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The Electron Trap Analysis in Thermoluminescent LiF Crystal

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Abstract

In the optical grade LiF crystal, the electron traps corresponding to the thermoluminescence(abbreviated to TL) glow peak develop as irradiation dose is increased. Originally the electron trap of the crystal has two levels but as the dose reaches to the order of 10^4 röntgen, it attains five levels as observed in the TL glow curves. The five trap depths are determined from the glow peak temperatures for two different heating rates, θ=6.6°C/sec and 3.4°C/sec. The electron trap depths have the following values

E_1=0.79 eV, E_2=0.93 eV, E_3=1.02 eV, E_4=1.35 eV, E_5=1.69 eV.

The special feature of thermoluminescence of optical grade LiF is that the traps, except E_1 and E_2 corresponding to 120°C glow peak and 150°C glow peak for θ=6.6°C/sec, have severe thermal instability, namely E_3, E_4 and E_5 levels disappear during bleaching process. These defects in the optical grade LiF crystal seem annealed out during the course of TL measurement.

The fresh or long time unused LiF(Mg) crystal shows only two glow peaks at 170°C and 230°C for θ=6.6°C/sec, but upon sensitization with γ-ray irradiation, it converts to the six glow peak state. The four electron traps, $\bar{E}_1$, $\bar{E}_2$, $\bar{E}_3$, and $\bar{E}_6$ created by γ-ray irradiation and corresponding to the glow peaks at T=100°C, 130°C, 150°C and 290°C are stable and not easily annealed out thermally. The sensitization essentially required to LiF(Mg) dosimeter is to give the crystal the stable six levels in the electron trap.

In optical grade LiF, the plot between logarithm of total TL output versus logarithm of γ-ray dose gives more supra-linear feature than that of LiF(Mg). However, if one takes the height of 120°C glow peak(θ=6.6°C/sec), instead of the total TL output, the curve becomes close to that of LiF(Mg).

요 약

光學級 LiF 單結晶의 熱螢光曲線은 γ 線照射線量이 增加함에 따라서 變化한다. 즉 線量이 적을 때는 2個의 glow peak 를 가지나, 線量이 점차 增加하여 10^5 röntgen

정도에 이르면 5個의 glow peak를 나타낸다. 이들 glow peak에 對應하는 energy 準位 E_i(i=1,2,3,4, 및 5)는 傳導帶 밑으로 부터의 깊이로 表示할 때 다음과 같은 값을 갖는다.

電子 trap의 energy depth(eV)	E_1	E_2	E_3	E_4	E_5
	0.79	0.93	1.02	1.35	1.69
Glow peak의 溫度 (θ=6.6°C/sec)	120°C	150°C	170°C	230°C	290°C

이들 E_i의 값은 加熱速度 θ_1=6.6°C/sec와 θ_2=3.4°C/sec에 對한 glow peak의 溫度를 얻은 다음, Randall-Wilkins의 理論에 따라서 計算되었다.

光學級 LiF 單結晶에서 E_1과 E_2 이외의 電子 trap은 熱的으로 不安定하며 LiF(Mg) 熱螢光線量計에 不可缺한 것으로 되어있는 sensitization의 効果가 거의 없다.

LiF(Mg)는 θ=6.6°C/sec 일때, 170°C와 230°C에 glow peak를 나타내며 이들에 對應하는 電子 trap $\bar{E}_4$와 $\bar{E}_5$ 이외에 放射線이 照射됨에 따라서 $\bar{E}_1, \bar{E}_2, \bar{E}_3$, 및 $\bar{E}_6$의 電子 trap이 形成되며 이들 값은 다음과 같다.

電子 trap의 energy depth(eV)	$\bar{E}_1$	$\bar{E}_2$	$\bar{E}_3$	$\bar{E}_4$	$\bar{E}_5$	$\bar{E}_6$
	0.72	0.84	0.93	1.02	1.35	1.69
Glow peak의 溫度 (θ=6.6°C/sec)	100°C	130°C	150°C	170°C	230°C	290°C

LiF(Mg)에서 放射線傷害 때문에 形成된 $\bar{E}_1, \bar{E}_2, \bar{E}_3$ 및 $\bar{E}_6$는 모두 상당히 熱的으로 安定하며, sensitization 過程에서 形成된다. 이 安定한 6準位系에서 LiF(Mg)에 依한 放射線 線量測定이 施行되어야 한다. $\bar{E}_1, \bar{E}_2, \bar{E}_3$ 및 $\bar{E}_6$의 安定性은 LiF 結晶內의 Mg^{++} 不純物의 影響으로 思料된다.

光學級 LiF 單結晶의 熱螢光에서 γ 線量의 對數表示量과 全熱螢光量의 對數表示 사이에 非線型性을 나타낸다. 그러나 熱的으로 安定한 120°C glow peak만을 고려하여 γ 線量의 對數表示量과 120°C glow peak의 높이의 對數表示量 사이에서는 非線型性이 減少되어, LiF(Mg)에 對한 曲線과 매우 類似한 曲線을 얻게 된다.

1. Introduction

Lately the thermoluminescence dosimeter has been used extensively in radiation dosimetry, and in many cases it has taken over completely the role of the conventional emulsion or film badge dosimeter. The latter, of course, has some specific advantages which can not be substituted with those of TL dosimeter, so that its application in specific varying occasions should continue[1].

CaF_2 series, LiF series, $CaSO_4$ series, Li_2O series *etc.* with the proper kind and amount of impurity element are the main TL dosimetric materials, but due to many advantages, such as easier crystal growing and its density near to human tissue and so on, LiF(Mg) has been used most widely. Further its TL emission temperature falls in the convenient temperature range(70°C~300°C) and its senistivity in the low dose range is excellent.

The present work is the continuation of that already reported elsewhere[2], and attention is paid particularly to the trap formation as γ-ray dose varies in the range of $R \approx 10^1 \sim 10^6$ röntgen. Further our special concern was of the difference between TL property of optical grade LiF {LiF(OG)} and LiF(Mg). Establishing that difference should provide better understanding of the many ambiguous features in TL properties of the crystal. Previous workers reported of the sensitization[3] process of LiF(Mg) crystal before application in TL dosimetry, but the reports did not clarify the physical significance of the process of sensitization in connection with changing trap system in the crystal.

J. R. Cameron[5] *et al* was the first to report of characteristics of TL of optical grade LiF. They reported the glow curve having a single glow peak was essentially same up to R=2,500 röntgen, but did not discuss about the further features of changing glow curve as the dose is beyond the order of 10^3 röntgen.

Another report of the preliminary work of LiF(OG) was made by one of the present authors[6]. They showed the annealing effect is very slight for TL of LiF(OG). In the report, although they showed correctly the TL emission curve of LiF(OG), the limited instrumental resolving power hampered detailed discussion of the glow curve.

At this point we point out specially that the comparison between the TL emission properties of LiF(OG) and LiF(Mg) is very useful in elucidating questions related to the mechanism of TL emission of LiF crystal.

Present work is based on the original and most used TL theory proposed by Randall-Wilkins[4]. The present authors derived some useful equations from this theory, which was reported in the reference 2.

2. Thermoluminescence Electron Trap in LiF Crystal

The TL emission curve or glow curve of a fresh LiF(Mg) crystal shows only two glow peaks at T=170°C and T=230°C for low dose. This is shown in Fig. 1. This indicates, according to the Randall-Wilkins theory, the electron trap of the fresh crystal has two levels.

The exactly same kind of the TL glow curve is obtained for $R \approx 10^1$ röntgen in a LiF

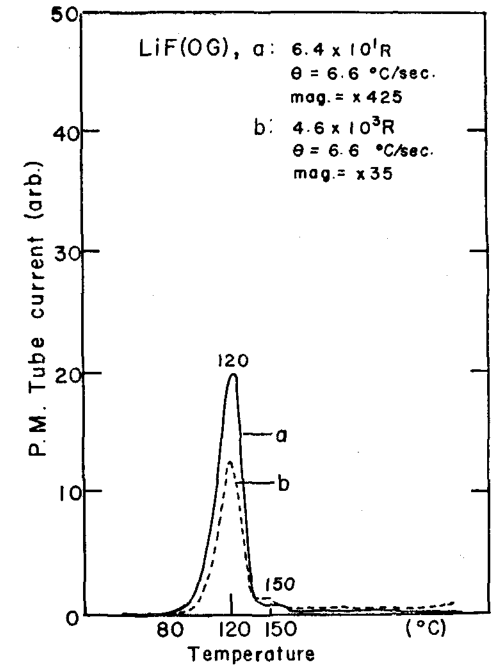

Fig. 1. TL glow curve of LiF(Mg)

(Mg) crystal, unused for a long time. This crystal was used previously repeatedly for some period of time and each time six glow peaks were identified. After that it was kept unused for six months. When this crystal is now again used successively for dose *R* only of the order of 10^1, the electron trap system of the crystal is then found, as seen in Fig. 1, to be converted to six levels system the glow curve showing six glow peaks. The crystal is then found showing stable six glow peaks for all values of dose. The TL dosimetry should be conducted with the LiF(Mg) with this six trap levels system. For this reason the fresh and the aged crystals have to be sensitized as reported[3]. However, the latter which was used previously but not used for long time requires small amount of irradiation ($R \approx 10^1$) for re-sensitization.

In Fig. 2, the peak at T=150°C may be regarded as the result of superposition of sides of the two glow peak curves centered at 170°C and at 130°C, but as D. W. Zimmer-

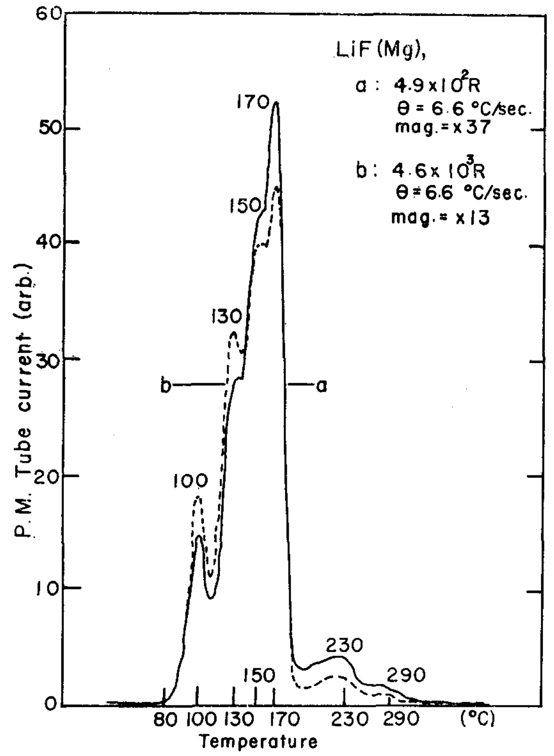

Fig. 2. TL glow curve of LiF(Mg)

Table 1. The glow peak temperature (θ=6.6 °C/sec) and the electron trap depth of LiF(Mg).

	Glow peak temperature (unsensitized)	Glow peak temperature (sensitized)	Electron trap depth in eV
$\bar{E}_1$	—	100°C	0.72 eV [2]
$\bar{E}_2$	—	130°C	0.84 eV [2]
$\bar{E}_3$	—	150°C	0.94 eV [2]
$\bar{E}_4$	170°C	170°C	1.02 eV [2]
$\bar{E}_5$	230°C	230°C	1.35 eV
$\bar{E}_6$	—	290°C	1.69 eV

man *et al*[7] indicated it is a separate glow peak also suitable for dosimetry as well as the peak at 170°C.

In Fig. 3, the glow curves of optical grade LiF crystal are shown. They all show two glow peaks at T=120°C and T=150°C for θ=6.6°C/sec for dose up to the order of 10^3 röntgen. In another words, the electron trap of the crystal has two levels. Those different

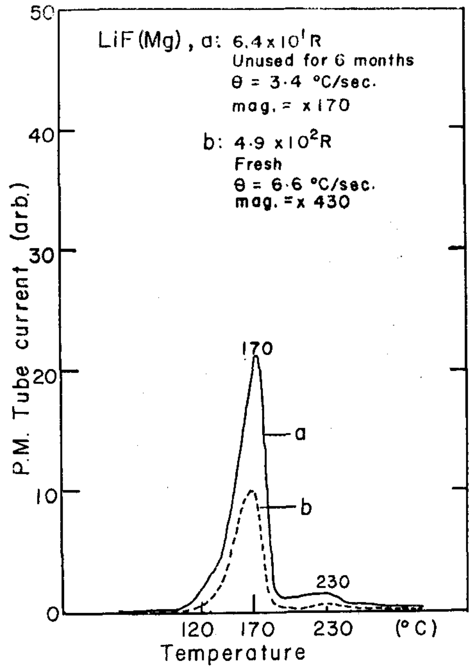

Fig. 3. TL glow curve of optical grade LiF

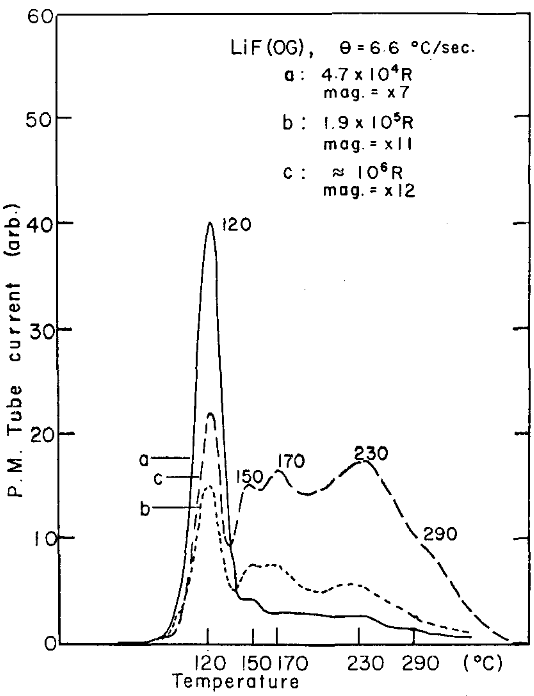

Fig. 4. TL glow curve of optical grade LiF

locations of the glow peaks are the distinctly different features of TL curve of LiF(OG) crystal from that of LiF(Mg) crystal. Further, as shown in Fig. 4, the glow curve changes as dose is increased to the order of 10^4, 10^5 and 10^6 röntgen, showing that the crystal takes the five levels electron trap system.

Table 2. The glow peak temperature(θ=6.6°C/sec) and electron trap depth of LiF (OG)

	10^1	10^2	10^3	10^4	10^5	10^6 röntgen	Electron depth trap
E_1	120°C	120°C	120°C	120°C	120°C	120°C	0.79eV
E_2	150°C	150°C	150°C	150°C	150°C	150°C	0.93eV
E_3	—	—	—	170°C	170°C	170°C	1.02eV
E_4	—	—	—	230°C	230°C	230°C	1.35eV
E_5	—	—	—	290°C	290°C	290°C	1.96eV

In the Fig. 5, the electron trap depths found in LiF(Mg) and Lif(OG) are plotted together with the glow peak temperature measured within the spread of 7%. Theoretically, this curve is given by $\frac{E}{kT}=\frac{s}{\theta}e^{-\frac{E}{kt}}$ derived from the Randall-Wilkins theory and treated elsewhere[2,4]. The graphical method of computing the trap depth was reported in the reference 2. The approximately linear relation between the trap depth, E, and the glow peak temperature, T, may be obtained from the above equation by ignoring the term kT which is of the order of 10^{-2}eV. Namely we take the logarithm of the equation and then differentiate with respect to T, then

$$\frac{dE}{dT}T(E+kT)=E(E+2kT)$$

is obtained assuming s is constant. Since E is of the order of $\approx 10^0$eV, $kT \approx 10^{-2}$eV may be neglected. Then the equation turns out to be $\frac{dE}{dT}=\frac{E}{T}$ which gives the aforementioned linearity in Fig. 5.

The optical grade LiF crystal used in this experiment was obtained from the Harshaw Chemical Co. The specimen was prepared out of the bulk optical crystal to be as close as possible the commercially produced LiF dosimeter, which has the dimension of 1/4″×1/4″×1/32″. Difference in shape and/or mass of the specimen may cause distortion in the glow curve.

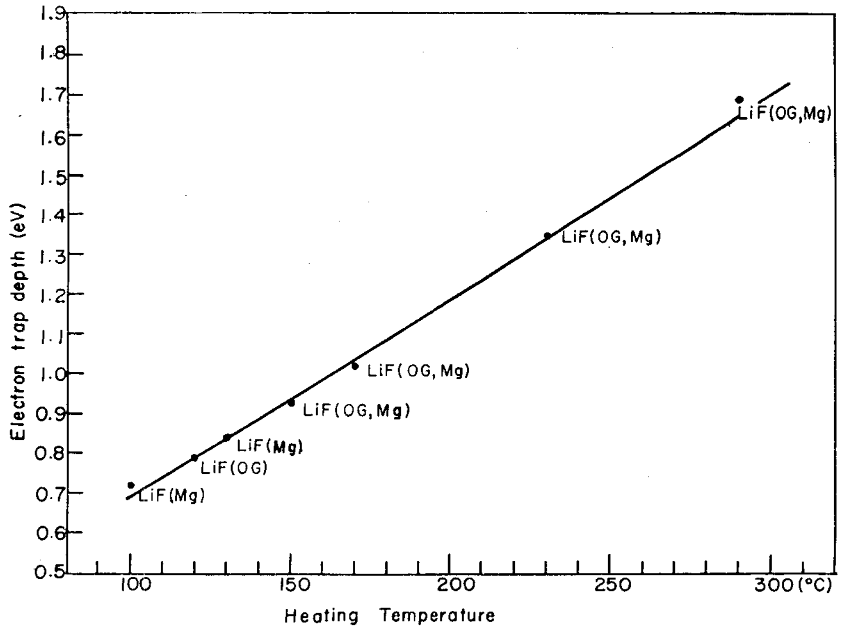

Fig. 5. The electron trap depth in LiF crystal

3. The Thermal Instability of the Electron Traps

The sensitization process is to give the fresh crystal comparatively large amount of dose of γ-ray and subsequent complete evacuation of electrons from traps through thermal treatment before regular dosimetric application of the crystal. The work about this process was reported by Cameron *et al*[3]. In their extremely laborous work, the process was treated thoroughly, but their report did not deal with the changing glow curve as a whole. but dealt with the change of the glow peak of LiF(Mg) at 170°C (θ=6.6°C/sec) alone. Namely little attention was paid to the way of changing of the rest of the glow peaks.

In the present work it is found the sensitization process for LiF(Mg) is nothing but the process converting the two levels electron trap system to the thermally stable six levels electron trap system shown in the Table 1. However, the six levels system is not absolutely permanent, but it can also be restored to the original two levels electron trap system through thermal treatment which includes the prolonged room temperature activation.

The conversion of two levels system in the used LiF(Mg) crystal to the six levels system requires only the dose of the order of 10^1 röntgen. This process is re-sensitization. However, for a fresh LiF(Mg) crystal, it was reported that the dose required for sensitization is of the order of 10^5 rontgen[3].

In optical grade LiF(OG), sensitization treatment has little effect, namely the glow

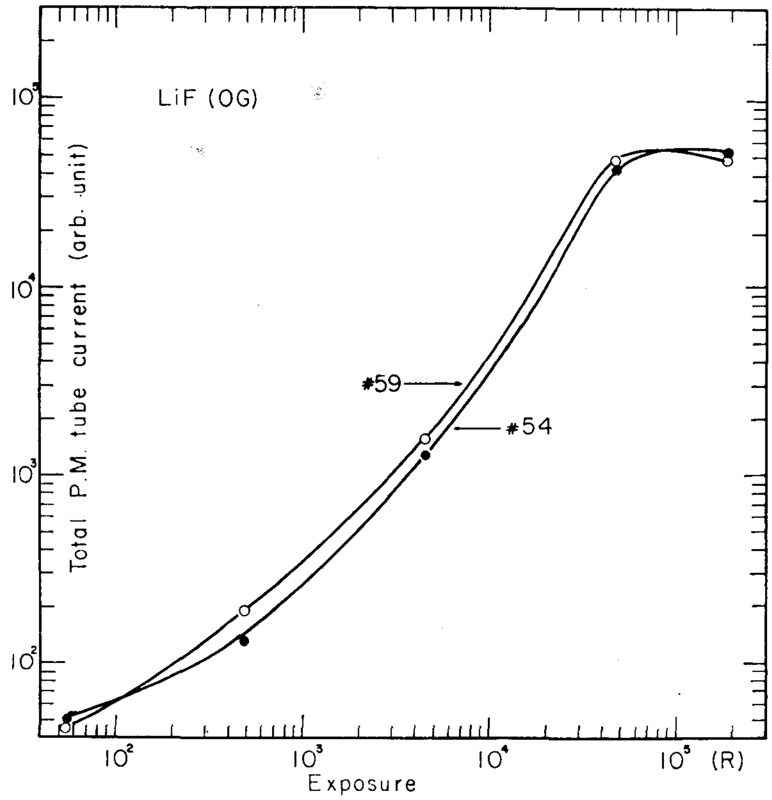

Fig. 6. Total P. M. tube current *v.s.* γ exposure for two optical grade LiF single crystals

curve is dependent almost solely on the amount of dose as shown in Fig. 3 and 4 and the Table 2. The electron traps, except E_1 and E_2 in the Table 2, are essentially dose-dependent only. In another words, the electron traps E_3, E_4 and E_5 in the Table 2 disappear during thermal treatment for TL emission and reappear only when the dose reaches to the order of 10^4 röntgen.

This thermal destruction of the traps is different from the thermal decay of trapped electron which follow the Randall and Wilkins' equation[4], $\exp(-\lambda e^{-\frac{E}{kT}})$.

4. Thermoluminescence Response of Optical Grade LiF Crystal

Our work on supra-linear TL response of LiF(Mg) crystal was reported elsewhere[2]. The present discussion will be concentrated on that of LiF(OG) crystal. It can be seen immediately that in LiF(OG), as the electron trap system is thermally unstable and the glow curve is dose-dependent, the TL response curve should acquire more supra-linearity. This is what we have found indeed in our present experiment. Fig. 6 is the plot between logarithm of total TL output versus logarithm of the dose and the graph reveals in the region of small R, the gradient is less than unity. In the reference 2, it was shown both experimentally and theoretically that in LiF(Mg) crystal, the gradient is unity for small R.

If one take height of the glow peak at $T=120°C(\theta=6.6°C/sec)$, which is corresponding to the electron trap inherently present in the crystal and thermally stable, the graph is practically identical with that of LiF(Mg)

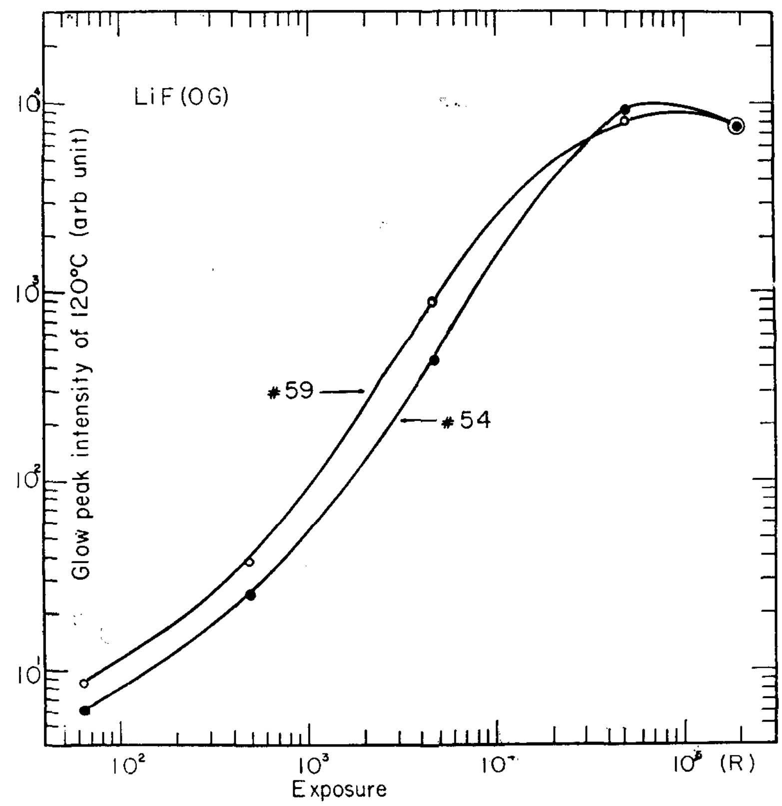

Fig. 7. Glow peak intensity of 120°C v.s. γ exposure for two optical grade LiF single crystals

reported in the reference 2. In Fig. 7, it is seen the gradient is closely unity.

For this peak we may propose the following analytical experssion in a similar way as proposed for LiF(Mg). Namely for the electron trapping process, we take the rate equation, $(1-e^{-\alpha R})$, α being the probability of electron trapping per röntgen, for increasing number of the electron traps, $(1-ge^{-\gamma R})$ and for increasing number of the hole traps, $(1-be^{-\beta R})$, so that TL emission at 120°C peak is proportional to

$$N_\beta N_\gamma(1-e^{-\alpha R})(1-be^{-\beta R})(1-ge^{-\gamma R})$$

which give the gradient for small R as below:

$$G=\frac{d(\log I)}{d(\log R)}\approx 1+R\left(-\alpha+\frac{b\beta}{1-b}+\frac{g\gamma}{1-g}\right)$$

From this equation it is seen $G\approx 1$ for small R, and it should become increasing for small R for

$$\left(-\alpha+\frac{b\beta}{1-b}+\frac{g\gamma}{1-g}\right)>0$$

In our previous work on LiF(Mg) crystal with the stable six levels electron trap system, $g=0$ was assumed. But as the number of electron trap increases with irradiation dose, it might be more general to assume a finite value for g. Indeed, we have found a sign that this peak has some sensitization effect. The similar argument can be extended to other unstable peaks or traps, but it requires more elaboration.

5. Discussion and Conclusion

The fresh LiF(Mg) dosimeter or that unused for a long time must be sensitized or irradiated and bleached thoroughly before application. The dosimeter crystal once used previously but not used for a long time requires relatively small amount of dose ($\approx 10^1$ röntgen) for re-sensitization purpose. With this sensitization process the crystal returns to the six levels electron trap system which is thermally stable. This thermal stability is, however, not permanent. In a long period time by thermal activation at room temperature the crystal may return to the two levels electron traps system which is not suitable for accurate dosimetry due to its dose dependent change in the TL glow curve.

In the optical grade LiF, the five levels electron trap system attained by the crystal at a large dose($\gtrsim 10^5$ röntgen) easily returns to the two levels system due to its thermal instability. So that LiF(OG) is basically not suitable for dosimetric application.

The deeply located four trap levels of LiF (Mg) and LiF(OG) have the same trap depths, but the two shallower traps of LiF(Mg) and one shallower trap of LiF(OG) have all different trap depths.

The traps develop due to the crystal defects produced as the consequence of interaction of γ-photon with the crystal, however, the thermal activations at room temperature, bleaching and annealing temperatures cure the defects, thus the LiF(Mg) crystal may return to original two traps system. The LiF (OG) converts to the original two levels electron trap system during the thermal bleaching process.

The traps corresponding to the glow peaks at $T=170$°C and $T=230$°C ($\theta=6.6$°C/sec) in LiF(Mg) and the traps in LiF(OG) corresponding to the glow peak at $T=120$°C and 150°C($\theta=6.6$°C/sec) are all thermally stable and they seem originated from inherent defects in crystals.

Although detailed experiments are not carried out yet, however, we have found a certain evidence that those peaks have some sinsitization effect.

The pronounced thermal instability in the TL property of LiF(OG) is, we believe, due to the relatively small concentration of impurity in the crystal, so that radiation damage, not as extensive as in the case of fast neutron irradiation or β-ray irradiation, can be cured easily. It is difficult to explain why the stable $\bar{E}_4$ and $\bar{E}_5$ trap levels in LiF(Mg) is not stable in LiF(OG), and conversely the stable trap E_2 in LiF(OG) is not so in LiF(Mg). Any attempt to elucidate this question should require extensive theoretical treatment of the crystal with impurity elements and the radiation induced lattice disorder, which is beyond the scope of the present work.

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