Thermoluminescence and Kinetics of Persistent Luminescence of Vacuum-Sintered Tb^{3+}-Doped and Tb^{3+},Ca^{2+}-Codoped Lu_2O_3 Materials

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The properties of green thermoluminescence (TL) and persistent luminescence of Lu_2O_3:Tb^{3+} and Lu_2O_3:Tb^{3+},Ca^{2+} materials sintered in vacuum at 1700 °C were investigated. The concentration of Tb varied in the range 0.1–3 mol %, and the Ca content was 1 mol %. Ca^{2+} codoping enhanced the room temperature persistent luminescence intensity and its duration as well as reduced the number of TL bands for lightly doped materials from four components covering about 50–400 °C range of temperatures to only one peaking around 100 °C. The Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) codoped material showed the most efficient persistent luminescence and TL, originating mainly from the $^5D_4 \rightarrow {}^7F_5$ transition at around 545 nm, among all the compositions investigated. For this material the persistent luminescence could be observed in the dark for about 15 h. There are indications that the efficient persistent luminescence of the codoped system is governed by tunneling mechanism, and the trapping centers are postulated to be $[Tb_{Lu}^{\times}-V_O^{\bullet\bullet}-2Ca_{Lu}^{'}]$ aggregates. Oxygen vacancies are supposed to serve as traps for free electrons giving F^+ $(e_O^{\bullet\bullet})$ or F $(V_O^{\times})$ centers while holes are temporarily immobilized in the vicinity of $Tb_{Lu}^{\times}$ giving $[Tb_{Lu}^{\times}-h^{\bullet}]$ entities. Alternatively, hole can be trapped in the $Ca_{Lu}^{'}$ site due to its negative net charge, giving $[Ca_{Lu}^{'}-h^{\bullet}]$. Air-sintered specimens did not show any significant persistent luminescence or TL, although they produce quite significant photoluminescence. Also, vacuum sintering at lower temperatures—1600 °C and below—was not sufficient to get efficient persistent luminescence.

1. Introduction

Phosphorescence and afterglow are luminescence processes with the decay times extending to seconds, minutes, or even hours after ceasing the excitation. Such an afterglow effect is unacceptable in many applications, yet persistent luminescence may be welcome in some others. In cathodoluminescence, in scintillation and X-ray-stimulated luminescence, in various displays, and in many other uses the persistent luminescence effect cannot be tolerated, and a lot of effort is needed to reduce the afterglow of the material to an acceptable level.[1] On the other hand, persistent luminescence is desirable if one wishes to keep an object visible for an extended time in dark or to store temporarily energy for luminescence extended in time. Such applications include watch dials or glowing road sings. The persistent luminescence effect can also be used in much more sophisticated instrumentation such as fiber-optic thermometers, for which the amount of material needed is small but the requirements as to its properties are very demanding and varied and thus hard to fulfill.[2] Intriguing at first, but the persistent luminescence can be useful even to supply light to solar cells in complete darkness.[3]

A persistent luminescence needs the presence of abundant traps able to intercept free carriers, i.e., electrons, holes, or pairs formed by them (the latter cannot be excluded although are only rarely considered),[4] and to immobilize them for an appropriately long time. Typically, the persistent luminescence is temperature dependent, and freeing a carrier from its trap is thermally stimulated then. However, an intercepted carrier may leave its trap through a tunneling mechanism. This may be a temperature-independent process or a temperature-assisted tunneling route, and in such circumstances it may produce persistent luminescence of high intensity.[5]

For temperature-stimulated processes, if the temperature is too low, the carrier cannot acquire enough energy to escape the trap and, consequently, the carrier cannot either move toward or pass the excessive energy to the luminescent center. On the other hand, if the temperature is too high, the trap is emptied too quickly and the persistent luminescence lasts for too short a time only. It is worth noting that the presence of deep stable traps able to immobilized the carriers

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permanently at room temperature is exactly what is required for efficient storage phosphors, which have already found important applications as photostimulated materials.[6,7]

While carrying out straightforward luminescence experiments on vacuum-sintered Lu_2O_3:Tb^{3+} it was noted that after excitation with UV radiation (wavelengths shorter than ca. 330 nm) the material exhibited persistent luminescence.[8] Depending on the terbium concentration, this effect could easily be seen by the naked eye for at least a few minutes after ceasing the excitation but sometimes for a noticeably longer time. Furthermore, in spite of being kept for one year in dark, the 0.1 mol % doped vacuum-sintered Lu_2O_3:Tb^{3+} material still stored some of the energy acquired previously, and this energy could be released upon stimulation with IR photons or red light.[8] This material demonstrated a behavior typical for storage phosphors.[6] The most efficient photostimulated green luminescence was obtained under irradiation of the material with 647 nm light. Photons of 980 nm wavelength were also able to stimulate the green Tb^{3+} emission, but this allowed recovering only a fraction of the total energy stored. These results were encouraging enough to initiate a more thorough investigation of the physical processes taking place in the material during and after excitation. This knowledge could be helpful when tailoring the properties of Lu_2O_3:Tb^{3+} as an efficient energy-storing or persistent luminescent material.

One way to tailor the properties of a persistent luminescent material is to introduce potential traps into the phosphor lattice by creating nonstoichiometry. Such an effect is usually achieved by introducing cations or/and anions with a charge different from those of the original constituents of the lattice. Several methods of investigations can be used to study the effect of such dopants. In this work, thermoluminescence was chosen as the main research tool since it has proven to be a very useful means to reveal valuable information about the traps and their role in determining the spectroscopic properties of materials.[9–12] The present paper summarizes the results of the work concerning the lutetium sesquioxide, Lu_2O_3, doped with trivalent terbium, Tb^{3+}, as well as codoped with divalent calcium, Ca^{2+} ions. The Kröger−Vink notation of defects[13,14] was chosen to be used throughout the entire report. It seems to be a good standard allowing to avoid confusions, possible when authors introduce their own ways of naming various defects.

2. Materials and Experiments

The Tb^{3+}-doped or Tb^{3+},Ca^{2+}-codoped Lu_2O_3 were prepared in the form of sintered pellets starting from nanocrystalline powders. The Tb^{3+} content was nominally set at 0.1, 0.5, 1, and 3 mol % with respect to the Lu^{3+} host cation. For the Ca^{2+}-codoped materials, the Ca^{2+} concentration was arbitrarily set at 1 mol % of the total amount of the tri- and divalent host cations. The nanocrystalline powders were synthesized through the combustion synthesis[8,15] using the aqueous metal (Lu^{3+}, Tb^{3+}, Ca^{2+}) nitrates and glycine as the reactants. The combustion process was carried out in a furnace preheated up to 650 °C. The powders were subsequently cold-pressed into pellets of 12 mm diameter and about 1 mm thick under 9 tons of load and then transferred into a furnace and annealed for 5 h at 1700 °C under a reduced pressure of about 5 Pa. The heating and cooling rates of the furnace were 3 °C min^{-1}. The materials were taken out of the furnace once it had cooled to the temperature of 200 °C or lower. Two additional Lu_2O_3:Tb,Ca (0.1 and 1 mol %, respectively) specimens were prepared in vacuum at 1500 and 1600 °C for comparison. One sample of Lu_2O_3:Tb^{3+} (0.1 mol %) was prepared by sintering in air and was used as a reference material. Aqueous rare earth nitrates were prepared using appropriate oxides (Lu_2O_3, 99.995%; Tb_4O_7, 99.99%) supplied by Stanford Materials and nitric acid of analytical purity. Calcium nitrate was prepared from $CaCO_3$ (99%).

The thermoluminescence (TL) experiments were carried out on 60−80 mg pieces of the ceramic Lu_2O_3:Tb^{3+}(,Ca^{2+}) materials. The TL intensity was eventually calculated for a mass unit (in mg) in order to get results easy to compare quantitatively. The thermoluminescence glow curves were measured with an upgraded Risø TL/OSL-DA-12 thermoluminescence system operating at a linear heating rate of 5 °C s^{-1} in the temperature range between 25 and 400 °C. The global TL emission from UV to 650 nm was monitored. Prior to the TL measurements, the materials were exposed to radiation from a combination of the Phillips TL 20W/05 (emission maximum at 360 nm) and TL 20W/03 (420 nm) UV lamps. Exposure times were varied from 10 to 120 s. In order to monitor the fading of the persistent luminescence, the TL glow curves of the materials were measured with selected delay times (3, 30, 60, and 120 min) after the exposure.

The decay curves of the persistent luminescence were measured with a FLS 920 spectrometer from Edinburgh Instruments. Prior to the measurements, the materials were irradiated with UV radiation at 270 nm for 10 min. The persistent luminescence was monitored at 545 nm (with a bandwidth of ±10 nm), which is the peak intensity of the Tb^{3+} emission from Lu_2O_3:Tb^{3+} [8] due to the strong $^5D_4 \rightarrow {}^7F_5$ transition.

3. Results and Discussion

The materials investigated were checked for the structural and phase purity. Only the cubic C-type oxide (lutetia) could be observed in the measured XRD powder patterns. The infrared spectra recorded on powdered materials obtained by grinding the ceramics did not either reveal the presence of any impurities (e.g., organic residues). All the materials freshly sintered in vacuum had a slightly brownish body color, even if they were taken out of the furnace after cooling them to room temperature in vacuum. The brownish body color is characteristic for the Tb^{3+}-doped Y_2O_3, too, and has

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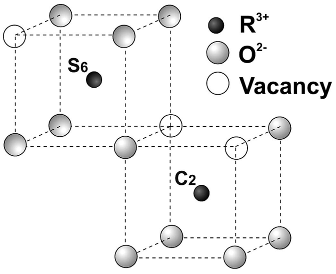

Figure 1. Schematic presentation of the two six-coordinated R^{3+} sites in cubic C-type Lu_2O_3.

been explained by the presence of residual Tb^{4+} ions.[16,17] This explanation seems to be reasonable also in the case of Lu_2O_3:Tb^{3+} since sintering in air resulted in materials of similar but much deeper brown color; i.e., the Tb^{4+} amount was then higher. The presence of the Tb^{4+} ion really embedded in the Lu_2O_3 lattice would necessitate a charge compensation. In order to maintain electrical neutrality, addition of interstitial oxygen is usually required. The exact position of the additional oxygen may be deduced in a convincing manner from the crystal structure of Lu_2O_3.

The crystal structure of the cubic C-type Lu_2O_3 (Figure 1) is related to the cubic fluorite (CaF_2) structure with oxygen vacancies. These vacant sites can be capable of accommodating the additional oxygen ions when tetravalent terbium ions are present. Furthermore, the charge compensation due to two Tb^{4+} ions replacing two Lu^{3+} ($2\mathrm{Tb}^{\bullet}_{\mathrm{Lu}}$) for one extra interstitial O^{2-} ion ($\mathrm{O}_{\mathrm{i}}''$) may lead to the formation of [$\mathrm{Tb}^{\bullet}_{\mathrm{Lu}}-\mathrm{O}_{\mathrm{i}}''-\mathrm{Tb}^{\bullet}_{\mathrm{Lu}}$] defect clusters due to electrostatic interactions between the O^{2-} and Tb^{4+} ions. It is evident from Figure 1 that it is possible to obtain quite a few slightly different clusters—considering their symmetry—not just one. On the other hand, these vacant oxygen sites may be occupied by an electron or electrons forming either negatively charged e′ and/or e″ centers, i.e., the vacant oxygen sites with one or two trapped electrons, respectively. The electrons would be bound to the Tb^{4+} ion with electrostatic forces, too, since the electrostatic attraction to Tb^{4+} is strong due to the high charge/size ratio of this ion. Once again, several slightly different $\mathrm{Tb}^{\bullet}_{\mathrm{Lu}}-\mathrm{e}'$ (or $2\mathrm{Tb}^{\bullet}_{\mathrm{Lu}}-\mathrm{e}''$) defect systems can be anticipated.

Once ceramics are formed in vacuum—a moderately reducing atmosphere—the existence of interstitial oxygen is not probable, as has been found for the rare earth cuprates.[18] In contrast, at high temperatures and with the help of vacuum, formation of yet additional *vacant* oxygen as well as vacant metal sites should be rather expected due to facilitated migration of atoms toward the surface, from where they may be expelled to vacuum.[19,20] The scientific literature is abundant with papers reporting such effects occurring at high temperatures, also for various Tb oxides for which nonstoichiometry is rather easily achievable.[21–26]

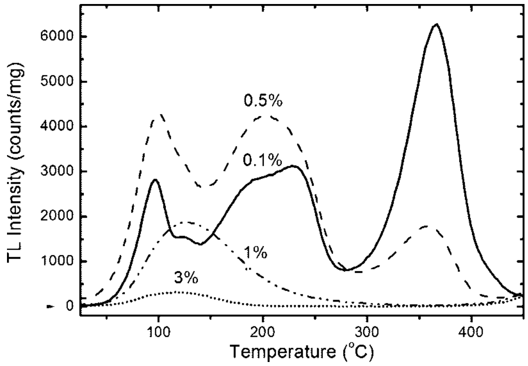

Figure 2. Thermoluminescence glow curves of the vacuum-sintered Lu_2O_3:Tb^{3+} as a function of the Tb^{3+} concentration.

3.1. Thermoluminescence of Tb^{3+}-Doped Lu_2O_3. The TL glow curves (Figure 2) of the Lu_2O_3 materials doped with Tb^{3+} at various doping levels were first measured to probe the effect of the terbium concentration on the thermally stimulated luminescence of these materials. It is immediately seen that the 0.1 and 0.5 mol % doped materials possess significantly more complex glow curves when compared to those containing higher amounts, i.e., 1 or 3 mol % of terbium. The TL glow curves of the materials with low terbium content exhibit three components located at ca. 100, 200, and 360 °C. The two low-temperature bands are clearly structured and are probably doublets. The materials with terbium concentration higher than 0.5 mol % show much simpler glow curves, essentially with only one band peaking around 125 °C.

The glow curves show concentration dependence: with increasing terbium concentration the intensity of the initially dominant high temperature band located at ca. 360 °C decreases and finally disappears completely. Moreover, the overall TL intensity decreases with increasing terbium content. For the 3 mol % terbium-doped material, the TL emission is several orders of magnitude weaker than for ceramics containing 0.1 and 0.5 mol % of the dopant. The glow curves reveal that there are several traps with rather different depths present in the lightly doped specimens able to intercept electrons and/or holes freed upon the UV excitation. Some of the traps are relatively shallow (100 and 125 °C) while the others are much deeper (200 and 360 °C). For the photostimulated phosphor application, the disappearance of the high-temperature TL bands is detrimental as is the enhancement of the TL intensity at the low-temperature range.

Both the photostimulated and persistent luminescence rely upon storing of the excitation energy for further use—in the case of persistent luminescence immediately after ceasing (or even simultaneously) the irradiation, whereas in the

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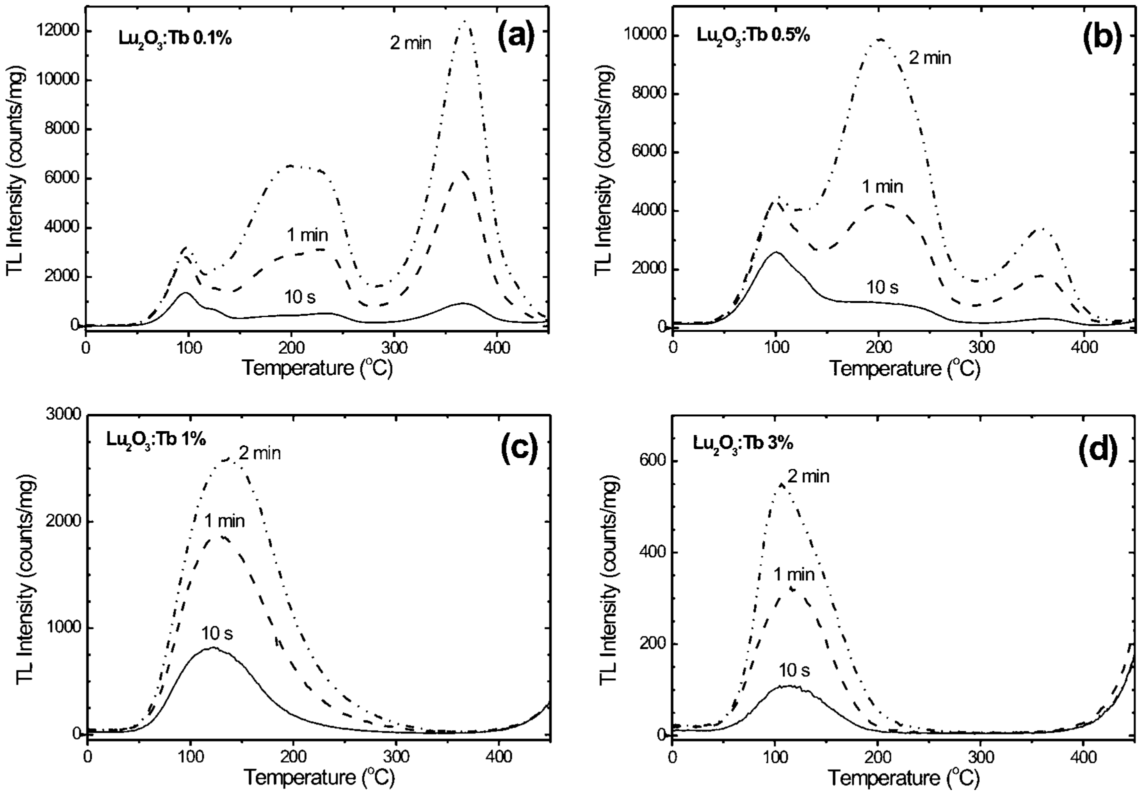

Figure 3. Thermoluminescence glow curves of the vacuum-sintered Lu_2O_3 doped with different Tb^{3+} amounts as a function of the UV irradiation time.

former case only after stimulation by a laser. It can be safely assumed that the energy storage occurs exclusively in electron and hole traps[6,7] in the forbidden energy gap of the host. Since both the storing and the electron–hole recombination process[6] leading finally to emission are of importance for the understanding of these processes as a whole, the knowledge of the traps present in the materials is crucial in the analysis of the excitation, storage, and release of energy.

Some indication as to the type of defects responsible for the carriers trapping in Lu_2O_3:Tb comes from the fact that the persistent luminescence appears only from materials heated at the reducing atmosphere of vacuum and only if the treatment is performed at temperatures around 1700 °C. Clearly, certain changes take place in the material when such high-temperature treatment is applied. Looking for these changes two effects, which are probable to happen, should be pointed out. First is the possibility to create vacancies, both metal and oxygen. Formation of such defects is strongly enhanced by the high temperature and vacuum. Both parameters facilitate the mobility of atoms, and those atoms which migrated to the surface may easily be expelled to vacuum, leaving increasing number of vacancies in the host. This was already discussed above.

Another effect which is probable to occur upon high-temperature treatment is an aggregation of defects. This may take place since, as was already stated, the high-temperature enhances the migration of the various species present in the material. Thermodynamically, aggregation and clustering of defects—vacancies, impurities, etc.—is usually advantageous. Evidently, appropriately high temperature not only increases the population of vacancies but also facilitates aggregation and clustering of the various defects present in the material.[20,27] Summarizing, it can be expected that after the high-temperature vacuum treatment cation and anion vacancies in Lu_2O_3:Tb ceramics will be rather abundant, and their distribution may well not be random. Most of all, because of opposite net charges, one should expect that cation and anion vacancies may agglomerate and cluster. The presence of Tb impurity may additionally enhance such aggregation and clustering.[20,27] This reasoning is especially important for the Tb,Ca-codoped materials analyzed below.

The irradiation time has usually a significant effect on the filling of traps provided the trap depths are sufficiently different. This effect can be used to differentiate and identify traps. For the Lu_2O_3 materials doped with terbium, the TL glow curves (Figure 3) are strongly irradiation time-dependent for each Tb concentration investigated. Yet, the basic differences in the TL glow curves as a function of terbium content are retained. The glow curves reveal the filling sequence of the traps present in the materials by carriers freed upon the impact of UV photons. The most complex sequences are for the lightly doped materials since their glow curve structures were originally more complicated. In general, the shallowest trap (at ca. 120 °C) is filled most readily. The deeper traps become more active in intercepting the freed carriers once the shallowest trap is already filled to a significant degree, even very close to saturation. Although the shallowest trap corresponding to the lowest temperature TL band is saturated with the present irradiation power and time, the other bands show no saturation of the corresponding traps. Evidently, higher irradiation power and/or time is

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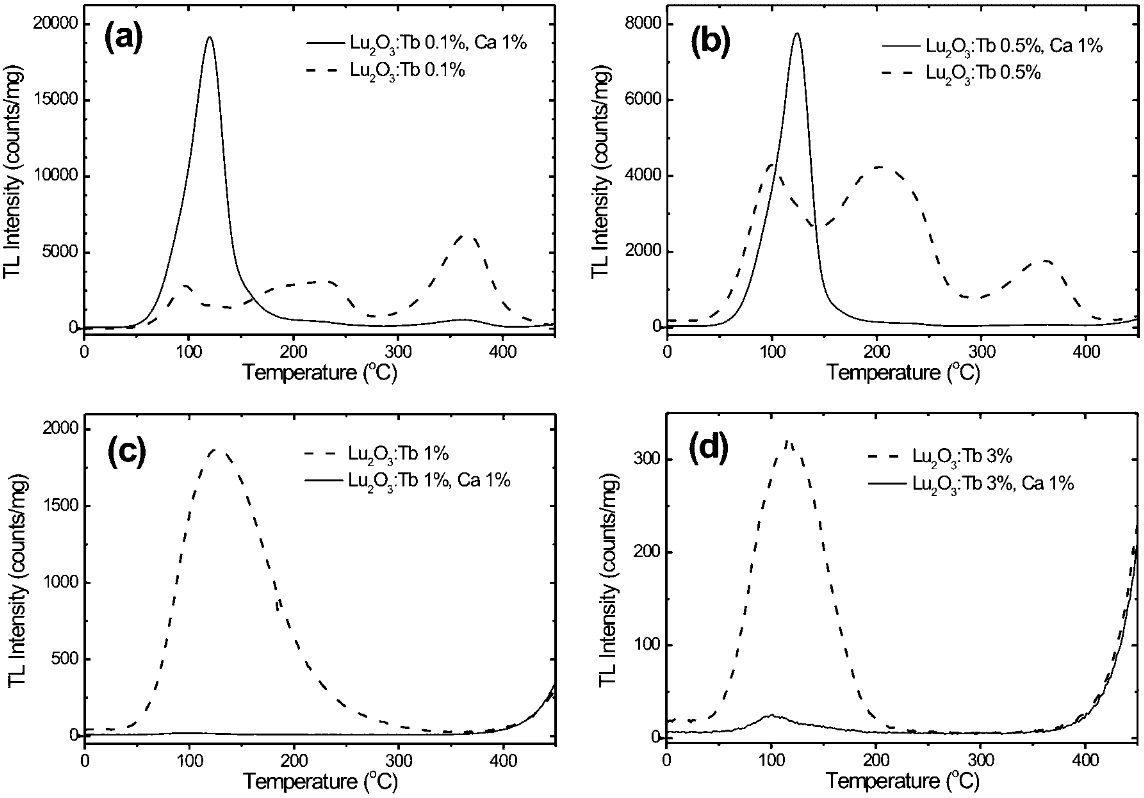

Figure 4. Comparison of the thermoluminescence glow curves of the Lu_2O_3:Tb^{3+} and Lu_2O_3:Tb^{3+},Ca^{2+} materials sintered in vacuum.

needed to saturate the traps corresponding to the TL band at ca. 200 and 360 °C. It was proven difficult to separate traps with similar depths by varying the irradiation time, unfortunately.

In spite of the fact that the trap structures of the materials containing 1 or 3 mol % of terbium are uncomplicated due to their rather simple TL glow curves, one can observe that, for the 1 mol % doped specimen, the TL band maximum moves from ca. 115 °C for the shortest irradiation time to ca. 140 °C for the longest one. For the 3 mol % doped material, an opposite shift is observed; i.e., with increasing irradiation time, the band maximum moves from ca. 115 to ca. 105 °C. It seems that in both cases the seemingly lone TL band comprises at least two strongly overlapping components. On the other hand, the slight shift observed may result from different kinetics[5] which explanation, however, needs further investigations to be validated. As the first approximation, the evolution of the TL band maxima as a function of the irradiation time for the 3 mol % terbium-doped material follows the second-order kinetics.[5]

The interpretation of the experiments presented above reveals that the most efficient thermoluminescence was obtained from the 0.1 mol % doped material. The problem with this specific material was, however, that its glow curve consists of several TL bands being significantly apart and covering a broad temperature range, from 50 to 450 °C. For practical applications, it would be much better if the total TL intensity could be retained, or even be increased, as a single band. For a storage phosphor, the trap(s) should be relatively deep to preclude the thermal release of the intercepted carriers at room temperature,[6,7] whereas for efficient persistent luminescence, the trap(s) should be rather shallow, corresponding to a TL band at somewhere between 100 and 150 °C to let the carriers be freed slowly by thermal energy at room temperature after being trapped.[4,28,29]

Taking into account these findings and considerations, it can be concluded that the Lu_2O_3 materials doped with Tb^{3+} fulfill the requirements of neither a good photostimulated (storage) phosphor nor a good persistent luminescence material. There is certainly a need to modify the trap structure of Lu_2O_3:Tb^{3+}. One of the most frequently used techniques to carry out these modifications is doping of the original material with ions (mainly cations) possessing a charge incompatible with the original cation, in this case the Lu^{3+} ion. The alkaline earths, Ca^{2+}, Sr^{2+}, and Ba^{2+}, are such cations and, what seems to be important, with no possibility for a change in the charge. These ions have no perturbing energy levels, either. Indeed, some interesting results were obtained for the Tb^{3+},Ca^{2+}-codoped materials to be dealt with in the following sections.

3.2. Ca^{2+}-Codoped Lu_2O_3:Tb^{3+}. In order to probe the modifications occurring in the trap structure due to the Ca^{2+} codoping, the TL glow curves of the Tb^{3+},Ca^{2+}-codoped vacuum-sintered Lu_2O_3 (Figure 4) were compared with those for the Tb^{3+}-doped materials. It is immediately seen that the Ca^{2+} substitution greatly changes the TL properties of all materials. For the two codoped specimens with low terbium content (0.1 and 0.5 mol %), the glow curves consist essentially of only one, but slightly asymmetric, band peaking

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at 120−125 °C. The shape of these bands might suggest that they result from a superposition of two components, with the less intense one peaking slightly below 100 °C. On the other hand, a similar asymmetry could indicate that the kinetics of the process is of the first order.[5]

In general, the Ca^{2+} codoping severely suppressed the TL intensity of the Lu_2O_3:Tb^{3+},Ca^{2+} materials with the exception of the lowest Tb^{3+} content (0.1 mol %). Despite the very simple TL band structure, the Ca^{2+} codoping enhanced the total TL intensity of this material. The Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) codoped material has a slightly higher TL intensity than the *sum* of all the TL bands of the Ca^{2+}-free material. For the 0.5 mol % Tb-doped ceramics, the Ca^{2+} codoping reduced the total TL intensity significantly, however. The TL efficiency became even weaker for the 1 and 3 mol % Tb-codoped materials, for which the thermoluminescence was almost totally quenched by the Ca^{2+} codoping. Thus, the influence of the Ca^{2+} codoping on the TL glow curves is indeed very significant, and the final goal of the codoping, i.e., the enhancement of the total TL intensity *and* the simplification of the TL glow curve, was fully achieved since the Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) codoped material produced the most efficient thermoluminescence among all the compositions investigated.

Before going to the detailed analysis of the TL glow curves, the structural consequences of the Ca^{2+} codoping should be considered. In fact, the plausible possibilities are very limited. For a six-coordinated site the ionic radii are as follows for Ca^{2+}, Tb^{3+}, and Lu^{3+}: 1.000, 0.923, and 0.861 Å, respectively.[30] Hence, it is unlikely that any significant number of Ca^{2+} ions occupy interstitial positions in the host lattice since the Ca^{2+} ions are relatively large. Clearly, calcium replaces Lu^{3+} in the regular cation site rather than squeezes into an interstitial position deforming strongly the lattice. It is true that the difference between the radii of Ca^{2+} and Lu^{3+} is close the experimental limit of 15% required to yield good solid solubility as stated by the Vegard's law.[31,32] Additionally, it should be expected that the solubility will diminish due to charge and structural incompatibility. Nevertheless, the rather low, 1 mol %, content of Ca should be quite easily accommodated by the lutetia host lattice without any separation as a new phase.

In contrast to the size, the Ca^{2+} codoping creates severe charge compensation problems in the Lu_2O_3 lattice. The most straightforward charge compensation scheme suggests that the lower charge of Ca^{2+} could be compensated by an oxygen vacancy, one for every two Ca^{2+}. Furthermore, since both Tb^{3+} and Ca^{2+} ions are slightly larger than Lu^{3+}, which they replace in the lattice, it is reasonable to expect that high temperature of the ceramics fabrication leads to clustering of both codopants and the oxygen vacancy ($V_O^{\bullet\bullet}$) owing to the facilitated migration of these species.[19,20] Consequently, it is reasonable to postulate that the unavoidable point defects aggregate spatially during the high-temperature sintering forming [$Tb_{Lu}^{\times}-V_O^{\bullet\bullet}-2Ca_{Lu}'$] clusters consisting of Tb^{3+} replacing Lu^{3+} (a neutral defect), a positive O vacancy, and two Ca^{2+} ions replacing Lu^{3+} (each a negative defect).

Another possibility for the charge compensation could be that Ca^{2+} codoping stabilizes the tetravalent terbium in the Lu_2O_3 lattice. This effect, if present, should be Ca concentration dependent: more Ca^{2+} should increase the concentration of Tb^{4+} (more numerous Ca_{Lu}' sites should raise the concentration of $Tb_{Lu}^{\bullet}$), and consequently the materials' brownish color should be more profound. For materials prepared in vacuum, varying the Ca content in the range 0.5–3 mol % such an effect was not observed (results are not presented here). On the other hand, for materials treated in air, indeed those with higher Ca content turned much darker. Therefore, this scheme of the charge compensation is rather insignificant for materials prepared in vacuum, which are of our concern. Hence, it is assumed that before irradiation Tb is present in the vacuum sintered ceramics as trivalent rather than tetravalent. This assumption gets further support from EPR spectra (not presented here), which, for the nonirradiated specimens, do not show any signal, which might be associated with the Tb^{4+} ion. It has been shown previously that Tb^{4+} gives a strong EPR spectrum similar to that characteristic for the isoelectronic Gd^{3+} ion.[33,34]

In the light of the considerations presented above, it is proposed that the high-temperature vacuum-sintered ceramics of Lu_2O_3:Tb^{3+},Ca^{2+} are rather abundant with the [$Tb_{Lu}^{\times}-V_O^{\bullet\bullet}-2Ca_{Lu}'$] clusters of point defects and that these clusters define the properties of the persistent luminescence of the Tb,Ca-codoped ceramics. In such agglomerates electron freed from Tb^{3+} ion upon UV photons may be easily trapped at the nearby located $V_O^{\bullet\bullet}$ site, giving $e_O^{\bullet}$ (or $V_O^{\times}$ after trapping of the second electron), while the hole left behind may become intercepted in the vicinity of the activator forming the [$Tb_{Lu}^{\times}-h^{\bullet}$] entity (Hosono[35] named it [$(Tb^{3+})^{+}$]). Holes are much less mobile than electrons,[35–37] and it is reasonable to expect that these carriers remain in the vicinity of their original Tb ions. Such a trapping scheme may be facilitated if the Ca^{2+} ion is positioned in the nearest vicinity of the Tb dopant, as was postulated above. The net negative charge of Ca_{Lu}' stabilizes the trapped hole. This strongly spatially correlated system is required since without that no hours-lasting persistent luminescence could be expected. Hence, it is postulated that after UV irradiation the energy is stored in electrons and holes trapped in defect clusters giving the following, spatially correlated entity: [$(Tb_{Lu}^{\times}-h^{\bullet})-e_O^{\bullet}-2Ca_{Lu}'$].

However, the very weak TL band centered at around 360 °C (Figure 4a) for Lu_2O_3:Tb^{3+},Ca^{2+} as well as analogously positioned but much weaker band for the Ca^{2+} free materials (Figures 2 and 3) can be a sign of holes trapped further from Tb^{3+} (holes which overcame the potential barrier and escaped further from their original Tb^{3+} ions) as might be the bands

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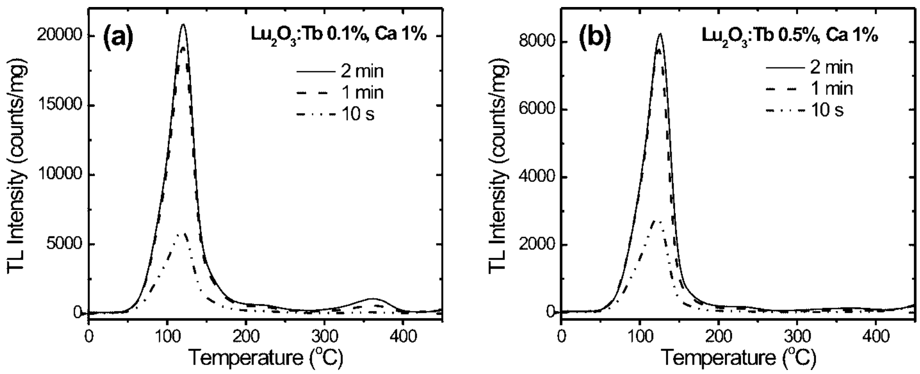

Figure 5. Comparison of the thermoluminescence glow curves of two vacuum-sintered Lu_2O_3:Tb^{3+},Ca^{2+} materials showing the strongest persistent luminescence with increasing UV irradiation time (dopant concentrations: Tb^{3+}: 0.1 and 0.5 mol %; Ca^{2+}: 1 mol %).

centered at between 200 and 250 °C for the Ca-free specimens. The high-temperature (~360 °C) band is completely absent for the Tb,Ca-codoped system containing 0.5 mol % of the dopant. This supports the conclusion that the 360 °C TL band results from carriers (probably holes) trapped far away from Tb. Yet, it cannot be excluded that holes are trapped at the $Ca_{Lu}^{'}$ site, whose negative net charge might facilitate such an entrapping. The ($Ca_{Lu}^{'}$−$h^{\bullet}$) or $Ca_{Lu}^{\times}$ center within the discussed [($Tb_{Lu}^{\times}$–$h^{\bullet}$)–$e_{O}^{\bullet}$–2$Ca_{Lu}^{'}$] defect cluster would still keep the hole close to the $Tb_{Lu}^{\times}$, which is important for efficient TL and consequently also intense persistent luminescence. At present, it is not possible to resolve which of the two postulated mechanisms of hole trapping indeed occurs. In any case both electrons and holes are trapped in the vicinity of the $Tb_{Lu}^{\times}$ site—serving as the carriers' recombination center.

As it was for the Ca-free materials, the TL intensity for the Tb,Ca-codoped specimens decreases with increasing Tb concentration. This observation indicates that a spatial separation between the energy-storing entities, [($Tb_{Lu}^{\times}$–$h^{\bullet}$)–$e_{O}^{\bullet}$–2$Ca_{Lu}^{'}$], is necessary to make the TL, and consequently persistent luminescence, efficient. In other words, efficient TL requires that the entities do not interact. If interaction between them appears due to a reduced distance, the traps are no longer so effective in keeping the carriers with their excessive energies. It will be seen later that the reduced distance makes the persistent luminescence decaying much faster, and its intensity diminished. Hence, a kind of concentration quenching of persistent luminescence is observed.

3.3. Effect of Irradiation Time. For the two materials yielding the strongest persistent luminescence, i.e., Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 0.5 mol % of terbium), the TL glow curves were measured with selected UV irradiation times, i.e., from 10 s to 2 min (Figure 5). The only difference observed is that the intensity of the TL band at around 120 °C increased for longer UV irradiation times. On the other hand, the saturation in filling the traps corresponding to the TL bands at low temperature is very close with the longest irradiation time, i.e., 2 min. For the lightest doped Lu_2O_3:Tb^{3+},Ca^{2+} material (0.1 and 1 mol %, respectively) a very weak TL band can be noted again at around 360 °C after a prolonged irradiation. The intensity of this band comprises only about 2–3% of the total TL intensity, and thus it may be considered insignificant from the practical point of view. For the heavier doped Lu_2O_3:Tb^{3+},Ca^{2+} material (0.5 and 1 mol %, respectively), this high-temperature band is practically absent. The position of this weak band coincides with the location of the highest temperature band for the Ca^{2+} free materials containing 0.1 or 0.5 mol % of terbium (Figure 2). It is evident that the number of these deep traps has radically been decreased by the Ca^{2+} codoping. Since addition of Ca^{2+} may only facilitate but not hinder the creation of Tb^{4+}, the least one can deduce from these TL curves is that the high-temperature traps are not related to the presence of Tb^{4+}.

The results presented above show that the most intense thermoluminescence comes from the Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) material and that the Ca^{2+} codoping greatly simplifies the trap structure when compared to the Ca^{2+}-free composition. Evidently, at room temperature, the position of the TL band for this composition favors the persistent luminescence over the energy storing, since for the latter application the trap is too shallow.

3.4. Fading of Thermoluminescence. The fading of thermoluminescence is due partly to the bleaching of the trapped carriers by thermal energy and partly by other processes, e.g., tunneling if the traps are deep enough and have distinct energies. The measurement of the TL glow curves with different delay times after ceasing the UV irradiation may give important information on the trap structure in the material. The TL glow curves (Figure 6) for the two Lu_2O_3:Tb^{3+},Ca^{2+} materials (0.1 and 0.5 mol % of terbium) are rather similar in form, and both indicate an expected decrease in the total intensity of the TL bands as the delay time increases. The glow curves reveal the presence of (at least) two traps with very similar depths. Since the fading of the TL band of the Lu_2O_3:Tb^{3+},Ca^{2+} material with lower Tb^{3+} content is clearly slower, this material yields the most efficient persistent luminescence when both the initial intensity and the duration are considered. When comparing the TL intensity after 120 min after ceasing the irradiation to the material with lower Tb^{3+} content, the TL band around 120 °C possesses about 30% of its original intensity. For the more concentrated system, this is only about 7%. The Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) vacuum-sintered ceramic possesses thus superior properties compared to any other material investigated here as far as the prerequisites for intense persistent luminescence are concerned.

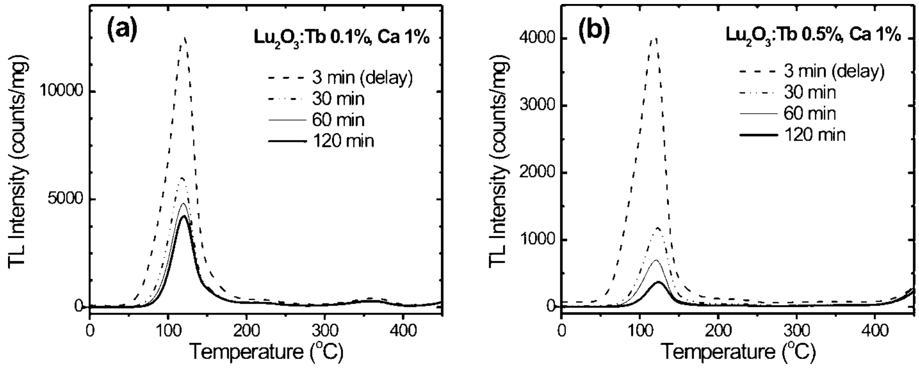

Figure 6. Comparison of the thermoluminescence glow curves of the best vacuum-sintered Lu_2O_3:Tb^{3+},Ca^{2+} materials (Tb^{3+}: 0.1 and 0.5 mol %; Ca^{2+}: 1 mol %) recorded with different delay times after the UV irradiation.

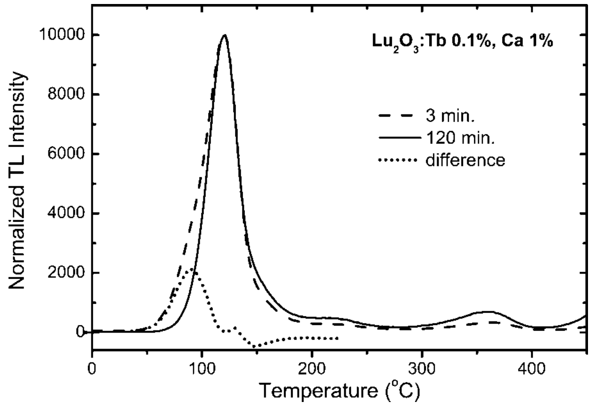

Figure 7. Comparison of the normalized thermoluminescence glow curves of the best vacuum-sintered Lu_2O_3:Tb^{3+}, Ca^{2+} material recorded 3 and 120 min after the UV irradiation and differential spectrum of the two.

It was already noted earlier that the TL band of the Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 0.5 mol % of terbium) ceramics located around 120 °C is asymmetric and gives an impression of a superposition of two strongly overlapping components. On the other hand, similar asymmetry is characteristic for the first-order mechanism. With the normalization of the two TL glow curves, measured 3 min and 2 h after ceasing the UV irradiation, one can calculate the difference curve (Figure 7). The TL band recorded with longer delay is narrower and lacks the low-temperature tail which observation is logical since the low-temperature component should fade faster, even if the feeding from the deeper traps is taken into account. At room temperature both traps give their contribution to the total observed persistence luminescence. Because there is no change in the position of the peak position of both TL bands, this observation ultimately confirms that the band around 120 °C is a superposition of at least two strongly overlapping components.

3.5. Kinetics of Persistent Luminescence. The room temperature persistent luminescence of the Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) material could be seen by naked eye in complete darkness for about 5–7 h, and if the eyes were use to the darkness, the luminescence was seen even after 15 h since ceasing the UV irradiation. Naturally, it would be of interest to find out the processes responsible for such a long persistent luminescence. Accordingly, the decay kinetics of the persistent luminescence (Figure 8) was recorded during the first 9 h after ceasing the excitation and was studied in detail. It turned out that fitting of the decay within the whole time range of the measurement was not possible even using a function of three exponential terms. Since the decay appeared nonexponential, an alternative approach was employed.

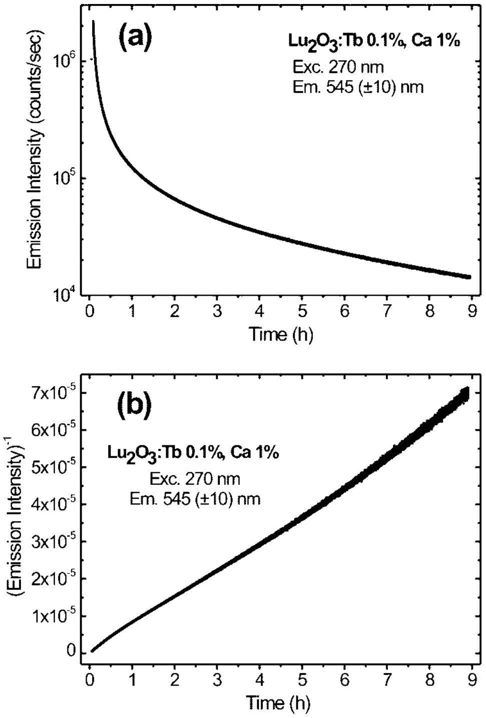

Figure 8. Decay curve of the persistent luminescence of the vacuum-sintered Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) material (a) and the time dependence of the reciprocal persistent luminescence intensity, I^{-1} (b). The linear relationship of $I^{-1}(t)$ indicates a tunneling mechanism of the process.

If the reciprocal of the luminescence intensity is presented as a function of time (Figure 8b), i.e., $I^{-1} = f(t)$, a striking, almost perfectly linear dependence is obtained within the whole range of time investigated. In the literature one can find examples of materials, whose persistent luminescence follows similar kinetics.[5,38–43] In more general terms, the intensity of persistent luminescence may decay according

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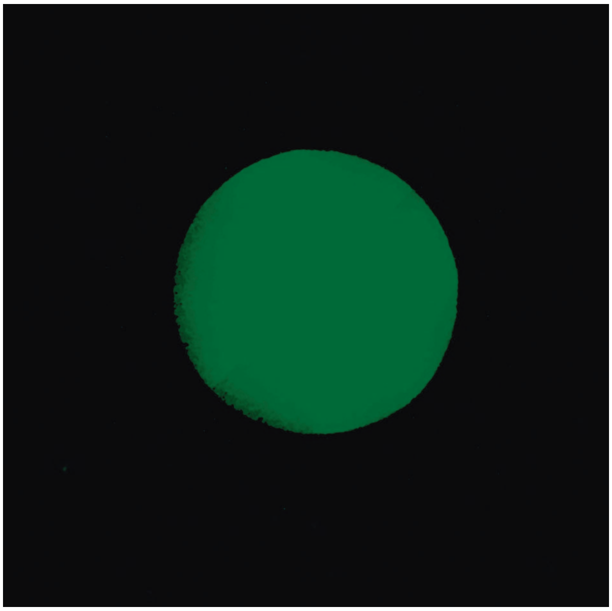

Figure 9. Picture taken in complete darkness with digital camera 8 h after ceasing the irradiation with UV light of the Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) ceramic material.

to the $I \sim t^{-a}$ dependence, with a varying between 0.5 and 1 usually and sometimes reaching even 2.[43] It appears that the linear dependence of I vs t^{-a} is a sign that the persistent luminescence occurs through a tunneling or temperature-assisted tunneling process.[5]

The tunneling probability is exponentially dependent on the distance between the involved centers,[39,44] which explains why the formation of the clustered defects, [$\mathrm{Tb}^{\times}_{\mathrm{Lu}}$–$\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}$–$2\mathrm{Ca}'_{\mathrm{Lu}}$], which was postulated and discussed earlier, is so important for getting efficient persistent luminescence. The presence of point defects randomly spread within the lattice is not enough to get efficient persistent luminescence. Only if clusters of the point defects are created, both types of carriers, electrons and holes, may be intercepted in the vicinity of Tb, and this, in turn, allows the tunneling to be efficient. The anticipated clustering also explains why only high-temperature treatment converts the investigated materials into efficient persistent phosphors: only then the individual point defects may migrate and form the clusters, reducing the separation of the trapping sites and Tb^{3+} ion. The existence of such clusters would also explain why the TL glow curves of the Tb,Ca-codoped materials are so much simpler when compared to that characteristic for the materials doped only with Tb. Namely, in the presence of the Ca^{2+} ions most of the carriers are trapped by the same type of trapping centers: [$\mathrm{Tb}^{\times}_{\mathrm{Lu}}$–$\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}$–$2\mathrm{Ca}'_{\mathrm{Lu}}$]. Altogether, the complex observations make up a complete and consistent picture.

Finally, in Figure 9 is presented a picture taken without any external light with a digital camera 8 h after ceasing the UV irradiation of the Lu_2O_3:Tb^{3+},Ca^{2+} (0.1 and 1 mol %, respectively) ceramic material prepared in vacuum at 1700 °C. The picture clearly shows that the green light is still being released from the material with significant intensity. This picture ultimately confirms that Lu_2O_3:Tb,Ca is a new persistent phosphor whose properties put it within a very limited group of novel persistent luminescent materials with intense emission lasting for many hours.

It should be noted that no material prepared by sintering in air showed any significant thermoluminescence/persistent luminescence. All such materials possessed much deeper brown body color than the vacuum-sintered materials. Despite the fact that the UV irradiation did not lead to thermoluminescence/persistent luminescence from the air-sintered ceramics, this excitation anyhow created the characteristic green emission of the trivalent Tb^{3+} ion with the most intense components around 480 and 545 nm corresponding to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions, respectively. Moreover, the Lu_2O_3:Tb^{3+}material prepared in vacuum at 1500 °C did not show any significant persistent luminescence, either. It appears clear that several requirements have to be *simultaneously* fulfilled to convert Lu_2O_3:Tb^{3+} into an efficient persistent luminescence phosphor: (i) the terbium content should be low, (ii) the sintering has to be carried out in vacuum, (iii) the temperature has to be about 1700 °C, and (iv) the material has to be codoped with Ca^{2+}. The lack of fulfilling any of these requirements makes the persistent luminescence much less efficient or even insignificant.

Finally, let us yet shortly comment on one detail. It was recently published[45] that although in photoluminescence of Lu_2O_3:Eu the activator ions placed in the C_2 position totally dominates the spectrum, in the afterglow spectra, the emission is mostly caused by the Eu^{3+} ions occupying the S_6 site, at least for the lower concentrations of europium. Consequently, both types of luminescence spectra differed significantly, indeed. In the presently investigated Tb-activated materials no similar behavior was observed. It seems that in Lu_2O_3:Tb^{3+} or Lu_2O_3:Tb^{3+},Ca^{2+} the activator ions occupying the two sites are rather equally active both in photoluminescence and in persistent luminescence.

4. Conclusions

The most efficient persistent luminescence was obtained from the vacuum-sintered Lu_2O_3 doped with terbium and codoped with calcium at the level of 0.1 and 1 mol %, respectively. This material is characterized by at least two overlapping bands in the TL glow curves centering at around 120 °C, which is quite ideal for room temperature persistent luminescence. The persistence lasts for about 15 h, as could be seen by eyes used to the darkness. Higher Tb contents are harmful for both the persistence and thermoluminescence intensity.

There occurs a very significant change in the TL glow curves due to the Ca^{2+} codoping, i.e., the high-temperature TL bands are suppressed. The removal of practically all deeper traps seems to be related to the clustering of individual defects into [$\mathrm{Tb}^{\times}_{\mathrm{Lu}}$–$\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}$–$2\mathrm{Ca}'_{\mathrm{Lu}}$] spatially correlated defect systems serving as efficient trapping centers for free carriers. The oxygen vacancy, $\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}$, would attract the free electron while the holes, h, would form the [$\mathrm{Tb}^{\times}_{\mathrm{Lu}}$–$\mathrm{h}^{\bullet}$] entity. On the

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other hand, it cannot be excluded that hole could be trapped in the $\mathrm{Ca}_{\mathrm{Lu}}'$ site due to its negative net charge, giving basically the neutral $\mathrm{Ca}_{\mathrm{Lu}}^{\times}$ or $\mathrm{Ca}_{\mathrm{Lu}}'$–$\mathrm{h}^{\bullet}$ site. This would still keep the trapped hole in the vicinity of $\mathrm{Tb}_{\mathrm{Lu}}^{\times}$ (as $\mathrm{Ca}_{\mathrm{Lu}}'$ is a part of the defect cluster) which is important for efficient tunneling and consequently also efficient persistent luminescence. The spatial correlation between the electron and hole trap centers as well as the activator ensures the surprisingly long persistence because tunneling—the most probable mechanism of persistent luminescence in Lu_2O_3:Tb^{3+},Ca^{2+}—may be efficient in such circumstances.

Finally, the optimization of both the composition and processing parameters of Lu_2O_3:Tb^{3+},Ca^{2+} should be carried out to find out whether the persistent luminescence characteristics can be further improved. Such a research is being conducted presently. Also, other than the Ca codopants are being tested, and the preliminary results are very encouraging.

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