

Preparation and characteristics of LiF:Mg,Cu,Na,Si thermoluminescent material

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Received 28 November 2007

Abstract. Lithium fluoride (LiF) thermoluminescent powder doped with Mg, Cu, Na, and Si as activators was prepared. X-ray diffraction analysis indicated that doping LiF with different activators makes crystal lattice somewhat expand. The dosimetric properties of the powder were studied. The main dosimetric peak of LiF:Mg,Cu,Na,Si appeared in the range of 227–247°C and the ratio of the height of the main peak to that of the other small peaks in the LiF:Mg,Cu,Na,Si is much greater than that in the LiF:Mg,Ti and LiF:Mg,Cu,P. The preparation conditions such as annealing temperature and duration, annealing atmosphere, doping with different activators etc. were investigated.

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].

Although LiF:Mg,Ti has proven to be a useful material for TLD, many researches for developing the more advanced TL materials have been accomplished. 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].

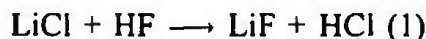
In the 1980s, Kim et al. developed a powdered type of LiF doped with four dopants: Mg, Cu, Na and Si [4]. This TL powders have about 2 times higher sensitivity in comparison with LiF:Mg,Cu,P. The LiF:Mg,Cu,Na,Si material with linear TL response over a wide dose range, low residual signal, and good stability to heat treatment is found to be a promising material for thermoluminescent dosimetry.

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In the present work, we prepared LiF powders activated with Mg, Cu, Na and Si and studied the dependence of the glow curve and the TL intensity on thermal treatment and the concentration of the dopants. The LiF:Mg,Ti and LiF:Mg,Cu,P powders were prepared for comparison.

2. Experimental

Four kinds of LiF powders have been prepared. Undoped LiF was prepared by means of the reaction:



The precipitated LiF was filtered, washed repeatedly and dried.

LiF:Mg,Ti powders were synthesized by co-precipitation method [5]. Aqueous solutions of LiCl, MgCl₂ and Ti + HF with required concentration were incorporated. The material precipitated was filtered, washed, dried, and was subjected to thermal treatment in an oven at 640°C for 1 hour, and then was annealed at 400°C for 1 hour.

LiF:Mg,Cu,P powders were prepared by the same method like in [6]. Aqueous solutions of MgCl₂, CuCl₂, and (NH₄)₂H₂PO₄ with required concentration were added to LiF precipitated by reaction (1). The material obtained was washed, dried, and was annealing in an oven at 700 °C for 1 hour, and then at 240 °C for 10 min.

The synthesis process for LiF:Mg,Cu,Na,Si TL powders is as follows [7]. The host LiF material was mixed with the compounds containing required activators MgCl₂, CuCl₂ and Na₂SiO₃ 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 10-40 minutes 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. According to [4, 7], the optimum concentration of the activators in powder-form LiF:Mg,Cu,Na,Si material were found to be Mg: 0.6 mol%, Cu: 0.6-0.8 mol%, Na: 1.8-2.0 mol% and Si: 1.8-2.0 mol%. In the present work, we prepared LiF powder activated with Mg 0.2-1.0 mol%, Cu 0.2-1.0 mol%, NaSi 1.6-2.4 mol% (NaSi was considered as a single dopant and its concentration was calculated as total of Na and Si because the compound Na₂SiO₃·9H₂O was added).

The X-ray diffraction (XRD) patterns of four kinds of the above mentioned specimens were obtained by using Cu-Kα (λ = 0.154056 nm) irradiation on an X-ray diffractometer D5005, Bruker, Germany. 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.

3. Results and discussion

Figure 1 shows XRD patterns of four kinds of the LiF powders. As shown in Fig. 1, all the XRD patterns can be well indexed to the face centered cubic structured LiF. In the XRD spectra are observed diffraction peaks from (111), (200), (220), and (311) crystal lattice planes.

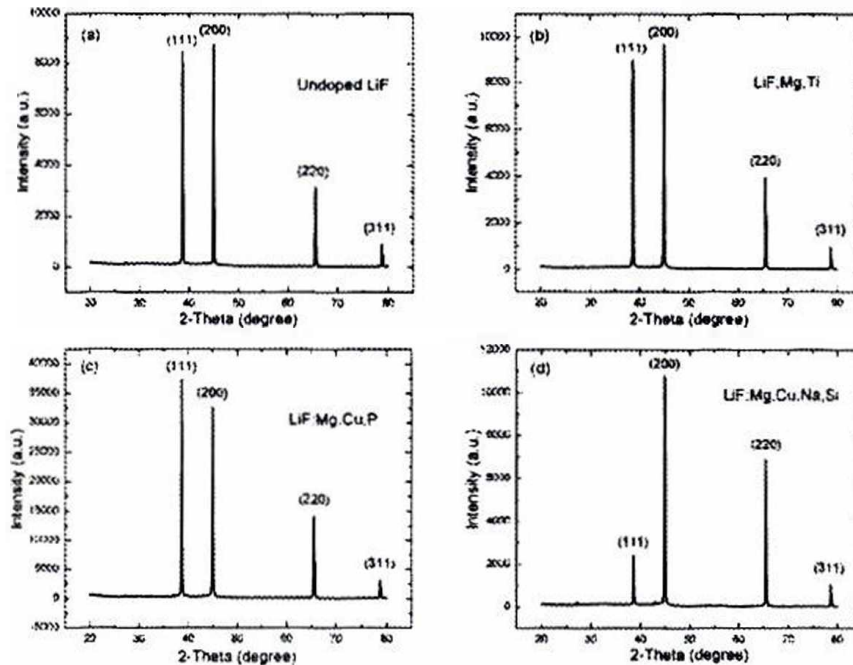


Fig. 1. XRD patterns of four kinds of LiF powders. a) Undoped LiF, b) LiF:Mg,Ti, c) LiF:Mg,Cu,P, and d) LiF:Mg,Cu,Na,Si.

Table 1. Crystal interplanar spacings and lattice constants for four kinds of LiF powders.

Sample	$d_{111}(\text{nm})$	$d_{200}(\text{nm})$	$d_{220}(\text{nm})$	$a(\text{nm})$
Undoped LiF	0.23267	0.20148	0.14245	0.40296
LiF:Mg,Ti	0.23273	0.20154	0.14247	0.40305
LiF:Mg,Cu,P	0.23279	0.20166	0.14253	0.40322
LiF:Mg,Cu,Na,Si	0.23291	0.20171	0.14261	0.40340

Table 1 shows the values of crystal interplanar spacing and lattice constants for the four kinds of LiF powders. From the table, it can be seen that doping LiF with different activators makes crystal lattice somewhat expand. The lattice constant of the undoped LiF is 0.40296 nm, while the lattice constant of the LiF:Mg,Cu,Na,Si is increased to 0.40340 nm, i.e. is increased 0.1 %. The reason for the lattice expansion is maybe that the dopant atoms occupy intersite positions or the dopant atoms replacing those of the host lattice have bigger atomic radii than that of the host lattice atoms.

Figure 2 shows the TL glow curves of the LiF powders with the optimum concentration of dopants: LiF (0.013 mol% Mg, 0.0003 mol% Ti), LiF (0.05 mol% Mg, 0.004 mol% Cu, 2 mol% P) and LiF (0.6 mol% Mg, 0.6 mol% Cu, 1.8 mol% NaSi). As can be seen from the figure that the glow curve of LiF:Mg,Cu,Na,Si powder shows some peaks in the range from 0 to 350 °C: the main peak usually used in dosimetry appears at 247 °C and the other small peaks are at 150, 205, and 280 °C. Comparing the glow curves shown in Fig. 2, one can note that the ratio of the height of the main peak to that of the other small peaks in the LiF:Mg,Cu,Na,Si is much greater than that in the LiF:Mg,Ti and LiF:Mg,Cu,P. This property makes LiF:Mg,Cu,Na,Si become an excellent material used in dosimetry.

In order to find optimum preparation conditions, the sample LiF: 0.6 mol% Mg, 0.6 mol% Cu, and 1.8 mol% NaSi was annealed in N_2 gas flow with a rate of 6 l/min at various temperatures: 750, 800, 830, and 850 °C. The results shown in Fig. 3 indicate that annealing temperature has strongly affected the TL intensity and the glow curve structure. At annealing temperature of 800 °C, the intensity of the main peak reaches a maximum value.

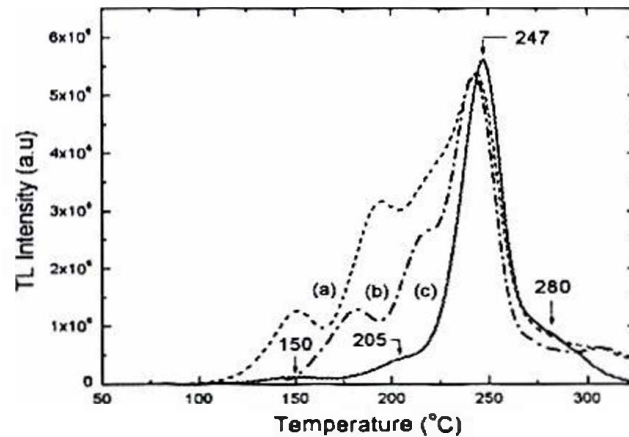


Fig. 2. Glow curves of a) LiF:Mg,Ti, b) LiF:Mg,Cu,P and c) LiF:Mg,Cu,Na,Si powders.

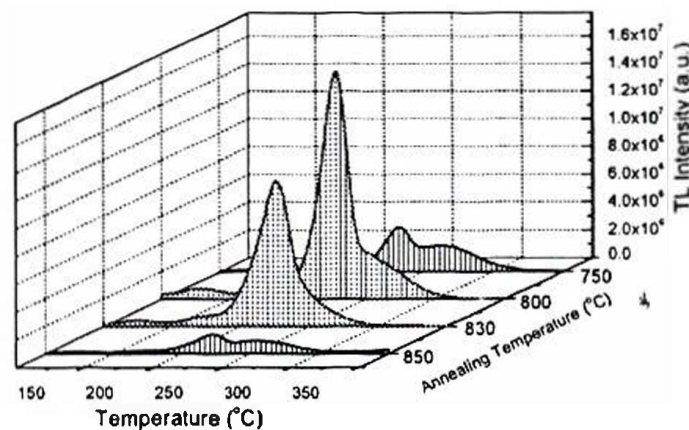


Fig. 3. Glow curves of LiF(0.6 mol% Mg, 0.6 mol% Cu, 1.8 mol% NaSi) TL powder annealed in N_2 gas flow with a rate of 6 l/min at various temperatures.

According to [8], annealing atmosphere may modify TL glow curve shape, and so annealing in inert atmospheres (helium (He) or nitrogen (N_2)) has been recommended to avoid the changes that were observed when the (LiF:Mg,Ti) TLD-100 chips were annealed in air. On the contrary, authors [9, 10] have reported that no significant differences were found between glow curve shapes of TLD-100 chips annealed either in He, N_2 or in air. It may be of interest to investigate the influence of annealing atmosphere on TL glow curve of our LiF:Mg,Cu,Na,Si powder. The powders were annealed at 800 °C for 15 min in air (no N_2 gas flowed) and in N_2 gas flow with different rates. After irradiation with X-ray, glow curves of the powders were recorded in air. Fig. 4 illustrates glow curves of LiF (0.6 mol% Mg, 0.6 mol% Cu, 1.8 mol% NaSi) TL powder annealed at 800 °C for 15 min as a function of N_2 flow rate. The results shown in Fig. 4 indicate that annealing atmosphere has strongly affected the TL intensity and glow curve structure. The powders annealed in N_2 flow have stronger TL intensity than the powders annealed in air do. From the figure, it can be seen that the optimum N_2 flow rate is 4 l/min. The height of the main peak in the sample annealed in N_2 flow rate of 4 l/min is 10 times greater than that in the sample annealed in air.

Annealing time is an important factor as well. Fig. 5 shows the glow curves for 1.5 g of LiF (0.6 mol% Mg, 0.6 mol% Cu, 1.8 mol% NaSi) TL powder annealed at 800 °C in N_2 gas flow with the rate of 4 l/min for various time intervals: 10, 20, 30, and 40 min. From Fig. 5 and the inset on it, it can be seen that for a sample amount of 1.5 g the optimum annealing time intervals at 800 °C are 20–30 min.

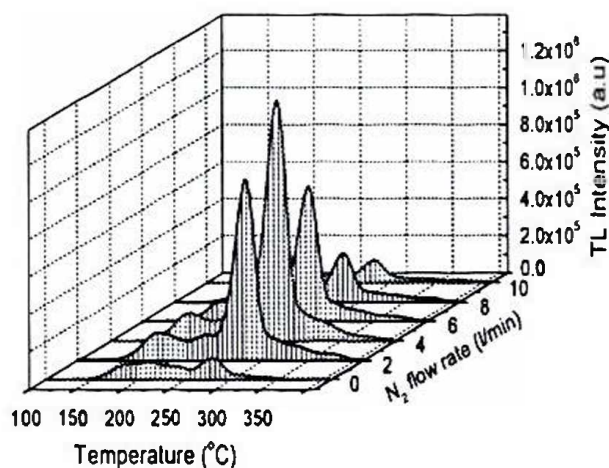


Fig. 4. Glow curves of LiF(0.6 mol% Mg, 0.6 mol% Cu, 1.8 mol% NaSi) TL powder annealed at 800 °C for 15 min as a function of N₂ gas flow rate.

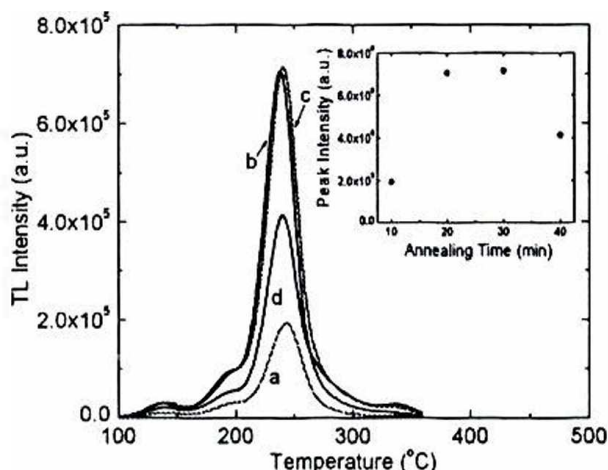


Fig. 5. Glow curves of LiF(0.6 mol% Mg, 0.6 mol% Cu, 1.8 mol% NaSi) TL powder annealed at 800 °C in N₂ gas flow rate of 4 l/min for various time intervals: a) 10, b) 20, c) 30, and d) 40 min.

After annealing process, the powder was stuck together and had the same blue-green colour as that of CuCl₂. The higher Cu concentration was, the colour was darker. It seems that the Cu dopants diffused not completely into LiF, the excess Cu dopant compound agglutinated to the surface of the LiF crystallites. Then the powder was washed with HCl solution. After washing with HCl solution the colour of the LiF:Mg,Cu,Na,Si TL powder was bluish, but turned white and the crystallites were separated from each other (Fig. 6). It indicates that the excess Cu compound was dissolved out of the powder during the HCl treatment.

In the powder without HCl treatment, the excess Cu compounds are not TL material but are an obstacle to the emission of TL, so TL intensity of this powder was weak. For the powder after treatment with HCl solution, in which the excess Cu compound was dissolved out of the powder, TL intensity becomes evidently stronger (Fig. 7).

The preliminary study on the effect of the dopants in LiF:Mg,Cu,Na,Si TL powder upon TL glow curve indicated that doping with activators has strongly affected the TL intensity and the glow curve structure of the powder. Fig. 8 illustrates glow curves of LiF TL powders undoped and doped with different activators. In the glow curve of the undoped LiF sample, the only strong peak was observed at 140 °C. For the LiF:Cu,NaSi sample, two strong peaks were observed at 140, 212 °C, while in the glow curve of the LiF:Mg,NaSi sample, 3 strong peaks were observed at 185, 230, 292

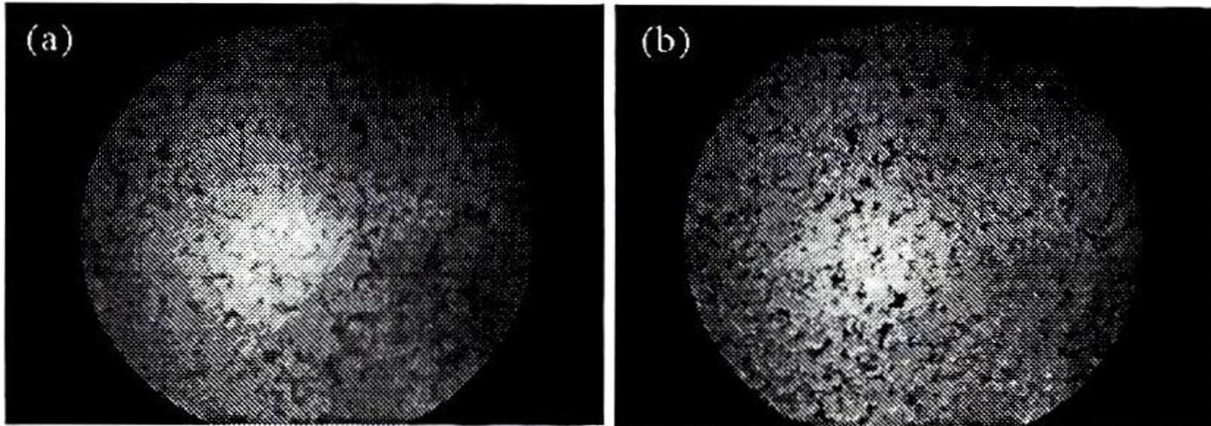


Fig. 6. The optical microscope images of LiF:Mg, Cu, Na, Si TL powder: a) Before washing with HCl, b) After washing with HCl.

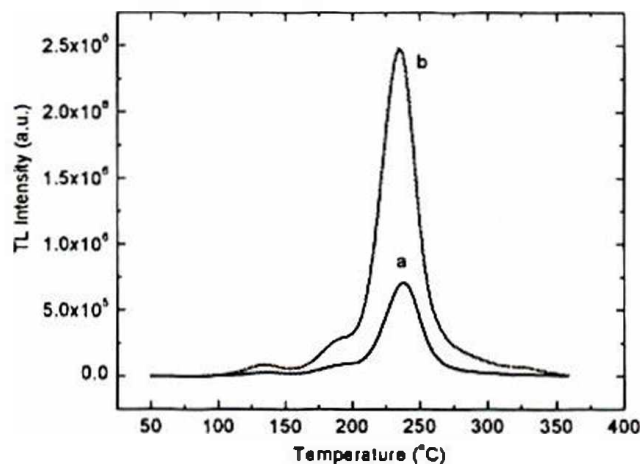


Fig. 7. Glow curves of LiF:Mg, Cu, Na, Si TL powders: a) Before washing with HCl solution, b) After washing with HCl solution.

°C. For the LiF:Mg, Cu sample, 2 overlaid strong peaks were observed at 240, 253 °C. Especially, the glow curve for LiF:Mg, Cu, Na, Si sample exhibits very strong dosimetric peak at 228 °C. The effect of the dopants in LiF:Mg, Cu, Na, Si TL powder upon TL glow curve will be reported in detail in other paper.

4. Conclusion

Lithium fluoride (LiF) thermoluminescent powder doped with Mg, Cu, Na, and Si as activators was prepared. X-ray diffraction analysis indicated that the LiF has the face centered cubic structure and doping LiF with different activators makes crystal lattice somewhat expand.

The dosimetric properties of the powder were studied. In the TL glow curve of LiF:Mg, Cu, Na, Si powder the main dosimetric peak appeared in the range of 227-247 °C and the ratio of the height of the main peak to that of the other small peaks is rather great.

In order to obtain high sensitive LiF:Mg, Cu, Na, Si TL powder, the optimum preparation conditions have been found. The optimum annealing treatment was to be at 800 °C, for 20–30 min in N₂ gas flow with rate of 4 l/min. After annealing treatment, the samples were washed with HCl solution.

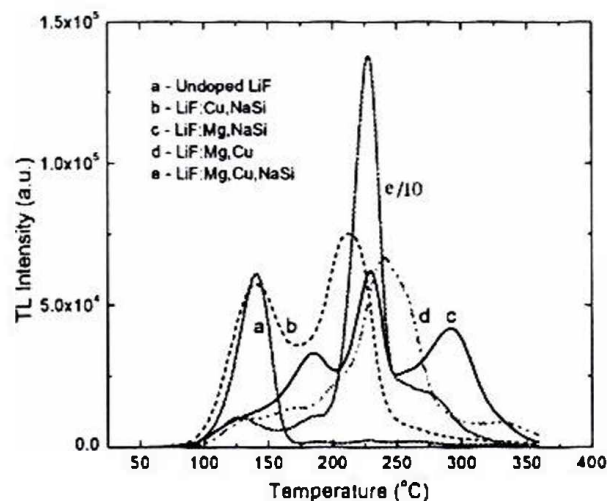


Fig. 8. Glow curves of LiF TL powders undoped and doped with different activators.

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