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Dependence of glow curve structure on the concentration of dopants in LiF:Mg,Cu,Na,Si thermoluminescent material

Vu Thi Thai Ha[1], Nguyen Thi Quy Hai[1], Nguyen Ngoc Long[2,*]

[1]*Institute of Materials Science, VAST, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam*
[2]*Center for Materials Science, College of Science, VNU, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam*

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Abstract. Lithium fluoride (LiF) thermoluminescent powder doped with Mg, Cu, Na, and Si as activators was prepared. The dopant concentrations were varied over the wide ranges as follows: Mg (0.05 - 1.0 mol%), Cu (0.01 - 1.0 mol%), Na,Si (0.3 - 2.4 mol%). The results indicated that the Mg and Cu activators are crucial dopants in the LiF:Mg,Cu,Na,Si phosphors. The LiF:Cu,Na,Si samples without Mg exhibit a peak at low temperature in the thermoluminescent glow curve and in the absence of Cu, the LiF:Mg,Na,Si samples exhibit a peak at high temperature. The Na,Si were effective dopants in producing the high intensity of the low-temperature peaks and the main peak. The emission spectrum measurements at each peak temperature of the TL glow curve were carried out for the LiF:Mg,Cu,Na,Si sample. The results showed that with increasing the peak temperature of the TL glow curve, the peak wavelength is generally shifted towards the low wavelength side.

1. Introduction

LiF-based thermoluminescent (TL) materials are widely used as a personal dosimetric material because of their low energy dependence, high sensitivity, stability and tissue equivalency. The thermoluminescent dosimetry (TLD) material based on LiF that has been studied most extensively is LiF:Mg,Ti, which is widely used in personal dosimetry and available in the market under trade names like TLD-100 and its variations (TLD-600 and TLD-700) [1]. Nakajima et al. [2] were the first to describe the properties of LiF doped with Mg, Cu and P impurities. This TL material combines two attractive properties, namely, a high sensitivity and a good tissue equivalency. This LiF:Mg,Cu,P material has been improved and commercialized by Chinese (GR-200), Japanese (NTL-500), Polish (MCP-N) and USA (TLD-600H and TLD-700H) [3].

In 1989, Kim et al. developed a powder-type of LiF doped with four dopants: Mg, Cu, Na and Si [4,5]. These TL powders have about 2 times higher sensitivity in comparison with LiF:Mg,Cu,P [6]. The LiF:Mg,Cu,Na,Si material with linear TL response over a wide dose range, low residual signal, and good stability to heat treatment is found to be a promising material for thermoluminescent dosimetry.

* Corresponding author. Tel: 0913038005.
E-mail: longnn@vnu.edu.vn

For doping the LiF, Nam et al. [7] and Kim at al. [8] used the following compounds: $MgSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ and $NaSiO_3 \cdot 9H_2O$ or $Na_2O \cdot 2SiO_2 \cdot 9H_2O$. They found that the change of the Mg content has a strong influence on the intensity of the main peak. The Cu activator has a strong influence on the glow curve structure: with increasing Cu concentration, the intensity of the main peak was rapidly intensified and the high-temperature peak was rapidly reduced. The Na,Si were effective dopants in producing the high intensity of the low-temperature peaks and the main peak. In order to understand the role of the dopants in TL mechanism, the light emission spectra during thermoluminescence (TL emission spectra) were measured and analysed for many TL materials [9–13].

In the present work, we prepared LiF powders activated with Mg, Cu, Na and Si using the following compounds: $MgCl_2$, $CuCl_2$, Na_2SiO_3. The influence of the dopants on the glow curve structure was investigated and the TL emission spectra were measured and analysed for LiF:Mg,Cu,Na,Si phosphors.

2. Experimental

The synthesis process for LiF:Mg,Cu,Na,Si TL powders described elsewhere [14] is as follows. The host LiF material was mixed with the compounds containing required activators $MgCl_2$, $CuCl_2$ and Na_2SiO_3 in distilled water. The mixture was mixed on a magnetic stirrer and was then dried at 150 °C for 15 hours. The dried material was annealed at temperature range of 750 - 850 °C for interval of 15 - 20 minutes in nitrogen (N_2) gas flow with the rate of 4 l/min and then it was quickly cooled to room temperature. Final product was pulverized, sieved to select grains having sizes in the range of 60 - 150 μm. In the present work, we prepared LiF powder activated with Mg (0.05 - 1.0 mol%), Cu (0.01 - 1.0 mol%), Na,Si (0.3 - 2.4 mol%). NaSi was considered as a single dopant and its concentration was calculated as total of Na and Si because the compound $Na_2SiO_3.9H_2O$ was added.

The specimens were irradiated by high energy radiation. The X-ray source of 20 kV – 1 mA was used as an irradiation source. Irradiation duration was 3 minutes. The TL glow curves of the samples were measured by using a Harshaw model 3500 TLD reader with a linear heating rate of 2 - 5 °C/s in temperature range from 50 °C to 360 °C. The TL emission spectra were measured by using a device which consists of a monochromator (with a diffraction grating 1302), photomultiplier tube and temperature control unit to thermally stimulate the samples with the heating rate of 0.2 °C/s.

3. Results and discussion

First, LiF material was doped with only one dopant. Figure 1 shows the glow curves of the undoped LiF and LiF doped with different dopants: Mg = 0.4 mol%, Cu = 0.2 mol% and Na,Si = 2.0 mol%. As seen from the figure, the undoped LiF shows a strong TL peak at low temperature (~143 °C). The Na,Si-doped sample exhibits two relatively strong peaks at temperatures below 200 °C (135 and 190 °C). The Cu-doped sample shows three strong peaks at both low and high temperatures (138, 228 and 261 °C), while the Mg-doped sample mainly exhibits a peak at 232 °C.

LiF samples doped with many dopants were prepared. The glow curves of the LiF:Mg,Cu,Na,Si; LiF:Mg,Cu; LiF:Mg,Na,Si; and LiF:Cu,Na,Si samples are represented in figure 2. The dopant concentrations for the samples are as follows: LiF:Mg,Cu (Mg = 0.4, Cu = 0.2 mol%); LiF:Mg,Na,Si (Mg = 0.4, Na and Si = 2.0 mol%); LiF:Cu,Na,Si (Cu = 0.2, Na and Si = 2.0 mol%) and LiF: Mg,Cu,Na,Si (Mg = 0.4, Cu = 0.2, Na and Si = 2.0 mol%). The relative TL intensities of the maximum peaks in the glow curves of the LiF:Mg,Cu,Na,Si; LiF:Mg,Cu; LiF:Mg,Na,Si and LiF:Cu,Na,Si samples were

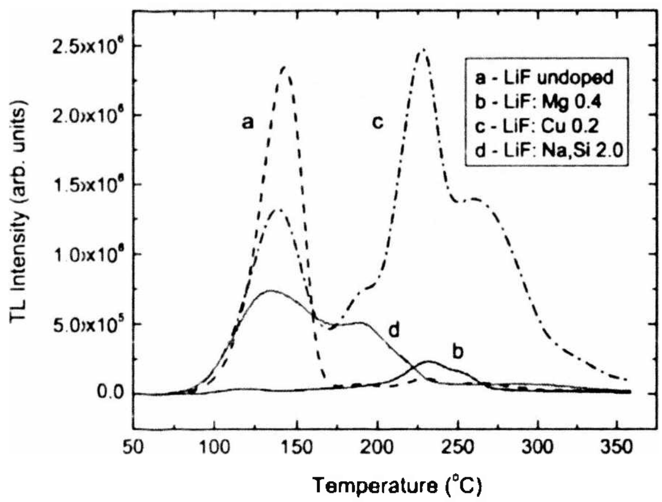


Fig. 1. The glow curves of the one-dopant samples: a) Undoped LiF, b) LiF:Mg, c) LiF:Cu and d) LiF: Na,Si.

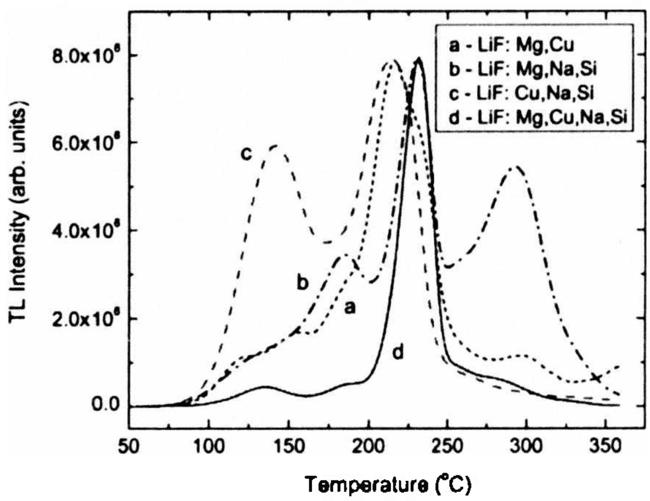
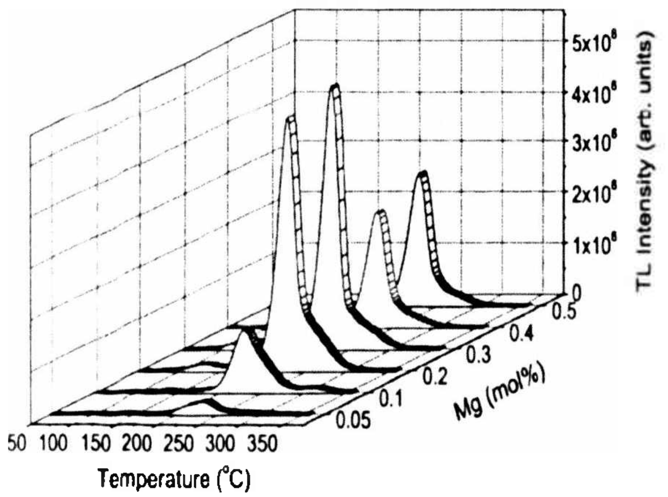


Fig. 2. The normalized glow curves of a) LiF:Mg,Cu, b) LiF:Mg,Na,Si, c) LiF:Cu,Na,Si and d) LiF:Mg,Cu,Na,Si samples.

1, 0.0016, 0.0116 and 0.0273, respectively. For a clear observation of the peak structure, in figure 2 the above-mentioned glow curves were normalized. It can be seen from the figure that Mg and Cu are crucial dopants in the LiF:Mg,Cu,Na,Si phosphors. But, without Na and Si the intensity of the LiF:Mg,Cu is about 0.16% of that of the main peak in the LiF:Mg,Cu,Na,Si sample. In addition, as shown in figure 2, in the absence of Mg the LiF:Cu,Na,Si sample (line c) exhibits a peak at low temperature (~141 °C) and in the absence of Cu the LiF:Mg,Na,Si sample (line b) exhibits a peak at high temperature (~293 °C).



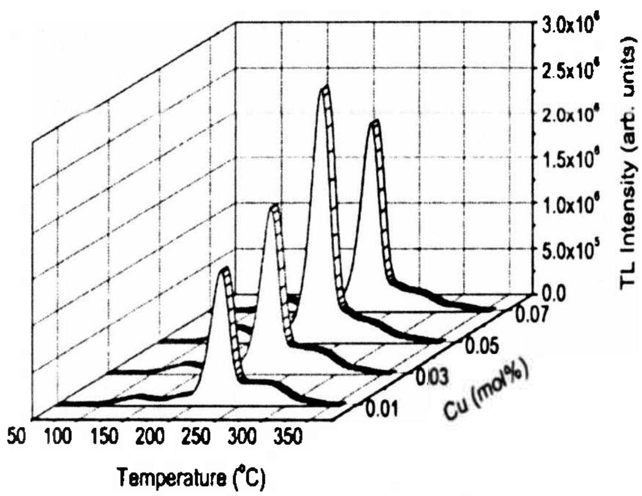


Fig. 3. The glow cuves for different Mg concentrations. Cu: 0.05 mol% and Na,Si: 0.9 mol%.

Fig. 4. The glow cuves for different Cu concentrations. Mg: 0.2 mol% and Na,Si: 0.9 mol%.

The following work is to study the dependence of the glow curves for LiF:Mg,Cu,Na,Si TL phosphor on dopants concentration. Figure 3 shows the glow curves for different Mg concentrations with a fixed Cu concentration of 0.05 mol% and Na,Si concentration of 0.9 mol%. The Mg concentrations were 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 mol%. As seen from the figure, the main peak intensity get very high values at the Mg concentrations of 0.2 and 0.3 mol%.

The glow curves for different Cu concentrations with a fixed Mg concentration of 0.2 mol% and Na,Si concentration of 0.9 mol% are represented in figure 4. The Cu concentrations were 0.01, 0.03, 0.05 and 0.07 mol%. It can be seen from the figure that the main peak intensity get maximum value at the Cu concertration of 0.05 mol%.

The glow curves for different Na,Si concentrations with a fixed Mg concentration of 0.2 mol% and Cu concentration of 0.05 mol% are demonstrated in figure 5. The Na,Si concentrations were 0.3, 0.6, 0.9, 1.2 and 1.5 mol%. As seen from the figure, the main peak intensity get very high values at the Na,Si concentrations of 0.6 and 0.9 mol%.

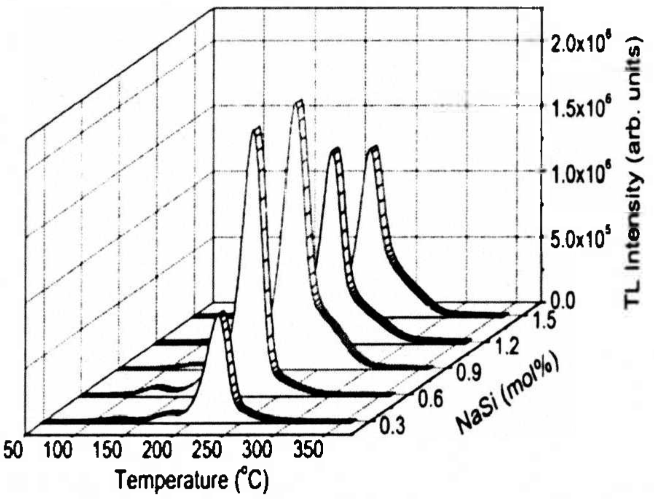


Fig. 5. The glow cuves for different Na,Si concentrations. Mg: 0.2 mol% and Cu: 0.05 mol%.

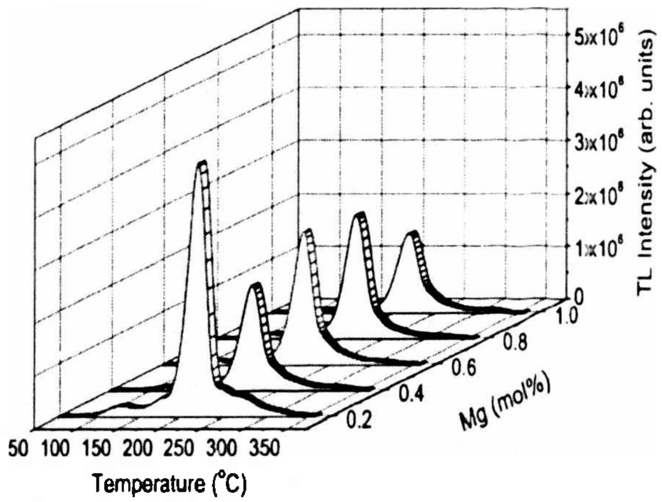


Fig. 6. The glow cuves for different Mg concentrations. Cu: 0.6 mol% and Na,Si: 2.0 mol%.

Consequently, in the low concentration region the optimum concentrations of dopants in the LiF:Mg,Cu,Na,Si TL material were Mg: 0.2 - 0.3 mol%; Cu: 0.05 mol%; Na,Si: 0.6 - 0.9 mol%. The above-mentioned results are in good agreement with that of Kim et al. [8].

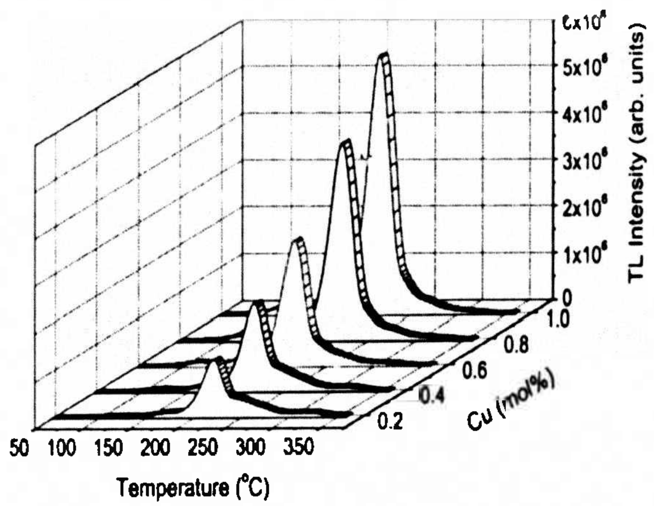


Fig. 7. The glow cuves for different Cu concentrations. Mg: 0.2 mol% and Na,Si: 2.0 mol%.

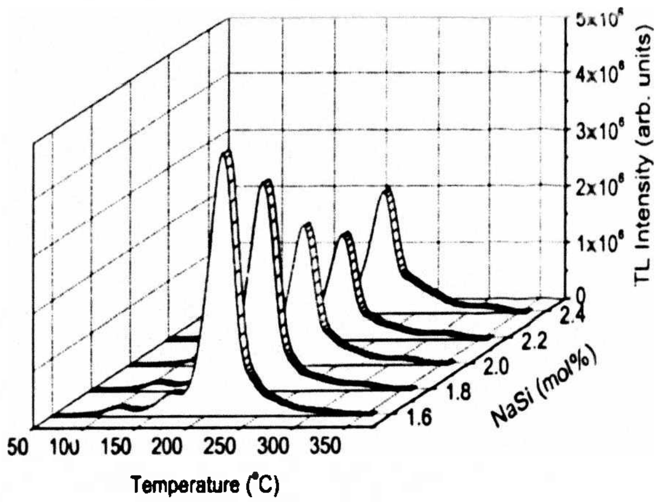


Fig. 8. The glow cuves for different Na,Si concentrations. Mg: 0.2 mol% and Cu: 0.6 mol%.

When the concentration of all dopants is increased, the dependence of the main peak intensity on the dopant concentration is varied.

The glow curves for different Mg concentrations with a fixed Cu concentration of 0.6 mol% and Na,Si concentration of 2.0 mol% are shown in figure 6. The Mg concentrations were 0.2, 0.4, 0.6, 0.8 and 1.0 mol%. As seen from the figure, the dependence of the main peak intensity on the Mg concentration exhibits a sharp maximum at 0.2 mol% as well.

Figure 7 represents the glow curves for different Cu concentrations with a fixed Mg concentration of 0.2 mol% and Na,Si concentration of 2.0 mol%. The Cu concentrations were 0.2, 0.4, 0.6, 0.8 and 1.0 mol%. It can be seen from the figure that the main peak intensity is increased with increasing the Cu concertration up to 1.0 mol%.

The glow curves for different Na,Si concentrations with a fixed Mg concentration of 0.2 mol% and Cu concentration of 0.6 mol% are demonstrated in figure 8. The Na,Si concentrations were 1.6, 1.8, 2.0, 2.2 and 2.4 mol%. As seen from the figure, the main peak intensity get very high values at the Na,Si concentrations of 1.6 and 1.8 mol%.

From these results, it can be noted that in the high concentration region the optimum concentrations of dopants in the LiF:Mg,Cu,Na,Si TL material were Mg: 0.2 mol%; Cu: 1.0 mol%; Na,Si: 1.6 - 1.8 mol%.

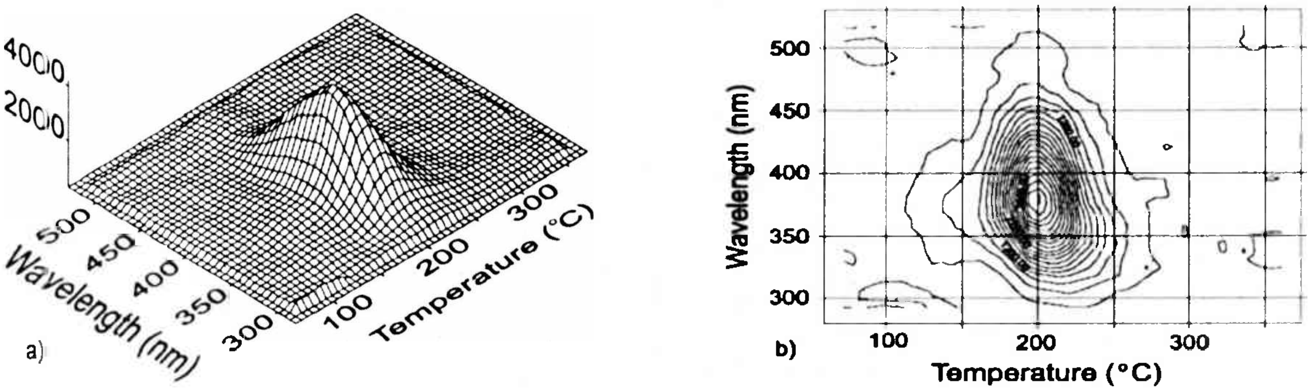


Fig. 9. (a) Isometric and (b) contour plot of the TL emission spectra from the LiF:Mg,Cu,Na,Si sample.

It is known that whereas the glow curves can give the information on the different detrapping processes occurring in the material, the TL emission spectra can provide the information about the different radiative recombination processes which are occurring. The three-dimensional TL emission spectrum of the LiF:Mg,Cu,Na,Si sample was demonstrated in figure 9. The dopant concentrations were Mg: 0.6 mol%, Cu: 1.0 mol% and Na,Si: 2.0 mol%. These spectrum data were recorded in the temperature range of 60 - 380 °C and wavelength range of 280 - 530 nm under the heating rate of 0.2 °C/s.

As shown in figure 9, a 340 - 400 nm luminescence is emitted at the temperature range of 150 - 250 °C. For a clear observation, the normalised spectra recorded at different peak temperatures: 150, 180, 205, 225 and 245 °C are represented in figure 10. It is found from figure 10 that, in general, as the peak temperature of the TL glow curves is increased from 150 °C to 245 °C, the peak position of the emission spectra is shifted towards the short wavelength side from 391 nm to 351 nm and the fullwidth at half maximum (FWHM) of the spectra is slightly increased, except the case of the peak temperature of 205 °C, the peak position of the emission spectra is shifted in the opppsite direction towards the long wavelength side. The reason of this fact is that there are not one, but a few radiative recombination centers in the material. Hence, the light emitted by the samples is a superposition of the lights emitted by the recombination centers existing in the sample. These luminescent centers can emit and dominate at different temperatures depending on their concentration, charge carrier capture cross-section and recombination probability, which results in a change in the position and shape of

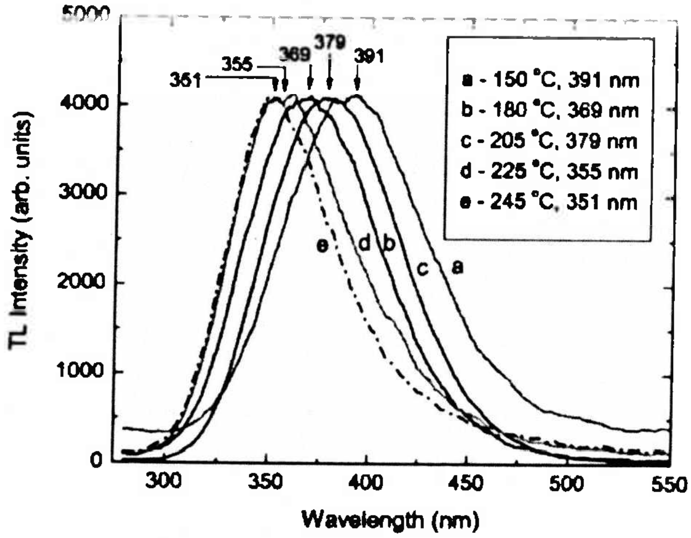


Fig. 10. The normalised TL spectra for the LiF:Mg,Cu,Na,Si sample according to the peak temperatures: 150, 180, 205, 225 and 245 °C.

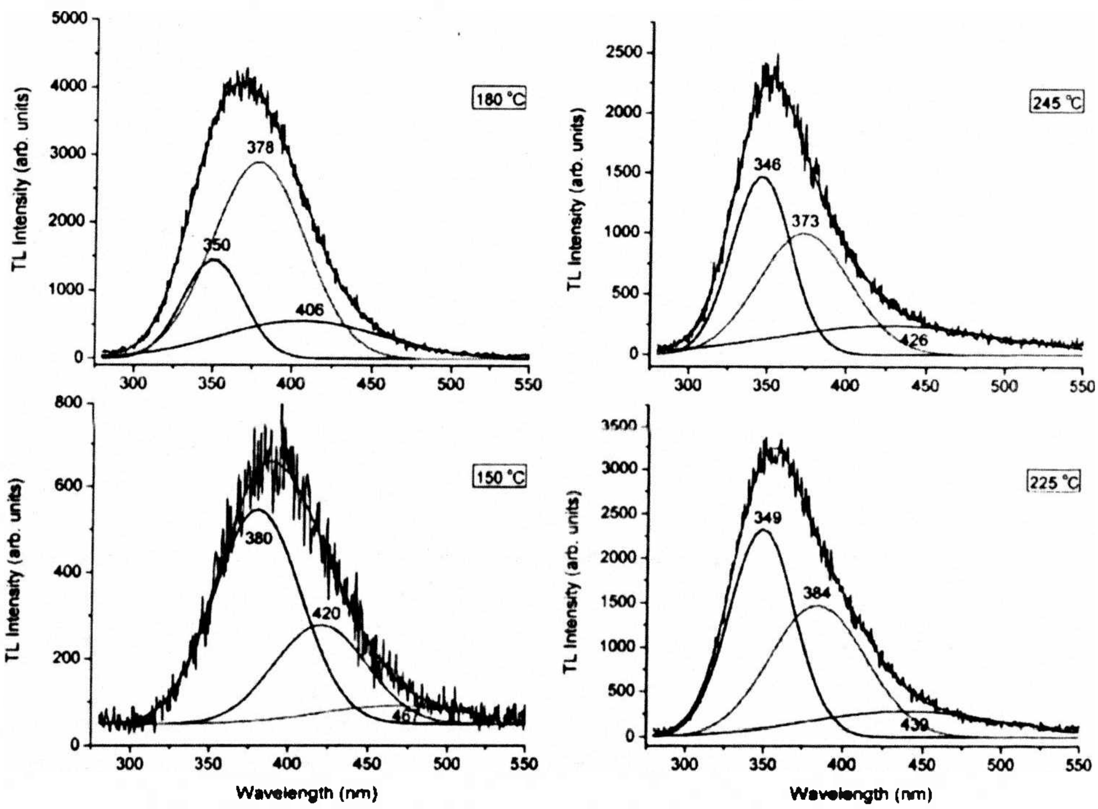


Fig. 11. The analysis of the emission spectra at each peak temperature of the TL glow curve: 150, 180, 225 and 245 °C.

the superposed peak. This phenomenon is clearly demonstrated in figure 11, where the TL spectra recorded at different temperatures are deconvoluted to three component gaussian curves peaking at various wavelengths. These components correspond with different luminescent centers. As seen from figure 11, when the temperature is increased up to 180 °C, a short wavelength (~350 nm) emission peak appears and becomes dominant in comparison with the 380 nm peak at the temperatures of 225, 245 °C, which results in a shift of the superposition peak wavelength to the shorter wavelength side. These results are in good agreement with that obtained by Lee et al. [10]. However at 205 °C the 380 nm peak (not shown in figure 11) is still dominant in comparison with the 350 nm peak, which results in a shift of the superposed peak position into the opppsite direction. The reason of this fact is not clear at present.

In order to varify the supposition on the existence of a few luminescent centers in the material, the photoluminescence (PL) measurements for the LiF:Mg,Cu,Na,Si samples were carried out and the results are shown in figure 12. The dopant concentrations in the sample were Mg: 0.2 mol%, Cu: 0.05 mol%, Na,Si: 0.9 mol%. The PL spectra were recorded at room temperature under excitation of 270 and 366 nm wavelengths. It can be observed from the figure that the spectra exhibit the emission bands centered at 356, 415 and 438 nm.

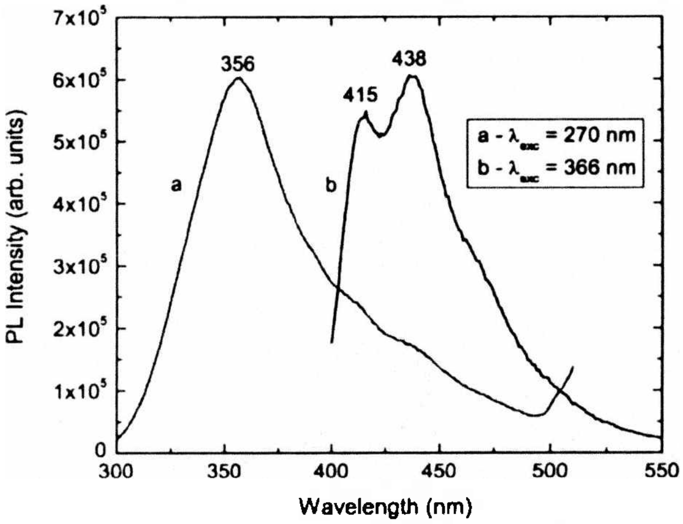


Fig. 12. The normalised PL spectra of LiF:Mg,Cu,Na,Si sample recorded at room temperature under excitation of 270 and 366 nm wavelengths.

4. Conclusion

The effect of the dopant concentrations on the TL glow curve in LiF:Mg,Cu,Na,Si phosphor was investigated. The results indicated that the Mg and Cu activators are crucial dopants in the LiF:Mg,Cu,Na,Si phosphors. The LiF:Cu,Na,Si samples without Mg exhibit a peak at low temperature and in the absence of Cu, the LiF:Mg,Na,Si samples exhibit a peak at high temperature. The Na,Si were effective dopants in producing the high intensity of the low-temperature peaks and the main peak. It was found that in the low concentration region the optimum concentrations of dopants in the LiF:Mg,Cu,Na,Si TL material were Mg: 0.2 - 0.3 mol%; Cu: 0.05 mol%; Na,Si: 0.6 - 0.9 mol%, but in the high concentration region the optimum concentrations of dopants in the LiF:Mg,Cu,Na,Si TL material were Mg: 0.2 mol%; Cu: 1.0 mol%; Na,Si: 1.6 - 1.8 mol%.

The TL emission spectrum measurements at each peak temperature of the TL glow curve were carried out for the LiF:Mg,Cu,Na,Si sample. The results showed that with increasing the peak temperature of the TL glow curve, the peak wavelength is generally shifted towards the low wavelength side. The reason of this fact is that there are not one, but a few radiative recombination centers in the material and therefore the light emitted by the samples is a superposition of the lights emitted by the recombination centers existing in the sample.

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