Radiation Protection Dosimetry
Vol. 100, Nos 1–4, pp. 451–454 (2002)
Nuclear Technology Publishing

TL EMISSION SPECTRA FROM DIFFERENTLY DOPED LIF:Mg DETECTORS

E. Mandowska†, P. Bilski‡, E. Ochab‡, J. Świątek† and A. Mandowski†
†Institute of Physics Pedagogical University
Armii Krajowej 13/15
PL 42-200 Częstochowa, Poland
‡Institute of Nuclear Physics
Radzikowskiego 152
PL-31–342 Kraków, Poland

Abstract — There are two widely applied types of thermoluminescent detectors based on LiF:Mg luminophor: Lif:Mg,Ti and highly sensitive LiF:Mg,Cu,P. The role of luminescence centres in these materials is usually attributed to defects connected with, respectively, titanium and phosphorus dopants. In order to check how composition of dopants introduced into the LiF lattice influences emission spectra, measurements on a series of variously doped LiF:Mg samples were performed. Apart from LiF:Mg,Cu,P and LiF:Mg,Ti detectors with different concentration of activators, an experimental sample being a kind of a 'hybrid' between both standard materials was also prepared. It was synthesised with concentrations of magnesium and copper identical to those used for LiF:Mg,Cu,P preparation, but instead of phosphorus it was doped with titanium (LiF:Mg,Cu,Ti). The measurements of the emission spectra were performed by using a liquid nitrogen cooled CCD 1024E detector with an SP150 spectrograph. During the measurements the samples were placed inside a cryostat in a vacuum. Resulting data were numerically deconvoluted for individual peaks with respect to the wavelength and the temperature. The glow curve shape of this material resembles that of LiF:Mg,Cu,P. while sensitivity is at the level of LiF:Mg,Ti. Preliminary results indicate that emission of the LiF:Mg,Cu,Ti sample is similar to that of LiF:Mg,Cu,P rather than to LiF:Mg,Ti, showing a maximum for wavelengths well below 400 nm.

INTRODUCTION

LiF with different dopants is the most common base material used for production of thermoluminescent detectors. LiF, in the form LiF:Mg,Ti (MT), has been the mainstay of the TLD industry for two decades and is the most widely used TLD material on the market since its first introduction more than 25 years ago. Even today it remains the most popular TLD material, especially for personal dosimetry. This popularity appears to be due to the near tissue-equivalence of the material, along with its overall reliability, in spite of the complexity of the glow curve and only a moderate sensitivity[1]. LiF doped with impurities Mg, Cu and P (MCP) is an ultra-sensitive, tissue-equivalent material suitable as a TL dosemeter with a sensitivity 20–50 times greater than that of TLD-100[2–4]. A disadvantage of this material, however, is that its TL sensitivity is found to be strongly influenced by annealing and readout procedures. Since the TL properties are critically dependent on dopant concentration and production technique[5] this conclusion may not hold for all MCP materials.

Detailed analysis of the emission spectrum for TL from TLD-100 has been carried out by Fairchild *et al*[6], and Delgado and Delgado[7]; both indicated the presence of two minor emissions at 427 nm and 459 nm. The TL emission spectrum for LiF:Mg,Cu,P was described by Meijvogel and Bos[8,9]. They indicate that the main emission band consists of two, overlapping Gaussian-shaped bands at 377 nm and 348 nm, of which only the intensity of the first one is strongly influenced by the annealing procedure and dominates the main glow peak. The latter, remaining fairly constant with different thermal treatments, is dominant in the high temperature region and is correlated with the residual signal. In this paper emission spectra for two groups of the samples are presented: with low Mg concentration ($\leq$0.02%) and with high concentration (0.2%). The measurements demonstrate that presumably P and Ti have less influence on the emission spectra then previously assumed. It is shown that Mg concentration also significantly affects the measured spectra.

Contact author Email: e.mandowska@wsp.czest.pl

EXPERIMENT

Sample preparation

The samples used in this study were prepared at the Institute of Nuclear Physics (INP) in Krakow, Poland. During preparation of the samples: LiF:Mg,Cu,P (MCP) and LiF:Mg,P with 0.2% Mg (here denoted as MC*P) the activators were applied in the form of the following compounds: $NH_4H_2PO_4$, $CuCl_2$ and $MgCl_2$. Doping was carried out by melting LiF at 1050°C in the presence of activators in an atmosphere of argon. The obtained polycrystalline material was powdered and sieved into grains of size 60–200 μm. Activation of LiF:Mg,Ti (MT) samples was performed during heating LiF together with dopants ($MgCl_2$, $TiCl_4$) in the presence of LiCl at the temperature 650°C in air. During this pro-

cess grains with average diameter ca. 100 μm are formed. Activation of the samples: LiF:Mg,Cu,Ti (MCT) and LiF:Mg,P (MP) with 0.02% Mg was performed during heating LiF together with dopants ($MgCl_2$, $TiCl_4$ and $CuCl_2$, $NH_4H_2PO_4$, respectively) in the presence of LiCl at the temperature of 650°C in argon. The prepared samples of activated LiF were turned into solid pellets of diameter 4.5 mm and a thickness of 0.9 mm using the method of cold pressing and sintering. LiF:Mg,Ti samples were annealed at 400°C for 30 min, while all others at 240°C for 10 min (these are conditions typical for LiF:Mg,Cu,P). Exposures were performed with ^{137}Cs gamma rays at the irradiation facility of the INP.

Emission spectra measurements

The TL measurements were carried out in a cryostat that enables sample temperature to be controlled between 78 K and 700 K. Cooling of the sample is done by using liquid nitrogen. The samples are in a vacuum of less than 10^{-5} torr. The linear temperature rise with respect to time is driven by the Autotuning Temperature Controller. The luminescent intensity was monitored using the spectrograph connected to the LN/CCD-1024E camera (chip format 1024 × 256, spectral range: 190–1080 nm). The CCD camera is liquid nitrogen-cooled. The work temperature of the camera is stabilised within the temperature range −70°C–130°C. Temperature and wavelength resolved TL signals are obtained using custom made software. The TL intensity was monitored while the sample was heated from 20 to 300°C at a constant heating rate of 0.7 $K.s^{-1}$. The resolution of the system was varied from 10 to 20 nm depending on the width of the spectrometer slit and the binning used for CCD camera that were choosen according to the intensities of the measured samples. The range of the measured spectra was cut down at 310 nm due to using of an IR blocking filter KG5 (Schott glass, transmission range 310–850 nm). The temperature resolution was about 3 K.

RESULTS

Figures 1 and 2 show the TL emission spectra for the samples MC*P and MCT. For MCT, concentrations of Mg and Cu are the same as for MCP and C_{Ti} is ten times higher than for MT. The MC*P sample is not a 'hybrid' material but rather should be considered as the MCP with C_{cu} =0%. The wavelength range of the emission spectra for these samples is similar. The emission maxima for MCP, MC*P and MCT were measured at 366 nm, 345 nm and 365 nm, respectively. It appears that for all the samples the measured emission can be very well fitted with Gaussian shaped bands in energy domain. Figures 3 and 4 show the emission spectra with one Gaussian band for MC*P and MCT taken at the maximum temperature of peak 4. The band A (having a maximum at 380 nm) and the band B (with a maximum at 351 nm) in the MCP sample are in agreement with earlier results[9,10]. MCT and MC*P were fitted using one Gaussian band (with the maxima at 365 nm and 345 nm respectively). The peak shapes of the emission spectra, the wavelength range and the emission maxima are similar in MCP, MC*P and MCT samples.

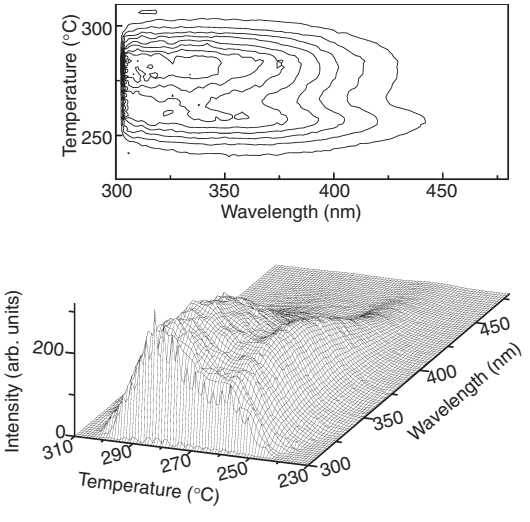

Figure 1. An isometric and a contour plot of TL emission from LiF:Mg,P (MC*P) samples with concentration of dopants: Mg 0.2%, Cu 0%, P 1.25% measured after a dose of 8.75 Gy. The spectra were recorded from room temperature up to 300°C.

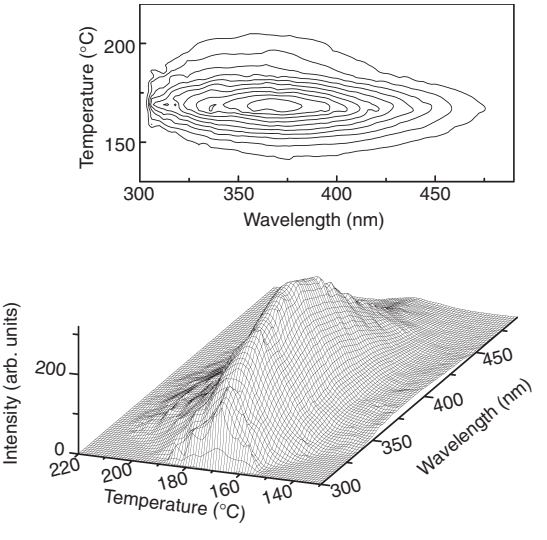

Figure 2. An isometric and a contour plot of TL emission from LiF:Mg,Cu,Ti (MCT) samples with concentration of dopants: Mg 0.2%, Cu 0.05%, Ti 130 ppm measured after a dose 8.75 Gy. The spectra were recorded from room temperature up to 300°C.

Figure 5 shows the TL emission spectrum of a MP sample. In MP, C_{Mg} was chosen in the range typical for MT, while P was kept at the level of MCP. The wavelength range for these samples is similar. The maximum emission appears at 436 nm for MT and 429 nm for MP samples. Figure 6 shows the emission spectra deconvoluted with two Gaussian bands in MP (at the maximum intensity). Band A has maximum at 473 nm and band B has a maximum at 399 nm in the MT sample. In the MP sample the bands A and B have maxima at 446 nm and 411 nm respectively. In MT, MP samples the maximum intensity appears at about 430 nm. The shapes of spectrally resolved spectra for MT and MP samples are similar. The intensity of TL for MC*P is greater than the intensity of MCT and MT samples. Probably it is also correlated with the greater concen-

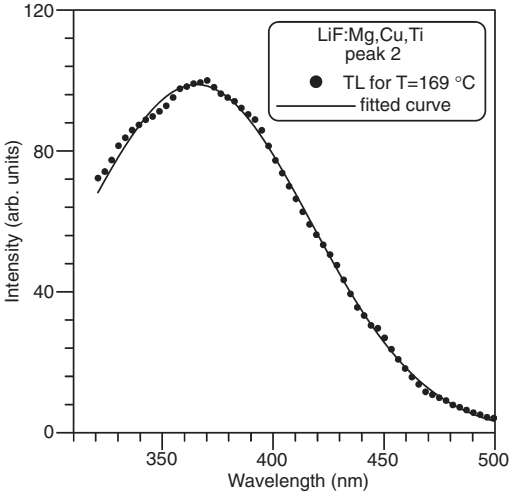

Figure 3. Analysed TL emission spectra of the main glow peak in LiF:Mg,P (MC*P) samples with concentration of dopants: Mg 0.2%, Cu 0%, P 1.25%. Emission of the TL was measured in the 255–258°C temperature range.

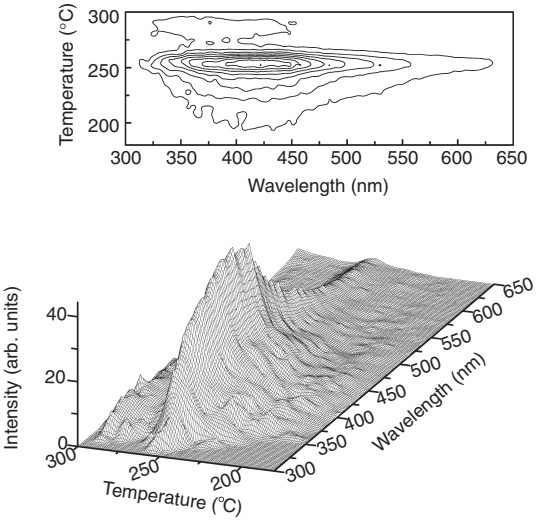

Figure 5. An isometric and a contour plot of TL emission from LiF:Mg,P (MP) samples with concentration dopants: Mg 0.02%, P 1.25% measured after a dose of 15.9 Gy. The spectra were recorded from room temperature up to 300°C.

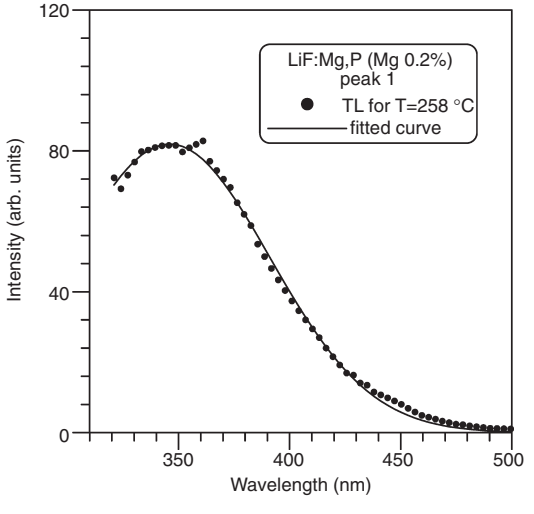

Figure 4. Analysed TL emission spectra of the main glow peak in LiF:Mg,Cu,Ti (MCT) samples with concentration of dopants: Mg 0.2%, Cu 0.05%, Ti 130 ppm. Emission of the TL was measured in the 166–169°C temperature range.

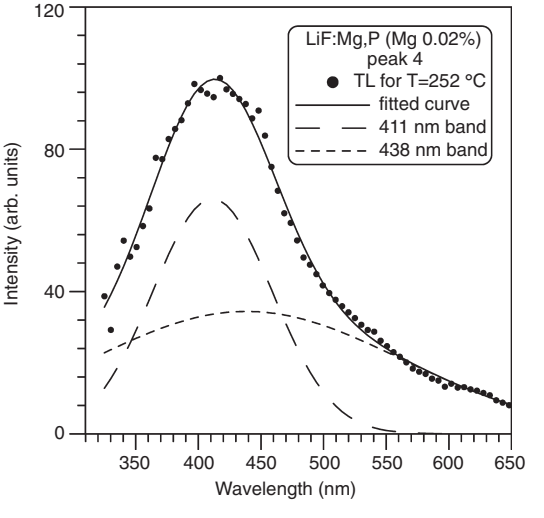

Figure 6. Analysed TL emission spectra of the main glow peak in LiF:Mg,P (MP) samples with concentration dopants: Mg 0.02%, P 1.25%. Emission of the TL was measured in the 246–252°C temperature range.

tration of Mg in MC*P compared with MT (about 10 times).

CONCLUSIONS

The obtained results revealed a strong influence of concentration of Mg on emission spectra. The analysed samples can be divided into two groups: for phosphors with low Mg concentration (≤0.02%) emission bands appears much above 400 nm, while for those with high concentration (0.2%) below 400 nm. It is remarkable that types of other dopants, which are usually assumed to be luminescence activators, seem to have less influence on emission spectra. The tested samples differ also in their dosimetric properties[10] and one may speculate if these effects are somehow related. Getting better understanding of the obtained results requires more experimental work on these and other samples (particularly LiF:Mg,Cu,P with various Mg concentration) and it is under way.

Table 1. Basic properties of TL emission spectra of LiF with various concentrations of different kinds of dopants (concentrations refer to amounts added in the activation process and are not results of any measurement). Δλ is the wavelength range in which the TL peak was observed. Peak emission maxima of bands A and B were found by computerised fitting (deconvolution) of the spectra with Gaussian shaped emission bands. The values are averages of three measurements.

Sample	Dose (Gy)	Peak	Δλ (nm)	λ (nm)
1. LiF:Mg,Ti (MT)	7.15	5	320–600	B 399
(Mg 0.012%; Ti 13 ppm)				A 473
2. LiF:Mg,P (MP)	15.9	5	320–650	B 411
(Mg 0.02%; P 1.25%)				A 446
3. LiF:Mg,Cu,P (MCP)	0.688	4	320–450	B 351
(Mg 0.2%; Cu 0.05%; P 1.25%)				A 380
4. LiF:Mg,P (MC*P)	8.75	1	320–450	345
(Mg 0.2%; P 1.25%)		2	320–450	
5. LiF:Mg,Cu,Ti (MCT)	8.75	4	320–480	365
(Mg 0.2%; Cu 0.05%; Ti 130 ppm)				

REFERENCES

1. McKeever, S. W. S., Moscovitch, M. and Townsend, P. D. *Thermoluminescence Dosimetry Materials: Properties and Uses*. (Ashford, UK: Nuclear Technology Publishing) (1995).
2. Nakijama, T., Murayama, Y., Matsuzawa, T. and Koyano, A. *Development of a New Highly Sensitive LiF Thermoluminescence Dosimeter, its Applications*, Nucl. Instrum. Methods **157**, 155–162 (1978).
3. Wang, S., Chen, G., Wu, F., Zha, Z. and Zhu, J. *Newly Developed Highly Sensitive LiF(MG,Cu,P) TL Chips with High Signal-to-Noise Ratio*, Radiat. Prot. Dosim. **14**, 223–227 (1986).
4. Bos, A. J. J. and Dielhof, J. B. *Does the Most Sensitive Thermoluminescent Material come from China? Some Characteristics of LiF:Mg,Cu,P (GR-200) TL Chips*. In: Proc. Symp on Thermoluminescent Dosimetry, Bilthoven, The Netherlands, pp. 43–48 (1989).
5. Zha, Z., Wang, S., Shen, W., Zhu, J. and Cai, G. *Preparation and Characteristics of LiF:Mg,Cu,P Thermoluminescent Material*. Radiat. Prot. Dosim. **47**, 111–118 (1993).
6. Fairchild, R. G., Mattern, P. L. and Levy, P. W. *Thermoluminescence of LiF TLD-100: Emission Spectra Measurements*. J. Appl. Phys. **49**, 4512–4521 (1978).
7. Delgado, L. and Delgado, A. J. *Photoluminescsence and Thermoluminescence of Ti Centers in LiF (TLD-100)*. Appl. Phys. **55**, 515–518 (1984).
8. Meijvogel, K. and Bos, A. J. J. *Influence of Thermal Treatments on Glow Curve and Thermoluminescence Emission Spectra of LiF:Mg. Cu,P*. Radiat. Meas. **24**, 239–247 (1995).
9. Meijvogel, K., Bos, A. J. J., Bilski, P. and Olko, P. *Thermoluminescence Emission Characteristics of LiF(Mg,Cu,P) with Different Dopant Concentrations*. Radiat. Meas. **24**, 411–416 (1995).
10. Bilski, P. *Lithium Fluoride: from LiF:Mg,Ti to LiF:Mg,Cu,P*. Radiat. Prot. Dosim. **100**(1–4), 199–206 (This issue) (2002).