Thermoluminescence Characteristics of Lu_2O_3:Pr,Hf Red Emitting Storage Phosphor

A. Wiatrowska[1] and E. Zych[1,2,*]

Abstract. *Lu_2O_3:Pr,Hf ceramics were prepared by means of high temperature sintering and their thermoluminescent characteristics were investigated. After stimulation with X-rays or deep-UV photons strong thermoluminescence bands peaking at around 110 ℃, 220 ℃ and 310 ℃ were observed. The lowest temperature peak was found to fade completely within first few hours. However, the other components of the glow curve showed measureable fading only after a few months in dark.*

Key words: thermoluminescence, Lu_2O_3:Pr, Hf, storage phosphor.

I. Introduction

Thermoluminescence (TSL) is a thermally stimulated emission of light and requires previous irradiation of the phosphor material with visible, ultraviolet or yet more energetic photons (X- or γ-rays) [1]. Analysis of glow curves allows obtaining valuable information about the possible interactions between the introduced impurities and other defects involved in the process. Lu_2O_3 possesses a high density (~9.42 g/cm^3) and high effective atomic number (Z_{eff} = 67.3) which makes it an attractive host for phosphors required to efficiently absorb ionizing radiation.

II. Sample Preparation

The investigated Lu_2O_3:Pr,Hf ceramics were fabricated by sintering at various temperatures of powders obtained by the Pechini method at 700 °C in air. The starting compounds were $Lu(NO_3)_3$•$5H_2O$, $Pr(NO_3)_3$•$6H_2O$, $HfCl_4$, citric acid and ethylene glycol. For sintering, 0.3 grams of raw powder was pressed into a pellet 8 mm in diameter under the load of 4 tons for 5 minutes. Such a tablet was heat-treated at different temperatures up to 1700 °C at different atmospheres for 5 hours. Structural measurements proved the expected cubic structure of Lu_2O_3:Pr, Hf (ICSD#96211-IA3) [2].

III. Results

A. Photoluminescence

Lu_2O_3:Pr,Hf ceramics produces strong red emission of Pr^{3+} ions in the range of 590-700 nm ($^1D_2 \rightarrow {}^3H_4$) and a trace around 700-770 nm ($^1D_2 \rightarrow {}^3H_5$) upon X-rays or UV photons [3]. The TSL (see Fig. 1) appears very similar to the PL.

B. Thermoluminescence

The right hand side panel in Fig. 1 presents TSL glow curve obtained with the heating rate of 4.5 °C/s after irradiation with X-rays. It contains three main bans peaking around 110, 220 and 310 °C.

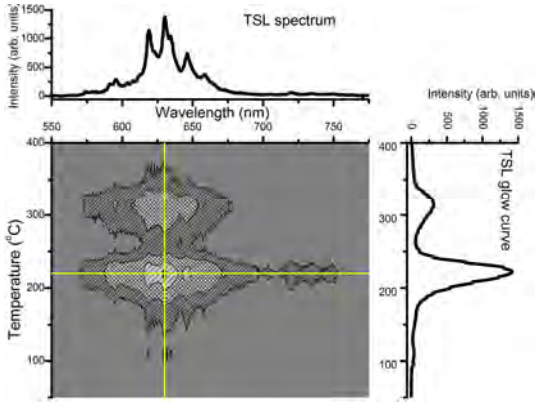

Fig. 1. Wavelength-resolved TSL of Lu_2O_3:0.05% Pr, 0.1% Hf ceramics recorded after irradiation with X-Rays. Heating rate was 4.5°C/s.

The experimental glow curve could be deconvoluted into five components of the first order kinetics [4] (Fig. 2). The trap parameters, such as trap depth (activation energy), *E*, and frequency factor, *s*, were thus found [4,5] and their values are listed in Table 1. The depths of the strongest components within each of the TSL glow bands reach about 1.1, 1.7 and 2.1 eV. The frequency factors for traps #2-5) are unusually high [6].

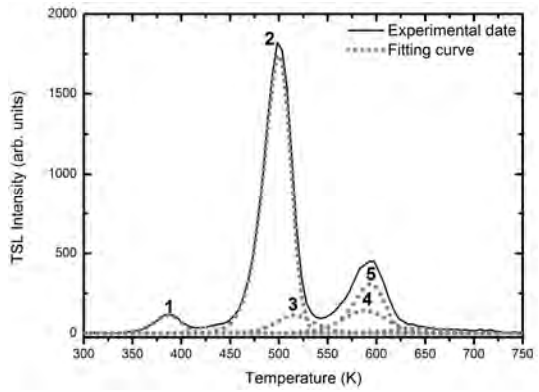

Fig. 2. TSL glow curve of Lu_2O_3: 0.05% Pr, 0.1% Hf ceramics recorded after irradiation with X-Rays. Deconvolution of the experimental curve with the First-Order Kinetics gave five main components (dotted lines).

Table 1. Parameters of the five traps of Lu_2O_3: 0.05% Pr, 0.1% Hf derived from the TSL glow curve using First-Order Kinetics.

Peak	*E* (eV)	*s* (s^{-1})
1	1.14	1×10^{14}
2	1.69	4×10^{16}
3	1.71	2×10^{16}
4	2.11	3×10^{17}
5	2.05	5×10^{16}

[1] Faculty of Chemistry, University of Wrocław, Wrocław, Poland
[2] Wrocław Research Centre EIT+, Wrocław, Poland
* eugeniusz.zych@chem.uni.wroc.pl

The synthesis conditions such an annealing temperature, atmosphere and materials composition as well as Pr and Hf concentrations were optimized for the TSL intensity. Undoped Lu_2O_3 prepared at the same synthesis conditions do not show any TSL. Also Lu_2O_3:0.1% Hf pellets have no TSL emission. Intensity of TSL of singly doped Lu_2O_3:0.05%Pr ceramics is by factor of at least 30 times lower than from the double activated Lu_2O_3:0.05% Pr, 0.1% Hf composition and appears only at the high temperature region of 280-440 °C. Hence, the presence of Pr in lutetia is sufficient to store some small amount of energy. The ionic radii of Pr^{3+} and Lu^{3+} are significantly different (0.99 and 0.861 Å, respectively [7]) which has to lead into a significant deformation of the host around the Pr^{3+} activator, which may in turn facilitate charge carriers trapping. The potential stability of Pr^{4+} oxidation state can also be favorable for such a trapping.

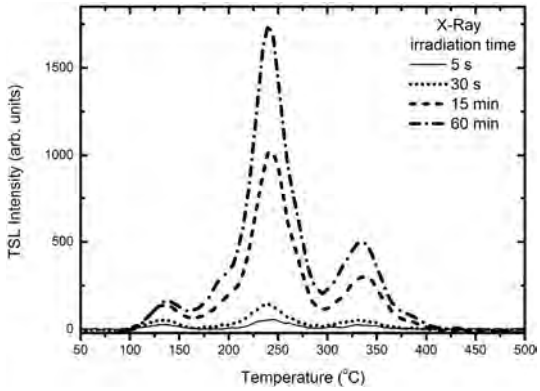

Fig. 3. TSL glow curves of Lu_2O_3:Pr, Hf ceramics as a function of irradiation time with X-Ray. The heating rate was 4.8°C/s.

TSL glow curves of Lu_2O_3:0.05% Pr, 0.1% Hf ceramics are presented in Figure 3 as a function of X-Ray irradiation time at room temperature. The signal around 130 °C seems to saturate first. Nevertheless, the most significant TSL appears always around 240 °C. Hence, it means that population of the trap with activation energy 2.1 eV is the highest. The position of the peaks in the TSL glow curves of Lu_2O_3:0.05% Pr, 0.1% Hf do not shift with increasing X-ray irradiation time/doses. It suggests that all of the glow peaks in the investigated region should be fit with the first-order kinetics [1].

Fig. 4 presents the comparison of the TSL glow curves of Lu_2O_3:0.05% Pr, 0.1% Hf ceramics recorded with different delay time after UV exposure (254 nm). 4 hours delay causes that the TSL around 130°C completely disappears. The TSL associated with the deeper traps giving maxima around 240 and 330 °C were not affected in such conditions. However, after 17 days the component around 240 °C (E = 1.7 eV) lost some of its original intensity. After three months both the 240 °C and the 330 °C components got less intense by about 35%. It may indicate that the carriers from traps

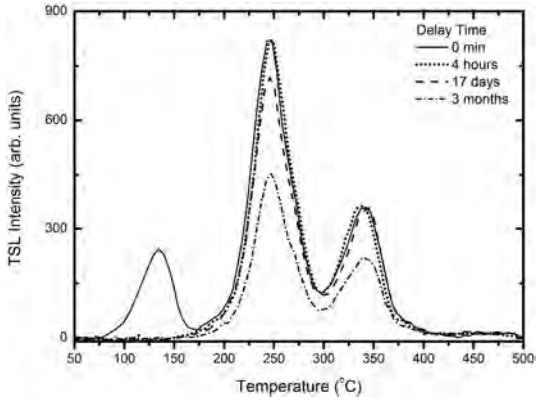

Fig. 4. TSL glow curves of Lu_2O_3:0.05% Pr, 0.1% Hf ceramics as a function of delay time after UV exposure (254 nm). Heating rate was 4.8 °C/s.

giving TSL around 330 °C sink to those producing thermoluminescence around 240 °C and finally escape also these traps.

IV. CONCLUSIONS

Lu_2O_3:Pr, Hf is a new red emitting storage phosphor and hafnium addition shapes its properties. The red emission created during the heating is related to the Pr^{3+} ion and it results from the $^1D_2 \rightarrow {}^3H_4$ and $^1D_2 \rightarrow {}^3H_5$ transitions. Reducing atmosphere and high synthesis temperature are favorable for energy storage in this ceramics. The shallowest trap with TSL peak at 110 °C completely vanishes at RT within 1-2 hours. However, the deepest traps giving TSL bands at 240°C and 330 °C store energy more permanently and only 30% fading is observed after 3 months.

ACKNOWLEDGMENT

The research was supported by Wroclaw Research Center EIT+ within the project "The Application of Nanotechnology in Advanced Materials" – NanoMat (POIG.01.01.02-02-002/08).

REFERENCES

[1] S.W.S. McKeever, *Thermoluminescence of solids*, Cambridge Solid State Science Series, Cambridge University Press, 1985.
[2] FindIt Database (ICSD#96211-IA3).
[3] C. de Mello Donega, A. Meijerink and G. Blasse, "Non-relative relaxation processes of the Pr^{3+} ion in solids", *J. Phys. Chem. Solids*, vol. 56, pp. 673-685, 1995.
[4] R. Chen and S.W.S. McKeever, *Theory of thermoluminescence and related phenomena*, Word Scientific, Singapore, 1997.
[5] C.M. Sunta, W.E. Feria Ayta, R.N. Kulkarni, T.M. Piters and S. Watanabe, "General order kinetics of thermoluminescence and its physical meaning", *J. Phys. D: Appl. Phys.*, vol. 30, pp. 1234-1242, 1997.
[6] A. Mandowski, "Topology-dependent thermoluminescence kinetics", *Radiat. Protec. Dosim.*, vol. 119, pp. 23-28, 2006.
[7] R.D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides", *Acta Cryst.*, vol. 32, pp. 751-767, 1976.