV photon bleaches on the TL glow curve in order to provide evidence which either supports or contradicts this correlation. The photon energy of 3.6 eV (instead of

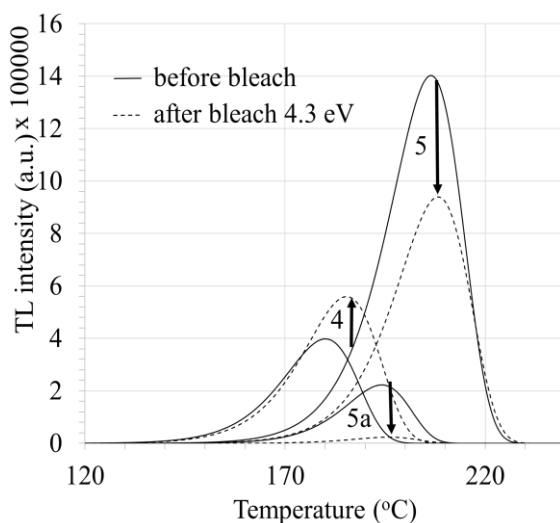
3.84 eV) was chosen as this energy lies outside the range of energies of the 4.3 eV band and could therefore be assumed to excite only the 3.84 eV trapped electrons. At 4.3 eV there is a slight overlap with the 3.84 eV band, however, this could not be avoided. The glow curves following the 3.6 eV and 4.3 eV bleaches are shown in Figure 6. Both glow curves are shifted somewhat to higher temperatures which is probably due to instrumental/measurement factors [10]. The increased intensity of peak 4 following the 4.3 eV bleach (relative to the 3.6 eV bleach) is visually obvious and is supported by the deconvolution analysis shown in Figures 7 and 8. In the case of both bleach energies, a shift of 3-4°C to higher temperatures in the value of the maximum intensity,  $T_{\max}$ , of the glow peaks was necessary to achieve an optimum fit using the figure of merit (FOM) criterion [11]. The shift to higher temperatures did not, however, significantly influence the relative results of the deconvolution analysis or the interpretation of these results.



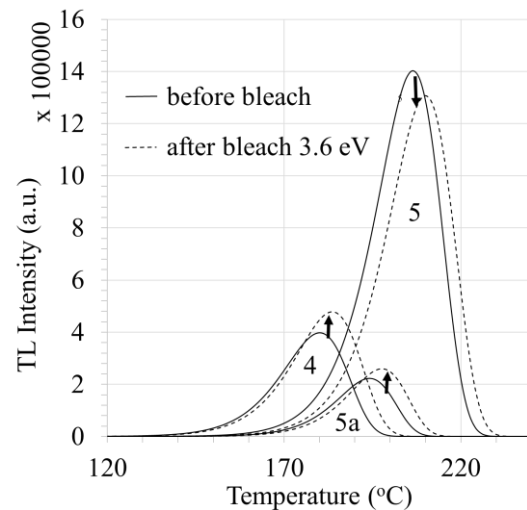
**Figure 5.** Ratio of the optical density of the 4.3 eV band to the 3.84 eV band as a function of dose. Reproduced from [1].



**Figure 6.** The measured TL glow curves showing the effect of the 3.6 eV and 4.3 eV bleach.

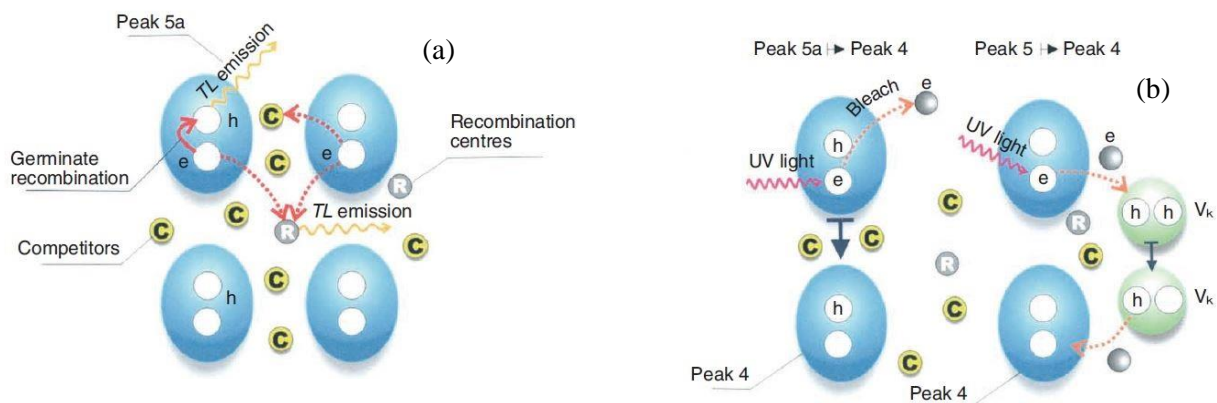


**Figure 7.** Representative deconvoluted TL glow curve showing the effect of the 4.3 eV bleach.



**Figure 8.** Representative deconvoluted TL glow curve showing the effect of the 3.6 eV bleach.

Figures 7 and 8 show representative (all measurements were carried out on the same experimental conditions) deconvoluted glow curves of peaks 4, 5a and 5 following gamma ray irradiation and the effect of the 4.3 eV and 3.6 eV bleaches on the relative intensities of these glow peaks. Figure 7 shows the effect of the 4.3 eV bleach averaged over four samples. The analysis reveals that this photon energy decreases peak 5 and peak 5a intensity by 32% and 80 % respectively whereas peak 4 increases by 36%. The increase in peak 4 (associated with the h-only configuration) and the decrease in peak 5a (associated with the e-h configuration) can be naturally explained by the removal of the electron from the e-h structure leaving the h-only configuration. The various occupied configurations of the trapping center/luminescent center giving rise to glow peaks 4, 5a and 5 and the effect of bleach are shown in figure 9. Following the 3.6 eV bleach shown in Figure 8, the results are dramatically different. The slight shift in the glow curve maxima was carried out to marginally improve the "goodness of fit" and did not have a significant effect on the results or their interpretation. The intensity of peak 5 is decreased by 19%, however no decrease in peak 5a is observed and peak 4 increases by only 7%.



**Figure 9.** Occupied configurations of the trapping center/luminescent center after irradiation (a) and after irradiation followed by bleach (b).

#### 4. Conclusions

The results strongly support the association of the glow peaks 4, 5a and 5 with the h-only, e-h (4.3 eV OA band) and e-only (3.6 eV OA band) configurations respectively. The bleach at 4.3 eV directly transforms the e-h configuration to a h-only configuration leading to the 80% decrease in peak 5a and the 36% increase in peak 4. A similar effect is not observed following the 3.6 eV bleach. Kinetic simulations of the bleach mechanisms will be carried out in the future to investigate the possible effect of  $V_3$ - $V_K$  transformation by capture of electrons in the 2-h  $V_3$  center and subsequent hole release [1]. This in order to further investigate the proposed association of the 3.84 eV and 4.3 eV OA bands with these glow peaks.

#### 5. References

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