

On thermoluminescence mechanism and energy leakage in Lu₂O₃:Tb,V storage phosphor



Justyna Zeler, Paulina Bolek, Dagmara Kulesza, Eugeniusz Zych*

Faculty of Chemistry, University of Wrocław, 14. F. Joliot-Curie Street, 50-383, Wrocław, Poland

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ABSTRACT

The energy storage properties of Lu₂O₃:Tb,V sintered materials when exposed to X-rays were investigated for the first time using a number of thermoluminescent techniques. Thermoluminescence was generated exclusively by the Tb³⁺ ions, which served also as hole-trapping centers. Two TL peaks at ~170 °C and 220 °C were found to be directly connected with V-electron traps and were assigned to the release of first (170 °C) and second (220 °C) electron from V_{Lu}^X. It was evidenced that each of the two TL bands results from strongly overlapping components showing continuous distribution of energies. Significant contribution from semi-localized transitions to carriers annihilation was also proved.

1. Introduction

Research on rare earth-doped Lu₂O₃ phosphors was pretty intense in last twenty years [1–8]. It was mainly related to scintillators/X-ray phosphors, up-converters, lasers, and persistent luminescence or energy storage phosphors. The last two were found especially efficient if activated with Tb or Pr and co-activated with aliovalent dopants: Ca/Sr/Ba (for persistent emission) or Ti, Hf, Nb, Ta (for permanent energy storage in deeper traps) [4,8–20].

The undertaken research allowed to understand many aspects of the mechanism of energy storage and subsequent controlled release by thermal or optical stimulation in these materials. Yet, the understanding of some details of the processes related to energy storage is still elusive. Besides, new compositions showing ability for carriers trapping are reported repeatedly. This also applies to the Lu₂O₃:Tb,V ceramics reported here.

It was concluded that hole trapping in these materials is describe by Eq. (1)



proving that Tb³⁺ (or Pr³⁺) is directly involved in this process. More recently, it was accepted that electrons trapping occurs by their localization at the co-dopants' (Hf, Ti, Nb, Ta) empty orbitals as schematically exemplified in Eq. (2) [3,8,21].



Then, the final states after the carriers trapping are Tb⁴⁺ and Ti³⁺/

Hf³⁺, in principle. In the case of co-doping with Nb/Ta two TL peaks clearly related to these impurities were systematically observed and were assigned to Ta/Nb traps filled with one (Ta_{Lu}ⁱ) or two (Ta_{Lu}^X) electrons [3,6,8,21]. Those conclusions accord with the recent developments of the Dorenbos semi-empirical model [22–25].

In this paper we present TL properties of the Lu₂O₃:Tb,V ceramics for the first time. A set of thermoluminescent experiments shall be presented to expose the traps structure and learn on the processes of energy storage and release in this material.

2. Experimental section

Lu₂O₃:Tb,V materials were prepared in the form of ceramic pellets ~8 mm in diameter and about 0.5 mm thick. The samples surfaces were ground and mirror-polished before measurements. Concentration of the V co-dopant was in the range of 0.05–0.2 mol% and that of Tb was fixed at 0.1 mol%. The sintering was performed at 1700 °C for 5 h in reducing atmosphere of N₂-H₂ (75%–25%) mixture. Some samples were prepared in air for comparison. The powders for sintering were synthesized by means of Pechini method [26]. More details on the synthesis and sintering can be found in papers published previously [2,3,6,8,18,21].

Crystallographic purity of all investigated compositions was tested by means of powder X-ray diffraction (XRD) method using a D8 Advance diffractometer from Bruker with Cu Kα₁ radiation of 1.54060 Å wavelength. TL glow curves, TL luminescence spectra and isothermal decay traces (ITDs) were recorded using Lexsygresearch Fully Automated TL/OSL Reader from Freiberg Instruments GmbH. It

* Corresponding author.

E-mail address: eugeniusz.zych@chem.uni.wroc.pl (E. Zych).

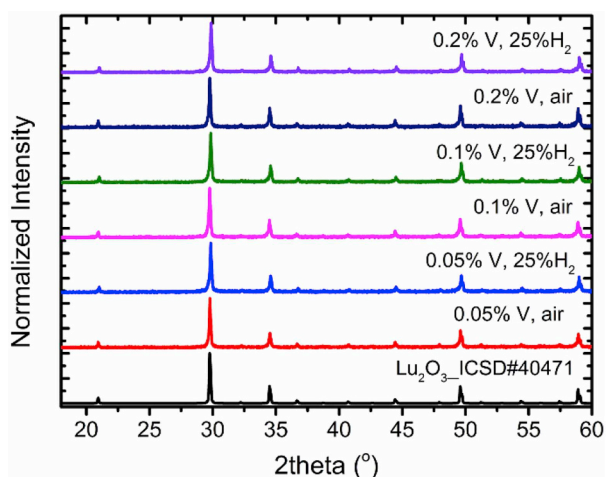


Fig. 1. The representative XRD patterns of the $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},x\%\text{V}$ sintered ceramics fabricated in indicated atmospheres together with a simulated diffraction pattern of the cubic structure of Lu_2O_3 (#ICSD 40471).

used Varian VF-50J RTG X-ray lamp with W-anode which operated under 30 kV and 0.1 mA. The TL glow curves and isothermal decays (ITDs) were collected with a 9235QB-type photomultiplier from ET Enterprises. TL spectra were recorded with an Andor DU420A-OE CCD Camera electronically cooled to -80°C . All experiments were controlled by means of LexStudio 2 software and resultant data were processed under LexEva 2 analytical software dedicated to the TL/OSL Reader and supplied by the manufacturer. Deconvolution of glow curves was executed using the Glowfit software [27].

3. Results and discussion

3.1. Structural analysis

In Fig. 1 the representative XRD diffraction patterns of the $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},x\%\text{V}$ ($x = 0.05\text{--}0.2$) sintered materials are shown together with a simulated pattern of the cubic C-type structure of Lu_2O_3 [28,29]. The results confirmed that fabricated ceramics were phase pure and the dopants dissolved in the host.

3.2. Thermoluminescence

In Fig. 2a the TL glow curves of X-ray irradiated $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},x\%\text{V}$ ($x = 0.05\text{--}0.2$) ceramics are presented. The samples were fabricated in

different atmospheres at 1700°C . It should be mentioned that TL intensity increases with temperature processing which is a common property of the Lu_2O_3 -based storage phosphors [3,6,8,18]. The most efficient TL was observed for samples prepared in reducing atmosphere and for low (0.05 mol%) concentration of V.

Two TL peaks were systematically observed at $\sim 170^\circ\text{C}$ and $\sim 220^\circ\text{C}$, see Fig. 2a. Their positions were independent on the co-dopant content and of the processing atmosphere proving that in all cases the same type of traps contributed to TL. For higher V concentrations (0.1–0.2%) the TL efficiency decreased very quickly and it virtually disappeared at V content of 0.2%, see Fig. 2a. Depending on the sintering atmosphere only small change in relative intensities of the two TL peaks was observed. Despite the two main peaks a low-intensity TL appeared around 90°C . This component was routinely observed in most TL glow curves of $\text{Lu}_2\text{O}_3:\text{Tb}$ -based ceramics and has intrinsic character [8].

Fig. 2b proves that the TL is produced exclusively by the Tb^{3+} activator with the main emission features around 540 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition) and 480 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$) and less intense groups of lines in the range of 575–700 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_{4,0}$). Hereafter, thermoluminescent data were collected on the most efficient $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},0.05\%\text{V}$ ceramics sintered in reducing atmosphere.

In Fig. 3 the TL glow curves of $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},0.05\%\text{V}$ as a function of X-ray irradiation time (dose) are presented. The TL intensity increases with the dose but the peak positions are firmly stable. This indicates a first order kinetics of the TL process [30]. Around 330°C a low-intensity component was systematically observed. Its relative intensity increased significantly for the highest dose. Studying it was beyond the scope of this research, however.

A rough estimation of the number of traps involved in the energy trapping can often be obtained by deconvolution of the experimental glow curves [31–33]. The results are presented in Fig. 3b for the $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},0.05\%\text{V}$ ceramics. Five components were needed to get a good quality fit. While the shallowest intrinsic trap (grey line in Fig. 3b) contributes only insignificantly to the total TL, the other 4 (V-related) components are all substantial, and are clearly connected with V impurity. The obtained trap depths, E , with values in the range of 1.15–1.35 eV and relative frequency factors, s , very close to $1.7 \cdot 10^{13} \text{ s}^{-1}$ – a theoretical value for the Lu_2O_3 host whose most energetic phonons have the energy of 580 cm^{-1} [34] – are listed in Table 1 and in Fig. 3b. The very good quality of the fit (FOM = 1.2%) implies that each of the two main TL experimental strongly overlapping peaks may indeed comprise two individual strongly overlapping components. This, however, shall be critically verified by experiments discussed below.

Two types of experiments are typically recommended in tracing strongly overlapping individual TL components. First of them is based

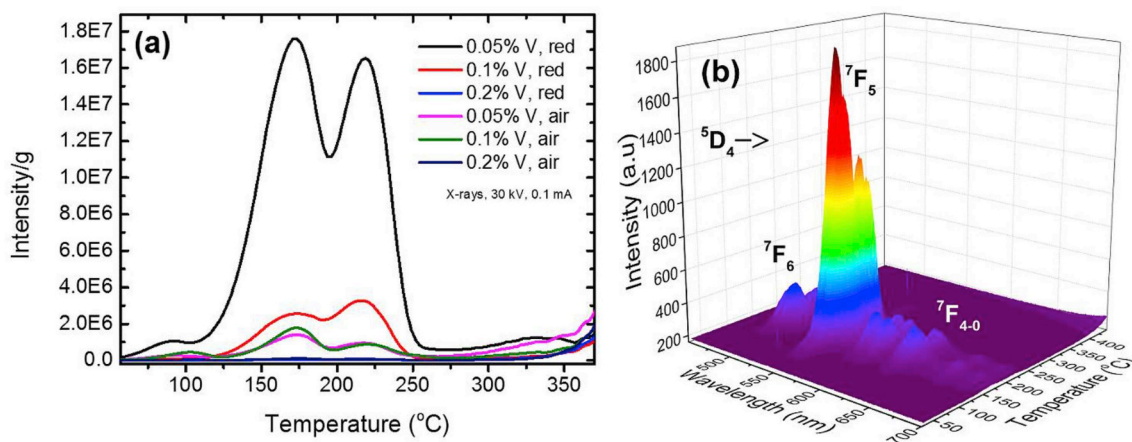


Fig. 2. (a) The TL glow curves of X-ray irradiated $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},x\%\text{V}$ materials sintered at indicated atmospheres. (b) 3D temperature- and wavelength-resolved thermoluminescence of $\text{Lu}_2\text{O}_3:0.1\%\text{Tb},0.05\%\text{V}$ sintered in reducing conditions.

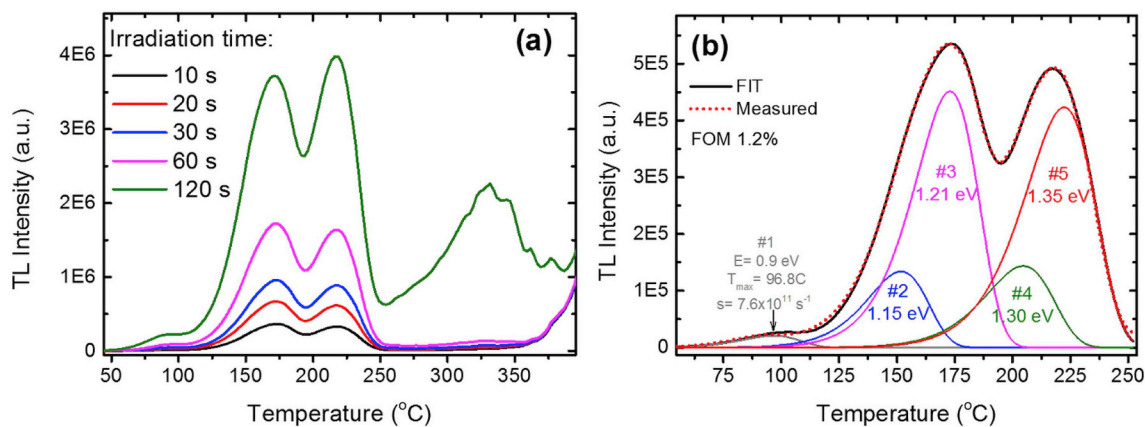


Fig. 3. (a) Dependence of the glow curves of Lu₂O₃:0.1%Tb,0.05%V on the X-ray dose (10–120 s). The glow curves were corrected for thermal quenching of the Tb³⁺ luminescence [8]. (b) Glow curve of Lu₂O₃:0.1%Tb,0.05%V ceramics and its deconvolution into five components. See also Table 1.

Table 1

Parameters of traps derived by deconvolution of the experimental glow curve of Lu₂O₃:0.1%Tb,0.05%V prepared in reducing atmosphere. Traps numbering as in Fig. 3b. FOM = 1.22.

Trap	T _m (°C)	E (eV)	s (s ⁻¹)	Trap lifetime (h/years)
Trap #2	151.8	1.15	1.6*10 ¹³	488/-
Trap #3	172.9	1.21	1.7*10 ¹³	4751/0.54
Trap #4	204.6	1.30	1.7*10 ¹³	158076/18
Trap #5	222.3	1.35	1.8*10 ¹³	1046000/120

parts of the T_{max}-T_{stop}, traps #2 and #4) and much more intense component composed actually of a set of traps with continuous distribution of energies (#3 and #5) [36–38]. The continuous distribution of trap energies is at first puzzling taking into account the very good quality of TL glow cure fit (deconvolution) presented in Fig. 3 and Table 1 with practically theoretical value of the frequency factor (see Table 1). We shall return to this problem discussing fading and heating rate-dependence of glow curves.

Next, room temperature fading of the TL signal and isothermal decays were measured to learn more about the mechanism of carriers releasing/time stability of their trapping. According to Arrhenius Eq. (3):

$$p = \tau^{-1} = se^{-\frac{AE}{kT}}, \quad (3)$$

where p is the rate of a trap depopulation, τ is the trap lifetime, s is frequency factor, AE is the trap depth, k is Boltzmann constant and T stands for temperature in Kelvins the lifetimes for the traps #2–5 were calculated and are listed in last column of Table 1. Generally, the lifetimes are long (Trap #2) or very long. The measurements of the TL signal fading critically verified these predictions.

Fig. 6a presents changes in TL glow curves within the first 10 h after exposure of the material to X-rays. It is immediately seen that the fading is significant and both TL peaks related to V co-dopant decrease in intensity substantially and continuously. The ~170 °C component decays faster but the ~220 °C TL peak reduces its intensity only slightly slower. Evidently, the experimental fading is by far more potent than predicted by the Arrhenius equation using the estimated parameters of traps (see Table 1 and Fig. 3b). This infers that the de-trapping process in the Lu₂O₃:Tb,V ceramics is governed by more complex - conceivably mixed - mechanism, and that a tunneling-like carriers annihilation may be involved and responsible for the fast fading [39–41].

In the context of the data presented in Figs. 4 and 5 it is noteworthy that the TL peaks recorded during fading experiments are firmly positioned at ~170 °C and ~220 °C. This implies that all the traps (remember about continuous distribution of their energies) generating each of the two TL components decay with essentially similar rate. In turn, this entails that the fading pathways occurs mostly if not exclusively by means of a local process without the use of the host conduction band [42–44], which at room temperature is practically unattainable for trapped electrons, especially those giving rise to the higher-temperature TL. This again brings us to the conclusion that a sort of tunneling is at work in the Lu₂O₃:Tb,V ceramic storage phosphor and causes the very significant fading of TL signal.

Furthermore, right after ceasing the sample irradiation the after-glow shows very low intensity, see Fig. 6b. This denotes that the observed significant fading has mostly non-radiative character [45,46].

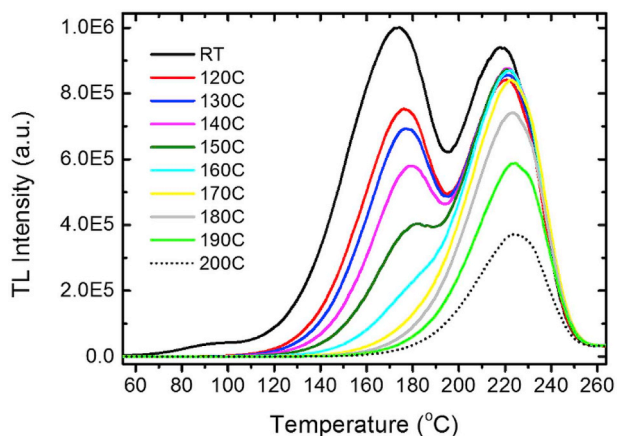


Fig. 4. The TL glow curves of Lu₂O₃:0.1%Tb,0.05%V ceramics after irradiation with X-rays at the indicated temperatures.

on TL glow curves measured after irradiation of the material under investigation at different temperatures and the other one is termed T_{max}-T_{stop} measurement [35–37]. Figs. 4 and 5 presents results of such experiments for the Lu₂O₃:0.1%Tb,0.05%V ceramics.

From Fig. 4 it is obvious that with increasing temperature of irradiation the glow curve gets narrower continuously losing its lower temperature part. Simultaneously, both TL peaks shift steadily to higher temperatures. This may indicate that both TL components are actually composed of many individual TL peaks due to continuous distribution of trap energies [33,35,38]. Irradiation at 170 °C leaves only the higher temperature TL peak. Its position also shifts continuously to higher temperatures as the irradiation temperature further increases.

In Fig. 5a the results of T_{max}-T_{stop} measurement are presented. The continuous shift of both TL peaks with increasing T_{stop} is perfectly evident from Fig. 5a. However, the detailed T_{max}-T_{stop} dependence presented in Fig. 5b shows that each of the two main TL peaks actually consist of a low intensity trap with a well-defined energy/depth (the flat

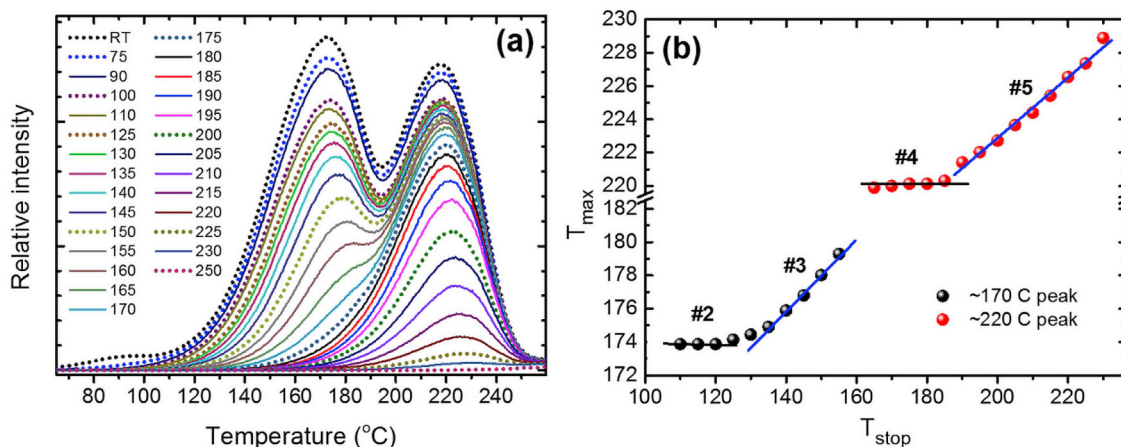


Fig. 5. (a) Glow curves of consecutive TL measurements recorded with increasing T_{stop} . Inset presents values of T_{stop} in °C. (b) $T_{max}-T_{stop}$ dependence derived from the data presented in (a).

Altogether, it appears that fading occurs when electron directly fills the hole immobilized at nearby located Tb and this process does not cause excitation of the dopant to its 5D_4 emitting level.

To further trace the thermoluminescence-related processes TL glow curves were recorded varying the heating rate (β) from 1 °C/s to 10 °C/s. The results are presented in Fig. 7. As expected the TL peaks shift to higher temperatures with increasing heating rate [33]. Another clearly seen effect is a continuous increase of the TL intensity with increasing β . This is a rare case described for the first time by Mandowski and Bos [45,47] and later by others [35,40,48]. Recently, analogous effect we observed in $Lu_2O_3:Tb,Ta$ [3].

Mandowski showed that such a situation occurs when regular radiative delocalized TL process competes with a non-radiative one which he termed semi-localized transition (SLT). This theory anticipates profound non-radiative fading and an anomalous dependence of TL intensity on heating rate – exactly as observed in the $Lu_2O_3:Tb,V$ ceramics.

However, SLT mechanism inevitably accelerates the de-trapping process and its characteristic effect is unusually large value of the frequency factor, s , related to the trap influenced by the SLT. However, as seen in Table 1, for all the four traps s had text-book values for Lu_2O_3 . Actually, this does not contradict the SLT mechanism in our case. Namely, the fitting/deconvolution of glow curve peaks was done using two components for each V-related TL peak. As we saw above, see Fig. 5, actually many more traps (of similar depths) contributes to each TL peak. Hence, the parameters of the traps obtained from the fit cannot be taken as real. At most, trap energies obtained from the fit might be

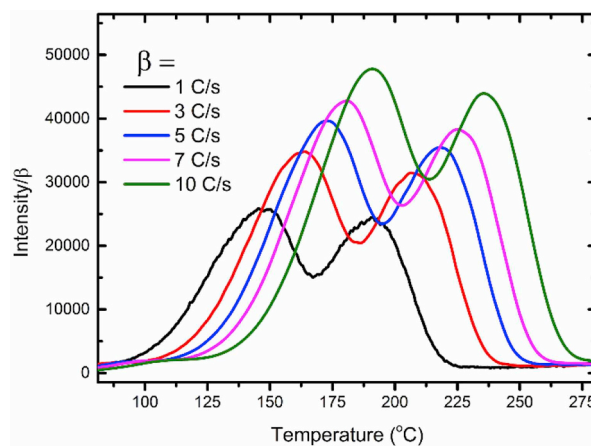


Fig. 7. Heating rate dependence on TL glow curve of $Lu_2O_3:0.1\%Tb,0.05\%V$ sintered in reducing atmosphere measured after the same X-rays dose. β stands for the heating rate.

considered as very rough estimations of their actual depths, but not the frequency factors, s . Hence, the results converge into a consistent picture of processes occurring upon irradiation of the $Lu_2O_3:Tb,V$ ceramics with X-rays and afterwards when natural fading or externally stimulated release of trapped carriers occur.

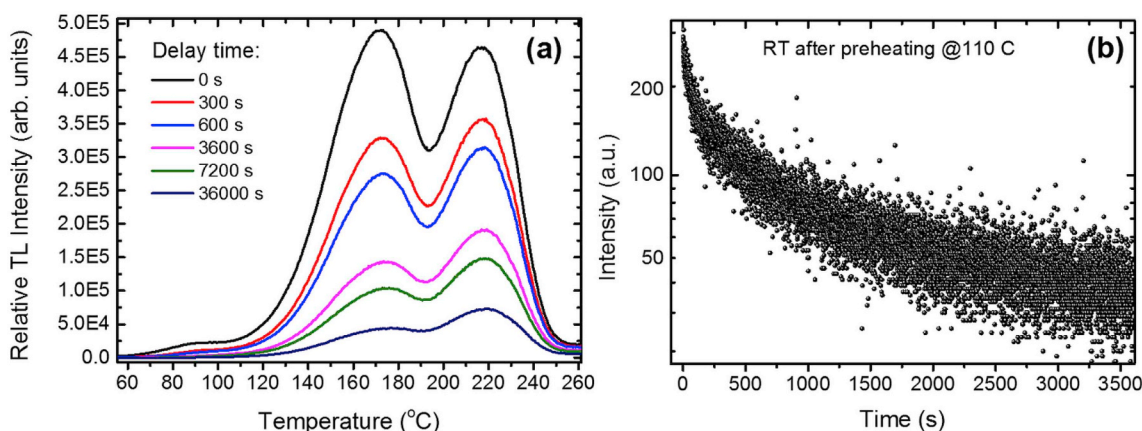


Fig. 6. (a) TL glow curves of $Lu_2O_3:0.1\%Tb,0.05\%V$ recorded with indicated delay time after irradiation with X-rays. (b) RT decay of afterglow signal after short preheating of the sample up to 110 °C.

4. Conclusions

This paper presents energy storage properties of $\text{Lu}_2\text{O}_3:\text{Tb},\text{V}$ sintered ceramics for the first time. The various processes were traced by a set of complementary thermoluminescent techniques. Two TL peaks around 170 °C and 220 °C were found to directly result from the presence of the V co-dopant. According to the results of previous research on $\text{Lu}_2\text{O}_3:\text{Tb},\text{Ta}$ and along the line with Dorenbos model—the two TL components were assigned to the release of first (170 °C) and second (220 °C) electron from the V-related. Each of the two TL peaks was found to result from a set of traps with some distribution of depths. Supposedly, the distribution is connected with varying distance of the hole- and electron-trapping centers – Tb and V impurities – engaged in the energy storage process. This accords perfectly with the proved contribution from the SLT process to the de-trapping.

There is every reason to accept that, in principle, the carriers trapping occurs according to previously presented schemes for other storage phosphors based on $\text{Lu}_2\text{O}_3:\text{Tb},\text{M}$. Thus, this is Tb^{3+} which attracts hole and V may immobilize up to two electrons. Their consecutive thermally-stimulated release give rise to the two main TL peaks. What differs the $\text{Lu}_2\text{O}_3:\text{Tb},\text{V}$ from $\text{Lu}_2\text{O}_3:\text{Tb},\text{Ta}$ or $\text{Lu}_2\text{O}_3:\text{Tb},\text{Nb}$ is much lower time-stability of the trapped electrons leading to unexpectedly high fading even from the deepest traps. Anomalous dependence of TL intensity with heating rate – increase of the TL signal when the rate increases – proved that semi-localized transitions occurs in $\text{Lu}_2\text{O}_3:\text{Tb},\text{V}$. This type of interaction between trapped electrons and holes was also blamed for the substantial and essentially non-radiative fading. This also explains why $\text{Lu}_2\text{O}_3:\text{Tb},\text{V}$ with higher concentration of dopants quickly lose its trapping capability.

$\text{Lu}_2\text{O}_3:\text{Tb},\text{V}$ storage phosphor with its two TL peaks might be interesting for temperature sensing in harsh conditions, as proposed recently [48–50]. Unfortunately, its profound fading is deleterious for such applications. At present, there is no obvious method to deal with this deficiency of the $\text{Lu}_2\text{O}_3:\text{Tb},\text{V}$ storage phosphor, however.

Acknowledgments

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