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Prompt isothermal decay properties of the $Sr_4Al_{14}O_{25}$ co-doped with Eu^{2+} and Dy^{3+} persistent luminescent phosphor

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ABSTRACT

Thermoluminescence (TL) techniques are very useful in the research of the persistent Luminescence (PL) phosphors research. It gives information about the existence of energy levels within the forbidden band, its activation energy, kinetic order, lifetime etc. The TL glow curve of $Sr_4Al_{14}O_{25}$: Eu^{2+},Dy^{3+} persistent phosphor, consists of two well separated glow peaks. The TL techniques used to evaluate activation energy were the initial rise, prompt isothermal decay (PID) of TL of each peak at elevated temperatures and the glow – curve fitting. The behavior of the PID curves of the two peak is very different. According to the results of the PID procedure and the subsequent data analysis it is suggested that the mechanism behind the low temperature peak is a delocalized transition. On the other hand the mechanism behind the high temperature peak is localized transition involving a tunneling recombination between electron trap and luminescence center.

1. Introduction

Persistent luminescence is the light emitted from a previously excited material for time periods ranging between seconds up to several hours after its excitation [1]. It can be considered as thermoluminescence (TL) measured at room temperature and it is also known as afterglow. Materials yielding persistent luminescence are called persistent phosphors and had attracted the extensive research interest from scientists of various topics like materials scientists, physicists, chemists and biologists [2] due to their widespread applications such as oxygen sensor, radiation dosimetry, light emitting diodes and others [3–5] as well as due to the special optical phenomenon itself.

Strontium aluminate is a very interesting persistent phosphor appearing in various forms as $Sr_4Al_2O_7$, $Sr_3Al_2O_6$, $SrAl_2O_4$, $SrAl_4O_7$, $Sr_4Al_{14}O_{25}$ and $SrAl_2O_{19}$. Usually, strontium aluminate in all aforementioned forms can be synthesized using appropriate precursor materials and heat treatments [6]. Recently $S_4Al_{14}O_{25}$ has attracted great interest because of its long afterglow time and brightness [7]. Their luminescence is obtained by adding specific rare earth elements as dopants, such as Eu^{+2} and Dy^{+3} into the host lattice of strontium aluminate [8]. The transitions between the ground state of $4f^7$ and the excited state of $4f^6 5d^1$ of Eu^{2+} ions provide broad emission bands and also enhance initial intensity of emission and luminescence lifetime.

In the framework of a multidisciplinary study of persistent phosphors, TL stands among the methods which can contribute in the characterization of such materials, enabling thus the calculation of the trap depths, as well as the potential assessment of the release rate of the carriers. For a recent review on the TL as a research tool in the study of persistent phosphors, the authors could refer to Bos [1].Besides TL, the prompt isothermal decay (PID) of TL at various temperatures can help calculating the values of the lifetimes of electron energy levels as a function of temperature. as well as the dependence of these lifetimes on the temperature [9,10]; the dependence of the lifetime on temperature leads to the evaluation of the energy trap depth of electron levels.

The aim of the present work is to apply TL techniques in order to investigate the electron trapping levels responsible for luminescence in the $Sr_4Al_{14}O_{25}$: Eu^{2+}/Dy^{3+} persistent phosphor. Additional aim is to analyze the results in the framework of both delocalized and localized tunneling recombination models.

2. Experimental procedure

2.1. Sample details

The material under investigation was $Sr_4Al_{14}O_{25}$: Eu^{2+}/Dy^{3+} persistent phosphor. The synthesis of Eu^{2+}/Dy^{3+} co-doped $Sr_4Al_{14}O_{25}$ was

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achieved by the sol-gel technique [11,12]. The main features of the multicomponent sol-gel process, being an efficient technique for the synthesis of phosphors, are the following: (a) the formation of a homogeneous solution before polymerization, (b) the relatively low processing temperatures, (c) the ease of powder production (d) the excellent mixing of starting materials and (e) the low cost [12–14]. Thus, the main outcomes of the sol gel technique due to all aforementioned features result not only in chemical homogeneity, which can be effectively achieved with absolute control over the final composition and tailoring of the surface characteristics of the product, but also in crystallization and lack of chemical decomposition. For more details regarding the synthesis as well as both structural and optical characterizations of the specific persistent phosphor, the readers could refer to Aydin et al. [3] and Demirci et al. [7].

2.2. Apparatus and measurement conditions

TL was induced by irradiation with Ultra Violet (UV) photons from a spectral mercury lamp. A limited number of irradiations were performed using a ^{90}Sr–^{90} Y beta ray source delivering 0.4 Gy/min. All TL measurements were performed using the TLD reader model 3500 of the Harshaw (Bicron) in a nitrogen atmosphere with a low constant heating rate of 2 °C/s, in order to avoid significant temperature lag; and the samples were heated up to the maximum temperature of 350 °C.

2.3. Experimental protocols

All PID measurements were performed according to the following protocol.

- Step 0: Test dose of 4 Gy and then TL measurement up to $T = 350$ °C at 2 °C/s.
- Step 1: The previously annealed aliquot is irradiated using the UV lamp, in order to populate the traps and the centers.
- Step 2: TL measurement up to a temperature T_{dec} at 2 °C/s. The sample is left to decay thermally for 300 s at this temperature, and the isothermal decay signal is measured.
- Step 3: After the end of the decay period, the sample is cooled down to room temperature.
- Step 4: TL measurement at 2 °C/s in order to obtain the residual TL glow curve (R-TL).
- Step 5: Repeat steps 1–4 for a new decay temperature T_{dec}.
- Step 6: Repeat step 0 in order to check for sensitivity changes.

The $Sr_4Al_{14}O_{25}$: Eu^{2+},Dy^{3+} has two prominent peaks at 80 °C and 170 °C.

The PID of the first peak was performed at temperatures 55, 60, 65, 70, 75, 80, 85 and 90 °C. For the PID study of the second peak an additional Step 1a involving a thermal cleaning up to 120 °C in order to remove the glow peak at 80 °C. The PID of the second peak was performed at temperatures 95, 100, 105, 110, 120, 125, 130, 135, 140, 145, 150, 155 and 160 °C.

The protocol runs in single aliquot mode. Step 0 and step 6 measure the initial and final sensitivity of each sample. Negligible sensitivity changes were observed for all samples.

3. Method of analysis

From the preliminary treatment of the experimental data in Section 4.1 it was recognized that all experimental PID curves have to be analyzed by two different models. (a) a delocalized recombination model and (b) a localized tunneling recombination model.

3.1. Delocalized recombination model

In the case of delocalized model, instead of the empirical general order kinetics analytical expression, the analytical expressions obtained from the solution of the one trap one recombination center (OTOR) model were used. The original analytical expression derived by Kitis and Vlachos [15] as a solution of the general one trap (GOT) semi-analytical equation, resulting from the OTOR model, is:

$$I(T) = \frac{N R}{(1-R)^2} \frac{p(t)}{W(z) + W(z)^2} \tag{1}$$

where N is the total concentration of electron traps, $W(z)$ is the Lambert W function [16] and $R = A_n/A_m$ with A_n the re-trapping probability, A_m recombination probability and $p(t)$ is a function describing the stimulation mode.

The expression for the factor z depends on the values of R.

When $R < 1$, denoting that re-trapping probability is less than recombination probability, then Eq. (1) holds for the first real branch of the Lambert W function and z given by

$$z = exp\left(\frac{R}{1-R} - ln\left(\frac{1-R}{R}\right) + \frac{\int_0^t p(t)dt}{1-R}\right) \tag{2}$$

Eq. (1) along with Eq. (2) are equivalent to what is conveniently known as empirical general order kinetics decay [17].

When $R > 1$, namely re-trapping probability gets values higher than recombination probability, then Eq. (1) holds for the second real branch of the Lambert W function and z given

$$z = -exp\left(\frac{R}{1-R} - ln\left(\left|\frac{1-R}{R}\right|\right) + \frac{\int_0^t p(t)dt}{1-R}\right) \tag{3}$$

Eq. 1 along with Eq. (3) is not, as the previous case, equivalent to what is conveniently known as general order kinetics, which in most cases fails to agree with it [18].

For the case of TL readout the function $p(t)$ is

$$p(t) = s \exp\left(-\frac{E}{k\,T}\right) \tag{4}$$

For a linear heating rate $T = T_0 + \beta t$ and for an asymptotic series approximation of the exponential integral [17] we have,

$$\int_0^t p(t)dt = \frac{s}{\beta}\int_{T_0}^{T} e^{-\frac{E}{k\,T}}dT = \frac{s\,k\,T^2}{\beta\,E} e^{-E/k\,T}\left(1-\frac{2k\,T}{E}\right) \tag{5}$$

For the case of isothermal TL at a stable temperature T_{dec} the function $p(t)$ is

$$p(t) = \lambda \tag{6}$$

and

$$\int_0^t p(t)dt = \int_0^t \lambda\, dt = \lambda\, t \tag{7}$$

Some problems may arise when the value of z is very high, so that e^z returns values that cannot be treated by some software packages. However, this problem with e^z values can be easily overcome, because the Lambert W function is a kind of logarithm, so that it can be very accurately approximated by a function of the form

$$W(e^x) = x - log(x) \cong x \qquad for \quad x > 500 \tag{8}$$

Eq. (1) along with Eqs. (2) and (3) are used to fit the experimental Isothermal decay curves. The adjustable fitting parameters are the decay constant λ and the ratio R (with $R \neq 1$).

The Lambert function $W(z)$, is, in modern software packages, among the usual built-in functions, similar to any other transcendental function like sine, cosine etc.[1] In the present work the ROOT data

[1] The Lambert function is termed ProductLog[(0,1),z] in Mathematica, Lambert w_0 and w_1 in MATLAB and EXCEL, gsl-sf-lambert-$w_0(z)$, gsl-sf-lambert-$w_1(z)$ in GNU GSL. w_0 and w_1 stands for the first and second real branch correspondingly.