UV light-induced thermoluminescence of Er + Li doped ZrO$_2$

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Abstract. Analysis of the thermoluminescence (TL) properties of ZrO$_2$ doped with Eu and Li has been conducted. Different quantities of lithium co-dopant have been added as Li$_2$CO$_3$ to a mixture of ZrO$_2$ with 1 wt% Er. Pellets sintered at a temperature of 1200°C have been prepared and the kinetic parameters of the phosphors have been studied after irradiation with UV light. It has been shown that the addition of 8 to 10 wt% of Li to the mixture of ZrO$_2$ with 1 wt% Er yields a maximum intensity of the peaks at 65°C and at 105°C. Spectral emission and spectral sensitivity of the phosphors have been studied. The analysis applied to TL glow curves, obtained from the UV irradiated phosphors and kept after the irradiation at different times in a dark storage, revealed that the peaks at 65°C and 105°C have relatively long fading. It is concluded that the phosphors thus obtained possess a good sensitivity to the UV emission and could be appropriate phosphors for detection and quantitative measurements of UV light.

1. Introduction

Thermally stimulated emission (thermoluminescence) of some crystals can be stimulated by irradiation with photons with lower than the X-rays’ and gamma-rays’ energies for instance ultra-violet (UV) emission. This case is interesting with respect to possible applications such as detection and quantitative measurements of the UV emission, holographic storage, etc.

It is known that an enhancement of the thermoluminescence (TL) emission of some phosphors can be achieved after co-doping with lithium [1, 2]. In this article we present the results from a study, conducted on the enhancement of the TL emission of ZrO$_2$ doped with Er and co-doped with Li, as a potential indicator, sensible to the UV light in the range of 290 nm – 400 nm.

2. Materials and methods

UV sensible phosphors have been produced from sintered pellets of ZrO$_2$ doped with 1 wt% of Er as Er$_2$O$_3$ according the procedure described in [3]. Different quantities of Li have been added to the

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mixture as Li$_2$CO$_3$, thus obtaining samples with Li concentrations of 2.5 wt%; 5 wt%; 10 wt% and 15 wt%. The mixtures, pressed in pellets with a diameter of 8mm and thickness of 1 mm, have been sintered at 1200°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 TL glow curves of the phosphors [4]. 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.

The kinetic parameters of the prepared phosphors have been studied analyzing their TL glow curves (GC) after irradiation with 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 in the interval 3 - 5 min. The alimentation of the XBO lamp was 75W maintained at lamp current of 5.4A, recommended by the manufacturer.

Kinetic parameters such as the activation energy and the kinetic order have been obtained applying glow curve decomposition analysis on each GC obtained. A single glow peak of a general order of kinetics was fitted using the equation [5]:

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

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 $\Delta = 2kT / E$, $\Delta_a = 2kT_m / E$; $Z_a = 1 + (b-1)/\Delta_a$ 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:

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

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 20°C. 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 exploiting conjugated gradients method for the peak decomposition technique described above.

3. Experimental results

A TL glow curve of ZrO$_2$, doped with Er$_2$O$_3$ and measured immediately after 3 minutes of irradiation with UV light from the XBO lamp at a distance of 10 cm, is shown in figure 1a). The GC, presented with a thick black line, has been obtained without annealing at a heating rate of 0.16°C/s. Three peaks have been revealed by the decomposition analysis: peak 1 at 65°C, peak 2 at 105°C and peak 3 at 150°C, indicated in the figures of this article as 1, 2 and 3 respectively. The resulting fit is presented with white line in the same figure.
Figure 1. Glow curves of ZrO$_2$ doped with 1 wt% Er$_2$O$_3$ and co-doped with different quantities of Lithium: a) without Li$_2$CO$_3$; b) with 5 wt% Li$_2$CO$_3$; c) with 10 wt% Li$_2$CO$_3$; d) with 15% Li$_2$CO$_3$.

The TL glow curves obtained from ZrO$_2$ doped with 1 wt% of Er and co-doped with 5 wt%; 10 wt% and 15 wt% of Li, are shown in figure 1b) - 1d) respectively. The curves have been measured immediately after the irradiation with UV light under the same conditions (time of UV irradiation and distance to the XBO lamp). The glow curves, presented with thick black lines, have been acquired without annealing at a heating rate of 0.160/s. The resulting three peaks at 65°C, at 105°C as well as at 150°C have significantly higher TL yields as it can be seen from the figures.

Figure 2. Spectral sensitivity of ZrO$_2$ doped with Er(1%) and Er(1%) +Li(10%).

Figure 3. Spectral emission of ZrO$_2$ doped with Er(1%) and Er(1%) +Li(10%).
The dependence of the TL emission with respect to the wavelength of the irradiating light (the spectral sensitivity) has been studied measuring the intensity of the whole TL glow curve for ZrO$_2$ doped with Er and for ZrO$_2$ doped with Er+Li. Interference filters for different wavelength were placed consecutively between the XBO lamp and the phosphors during each irradiation. The measured total TL glow curves intensities versus the wavelength of the irradiating light are shown in figure 2. Thus the obtained spectral sensitivities of the crystals reveal a wavelength limit for the irradiating light around 380 nm. The later fact shows that the TL emission of the phosphors is caused only by the UV component of the emission of the XBO lamp.

Figure 3 shows the emitted total TL light intensity of Er doped ZrO$_2$ and Er+Li doped ZrO$_2$ with respect to the wavelength (the spectral emission). The TL emission has been measured during the crystal heating after 5 min irradiation of the crystal with XBO lamp. A set of interference filters has been placed in front of the photomultiplier tube of the TL reader during the acquisition and the total number of counts for a heating cycle (30°C – 200°C) has been registered immediately after the irradiation. Corrections for the light attenuation in the filters and for the spectral response of the photomultiplier tube have been made to the measured total number of counts.

The analysis of the measured peak intensities from the glow curves of the sintered ZrO$_2$ doped with 1% Er form Er$_2$O$_3$ and the co-dopant Li from Li$_2$CO$_3$ in quantities of 2.5 wt%, 5 wt%, 10 wt% and 15 wt% shows that the quantities around 10wt% of Li co-dopant generate maximum intensities of the GC peaks. A plot of the peak intensities (integrated counts in the corresponding peak areas) for Peak 1 and Peak 2 from fig 1, as a function of the quantity of Li co-dopant, is shown in figure 4.

The calculated kinetic parameters for the peaks appearing in the TL glow curves of ZrO$_2$ doped with Er$_2$O$_3$ and Li$_2$CO$_3$ are shown in Table 1.

| Peak reference | Peak position (°C) | Activation energy (eV) | Kinetic order |
|----------------|--------------------|------------------------|---------------|
| Peak 1         | 65 ± 2.0           | 0.52 ± 0.07            | 1.1 ± 0.15    |
| Peak 2         | 105 ± 1.8          | 0.96 ± 0.03            | 1.6 ± 0.29    |
| Peak 3         | 150 ± 1.3          | 1.03 ± 0.09            | 2.0 – 0.02    |

**Figure 4.** Measured net area of Peak 1 and Peak 2 of the TL glow curves from Er-doped ZrO$_2$ as a function of the quantity of Li co-dopant.

**Figure 5.** Fading of Peak 1 and Peak 2 of phosphors from sintered ZrO$_2$ doped with 1 wt% Er and 10 wt% Li.
Finally the fading measurements about the observed Peak 1 and Peak 2 in fig 1 have been performed plotting the peak areas from the TL glow curves versus the storage time of the phosphors from sintered ZrO$_2$ doped with 1 wt% Er and 10 wt% Li. (figure 5). To perform these 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. The maximum storage time interval was 12 hours. Form figure 5 is seen that peak 1 and peak 2 fade completely for about 12 hours.

4. Conclusion
The analysis of the TL glow curves of the sintered crystals shows that the presence of Li ions as a co-dopant enhances significantly the TL emission of ZrO$_2$ doped with Er$_2$O$_3$ with respect to the UV light. Quantities between 8 wt% and 10 wt% of Li$_2$CO$_3$ induce higher thermoluminescence emission of the peaks at 65 °C and 105 °C.

An interesting fact, analogical to the one, described in [2] is observed in the TL glow curves in figure 1: the increase of the TL emission of the two peaks is followed by the decrease of the higher-temperature TL peaks, where the deconvolution procedure is difficult to be conducted due to the higher thermal emission of the samples.

The measurements carried out for the fading of the peaks showed that the peak 1 has a fading of approximately 9 hours and the peak 2 has slightly longer fading – about 12 hours. This fact together with the higher sensitivity with respect to the UV light, shows on the possibility to use the sintered pellets of ZrO$_2$ doped with 1 wt% Er and co-doped with 8 to 10 wt% of Li as a potential phosphor for UV thermoluminescence measurements.

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