Thermoluminescence properties of Eu and Li co-doped Gd2O3, induced by UV light

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Abstract. For some specific biomedical applications, connected with in-situ measurements of the absorbed dose of ultraviolet (UV) light, we have developed materials, sensitive to the light emission with a wavelength up to 320nm. Thermoluminescence (TL) yield of Gd2O3, doped with Eu and Li has been analysed with respect to the quantity of Li co-dopant. Lithium has been added as Li2CO3 to a mixture of Gd2O3 with 10 wt% Eu2O3. Pellets with the mixture have been sintered at a temperature of 1000ºC. The kinetic parameters of the phosphors thus obtained have been studied from the TL glow curves after irradiation with UV light. It has been demonstrated that the addition of 16 wt% of Li2CO3 to the Eu-doped Gd2O3 yields a maximum intensity of the peaks at 87ºC and at 145ºC. Studies on the kinetic parameters as well as the TL properties of Eu-doped Gd2O3 with the addition of 16% of Li2CO3 have been conducted. It has been measured that two of the TL peaks of this phosphor have relatively long fading. Analysis of the TL properties of the phosphors obtained from Gd2O3, doped with Eu and Li, shows that they possess good sensitivity to the UV emission and could be used as appropriate phosphors for detection and quantitative measurements of UV light.

1. Introduction
During the process of thermally stimulated luminescence (thermo-luminescence or TL) a release of luminescence light from some compounds (phosphors) is observed when they are heated. The emitted light is proportional to the accumulated energy from primary irradiation (x-rays, gamma rays, etc.), absorbed by the phosphor. The plots of the emitted light intensity with respect to the linearly increasing temperature are known as “glow curves” (GC). These curves usually have a complex shape, compounded by superimposed TL peaks. The intensity of these peaks is as a rule linearly correlated to
the quantity of radiation absorbed by the material. TL is largely exploited at present for applications in
dosimetry, in nuclear medicine, in archaeology in environmental studies, etc.

A very promising TL property of some materials is their ability to accumulate energy from photon
sources with “softer” than the X-rays’ and gamma-rays’ energy such as ultraviolet (UV) and even
visible light. It has been shown that some sintered materials from ZrO$_2$ doped with Er and Li could be
used as appropriate detectors for ultra-violet (UV) light [1-3].

Studies about the influence of some co-dopants on the TL emission of some materials have shown
that the presence of some ions in the matrix of the phosphors enhances the intensity of the TL. This
effect is probably due to the presence of traps in the band gap created by the ions. The effect of co-
doping with lithium ions is shown for a number of materials [4,5]. Following the idea to enhance the
TL emission of the materials with addition of Li ions, in our previous publications we have
demonstrated that quantities of lithium co-dopant, added as Li$_2$CO$_3$ to a mixture of ZrO$_2$ with 1wt%
Er, improved the TL intensity of the sintered material [6]. In this article we present the enhancement
of the TL emission of Gd$_2$O$_3$ doped with Eu and co-doped with Li (some preliminary results have
already been reported in [7]). We discuss the opportunity such material to be exploited as a potential
quantitative indicator, sensible to the ultraviolet light in the range of 290nm—340nm.

2. Materials and methods

To obtain the TL materials sensitive to the UV emission we have applied a simple sinterization
procedure, similar to the one described in [1]. UV sensible phosphors have been made from sintered
pellets of Gd$_2$O$_3$ doped with 10% Eu$_2$O$_3$. Quantities of Li have been added as Li$_2$CO$_3$, obtaining thus a
set of samples with the following quantities of Li: 10%; 12%, 14%; 16% and 18%. The mixtures have
been pressed in pellets with a diameter of 8mm and a thickness of about 1 mm using 5 ton press.
Finally the pellets have been sintered at 1000°C for 8 hours.

A setup for precise TL measurements (TL reader) developed in the Laboratory for nuclear physics
and radioecology (LNPR) at the University of Shumen has been used to obtain the glow curves of the
phosphors [8]. The system consists of a setup for sample heating, a glow curve measuring device on
the basis of photomultiplier tube, and a setup for sample irradiation with higher-intensity ultraviolet
(UV) light. The operation and control of the system has been realized on the basis of PIC16F876
microcontroller as well as on original forward/backward feedback method, based on the so-called
model predictive controllers, in order to achieve higher temperature stability and repeatability of the
analyses conducted.

Trap parameters of the phosphors have been studied using initial irradiation with ultraviolet light
from a xenon short-arc lamp type XBO 75 W/2 from OSRAM. The crystals have been placed at a
distance of 10 cm and the time of irradiation was 5 min.

The intensity of the TL emission as a function of the linear increase of the temperature, known as
TL glow curve (GC), is used to analyze some important parameters of the materials. Kinetic
parameters such as the activation energy and the kinetic order are obtained applying glow curve
decomposition analysis on each GC. Following [9] a single glow peak of a general order of kinetics is
fitted using the formula:

$$I(T) = I_m b^{b-1} \exp \left[ \frac{E}{kT} \frac{T - T_m}{T_m} \right] \left[ (b - 1) T_m^2 \exp \left[ \frac{E}{kT} \frac{T - T_m}{T_m} \right] + Z_m \right]^{b-1},$$

where $I(T)$ is the glow-peak intensity, $I_m$ is the maximum glow-curve intensity, $E$ (eV) is the activation
energy, $k$ is the Boltzmann constant, $T$ (K) is the temperature, $T_m$ (K) is the value of the temperature at
the peak maximum, with $\Delta = 2kT / E$, $\Delta_m = 2kT_m / E$ ; $Z_m = 1 + (b-1)/\Delta_m$ and the parameter $b$ ($1 < b \leq 2$) is the so-called kinetic order.
When the glow peak is a composite peak, compounded by \( m \) overlapping glow peaks, the method consists of a minimization of the \( \chi^2 \) function:

\[
\chi^2 = \sum_{i=1}^{n} \left( I_i - \sum_{j=1}^{m} I_j(T_i) \right)^2,
\]

where \( I_i \) are the measured GC intensity values, \( I_j(T_i) \) are the values of each partial GC at the temperature \( T_i \), \( n \) is the number of the experimental points and \( m \) is the number of the partial glow peaks compounding the observed peak.

The fading of the peaks in the TL glow curve (GC) has been obtained calculating the intensity of the corresponding partial TL emission (the net peak area) from the phosphors, kept for a certain time after the irradiation in a dark storage at a temperature of 20ºC. Glow curves, obtained with the TL reader, have been analyzed using a developed in the LNPR computer program implementing data smoothing using a Savitzky-Golay filtering and subsequently applying a minimization procedure based on conjugated gradients method for the TL peak decomposition technique.

3. Experimental results

Glow curves of \( \text{Gd}_2\text{O}_3 \), doped with 10% of \( \text{Eu}_2\text{O}_3 \) and co-doped with different quantities of Li from \( \text{Li}_2\text{CO}_3 \) have been obtained measuring the TL emission immediately after 5 minutes of irradiation with UV without annealing. The GC, presented with small circles in figure 1, have been obtained at a heating rate of 0.16ºCs\(^{-1}\).

![Figure 1](image_url)  
**Figure 1.** Glow curves of \( \text{Gd}_2\text{O}_3 \), doped with 10 wt% of \( \text{Eu}_2\text{O}_3 \), obtained after irradiation with UV light. The material is co-doped with: a) 12% Li from \( \text{Li}_2\text{CO}_3 \); b) 14% Li from \( \text{Li}_2\text{CO}_3 \); c) 16% Li from \( \text{Li}_2\text{CO}_3 \); d) 18% Li from \( \text{Li}_2\text{CO}_3 \).
Three peaks, shown with a broken line in figure 1, have been revealed by the decomposition analysis of the glow curves (using formula (1) and (2)): peak 1 at 47ºC, peak 2 at 87ºC and peak 3 at 145ºC, indicated as 1, 2 and 3 respectively. Another peak with higher values of the maximum temperature position, indicated as 4 in figure 1, has also been detected. The resulting fit, which is a sum of all peaks, is presented with thick line in the same figures.

**Figure 2.** A plot of Peak 2 and Peak 3 intensities as a function of the quantity of Li co-dopant.

A plot of the calculated peak intensities (the integrated counts in the corresponding peak areas from figure 1(a) to figure 1(d)) as a function of the quantity of Li co-dopant is shown in figure 2. From the figure it is clearly seen that the highest TL emission of peak 2 and peak 3 is observed for the pellet co-doped with 16% Li from Li2CO3. The calculated kinetic parameters for the peaks appearing in the TL glow curves are shown in Table 1.

**Table 1.** Calculated kinetic parameters of the peaks in TL glow curves of Gd2O3 co-doped with Eu and Li

| Peak reference | Maximum temperature position (ºC) | Activation energy (eV) | Kinetic order |
|----------------|-----------------------------------|------------------------|--------------|
| Peak 1         | 47 ± 2                            | 0,6 ± 0,2              | 2,0 – 0,1    |
| Peak 2         | 87 ± 1,8                          | 0,7 ± 0,1              | 1,8 ± 0,1    |
| Peak 3         | 145 ± 1,3                         | 1,1 ± 0,08             | 1,2 ± 0,1    |

The dependence of the TL emission on the wavelength of the irradiating light (the spectral sensitivity) has been studied measuring the intensity of the TL glow curves for Gd2O3 doped with 10 wt% Eu from Eu2O3 and co-doped with 16wt% Li from Li2CO3. Interference optical filters for different wavelength were placed consecutively between the XBO lamp and the crystals during each irradiation. To perform these measurements the phosphors have been exposed to irradiation from the XBO lamp for a long enough time, ensuring thus saturation of the states. The calculated intensities for
peak 1, peak 2 and peak 3 from the measured TL glow curves versus the wavelength of the irradiating light are shown in figure 3. The obtained thus spectral sensitivity of the material reveals a wavelength limit for peak 2 and peak 3 around 320 nm. The corresponding irradiation wavelength limit for peak 1 is about 400 nm. The later fact shows that the appearance of peak 2 and peak 3 in the TL glow curve spectrum is caused by the UV emission from the XBO lamp only.

Figure 3. Spectral sensitivity of Gd\textsubscript{2}O\textsubscript{3} doped with 10 wt\% Eu from Eu\textsubscript{2}O\textsubscript{3} and co-doped with 16 wt\% Li from Li\textsubscript{2}CO\textsubscript{3}.

Figure 4. Fading of Peak 1, Peak 2 and Peak 3 intensities as a function of the storage time.
Measurements to determine the fading of the observed peaks in fig 1 have been conducted for several sintered pellets, containing Gd$_2$O$_3$ doped with 10 wt% Eu from Eu$_2$O$_3$ and co-doped with 16wt% Li from Li$_2$CO$_3$. To perform this kind of measurements the phosphors have been irradiated each time with an equal amount of light (5 min) from the XBO lamp. After the irradiation the crystals have been kept for certain time periods in dark place at a temperature of 20°C. A plot of the areas of the three peaks, calculated from the fits of the TL glow curves versus the storage time of the phosphors from is shown in figure 4. The maximum storage time interval was 120 hours.

4. Conclusions
The analysis of the fading of the three peaks of Gd$_2$O$_3$, co-doped with 10% of Eu and 16% of Li reveals that the low-temperature peak 1 disappears rapidly (in two hours). Peak 2 fades completely for about 50 hours, while peak 3 fades for about 120 hours. Both last peaks possess relatively good count-rate statistics. They have sufficiently long fading, allowing quantitative TL measurements within a couple of days.

We also compared the TL yield of Gd$_2$O$_3$ co-doped with 10% of Eu and 16% of Li with respect to the TL yield of ZrO$_2$ co-doped with 1% Er and 8% of Li from our previous studies [7]. Equal size pellets from both kinds of materials were tested using excitation with XBO lamp at equal other excitation conditions such as time of irradiation and source-to-detector distance. It was shown that the material from Gd$_2$O$_3$, co-doped with 10% of Eu and 16% of Li possesses higher TL yield. This fact and the relatively long enough fading of peak 2 and peak 3 open a reasonable opportunity to exploit such a material as a potential phosphor for short-term UV measurements.

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