Chapter 4

The Sensitivity of Ln₂O₃ to UV Radiation

4.1 Introduction

Ln₂O₃ phosphors are used in the manufacturing of lamps, cathode ray tubes, image amplifier tubes, and other visual display devices such as color television tubes. Recently, Yeh (1996) suggested using some of them in UV dosimetry. One advantage of these compounds is the high thermal stability in the atomic structure. For instance, the thermal stability of La₂O₃ and Y₂O₃ is greater than 2000 ^oC. Another advantage of these compounds is their price per gram which is cheaper than commercial TLD phosphors. The disadvantage of these materials is their high degree of toxicity.

4.2 Sensitivity to UV lamp

Three types of Lanthanide oxide (Ln_2O_3) phosphors doped with different rare earth (RE) materials each showed different sensitivity to UV radiation. The most common result of these phosphors is their sensitivity to UV radiation when they were doped with presidium (Pr). For instance, the sensitivity of Y_2O_3 :Pr³⁺ to UV radiation was negligible. No clear glow peak was observed in the glow curve although it has been exposed to UV radiation for more than one hour.

The sensitivity to UV radiation of these phosphors doped with different rare earth elements is shown in more detail in the following sections.

4.2.1 Y₂O₃

This host phosphor has same range of sensitivity to UV radiation for different dopants except for presidium (Pr).

The sensitivity of Y_2O_3 :Tm³⁺ to UV radiation is shown in figure (4.1, B). The range of linearity was just for a few minutes (~10 minute) of exposure time to UV lamp. The small change in TL intensity against exposure time was observed after that time. TL intensity for Y_2O_3 :TD³⁺ and Y_2O_3 :Eu³⁺ reached its maximum value after one hour of exposure as shown in figure (4.1, A and D). The range of linearity was during first one hour of exposure time to UV lamp. The gradual decrease of the curve after its maximum is due to UV induced bleaching over the UV induced build up (Scarpa 1971).



Figure (4.1): The sensitivity of Y_2O_3 :RE³⁺ to UV lamp

 Y_2O_3 : Er^{3+} showed linear response to exposure time to UV lamp as shown in figure (4.1, E). The high sensitivity of this phosphor to UV radiation was observed after a few minutes of exposure to a UV lamp.

It is possible that thulium (Tm) ion created less trap center in the structure of the host phosphor Y₂O₃ (C-type) compared to terbium (Tb) ion and europium (Eu) ion. Erbium (Er) ion created high number of trap centers which still vacant after long exposure to UV lamp (Mckeever 1985).

4.2.2 La₂O₃

The response of this host phosphor to UV radiation was similar for different dopants except for presidium (Pr) and europium (Eu).

La₂O₃:Eu³⁺ and La₂O₃:Pr³⁺ showed low sensitivity to UV lamp although they were exposed to UV radiation for one hour as shown in figure (4.2, C and D). The change in TL intensity was almost around the background reading of the materials. La₂O₃:Tb³⁺, La₂O₃:Tm³⁺ and La₂O₃:Er³⁺ had linear response range during first one hour of exposure to UV lamp and reached the maximum response after that time as shown in figure (4.2, A, B and E). The gradual decrease of the curve after its maximum is due to UV induced bleaching over the UV induced build up (Scarpa 1971). Among these materials, La₂O₃:Tb³⁺ showed high sensitivity to UV radiation. The high sensitivity of La₂O₃:Tb³⁺ to UV radiation could be due to the creation of a high number of trap centers in the structure of the host phosphor La₂O₃ (A-type) by terbium (Tb) ion compared to thulium (Tm) ion and erbium (Er) ion (Mckeever 1985).



Figure (4.2): The sensitivity of La_2O_3 :RE³⁺ to UV lamp

4.2.3 Gd₂O₃

The Same result was found in this host phosphor as in Y_2O_3 . The host phosphor has the same range of sensitivity to UV radiation for different dopants except for presidium (Pr). The difference was in the response of these compounds to UV radiation.

 Gd_2O_3 :Tm³⁺ showed a linear response in TL intensity against exposure time to UV lamp as shown in figure (4.3, B).

 Gd_2O_3 :Eu³⁺ showed a small range of linear response and small change in TL intensity after 10 minutes of exposure to UV lamp as shown in figure (4.3, D), this result was found previously by Yeh (1996).

The linear response for Gd₂O₃:Tt³⁺ and Gd₂O₃:Er³ was during first one hour of exposure to UV lamp and reached their maximum response after that time as shown in figure (4.3, A and E). The gradual decrease of the curve after its maximum is due to UV induced bleaching over the UV induced build up (Scarpa 1971).

It is possible that erbium (Er) ions and terbium (Tb) ions create the same number of trap centers in the structure of the host phosphor Gd₂O₃ (C-type). Europium (Eu) ions create high numbers of trap centers that are totally filled by electrons after a few minutes of exposure time to UV lamp. Thulium (Tm) ions create high numbers of trap center that are still vacant after long exposures to UV lamp, which may explain the long range of its linear response (Mckeever 1985).



Figure (4.3): The sensitivity of Gd₂O₃:RE³⁺ to UV lamp

4.3 Sensitivity to sunlight

4.3.1 Long period of exposure

The sensitivity and the response of these phosphors to sunlight were found to be different from that when they were exposed to UV lamp. It is possible that visible light can play an important role in the fading of TL intensity.

The UV sensitivity of these phosphors can be classified into three groups.

The first group includes $Y_2O_3:Eu^{3+}$, $Y_2O_3:Er^{3+}$, $Y_2O_3:Tm^{3+}$ and $Gd_2O_3:Er^{3+}$. They did not show any change in TL intensity with exposure time to sunlight as shown in figure (4.4, C). It is possible that they are sensitive to wavelengths less than 290 nm, which does not exist in the earth surface, or the high TL fading caused by the high intensity of visible light of solar radiation, which can remove some TL intensity caused by solar UV radiation.

The second group includes La₂O₃:Er³⁺, La₂O₃:Tm³⁺ and Gd₂O₃:Tb³⁺. The change in the TL intensity was small with the exposure time to sunlight as shown in figure (4.4, B).

The last group includes Gd₂O₃:Tm³⁺, Gd₂O₃:Eu³⁺, La₂O₃:Tb³⁺ and Y₂O₃:Tb³⁺. They are sensitive to solar UV radiation as shown in figure (4.4, A).



Figure (4.4): The sensitivity of Ln_2O_3 :RE³⁺ to the sunlight (long term).

4.3.2 Short period of exposure

According to the result in section (4.3.1), Y_2O_3 : Tb^{3+} , La_2O_3 : Tb^{3+} , La_2O_3 : Tm^{3+} and La_2O_3 : Er^{3+} and Gd_2O_3 : Tb^{3+} , Gd_2O_3 : Tm^{3+} and Gd_2O_3 : Eu^{3+} have been exposed to sunlight around noontime to check their sensitivity to sunlight.

 Y_2O_3 :Tb³⁺, La₂O₃:Tm³⁺, La₂O₃:Er³⁺ and Gd₂O₃:Tb³⁺ showed fluctuations in their response with the exposure time to sunlight as shown in figure (4.5).



Figure (4.5): The sensitivity of $Ln_2O_3{:}RB^{3+}$ to sunlight (short periods) as compared with UM-25 UV-meter.

For La₂O₃:Tb³⁺, Gd₂O₃:Tm³⁺ and Gd₂O₃:Eu³⁺, the TL intensity reading has small change and the response was linear to exposure time to sunlight as shown in figure (4.5).

The low sensitivity of this phosphor to the sunlight could be due to the high light fading due to heating by the visible light. See section (4.6) for more details in light fading.

4.4 Glow curve

4.4.1 Glow curve after direct exposure to UV light

The glow curve for $Y_2O_3:RE^{3+}$ after direct exposure to UV lamp showed three glow peaks. La₂O₃:RE³⁺ and Gd₂O₃:RE³⁺ showed two glow peaks as shown in figure (4.6). The maximum temperature of the glow peaks for these materials is shown in table (4).

The glow curve for $Y_2O_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ was found to be similar to that mentioned previously by Yeh (1996). It is possible that rare earth (RE³⁺) elements create or enhance three trap levels at different energy depths in the structure of Y_2O_3 (C-type), and two trap levels with different energy depth in the structure of La_2O_3 (A-type) and Gd₂O₃ (C-type).

For Y_2O_3 , different rare earth creates different number of trap levels at different energy depth. For instance, Europium (Eu) ion creates more trap levels at shallow energy levels compared with erbium (Er) ion that creates more trap levels at deep energy levels as shown in figure (4.6).



 Figure (4.6): The glow curve for Ln₂O₃:RE³⁺ after direct exposure to UV for 10 minute.

 (-----)

 (-----)

 Tb³⁺, (-----)

 Eu³⁺, (-----)

 Eu³⁺, (-----)

It can be concluded that each rare earth element creates different number of trap levels at different energy depth in the host phosphor of Ln₂O₃.

Most glow peaks at low temperatures for these phosphors are not stable at room temperature. It fades after 24 hours. The glow peak at high temperature is stable and can be used in UV dosimetry.

4.4.2 Glow curve for Y2O3 after 24 hours of exposure

The glow curves were similar for gamma rays (intermittent line) and UV light (solid line) except for $Y_2O_3:Eu^{3+}$ as shown in figure (4.7). It has a peak and a shoulder at high temperatures for $Y_2O_3:Tm^{3+}$ and $Y_2O_3:Er^{3+}$, figure (4.7, B and D), whereas one glow peak for $Y_2O_3:Tb^{3+}$, figure (4.7, A). The glow curve for $Y_2O_3:Eu^{3+}$ showed different glow curves for gamma ray and UV light (Yeh 1996). The first peak at lower temperature was sensitive to gamma rays, whereas the second peak at higher temperature was sensitive UV light as shown in figure (4.7, C)

It was observed that the first glow at lower temperature for Y_2O_3 :Tm³⁺ and Y_2O_3 :Er³, which is stable at room temperature can be removed by visible light. This effect becomes clear when the materials were exposed to sunlight (dotted line), where the first peak was removed. The same glow curve was obtained when they were exposed to the ordinary lamp without any filter. The first peak is also sensitive to gamma ray and became clear after long exposures to this radiation.

For Y₂O₃:Tb³⁺, the first peak was not affected by the visible light and it was not sensitive to it.



Figure (4.7): Glow curve for $Y_2O_3:RE^{3+}$ (------) After 24 h of exposure to UV lamp, (------) After 24 h of exposure to Gamma-ray, and (------) After 24 h of exposure to sunlight.

4.4.3 Glow curve for La2O3 after 24 hours of exposure

The glow curve was similar for both gamma rays (intermittent line) and UV light (solid line) for all La₂O₃:RE³⁺ as shown in figure (4.8). The visible light could remove the TL intensity of the glow peak at low temperatures, and the effect became clear after exposure to sunlight (dotted line). For La₂O₃:Tb³⁺ and La₂O₃:Tm³⁺, the glow curve has a peak and a shoulder at high temperatures as shown in figure (4.8, A and B).

The first glow peak at low temperatures is sensitive to gamma rays. The glow curve of $La_2O_3:Er^{3+}$ has small glow peaks at lower temperature and high glow peak at high temperatures as shown in figure (4.8, C). Both peak are sensitive to gamma ray.

4.4.4 Glow curve for Gd₂O₃ after 24 hours of exposure

Most of the glow curve of Gd₂O₃:RE³⁺ material has a shoulder and a peak at high temperature as shown in figure (4.9).

The shoulder became clear after exposure to gamma ray. Same result was found in $Gd_2O_3:RE^{3+}$, where the shoulder can be removed by the visible light.

It was observed that the glow peak at high temperatures was stable and can be used for UV dosimetry.



Figure (4.8): Glow curve for $La_2O_3:RE^{3+}$ (------) After 24 h of exposure to UV lamp, (------) After 24 h of exposure to Gamma-ray, and (------) After 24 h of exposure to sunlight.



Figure (4.9): Glow curve for $Gd_2O_3:RE^{3+}$ (------) After 24 h of exposure to UV lamp, (------) After 24 h of exposure to Gamma-ray, and (------) After 24 h of exposure to sunlight.

4.5 Stability of TL intensity at room temperature

Most of the glow peaks of the host phosphor at high temperatures showed low fading, on the other hand, the glow peaks at low temperatures showed high thermal fading and are not stable in the dark at room temperatures after a storage time of 24 hours as shown in figure (4.10).

The high thermal fading of the glow peaks at low temperature is due to the nonstability of the shallow trapped electrons at room temperature and usually it is not suitable for dosimetry.

Some of these phosphors showed low thermal fading, for instance, the glow peak at high temperature for Y_2O_3 : Er^{3+} has low thermal fading compared with the rest of Ln_2O_3 : RE^{3+} powder as shown in figure (4.10, A).

Figure (4.10) shows that the high thermal fading for the first glow peak during the first 10 hours after exposure to UV lamp. The constancy in the value of TL intensity after ~10 hour of exposure to UV lamp represents the TL intensity for the glow peaks at high temperatures.

The residual TL intensity almost represents the glow peak at high temperatures. See figure (4.10) and table (4.1) to check the residual TL intensity and the percentage area of glow peak under the second or third peak.



Figure (4.10): Thermal fading of Ln₂O₃:RE³⁺

TL material	Area under Glow peak (%)			TL material	Area under Glow peak (%)		
	1st	2nd	3rd	1L material	1st	2nd	3rd
Y ₂ O ₃ :Tb ³⁺	60.0	40.0	-	La2O3:Er3+	75.7	24.3	-
Y ₂ O ₃ :Tm ³⁺	38.4	36.6	25.0	Gd ₂ O ₃ :Tb ³⁺	40.0	60.0	-
Y ₂ O ₃ :Eu ³⁺	94.1	5.90	-	Gd ₂ O ₃ :Tm ³⁺	69.1	30.9	-
Y ₂ O ₃ :Er ³⁺	19.4	82.6	-	Gd ₂ O ₃ :Eu ³⁺	82.4	17.6	-
La ₂ O ₃ :Tb ³⁺	93.2	6.80	-	Gd ₂ O ₃ :Er ³⁺	69.0	31.0	-
La2O3:Tm3*	75.7	24.3	-				

Table (4.1): The percentage of the area under each glow peak for the Ln_2O_3 :RE³⁺.

4.6 Effect of the light on TL intensity

In general, light can cause severe fading in TL intensity.

Except $Y_2O_3:Tb^{3+}$, most of these materials have high light fading compared to TLD-900 and TLD-200. The visible light of 100W bulb can remove ~60% of the TL intensity of the dosimetry peak as shown in figure (4.11). After ~50 minutes of light exposure, the TL intensity is approximately stable, where the visible light has no effect. This result could be an explanation for the small change in TL intensity with exposure time to sunlight as shown in figure (4.5).

4.7 Conclusion

It is possible that rare earth materials play an important role as trap levels in the structure of the host phosphor. Some of them increase the sensitivity of the host phosphor to UV radiation. And others did not show any change in sensitivity of the host phosphor to UV radiation. The sensitivity of these phosphors to UV lamp and sunlight is summarized in the table (4.2).



Figure (4.11): The light fading for Ln₂O₃:RE³⁺

TL material	Sensitivity t	o UV radiation	TL material	Sensitivity to UV radiation		
	UV lamp Sunlight		I L material	UV lamp	Sunlight	
Y ₂ O ₃ :Tb ³⁺	sensitive	Sensitive	La2O3:Eu3+	Not sensitive	Not sensitive	
Y ₂ O ₃ :Tm ³⁺	Sensitive	Not sensitive	La2O3:Er3+	sensitive	Sensitive	
Y ₂ O ₃ :Pr ³⁺	Not sensitive	Not sensitive	Gd ₂ O ₃ :Tb ³⁺	Sensitive	Sensitive	
Y ₂ O ₃ :Eu ³⁺	Sensitive	Not sensitive	Gd ₂ O ₃ :Tm ³⁺	Sensitive	Sensitive	
Y2O3:Er3+	Sensitive	Not sensitive	Gd ₂ O ₃ :Pr ³⁺	Not sensitive	Not sensitive	
La ₂ O ₃ :Tb ³⁺	Sensitive	Sensitive	Gd ₂ O ₃ :Eu ³⁺	Sensitive	Sensitive	
La2O3:Tm3+	Sensitive	Sensitive	Gd ₂ O ₃ :Er ³⁺	Sensitive	Not sensitive	
La ₂ O ₃ :Pr ³⁺	Not sensitive	Not sensitive				

Table (4.2): The sensitivity of Ln₂O₃:RE³⁺ to UV lamp and sunlight.