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Thermoluminescence and scintillation properties of LuAP and YAP

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Abstract

In this communication we report on the application of low temperature thermoluminescence (ltTL) associated with shallow traps in the research on scintillation properties of cerium doped LuAP and YAP crystals. We show that existence of shallow traps and their interference with the scintillation process readily explain changes in light yield and time profiles with temperature. The analysis of two major glow peaks at 183 and 270 K of LuAP:Ce yields trap parameters: The activation energy $E=0.507$ eV; the frequency factor $s=3.65\times10^{12}$ s^{-1} and $E=0.786$ eV; $s=1.77\times10^{13}$ s^{-1}, respectively. A glow curve of YAP:Ce also shows two major glow peaks at 108 K and 154 K, although this case is more complex and involves a distribution in the energies. Assuming a Gaussian distribution with the standard deviation $\sigma\cong0.018$ eV we find trap parameters to be: $E=0.30$ eV (the mean); $s=5\times10^{12}$ s^{-1} and $E=0.5$ eV; $s=7\times10^{14}$ s^{-1}, respectively. Then using the obtained trap parameters we calculate examples of time profiles and light yield characteristics to compare them to the experimental results.

Keywords: Recombination and trapping; Thermal analysis; Luminescence; Phosphors

1. Introduction

It has recently been recognized that existence of shallow charge traps can negatively affect efficiency and time properties of scintillation emission [1–3] modifying such key parameters as light yield, rise and decay times of scintillation response pulse that are important for evaluation of scintillators in modern applications (e.g. PET cameras). Variations of these parameters were observed in cerium doped $LuAlO_3$ (LuAP) and $YAlO_3$ (YAP) crystals. Despite the fact that LuAP and YAP are two isostructural crystals their scintillation properties differ significantly. The room temperature light yield of LuAP suffers about 30% loss against that of less dense YAP; on the other hand its scintillation decay time is equal to the radiative decay time of the Ce^{3+} allowed d–f transition (~19 ns) whereas scintillation emission of YAP:Ce is characterized by an unexpectedly longer decay time (~25–38 ns). On the contrary, the rise time of LuAP:Ce scintillation time profile is longer than in the case of YAP:Ce. Based on a simple kinetic model of the scintillation process that includes shallow electron traps these differences have been successfully explained [1–3].

In this paper we employ the ltTL associated with shallow traps in the course of research on scintillation properties of Ce^{3+}-activated LuAP and YAP crystals. Although the presence of some shallow traps in LuAP:Ce had been anticipated from light yield experiments [1,2] and in one particular case confirmed in an ltTL measurement later on [4], the actual glow curve has never been analyzed in the frame of any kinetic model. On the other hand, the glow curve of YAP:Ce has undergone such an interpretation albeit an apparent distribution in trap depths was neglected and a two-trap model was introduced for the sake of simplicity [3]. Now we apply an extended analysis by including an observed trap distribution.

2. Experiment

The measurements of ltTL and ITD were preceded by irradiation of samples with either an ^{241}Am X-ray source or a 180 nm VUV light at 4 K temperature. For both the ltTL and ITD experiments the total emission of a sample was recorded with the detection monochromator set to the zeroth order. The ltTL measurements were performed in the range of 10–370 K at a linear heating rate of 0.15 K/s.

In scintillation light yield measurements we used a ^{137}Cs radioactive source (10 μCi). The samples were excited by γ-photons from the source at various temperatures in the range 20–300 K. The light generated by a γ-photon was

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integrated over the time window determined by a 0.5 μs shaping time.

The scintillation and emission time profile measurements used the standard method of synchronous photon counting. Scintillation time profiles (STP) were performed employing the same set-up as the scintillation light yield measurements. Emission time profiles (TP) were measured under the pulsed synchrotron excitation on the same set-up as for luminescence at the SUPERLUMI station of the HASYLAB [7]. The instrumental time response of this set-up is below 1 ns.

3. Theory

In the first order kinetic model provided by Randall and Wilkins a single trapping level can be described by two parameters, the activation energy (E) and frequency factor (s) [5]. The intensity of a glow curve is given by:

$$\mathrm{I}(\mathrm{T}-\delta T) = ns\exp\left(-\frac{E}{kT}\right) \times \exp\left[-\left(\frac{s}{\beta}\right)\int_0^T \exp\left(-\frac{E}{kT'}\right)\mathrm{d}T'\right], \quad (1)$$

where n is the initial concentration of filled traps, k the Boltzmann constant, β the linear heating rate and δT the thermal lag. The rate of carrier's escape from the trap (γ), equal to the reciprocal of carrier's lifetime in the trap (τ_t), is described by the following equation: $\gamma=\tau_t^{-1}=s\times\exp(-E/kT)$. If the heating cycle is stopped at some particular temperature in the range of a glow peak (at T_0), we can record the decreasing intensity of emission against time. In this case Eq. (1) assumes a simpler form:

$$I(t)|_{T_0} = \frac{n}{\tau_t}\exp\left(-\frac{t}{\tau_t}\right). \quad (2)$$

This formula describes the so-called isothermal decay traces, from which the τ_t constant can be extracted. If we then subsequently assume that the carrier released from a trap goes directly and instantaneously to a recombination centre, then we can treat a trap–centre system as a donor–acceptor system and the time profile of its emission can be described as follows [6]:

$$I(t) = \frac{n}{\tau_{\mathrm{Ce}}-\tau_t}\left[\exp\left(-\frac{t}{\tau_{\mathrm{Ce}}}\right)-\exp\left(-\frac{t}{\tau_t}\right)\right]. \quad (3)$$

This equation is valid in the entire range of temperatures, whether the τ_t is shorter (introducing the rise time) or longer (introducing slower component) than τ_{Ce}. Of course, the experimental time profile traces include the prompt component of emission (directly excited Ce ions) as well. If we integrate Eq. (3) over a collection time t_{col} we will get a formula that accounts for changes of light yield against temperature [1–3]:

$$I\int(T) \approx n\frac{\tau_{\mathrm{Ce}}}{\tau_{\mathrm{Ce}}-\tau_t}\left\{1+\frac{\tau_t}{\tau_{\mathrm{Ce}}}\left[\exp\left(-\frac{t_{\mathrm{col}}}{\tau_t}\right)-1\right]\right\}. \quad (4)$$

Note that the direct component is not included in this equation. Since this component does not change with temperature we include it in the background.

To consider a trap distribution we assume that traps within the distribution do not interfere with each other. Consequently, the final result can be described as a linear combination of traps of different energy and concentration, the last determined by a distribution function. For our purpose we choose a Gaussian. Naturally, the linear combination is achieved by integration of all the above equations over appropriate energy range. The only problem is caused by Eq. (2), where the most serious difficulty with this approach is related to the distortion of the initial distribution of traps caused by the heating of the sample necessary to reach the predetermined temperature of a measurement. The concentration of shallower traps is depleted stronger than that of the deeper traps. Thus this effect must be included into our equation. Simple consideration leads us to the following formula:

$$I(t)|_{T_0} = \int_{E_1}^{E_2}\frac{G(E)}{\tau_t}\exp\left(-\frac{s}{\beta}\int_0^{T_0}\exp\left(-\frac{E}{kT}\right)\mathrm{d}T\right) \times \exp\left(-\frac{t}{\tau_t}\right)\mathrm{d}E, \quad (5)$$

where $G(E)$ is the normalized Gaussian distribution and the additional exponential expression accounts for changes in the concentration of occupied traps with temperature.

4. Results and discussion

4.1. TL and ITD of LuAP:Ce

The glow curve of LuAP:Ce presented in Fig. 1 contains two major peaks, the fist, dominant one is peaking at 183 K (a) and the second one at 266 K (b). In addition there are two minor peaks at 55 K (α_1) and 95 K (α_2). The curve was recorded using a sample irradiated with the VUV light at 4 K. The irradiation with X-rays leads to a similar curve although the ratio of the peaks can slightly differ. In order to find the parameters E and s of the major peaks we conducted ITD experiments at temperatures in the vicinity of these peaks: (a) 180, 185, 190 K and (b) 250, 262 and 266 K. The fitting procedure (Eq. (2)) applied to the measured traces yielded the following values of τ_t: (a) 278, 46, 7 s and (b) 400, 72, 46 s that in turn were plotted on an Arrhenius type diagram. The subsequent analysis of this diagram led to the following trap parameters: (a) $E=0.507$ eV; $s=3.65\times10^{12}$ s^{-1} and (b) $E=0.786$ eV; $s=1.77\times10^{13}$

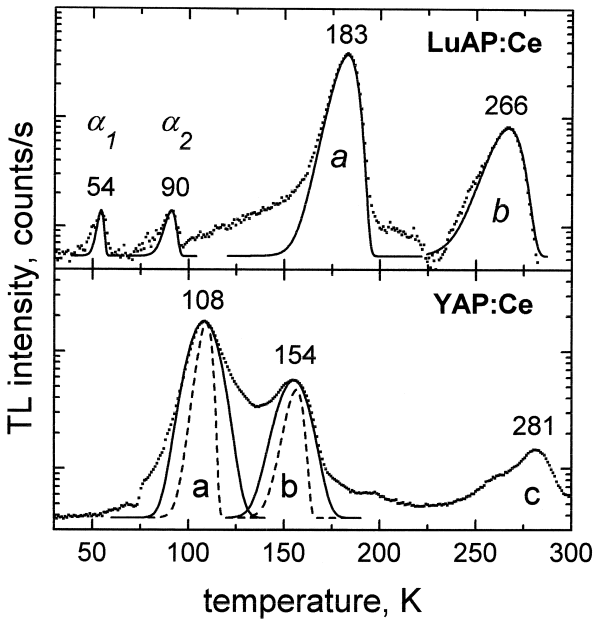

Fig. 1. ltTL glow curves of LuAP:Ce and YAP:Ce. Dots are experimental points. Eq. (1) was used to calculate the solid lines for LuAP:Ce and dashed lines for YAP:Ce. In the case of YAP:Ce the solid lines were calculated using convoluted Eq. (1). We assumed the thermal lag of 2.05 and 1.9 K for LuAP:Ce and YAP:Ce, respectively. The heating rate β is 0.15 K/s.

s^{-1} (summarized in the lower part of Table 1). Having these parameters we calculated the two glow curves (solid lines in Fig. 1) using Eq. (1). The only parameters adjusted were the initial concentration (n) and thermal lag $\delta T = 2.05$ K. The match to the experimental points is very good, although the (b) peak would be better represented by a pair of glow peaks rather than just one. The values of parameters obtained by this method in the case of the (a) peak are very close to parameters found previously [1–4] (the upper part of Table 1), whereas for the (b) peak they differ substantially. This fact can be explained in terms of differences in a fitting procedure (in Ref. [4] a fitting procedure to a single glow peak was performed). Unfortunately, the used method cannot be applied to determine the trap parameters of the remaining traps – α_1 and α_2. The intensity of these traps is very low and so far we have failed to measure ITD traces. The quality of TL spectra does not allow using a fitting routine to particular glow peaks, neither. Hence we decided to perform a simple simulation that reproduces the maxima of peaks with the frequency factor preset to that of the (a) peak (solid lines in Fig. 1). We find the activation energies of the α_1 and α_2 traps to be 0.141 eV and 0.244 eV, respectively. The position and activation energies of either of these traps is close to the predicted α trap although none of them have the expected from LY experiments intensity [1,2].

4.2. TL and ITD of YAP:Ce

The glow curve of YAP:Ce (irradiated with the X-ray source at 4 K) showed in Fig. 1 also contains two major glow peaks although they are shifted toward lower temperatures. The dominant peak (a) is located at 108 K and the second peak (b) at 154 K. At higher temperatures, 261 and 281 K (c) there are two other peaks of smaller intensity. The α trap (the upper part of Table 1) anticipated from other experiments at around 51 K is not detected but we must say that this value was calculated using a preset frequency factor. After ceasing an irradiation of a YAP:Ce crystal at 4 K we observed an apparent phosphorescence, that could be due to this trap if the actual frequency factor was higher than assumed. Highly symmetric shapes of the major glow peaks (a, b) lead us to conclusion that there is a distribution in the energies associated with these traps (we have excluded the possibility of second order kinetic). Because both peaks can be accurately fitted with a Gaussian, we chose it as our distribution function. It means that any of curves described by Eqs. (1)–(4) have to be convoluted with a Gaussian function, with a special instance of an ITD curve that must follow Eq. (5). Because of the trap distribution involved

Table 1
Summary of trap parameters of LuAP and YAP doped with Ce^{3+} [a]

LuAP:Ce					YAP:Ce				
Trap	E [eV]	ln s [s^{-1}]	T_{max} [K]	Ref.	Trap	E [eV]	ln s [s^{-1}]	T_{max} [K]	Ref.
α	0.205	28.90	(75)	[1,2]	α	0.119	?	(–)	[1,2]
a	0.485	28.90	(173)	[1,2]	α	0.13	27.27	(51)	[3]
a	0.51	28.90	183	[4]	a	0.309	29.20	(110)	[1,2]
b	0.64	23.70	265	[4]	a	0.28	27.27	105	[3]
α_1	0.141	28.93	54	–	b	0.4	27.27	152	[3]
α_2	0.244	28.93	90	–	a	0.30	29.24	108	–
a	0.507	28.93	183	–	b	0.50	34.18	154	–
b	0.786	30.50	266	–	c	–	–	281	–

[a] The parameters in the upper part of the table are taken from previous publications [1–4]. The maxima of peaks (T_{max}) in brackets are derived from experiments other than TL. In the lower part of the table we present results obtained from fits and simulations to ITD and ltTL experiments described in this paper. In the case of YAP:Ce the activation energy E represents the mean of a normalized Gaussian with the standard deviation $\sigma = 0.0175$ (a) and 0.0195 (b).

we cannot exercise the same simple routine used for LuAP:Ce. For that reason we have decided to look for the best simulations with a given set of parameters to both a glow peak and ITD traces. For the (a) peak we find that the TL and ITD simulations with $E=0.30$ eV (the mean); $s=5\times10^{12}$ s^{-1} and the standard deviation $\sigma=0.0175$ give fairly good match to the experimental points (with $\delta T=1.9$ K). A glow peak calculated with the above values is drawn in Fig. 1 by the solid line. For a comparison the non-convoluted glow peak is also showed by the dashed line. In Fig. 2 we show two ITD traces measured in the vicinity of the (a) peak at temperatures of 105 K and 110 K that we used in our procedure (small peaks superimposed on the 110 K trace are experimental artifacts). The calculated curve for the 105 K trace (solid line) closely follows the experimental points whereas the one for the 110 K trace at some point (~500 s) goes lower than the experimental points. This effect can be explained by the existence of slightly deeper traps (~132 K) that provide longer components. Employing the same method we find parameters of the (b) peak: $E=0.5$ eV; $s=7\times10^{14}$ s^{-1} and $\sigma=$ 0.0195. ITD curves measured at 150 and 153 K (not showed) have a good match to the experimental points. The simulation of the (b) glow peak is drawn in Fig. 1 by the solid line (the dashed line shows a non-convoluted simulation). The ratio of intensities of both glow peaks is ~76:24 (a:b).

4.3. Comparison of LuAP:Ce and YAP:Ce

At this point it is interesting to examine if the observed traps can actually interfere with the scintillation process and modify scintillation properties. In Fig. 2 we present an STP of YAP:Ce measured at 260 K. We chose this temperature so that the influence of mainly one trap, the (a) trap can be observed. With the values of trap parameters given above we calculated a TP curve presented in Fig. 2 by the solid line. It contains three components, each one in the form of Eq. (3). The first component accounts for the prompt emission (here, we assumed $\tau_t=0$) and takes ~47% of the total intensity. The other two correspond to delayed emissions due to the (a) (37%, dotted line) and (b) (13%, dashed line) trap. The ratio of intensities was derived from the LY and TL experiments and the only adjusted parameters were the total concentration and background. We observe that the match between the experimental points and the solid line is very good. As the temperature increases the delayed components get shorter and at some point a rise time is introduced. In Fig. 3 we show TPs of YAP:Ce (360 nm emission) measured under a synchrotron pulsed excitation with the 78 nm light. In this case, as the synchrotron radiation just simulates the high energy excitation but is not the same, the intensity of prompt emission is substantially reduced and the trap

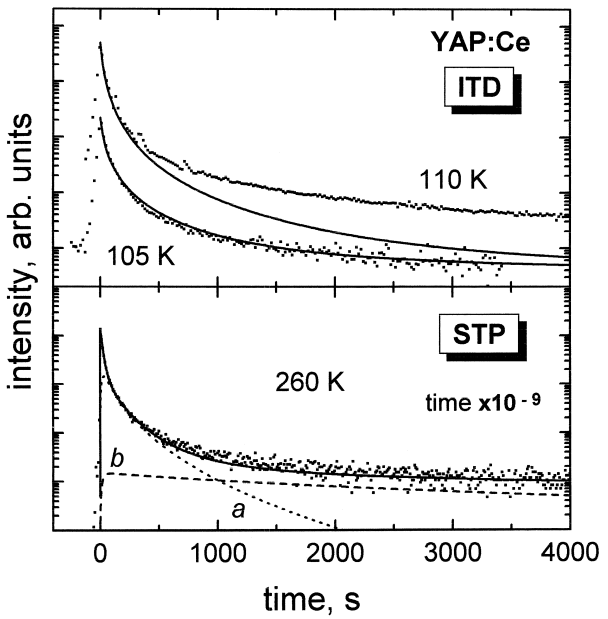

Fig. 2. ITD traces measured at 105 and 110 K and STP taken at 260 K of YAP:Ce. Dots represent experimental points and solid lines simulations calculated from Eqs. (2) and (3) for ITD and STP, respectively. In the case of STP the dotted and dashed lines correspond to the components introduced by the (a) (mean $\tau_t=128$ ns) and (b) (mean $\tau_t=680$ μs) trap, respectively.

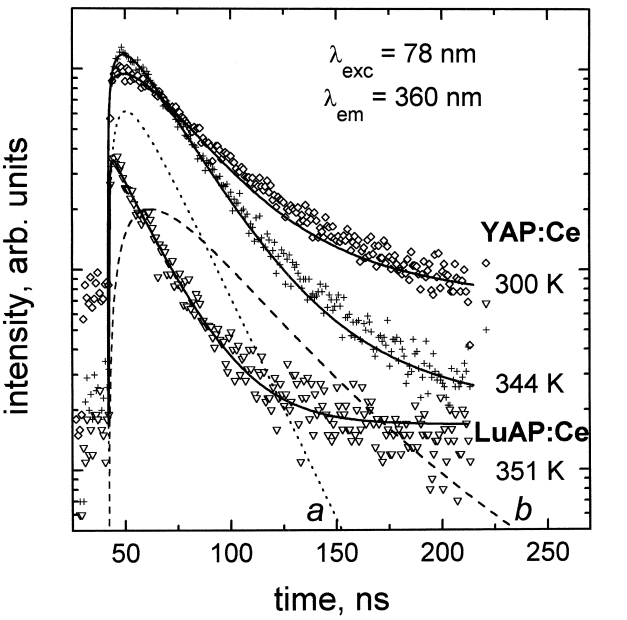

Fig. 3. Time profiles of YAP:Ce and LuAP:Ce under the 78 nm excitation of 360 nm emission recorded at two temperatures. Points are experimental data. The solid line in the case of LuAP:Ce is a simple fit to Eq. (3) that yielded the values of 19.5 ns and 0.6 ns for decay and rise time, respectively. In the case of YAP:Ce the solid line represents the sum of three components (see text). The dotted and dashed lines are examples of delayed components at 344 K due to the (a) (mean $\tau_t=4.8$ ns) and (b) (mean $\tau_t=29.2$ ns) trap, respectively.

induced effect can be easily observed. Solid lines represent calculated TPs that again contain three components (the prompt component calculated with the decay and rise times equal to 19 ns and 0.5 ns, the last introduced by the set-up and was determined in other experiments). The match between the calculated curves and the experimental points is good, although contrary to the STP experiments the ratio of intensities is different and was estimated on the best fit approach to 12 TPs measured at different temperatures (260–353 K). The prompt component takes only 25% of the total intensity whereas the delayed components seize 60% (a) and 40% (b).

Quite to the contrary the presented TP of LuAP:Ce (measured with the same settings) does not change under the 78 nm excitation between 300 and 350 K. In Fig. 3 we show only one trace measured at 351 K that can be fitted accurately to Eq. (3) with the time constants 19.6 ns (τ_{Ce}) and 0.5 ns.

The changes in long components and thermal stability at RT are best depicted by a LY curve (Eq. (4)) that represents variations of integrated light emitted by a sample with temperature. The experimental points (dots) and simulations calculated with the parameters obtained above (lines) are showed in Fig. 4. The LY of LuAP:Ce exhibits two steps at ~150 K and ~350 K. As expected the first step can be approximated by any of the α_1 or α_2 trap and the second step by the (a) trap although in the last case the fit is not as good as we have expected. Additionally, at even higher temperatures according to our theory there should be another step due to the (b) trap (of amplitude equal to 1/3 of the (a) step amplitude, following the ratio of ltTL peaks). It is easy to see that in this case there is a strong mismatch as the experimental points go below of the calculated line. This drop of the LY intensity in both regions ~300 and 500 K can be explained by the change in value of the capture cross-section of a carrier with temperature. In the case of YAP:Ce as the major glow peaks are shifted toward lower temperatures the steps are shifted as well. In Fig. 4 we show two theoretical curves: Non-convoluted (dotted line) and convoluted (solid line). Both curves have the intensity ratio equal to that of the glow peaks concentrations ratio 76:24 (a:b) and follow the experimental points well with the advantage of convoluted curve. It is easy to see that in the region of 300–350 K the LY of LuAP is rather stable while the LY of YAP still grows. This is consistent with our observations of TPs in Fig. 3.

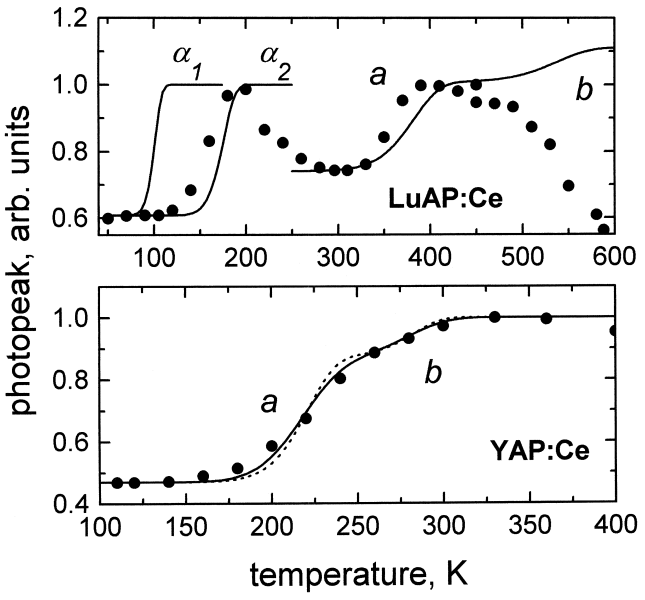

Fig. 4. Light yield of LuAP:Ce and YAP:Ce against temperature. Dots are experimental points. The solid line for LuAP:Ce and the dashed line for YAP:Ce are calculated curves according to Eq. (4) with the parameters of traps as showed in the figure. In the case of YAP:Ce the solid line represents simulated curves but this time convoluted with a Gaussian. Note the level of background indicating the ratio of prompt and delayed components.

5. Conclusions

Although LuAP:Ce and YAP:Ce are two isostructural materials their scintillation properties differ. In this paper we have showed that these differences can be explained by the existence of shallow electron traps. In these crystals the recombination process is based on a sequential charge carrier capture where Ce^{3+} ion acts as a hole trap first and electron is captured in the second step by an already created Ce^{4+} ion. Because a number of electrons is intercepted and released later by the investigated traps the recombination process is distorted and the scintillation properties changed. Using the ltTL and ITD experiments we derived parameters (summarized in Table 1) associated with the traps responsible for the described effects and showed that they can be successfully applied in calculations of time profiles and light yield characteristics.

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