Energy Recovery from Lu_2O_3:Tb,Hf Ceramic Storage Phosphors

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Lu_2O_3:Tb,Hf ceramics were investigated as energy storage materials. It was shown that X-rays caused a significant thermoluminescence with a main band around $250\,^{\circ}$C at a heating rate of $4.8\,^{\circ}$C$\,$s^{-1}. 780 nm radiation released up to about 75% of the stored energy, while 420 nm light liberated all the stored energy in the form of green photons produced by the Tb^{3+} ions.

Key words: Storage Phosphors, Optically Stimulated Luminescence, Thermoluminescence, Thermal Quenching

Introduction

Storage phosphors form a specific class of luminescent materials. They are able to temporarily immobilize excited carriers in energy traps formed by specific defects [1, 2]. The time a carrier spends in a trap is defined by the trap properties, mainly its energy depth, E, frequency factor, s, and the temperature. After immobilization, the frozen energy may be subsequently recovered by an external stimulation, either thermal or optical, leading to the generation of luminescent photons [3, 4]. Upon heating, however, some energy may be (and usually is) lost in nonradiative processes, whose probability raises with temperature. This effect is known as thermal quenching of photoluminescence [5 – 7]. Therefore, there are two contradictory requirements for the storage phosphors: deep traps are preferred, from which the immobilized carriers are less prone to leak out without an intentional external stimulation. Yet, the deeper the traps, the higher the heating temperature required to free all the trapped carriers to recover their energy. This, however, ends up with an increasing energy loss through thermal quenching. In an extreme case, the traps may be so deep that thermal stimulation does not produce any luminescence at all, as the temperature needed to free the carriers is higher than that needed to totally quench the emission.

Fortunately, there is an alternative possibility to free the trapped carriers. This may be done by *optical* stimulation, which needs photons whose energy is high enough to exceed the trap energy barrier. This typically occurs at room temperature, so that thermal quenching is either absent or insignificant. Consequently, thermal and optical stimulations are used complementarily, both in applications and in research on storage phosphors.

Typically, the stimulating radiation energy is lower than the energy of the finally emitted photon [3, 4]. Therefore, special and rather expensive filters are used to remove the scattered infrared/red (usually) stimulating photons from the visible emission they cause. An opposite situation, where the optical stimulation can be efficiently performed with radiation of wavelength shorter than characteristic for the emitted light, has not been reported in literature on storage phosphors.

In this paper we show how energy entrapped in Lu_2O_3:Tb,Hf ceramic storage phosphors may be recovered by means of thermal and optical stimulations. Interaction of stimulating radiation photons of various energies with the trapped carriers are tracked and discussed. A detailed analysis of the physics behind the processes of trapping and detrapping carriers and of the trap parameters have previously been presented [8].

Results and Discussion

Fig. 1 presents thermoluminescence (TL) glow curves of Lu_2O_3:Tb,Hf ceramics recorded applying
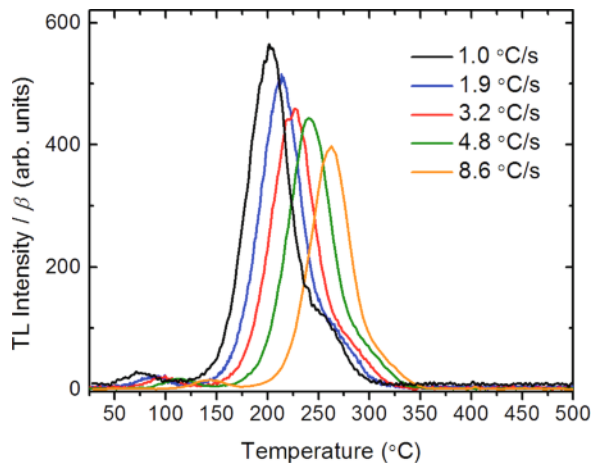
Fig. 1 (color online). Thermoluminescence (TL) glow curves of Lu$_2$O$_3$: 0.1 % Tb, 0.2 % Hf ceramics recorded applying different heating rates after irradiation with X-rays for 3 min. Note the systematic shift of the peak positions and the reduced intensity with increasing heating rate.

different heating rates. As expected [9], the TL band maximum moves towards higher temperatures as the heating becomes faster. At the same time, the intensity gets reduced, which is an anomalous behavior unless a luminescence thermal quenching takes place. Fig. 2 shows how the luminescence decay curves (Fig. 2a) change with the sample temperature and how the average decay time constant decreases with increasing temperature (Fig. 2b).

Clearly, the green Tb^{3+} emission experiences a significant thermal quenching, especially above 150 °C. Near 400 °C the effect is so significant that the luminescence practically disappears. Combining the observations depicted in Figs. 1 and 2, it appears that the decreasing TL intensity with increasing heating rate results from the thermal quenching of the luminescence, *e. g.* increased draining of the energy from the emitting $^5D_4$ level of Tb^{3+} by means of nonradiative relaxation. Indeed, after correction of the glow curves for this effect (not presented here), the intensity – representing the amount of energy stored in the material – is stable within a few percent. All these observations indicate that during the thermoluminescence some energy is lost due to nonradiative processes. This would reduce the sensitivity and accuracy of the storage phosphor if applied in thermoluminescent dosimetry of ionizing radiation.
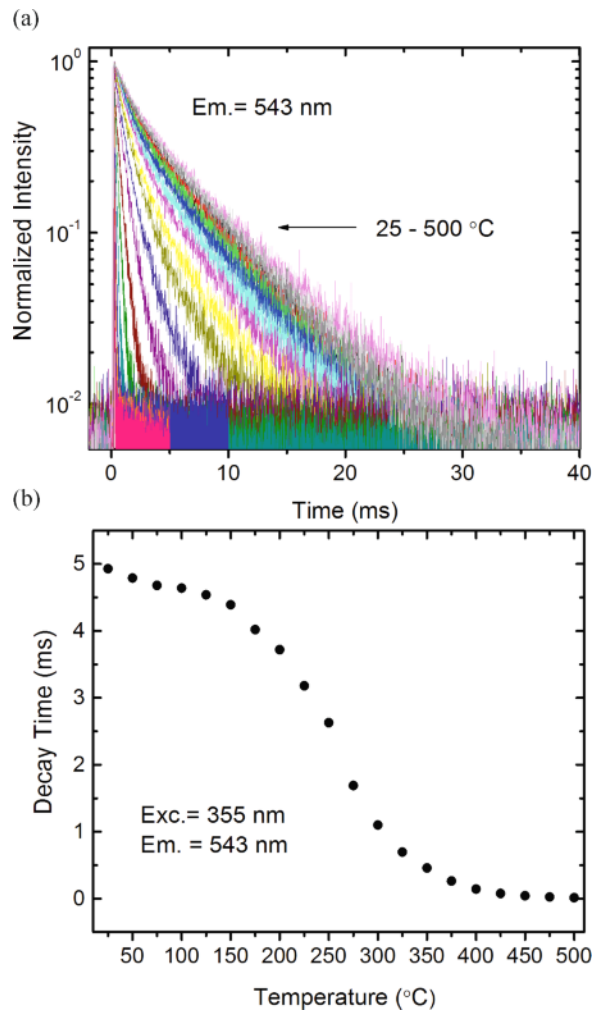

Fig. 2 (color online). Decay traces of the Tb^{3+} main photoluminescence at 543 nm in Lu$_2$O$_3$:Tb,Hf ceramics (a), and average decay time constants derived from these traces (b). Note the continuously increasing loss of energy in nonradiative processes due to thermal quenching above 150 °C.

Thus, the question arises if there may be another way of releasing the energy stored in Lu$_2$O$_3$:Tb,Hf ceramics. As we already stated in the introduction, optically stimulated luminescence might be such an alternative. For this the most useful energy of the stimulating photons needs to be determined. Some indication on what the energy (wavelength) should be may originate from the absorption and excitation spectra recorded for specimens freshly prepared and irradiated with X-rays. The results are given in Fig. 3a (absorption) and Fig. 3b (excitation).
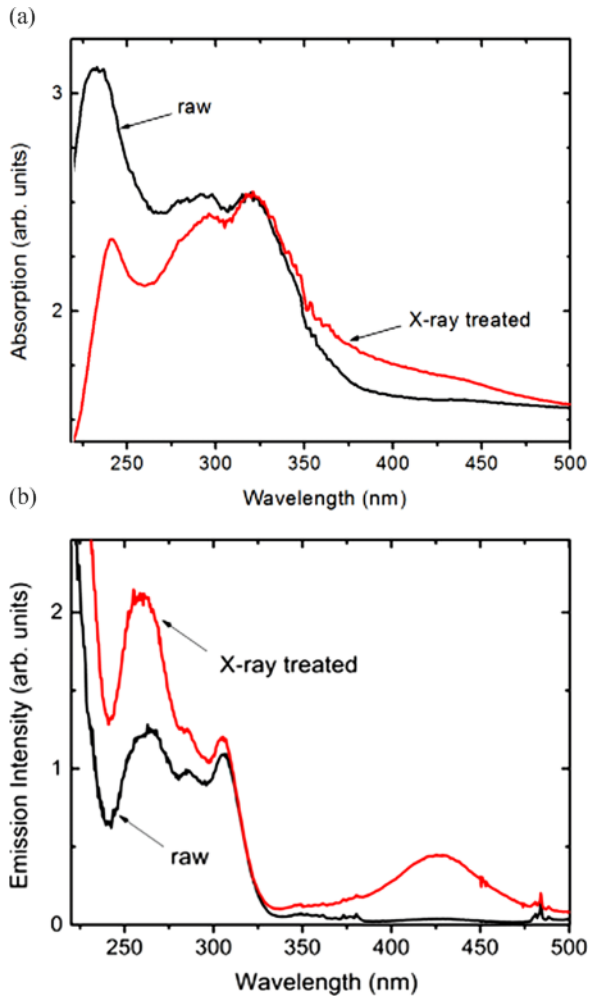
(a)

(b)

Fig. 3 (color online). Absorption (a) and luminescence excitation (b) spectra of fresh and X-ray-treated specimens. Note the extrinsic absorption/excitation feature induced by X-rays around 420 nm. The decrease of absorption of material X-rayed below ~ 300 nm is mirrored by an increase of the excitation efficiency in this region (see text).

It is immediately obvious that irradiation with ionizing radiation induces a broad band covering the long-UV and short-Vis range of wavelengths, somewhere around $400-450$ nm. The extrinsic absorption/excitation band has significant intensity, and its appearance is mirrored by a decrease of the $f \rightarrow d$ absorption intensity below ~ 310 nm and – surprisingly at first – an increase of excitation intensity in the $f \rightarrow d$ range. Above 550 nm the absorption spectra did not show any measurable new absorption

bands. Hence, ionizing radiation did not cause substantial variations in absorption above about 550 nm. Yet, due to a significant scattering of the sintered pellets we investigated, some tiny changes might be easily obscured. Therefore, at this point, it is not excluded that some variations in the absorption above about 550 nm do occur. Consequently, in the next step emissions of specimens irradiated with X-rays were measured upon stimulation with 420 nm light as well as using 980 and 780 nm IR radiation from diode lasers.

In each case the optically stimulated green Tb^{3+} luminescence (OSL) was observed, which indicated that each of the three wavelengths/energies were able to release at least some of the trapped carriers and let them pass their excessive energy to the emitting Tb^{3+} ion. However, the intensity of the OSL emission varied strongly for the three wavelengths, the highest being observed upon stimulation around 420 nm. The IR stimulations – 980 or 780 nm – produced much less green OSL emission. Especially the former was truly weak.

It is noteworthy that, since the Tb^{3+} luminescence appears above ~ 470 nm, it is easy to filter out the most effective stimulating radiation in OSL ~ 420 nm from the green emission it causes. This, combined with the significant intensity of the ~ 420 nm excited OSL, makes the 420 nm stimulation a very practical one.

Thus, in the case of the Lu$_2$O$_3$:Tb,Hf storage phosphors, the most useful optical stimulation to recover the energy entrapped in the material is by means of ~ 420 nm radiation. Fig. 4 presents the decay of the green OSL emissions upon irradiating at 980 nm (Fig. 4a), 780 nm (Fig. 4b) and 420 nm (Fig. 4c). Only upon stimulation at 420 nm the OSL signal could be reliably measured for a relatively long time, as only such stimulation produced truly intense, long-lasting OSL. This property makes the Lu$_2$O$_3$:Tb,Hf ceramics unique, as usually the useful stimulation in OSL emission is of longer wavelength than the emitted light, as was already mentioned.

Since OSL upon irradiation at 980, 780 and 420 nm generated green emission of Tb^{3+} (though of very different intensities), some changes in TL should be expected as a result of such prolonged stimulations. Indeed, as shown in Fig. 5, each of the three types of stimulations reduced the intensity of the main TL band located around 250 °C. Yet, the 980 nm photons lessened the TL only slightly. However, 30 min stimulation with the 780 nm radiation diminished the TL signal
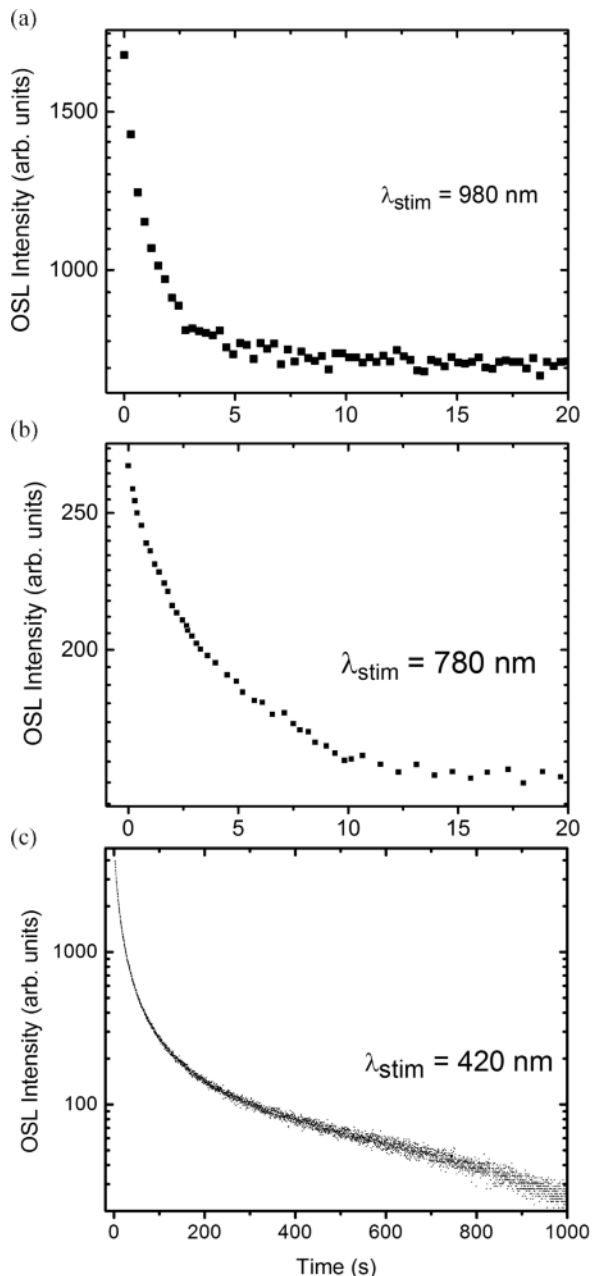
(a)

$\lambda_{stim} = 980$ nm

(b)

$\lambda_{stim} = 780$ nm

(c)

$\lambda_{stim} = 420$ nm

Fig. 4. Decay traces of green OSL of Lu₂O₃:Tb,Hf upon prolonged stimulation at 980 nm (a), 780 nm (b) and 420 nm (c). Only the most energetic (~ 420 nm) stimulation allowed to free carriers from all traps (see Fig. 5).
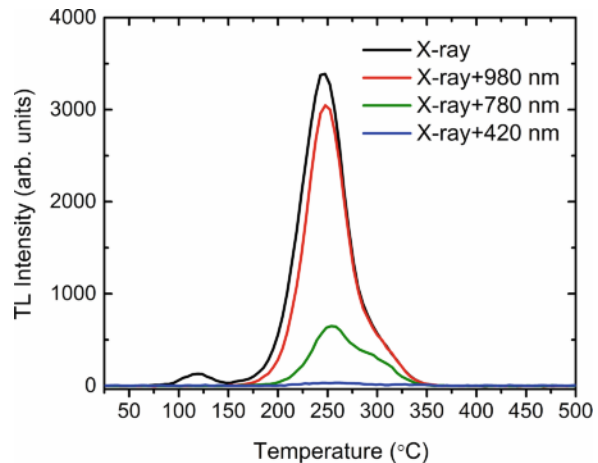

Fig. 5 (color online). TL glow curves measured following X-ray irradiation and subsequent stimulation with 980 and 780 nm diode lasers and 420 nm light of a xenon arc lamp for 30 min (see Fig. 4).
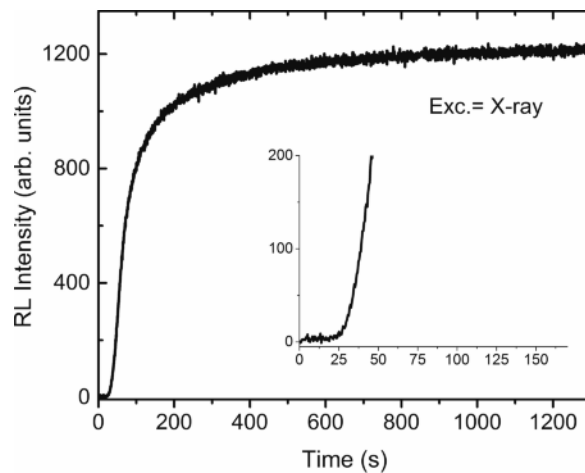

Fig. 6. Dependence of the radioluminescence intensity on the irradiation time of Lu₂O₃:Tb,Hf ceramics.

by about 75 %. Hence about 3/4 of the energy previously trapped in the Lu₂O₃:Tb,Hf ceramic phosphor was released with 780 nm radiation. Only upon stimulation with 420 nm radiation a total recovery of the stored energy was possible, which led to complete disappearance of a TL signal.

Hence, it is the ~ 420 nm stimulation which is capable of freeing all the stored energy to produce green photons by the Lu₂O₃:Tb,Hf storage phosphor. The 780 nm radiation is useful to release only a fraction of the stored energy.

It is yet interesting how efficiently the energy of the incoming X-rays is stored in the Lu₂O₃:Tb,Hf ceramic

material. Fig. 6 presents the development of the radio-luminescence intensity upon X-ray irradiation. At the early stages of the irradiation hardly any radioluminescence was recorded. Only after about 30 s the intensity of RL began to grow. Thus, it appears that when the traps are empty the energy delivered by X-rays is almost totally transferred to the traps.

When an increasing fraction of the traps becomes filled with carriers, continuously more energy is used to produce regular radioluminescence. Thus, we conclude that Lu$_2$O$_3$:Tb,Hf is very efficient in energy storage, and the traps generated by co-doping lutetia with Tb and Hf are very attractive for free carriers, electrons and holes, produced upon the impact of X-ray photons.

Finally, it should be stated that all the effects were observed repeatedly and no material aging was noticed. Also after repeated heatings of the ceramics up to 500 °C no degradation of their storing properties was observed. After recovering of the stored energy, either by heat treatment or by stimulation with 420 nm light, no extra procedure was needed to retain the ability of energy storage by the phosphor. This makes Lu$_2$O$_3$:Tb,Hf very convenient for practical usage.

Conclusion

We have shown that Lu$_2$O$_3$:Tb,Hf ceramics are efficient storage phosphors producing green emission when stimulated with heat or with 780 or $\sim$ 420 nm radiation. The latter is more suitable as it is able to release all the energy previously stored in the material, and the emission may be easily filtered out of the generated green photons upon such a stimulation. Irradiation with X-rays causes appearance of a strong extrinsic absorption around 420 nm, which may be bleached out by the $\sim$ 420 nm photons as well as by heating the materials up to about 350 °C. Repeated usage does not degrade the energy storage ability of Lu$_2$O$_3$:Tb,Hf ceramics.

Experimental Section

Thermoluminescence measurements were performed in the range of 25 – 500 °C with 4.8 °C s^{-1} heating rate. In a few cases different heating rates were used in the range of 1 – 8.6 °C s^{-1}. Prior to the TL measurements the ceramics were irradiated with white X-rays from a Cu tube for

3 min. The 543 nm photoluminescence decay traces were measured in the 25 – 500 °C temperature range using the third harmonic (355 nm) of the YAG:Nd laser for excitation and a PMT R928P side-on-type photomultiplier as a detector. The absorption spectra were recorded using a Cary-Varian 500 spectrophotometer with 0.1 nm resolution. The absorptions were detected for a freshly prepared sample as well as after irradiation with X-rays for 3 min. For the similarly treated sample (before and after irradiation) excitation spectra of the 543 nm emission were measured using a 450 W xenon arc lamp as an excitation source coupled with a 275 mm excitation monochromator equipped with a 1800 lines per mm grating blazed at 250 nm. Excitation spectra were corrected for the incident light intensity. Also optically stimulated luminescence (OSL) decay traces were measured for a sample irradiated with X-rays for 3 min by stimulating it with 980, 780 or 420 nm radiation. In the two first cases, 1 mW diode lasers were used, while for Vis excitation the 420 nm light was selected using a monochromator and a 450 W Xe arc lamp. Influence of the 980, 780 and 420 nm radiation on the thermoluminescence intensity was investigated recording the TL glow curves for samples irradiated for 3 min with X-rays and subsequently for 30 min with IR or Vis radiation. All the thermoluminescent experiment and OSL decay trace measurements were performed using an Ocean Optics HR2000 CG spectrometer equipped with 25 μm slits providing a resolution of about 1.2 nm. The temperature of the measurements was controlled using a custom-made setup.

Preparation of Lu$_2$O$_3$:Tb,Hf

Sintered ceramics of Lu$_2$O$_3$:Tb,Hf were prepared using nanocrystalline powders made by the standard Pechini method [10]. 4.9850 g of Lu(NO$_3$)·5H$_2$O, 0.0050 g of Tb(NO$_3$)·6H$_2$O and 0.0071 g of HfCl$_4$ were dissolved in 2 M citric acid with some ethylene glycol at 80 °C. Upon further heating the condensation led to the formation of a solid resin, which was finally burned in air at 700 °C for 5 h. About 0.5 g of the received powder was compacted to a pellet 12 mm in diameter under the load of 9 tons applied for 5 min and subsequently sintered in a tube furnace at 1700 °C for 5 h in a vacuum of about 10^{-2} hPa. The Tb^{3+} and Hf^{4+} contents were 0.1 and 0.2 mol-%, respectively.

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