The role of Ti in charge carriers trapping in the red-emitting Lu$_2$O$_3$:Pr,Ti phosphor

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**A B S T R A C T**

Lu$_2$O$_3$:Pr,Ti storage phosphors were prepared by means of high temperature (1700 °C) sintering both in a reducing atmosphere of the N$_2$-H$_2$ mixture (3:1 by volume) and in ambient air. Their thermoluminescent (TL) properties were presented and discussed. Pr singly-doped material showed only very inefficient TL. Ti co-doping boosted the TL efficacy, and the most potent TL was observed for ceramics containing 0.05 mol% of Pr and 0.007 mol% of Ti and made in the reducing atmosphere. Samples prepared in air produced noticeably less intense TL. The glow curves of both materials consisted of one broad asymmetric band with the maximum around 357 °C for the heating rate of 4.7 °C/s. The glow peaks could be fitted with three (reduced samples) or two (air-sintered) components. The latter lacked the high-temperature part of TL compared to the former. Tmax-Tstop experiments indicated that the TL is connected with continuous distribution of trap depths, which were estimated to cover the range of ~1.7 to 2.3 eV, and their specific values were slightly dependent on the methodology. Anomalous dependence of the TL intensity on the heating rate made the semi-localized transition the likely mechanism affecting the TL properties of Lu$_2$O$_3$:Pr,Ti ceramics. The collected data allowed to construct vacuum referred binding energy (VRBE) level scheme with Pr$^{3+}$ and Ti$^{3+/4+}$ energy levels in the band gap of Lu$_2$O$_3$ host that could explain the TL mechanism in Lu$_2$O$_3$:Pr,Ti ceramics.

1. **Introduction**

Persistent luminescent and storage phosphors/dosimeters form a unique class of luminescent materials whose physics is probably still the least understood among all phosphor materials nowadays [1–5]. Consequently, practically all the practically utilized materials – in environmental, personal or medical dosimetry, computed radiography, bioimaging etc. – were discovered by chance rather than by deliberate research. Nevertheless, last 20 years brought a significant progress in understanding of the mechanisms standing behind energy storage and its controlled, on demand, recovering by means of thermal or optical stimulation. The mentioned progress in this field became possible due to the discovery of new families of persistent luminescent and storage phosphors in the last decade of the XX century and later, and their thorough investigation in many research groups [3,4,6–12]. In this context, a special attention should be given to a semi empirical methodology proposed by Thiel [13,14] and greatly developed by Dorenbos [4,15–19]. This procedure enables to position energy levels of Ln$^{3+}$ and Ln$^{2+}$ ions against valence and conduction bands of the host lattice. This, in turn, permits prediction of electron- or hole-trapping abilities by the Ln ions introduced to the various hosts. Recently, transition metals with empty 3d, 4d or 5d orbitals were also involved and consistent results were obtained [20–22].

While fabrication techniques and parameters are always important for the final product properties, in the case of persistent and storage phosphors they play an extraordinary role [23–25]. Properties of such materials are extremely sensitive to their processing, presence of impurities (intentionally or unintentionally introduced) and their concentrations.

Following a first summary report [26], in this paper we trace and discuss the TL-related processes in Lu$_2$O$_3$:Pr,Ti red-emitting ceramic storage phosphor in more detail. This composition falls into a larger family of Lu$_2$O$_3$-based storage and persistent luminescent materials [23–25,27–31] on which we reported previously. The experimental data and their analysis presented here gives a greater insight to physics behind the thermoluminescence in this material.

2. **Synthesis**

The starting powders of Lu$_2$O$_3$:Pr,Ti were prepared by the classic

Pechini method [32]. Stoichiometric amounts of lutetium(III) nitrate pentahydrate, (Lu(NO3)3·5H2O, 99.99%), praseodymium(III) nitrate hexahydrate, (Pr(NO3)3·6H2O, 99.99%) and 1% solution of titanium isopropoxide (Ti[(OCH)(CH3)2]4, 99.999%) (in aqueous citric acid solution) were dissolved in 2 M aqueous citric acid solution to complex the metal ions and then ethylene glycol was added to that solution. Next, the mixture was slowly heated up to 100 °C on a hot plate to remove water. Afterwards, the temperature was gradually increased to ~ 600 °C to form resin at first and then burn most of the organics. The final traces of organics were removed by heat-treatment in a chamber furnace at 700 °C for 5 h in air. The obtained powders were white. Portions of about 0.2 g of powders were pressed into pellets 8 mm in diameter under the load of 4 t for 5 min. Each pellet was sintered in a furnace at 700 °C for 5 h in air. The obtained powders were white.

Material characterization

The phase purity of all samples was tested by powder X-ray diffraction (XRD) method using a D8 Advance diffractometer from Bruker with Nickel-filtered CuKα radiation (λ = 1.540596 Å). Measurements were performed in the range of 2θ = 10–80°. TL glow curves were measured using custom-made TL set-up in the range of 25–500 °C with the heating rate of β = 4.7 °C/min. The set-up consisted of a custom made temperature controller allowing for a linear heating, an Ocean Optics HR2000 CG spectrometer operating under the OOIBase dedicated software and 74-UV lens coupled to a QP600-1 SR waveguide which collected and transferred the light emitted by the sample to the CCD detector. The system spectral resolution was about 1.2 nm. Before TL measurements the ceramics were irradiated with 254 nm radiation from a 12 W mercury lamp equipped with a Co filter. TL intensity was monitored for the red emission of Pr3+. Fading was registered using RISO TL/OSL reader model DA-15 and controller model DA-20. Sample was irradiated with 90Sr/90Y β-source with a dose rate of 0.7 mGy/s. Measurements were performed in nitrogen gas atmosphere with a heating rate of 5 °C/s. Absorption spectra were obtained using Cary 5000 Scan UV–vis–NIR spectrophotometer for raw (non-irradiated) material and after irradiation with 254 nm for 5 min. Photoluminescence excitation (PLE) and emission (PL) spectra of Lu2O3:Pr, Ti and Lu2O3:Ti samples – raw and after its exposure to UV radiation for 5 min – were recorded using FLS 980 spectrofluorometer from Edinburgh Instruments equipped with a Xenon arc lamp as an excitation source.

4. Results and discussion

XRD patterns of all specimens perfectly agreed with the cubic C-type structure of Lu2O3 [34,35]. This was also true for higher dopant contents (up to 2%). Consequently, we assume that both dopants, Pr and Ti, dissolve in Lu2O3 host material forming solid solutions. Let us recall that there are two non-equivalent positions of Lu3+ ion in the cubic Lu2O3 host: centrosymmetric Cu1 and non-centrosymmetric Cu2, whose populations ratio is 1:3 [34,35]. Obviously, the dopants may share between the sites in a ratio to some extent different, as was shown for Eu in the same host [36]. Each Lu atom is placed in the center of a cube whose six corners contain oxygen atoms and two others are empty. These may be easily used to compensate higher charges of dopants, +4, or even +5 [26].

At first, we experimentally recognized the effect of the dopants, Pr and Ti, concentrations as well as the atmosphere of the ceramics fabrication on their TL efficiency. We found, see Fig. 1, that TL efficiency is very much dependent on both Pr and Ti concentrations. In general, high-intensity TL is produced by diluted systems only. When Pr content reached 0.2% TL almost completely disappeared. The TL efficiency was even more sensitive to Ti content, and practically disappeared when Ti concentration reached also 0.2%. It is important that the decay time of photoluminescence (not presented) hardly changes for the investigated concentrations and photoluminescence is very efficient for all investigated concentrations. Thus, the disappearance of TL for higher concentrations is not due to concentration quenching of the luminescence but must be related to decreased ability of carriers trapping rather. Finally, it was found that the TL intensity was the highest for two ceramics Lu2O3:0.05%Pr,0.007%Ti and Lu2O3:0.05%Pr,0.015%Ti. The singly activated Lu2O3:Pr ceramics, similarly to Lu2O3:Tb [27], shows weak TL. It is about two orders of magnitude lower than from the (Pr,Ti) co-doped specimens (compare Fig. 2a and b). Also the shapes of TL glow curves of the singly- and doubly-doped Lu2O3 are much different. In the case of the former two low-intensity narrow peaks peaking around 150 °C and 350 °C are present. In contrary, (Pr,Ti) co-doping
leads to just one broad structured TL component peaking around 355–360 °C. This clearly shows that the Ti co-doping greatly affects the ceramics capabilities of charge carriers trapping, thus the trap parameters and populations.

In Fig. 2b TL glow curves of the Lu₂O₃:0.05%Pr,0.007%Ti ceramics sintered either in reducing (N₂-H₂ mixture, black line) or in oxidizing (air, solid blue line) atmospheres are compared. It is noteworthy that the oxidized sample showed slight brown-yellow coloration, presumably resulting from oxidization of some praseodymium into Pr⁴⁺.

A higher TL intensity, by about an order of magnitude, was recorded for the reduced material. Apparently, the reducing atmosphere enhances the population of trapping sites in Lu₂O₃:Pr,Ti. This observation might be rationalized keeping in mind that the high-temperature radiation time (dose). Accordingly, fits of the linear parts of the low-temperature onset of TL glow curves in Arrhenius plots for different doses (see Fig. 3c) allowed to calculate trap depths according to Eq. (1):

\[
I(T) = C \exp(-\frac{E_t}{kT}).
\]

where, C is a constant (includes frequency factor assumed to be independent on the temperature), Eₜ is trap depth, k is the Boltzmann constant and T is temperature in Kelvin [2]. Inset in Fig. 3c shows trap depths obtained using the initial rise method for the various doses. All the obtained values are very similar and locates between 2.0 and 2.1 eV.

From the presented data it is clear that the TL glow curves are composed of a few strongly overlapping components. The fitting was performed both for the ceramics sintered in forming gas (Fig. 4a) and in air (Fig. 4b). For the reduced material three components were needed while for the air-sintered ceramics it was enough to use two peaks to get a reasonable fit. This accords with the differences of the respective glow curves presented in Fig. 2b. The trap parameters – depths and frequency factors - are given in Table 1 together with lifetimes at RT and at 300 °C calculated according to the Arrhenius function [5] given by Eq. (2):

\[
\tau = s^{-1} \exp\left(\frac{E}{kT}\right).
\]

where s is frequency factor (s⁻¹), r is a time a carrier spends in its trap of depth E. It appears that the traps #1 and #2 have very similar parameters (E and s) in both materials (oxidized and reduced). This adheres with the observation made discussing data in Fig. 1b – the low-temperature part of TL in both materials is due to the same type of traps. The trap depths cover the range of 1.7–2.1 eV for reduced specimen and 2.0–2.15 eV for the air sintered one. What is peculiar, however, is that using this method the traps giving TL at lower temperatures were found deeper than those with Ti at higher temperatures. Simultaneously, the frequency factors of the traps were also decreasing noticeably from trap #1 to #3 (see Table 1). For the regular first-order kinetics of TL in Lu₂O₃:Pr,Ti the expected value of s would be ~1.7 × 10¹³ s⁻¹, as the cut-off frequency of Lu₂O₃ is ~580 cm⁻¹ [41]. Thus, the quite different values of s for the various traps, rather high value of s for the first trap and low for the third one (reduced sample) may imply that the TL mechanism may be more complicated and that
the derived trap parameters are good fit parameters but not related to physical quantities. It was recognized that higher values of \( s \) may indicate that a semi-localized transition (SLT) plays a role in the TL of Lu\(_2\)O\(_3\):Pr,Ti [42–45]. On the other hand, Pagonis showed that TL occurring with the use of common excited state of the hole- and electron-traps upon fitting tended to produce lower-energies for traps producing TL at higher temperatures [46] — exactly as in our case, see Table 1. We shall return to this problem later discussing the proposed model of TL processes in Lu\(_2\)O\(_3\):Pr,Ti.

Releasing of trapped charge carriers may be executed not only by thermal, but also (although not in all storage phosphors) by proper optical stimulation. Upon charging the traps in Lu\(_2\)O\(_3\):Pr,Ti a broad absorption and excitation bands covering near-UV and bluish-cyan part of spectrum (see Fig. 5a, b) is developed (it partially overlaps with the 4f→5d bands of Pr\(^{3+}\), see Fig. 5b). Evidently, it is connected with the charge carriers trapping. Thus, we also applied controlled optical bleaching into this band to monitor the traps’ cleaning. Fig. 5c compares glow curves of freshly irradiated Lu\(_2\)O\(_3\):Pr,Ti ceramics with 254 nm and after its subsequent bleaching with either 490 nm or 395 nm radiation. The latter light (~ 3.14 eV) empties the traps completely — the TL is no longer observed. Yet, the 490 nm (2.53 eV) radiation liberates only part of the stored carriers without releasing those giving rise to the high-temperature part of TL, presumably those in trap #3 (Table 1). Thus, the optical stimulation wavelength determines which trapped carriers are released depending on the depth of traps. Let us stress that, whichever the stimulation is, emission comes from Pr\(^{3+}\) ions exclusively, as in the case of TL. Accordingly, the broad absorption generated during energy storage (carriers trapping) (Fig. 5a) seems to be a superposition of overlapping components related to traps of different depths. Partial thermal cleaning discussed below will bring more data on the problem of energetic structure of traps in Lu\(_2\)O\(_3\):Pr,Ti.

For TL bands composed of overlapping components McKeever introduced the so-called \( T_{\text{max}}-T_{\text{stop}} \) method [1,47]. The results for our reduced material are presented in Fig. 6a and the \( T_{\text{max}}-T_{\text{stop}} \) dependence is given in Fig. 6b. Data in Fig. 6b show that up to the \( T_{\text{stop}} = 290 \) °C the TL peaks are firmly located at ~ 352 °C. This reflects the trap #1 (Table 1) giving rise to the TL at lowest temperatures. However, for \( T_{\text{stop}} > 290 \) °C the peak position moves continuously to higher temperatures without forming a clear plateau. This is characteristic for a set of traps with very similar parameters (depths) furnishing so called quasi-continuous distribution of trap depths [47]. In the analysis presented in Fig. 4 and Table 1 this complex is indicated by traps #2 and #3 and we shall continue using this terminology.

To learn more about the trap depths, taking advantage of data in Fig. 6a, we employed the initial raise method on partially cleaned glow

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**Table 1**

Trap parameters derived from fitting of TL glow curves of the Lu\(_2\)O\(_3\):Pr,Ti ceramic assuming first-order kinetics together with lifetimes at RT and 300 °C.

<table>
<thead>
<tr>
<th>Trap #</th>
<th>( T ) (°C)</th>
<th>( E ) (eV)</th>
<th>( s ) (s(^{-1}))</th>
<th>Lifetime @ RT (years)</th>
<th>Lifetime @ 300 °C (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>350</td>
<td>2.1</td>
<td>( 3.0 \times 10^{16} )</td>
<td>3.5 \times 10^{11}</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>371</td>
<td>1.9</td>
<td>( 1.9 \times 10^{14} )</td>
<td>2.3 \times 10^{10}</td>
<td>267</td>
</tr>
<tr>
<td>3</td>
<td>393</td>
<td>1.7</td>
<td>( 1.6 \times 10^{12} )</td>
<td>1.1 \times 10^{9}</td>
<td>560</td>
</tr>
</tbody>
</table>

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**Fig. 3.** The charging curve of Lu\(_2\)O\(_3\):Pr,Ti recorded upon 254 nm irradiation monitoring 631.5 nm emission (a) influence of irradiation time with 254 nm radiation on the TL glow curve of Lu\(_2\)O\(_3\):Pr,Ti ceramics (b) TL glow curves plotted in Arrhenius diagram and (in inset) estimated trap depths in Lu\(_2\)O\(_3\):Pr,Ti for the various irradiation times calculated from the slope of the initial rise range.

**Fig. 4.** TL glow curve of Lu\(_2\)O\(_3\):Pr,Ti registered after 5 min irradiation of 254 nm radiation (solid line) sintered in a H\(_2\)-N\(_2\) mixture (a) and in air (b). Dotted lines show result of first-order kinetic fitting.
curves [1]. Using this procedure we plotted glow curves in the Arrhenius diagram (Fig. 6c) and calculated the trap depths (according to Eq. (1)). We obtained a group of points with similar energies in the range of 2.1 ± 0.1 eV within the whole range of Tstop temperatures (see inset in Fig. 6c). At first it may be implausible that the data produced actually one energy for the whole set of traps – their existence was evidently proved above. Yet, van den Eeckhout et al. [48] investigated the effect of the trap depths distribution on the traps energies obtained using the initial rise method. Their analysis showed that for continuous traps distribution the initial rise procedure actually gives just one trap energy (depth) and its value coincides roughly with the shallower of the traps [40]. Concluding, all the data presented above conform with the concept that in Lu2O3:Pr,Ti a continuous distribution of traps contributes to TL and shallowest of them are characterized by depths of ~2.0 to 2.1 eV. Nevertheless, we should note that quite similar characteristics as in the inset of Fig. 6c can be observed when localized, thermally activated tunneling process is involved, as was shown for (Lu,Y)AlO3:Ce [49].

In a regular delocalized Randal-Wilkins mechanism a higher heating rate will cause a shift of the glow peak(s) towards higher temperatures [1]. However, the intensities of TL peaks (when TL/β vs. temperature is plotted) are supposed to be independent on the heating rate and only their shift to higher temperatures should be seen [42].

Fig. 7 presents TL glow curves (corrected for thermal quenching) of Lu2O3:Pr,Ti ceramics taken applying three heating rates (β = 1, 4.7 and 9.1 °C/s). As expected, we observe a shift of the TL maxima towards higher temperatures but, surprisingly, increase of all TL peak intensities with increasing heating rate. This rather rare effect was treated by Mandowski and Bos [42-44] as well as Pagonis [45] in the past. They showed that such a behavior may result from a significant involvement of semi-localized transitions (SLT) through where trapped carriers recombine, presumably non-radiatively, by means of a localized process. Consequently, a low heating rate makes the TL less efficient as then the SLT non-radiative energy dissipation is most significant. Then, with increasing heating rate a growing importance is gaining the regular radiative recombination through the delocalized process in which carriers are liberated to the host conduction/valence band. This is exactly what we see in experiments presented in Fig. 7. Furthermore, since the concentrations of both co-dopants are very low we infer that they show tendency to get spatially correlated (paired) as the SLT needs their interaction, which may occur over limited distances.

In the context of above findings it is important to learn about fading in Lu2O3:Pr,Ti ceramics. While the high temperature of TL and large trap depths should lead to negligible fading, the SLT process and deduced tendency for coupling of the co-dopants raise question about their effect on the trapped carriers leakage in time [2]. The results of precise measurements of fading during the first ~ 6.5 h are presented in Fig. 8. Due to a higher sensitivity of the set-up used in these experiments two low-intensity TL components are observed around 150 °C and 230 °C. The fading within the ~ 6.5 h after the irradiation reaches
~ 12%. This is more than could be predicted from the trap parameters (see Table 1) and indicates the localized transitions. The leakage is at least partly radiative as we could measure some non-exponentially decaying luminescence from the irradiated sample for a few hours by means of the FLS980 spectrometer. Yet, we should note that even the lowest temperature (~ 150 °C) TL peak lasts till the end of the fading experiments. Thus, the RT afterglow is probably mostly due to this low-temperature TL band. This precludes observation and analysis of fading emission spectrum (or its lack) related exclusively to the most intense high-temperature TL band. So we cannot fully exclude a thermally-assisted tunneling. From Fig. 8b it can be seen that at Room Temperature these transitions have a limited effect on the durability of charge carriers storage in Lu₂O₃:Pr,Ti ceramics. It may be considered a high-temperature TL storage phosphor.

One of the main questions regarding storage or persistent luminescent phosphors is about the charge carriers trapping mechanism and defect sites involved in this process. According to the experimental data presented above, the possible pathways of trapped carriers release in Lu₂O₃:Pr,Ti ceramics are indicated in Fig. 9. Since Pr³⁺, similarly to Tb³⁺, is known for its tendency to oxidize to Pr⁴⁺ it is perfectly reasonable to assume that it serves as a hole trapping center [4,23] at which recombination of carriers occurs in the TL process. Taking into account the glow curves presented in Fig. 2a, b it is reasonable to assume that Ti serves as electron-trapping center.

Taking advantage of the Dorenbos model [21,22,51–53] and spectroscopic data on Lu₂O₃-based phosphors [54–56] a scheme of vacuum referred binding energy (VRBE) of Pr³⁺ electronic levels and Ti³⁺/⁴⁺ ground state together with the Lu₂O₃ host valence and conduction bands could be presented in Fig. 9. The position of the Pr³⁺ electronic levels in Lu₂O₃ was determined according to the Dorenbos’ model [51]. To position the ground state of the supposed Ti-related electron trap an absorption/excitation spectrum of Lu₂O₃:Ti was needed. Since the samples are not transparent or translucent we have chosen to record its emission and excitation spectra. They are presented in Fig. 10. The emission peaks around 460 nm and is very broad as expected for charge transfer (CT) luminescence. It is composed of two components which seems to reflect the two metal sites of the host lattice. Also the excitation spectrum of Lu₂O₃:Ti shows two bands peaking around 300 nm (4.13 eV) and 265 nm (4.68 eV), which makes the results of these experiments consistent. The PLE bands should be attributed to O²⁻→Ti⁴⁺ CT transitions, then. Their energies agrees with the recent studies presented by Dorenbos and Rogers [21,22] who found that independently on the host, the energy of O²⁻→Ti⁴⁺ CT transition is slightly (few tenths eV) lower than energy of analogous O²⁻→Eu³⁺ CT bands. The latter was reported to appear in Lu₂O₃:Eu around 228–238 nm for C3i site and around 245–248 nm for C3 [55,56]. Thus, our findings are fully consistent with the Dorenbos model. While the presence of two sites in Lu₂O₃ complicates the quantitative analysis the Ti-related electron trap may be reasonably positioned ~ 4.1 eV above the host valence band, as presented in Fig. 9. a is worthwhile to notice that with the positioning of the Ti level with the help of the CT band the trap depths represented by Ti³⁺/⁴⁺ e-traps band in Fig. 9 lie between 1.7 and 2.2 eV which is in perfect agreement with the values in Table 1.

Fig. 8. Fading of TL in Lu₂O₃:Pr,Ti ceramics at RT (a) Decrease of the 260–450 °C band TL (in %) as a function of time (b).

Fig. 9. VRBE level scheme with Pr³⁺ and Ti³⁺/⁴⁺ energy levels relative to the Lu₂O₃ host valence and conduction bands. The proposed mechanism of releasing trapped carriers in Lu₂O₃:Pr,Ti ceramics by means of semi-localized transition competing with the regular delocalized process with the use of conduction band is depicted. After Dorenbos [21,50], the Ti³⁺/⁴⁺ trap represents the ground state of Ti⁴⁺ ion attained after trapping an electron by Ti⁴⁺.

Fig. 10. PLE and PL spectra of Lu₂O₃:Ti ceramics. The emission was excited at 255 nm and for PLE spectrum 450 nm luminescence was monitored.
Thus, all the data appear internally consistent and also correspond quite well quantitatively. Consequently, using the Kröger-Vink notation \([57,58]\), the trapping processes might be described according to Eqs. (3) and (4):

\[
P_{\text{Pr}} + \text{X} \rightarrow P_{\text{Pr}}\text{X} + \text{Pr}^3+ \quad (3)
\]

\[
T_{\text{Lu}} + \text{e} - \rightarrow T_{\text{Lu}}\text{X} + \text{Lu}^3+ \quad (4)
\]

Upon subsequent heating the electron in \(T_{\text{Lu}}\) may acquire enough energy to be liberated to the conduction band and diffuse to the \(P_{\text{Pr}}\) to recombine with the hole trapped there and produce a photon of red light. However, a competitive SLT process appears to occur allowing some of the trapped electrons to fill the hole in \(P_{\text{Pr}}\) by means of non-radiative SLT process. The occurrence of energy dissipation via the SLT mechanism may be justified by the fact that the \(T_{\text{Lu}}\) entity, with its similarity to the \(O^2-\rightarrow Ti^{4+}\) charge transfer state, has to spatially spread which facilitates interaction of the electron and hole traps over larger distances. This would also explain why higher concentrations of Ti quickly diminishes the TL (as carriers trapping) efficacy, as we earlier mentioned. What is more, the \(Ti^{3+/4+}\) entity is expected to have its own \(3d^6\) excited level denoted with * in Fig. 9, which – according to the theory of TL transitions – may serve for non-radiative energy flow to \(P_{\text{Pr}}\) competitive to the regular delocalized (with the use of conduction band) radiative process generating TL. Accordingly, all the observations related to TL of Lu2O3:Pr:Ti may be combined into a consistent picture.

What might be considered not fully clear is the presence of continuous traps distribution, which indicates the presence of many electron-traps needing slightly different energies for their electrons to escape This cannot be justified by the two metal sites present in Lu2O3 \([34,35]\). What may differentiate the electron traps is their distance from the \(T_{\text{Lu}}\) recombination center. By itself it does not change their depths defined as energy needed to reach the bottom of conduction band. Yet, if the transfer of electron from \(T_{\text{Lu}}\) to \(P_{\text{Pr}}\) could occur by means of more localized mechanism – with a use of a common excited state for example - the energy needed to overcome the barrier might be then distance-dependent \([1,2,59]\). While such interactions between \(T_{\text{Lu}}\) and \(P_{\text{Pr}}\) traps centers are conceivable and could be considered as versions of intervallence charge transfer interactions \([22,60]\) a further research is needed to verify this hypothesis.

5. Conclusions

Thermoluminescent properties of Lu2O3:Pr:Ti ceramics were presented and their ability to efficiently store excited charge carriers was proved. The presence of Ti is crucial for generation of high population of energy trapping sites. From our previous study we know that \(Pr^{3+}\) is the recombination center. This study reveals the role of Ti dopant as electron-trapping center. The vacuum referred binding energy levels of trapping centers – \(Pr^{3+}\) and \(Ti^{3+/4+}\) - were positioned in Lu2O3 host. The most efficient TL shows the composition containing 0.05 mol% of Pr and 0.007 mol% of Ti and sintered at high temperatures \((1700°\)C) in reducing atmosphere of forming gas. Glow curve of Lu2O3:Pr:Ti ceramic contains one broad band with maximum around 357° C. The broad band is the result of a continuous distribution of trap depths present in the storage phosphor. Their activation energies were found to start ~ 2.0 eV. Anomalous dependence of TL intensity on heating rate was demonstrated and explained by semi-localized transition model. Fading of TL was not significant and reached 12% after 6.5 h.

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