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Thermal quenching of luminescence in $(\text{Lu,Gd,Y})_3(\text{Ga,Al})_5\text{O}_{12}:\text{Ce}$ complex garnet ceramics at high and low temperatures

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Abstract. Cerium-doped complex garnets with the general formula $(\text{Lu,Y,Gd})_3(\text{Ga,Al})_5\text{O}_{12}:\text{Ce}$ are promising materials to be used in PET and CT scanners. By modifying garnet composition (bandgap engineering), one can adjust its scintillation properties to fit a specific set of requirements. In certain compositions, Ce^{3+} luminescence intensity can decrease upon cooling (negative thermal quenching). The reason for that is still a matter of active debate. This article is focused on negative thermal quenching in Ce-doped $(\text{Lu,Gd})_3(\text{Ga,Al})_5\text{O}_{12}$ garnet ceramics. We have measured thermally stimulated luminescence, temperature dependence of the X-ray excited luminescence intensity, and other scintillation properties of samples which have different Lu and Ga content and were annealed in different conditions. We discuss that negative thermal quenching in our samples can be attributed to the process of charge carrier localization on traps at lower temperatures.

Keywords: complex garnet ceramics, Ce-doping, annealing, radioluminescence spectra, negative thermal quenching, thermal ionization.

Introduction

Cerium-doped complex garnets with the general formula $(\text{Lu,Gd,Y})_3(\text{Ga,Al})_5\text{O}_{12}:\text{Ce}$ are very promising materials to be used as scintillators (Ronda et al. 2016) and persistent phosphors (Ueda, Tanabe 2019). This class of materials is actively studied by many research teams (Nikl, Yoshikawa 2019; Ueda, Dorenbos, Bos, Kuroishi et al. 2015). The interest of researchers is stirred by the need to improve the scintillation properties of complex garnets used in medical tomography (Wieczorek et al. 2020). The available studies usually focus on the energy resolution and timing performance of scintillators. However, it is also important to study temperature stability of their luminescence properties, since that is one of the key requirements for practical applications. Scintillation detectors used in computer or positron emission tomography scanners are exposed to heat which emanates from high voltage electronics, moving mechanical parts, etc. A change in the temperature of the detector causes a change in its main properties—i.e., light output and decay time (Venetsev et al. 2017). A reliable operation of PET or CT scanners requires scintillation detectors to be minimally affected by temperature variations. Thermal stability can be ensured by the selection of the optimal chemical composition of the scintillator, which requires a detailed study of the physical processes occurring in scintillators.

In the current work, we study the temperature dependence of the main properties of $(\text{Lu,Gd,Y})_3(\text{Ga,Al})_5\text{O}_{12}:\text{Ce}$ scintillators. We specifically focus on the least studied low-temperature region, where negative thermal quenching (NTQ) has been observed.

In our previous research, we have been able to show several examples of garnet compositions in which NTQ takes place. In $(\text{Gd,Y})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (Venetsev et al. 2017), NTQ is very pronounced in a wide range of temperatures from 90 to 450 K, especially in the basic YAG:Ce composition. Those results have shown that although Gd has a significant influence on Ce emission intensity, it does not directly participate in NTQ. Gd^{3+} ions have an emission line at 311 nm which can overlap with $\text{Ce}^{3+} 4f \rightarrow 5d_2$ excitation band around 300–400 nm resulting in an efficient resonant energy transfer. This overlap increases at higher temperatures due to broadening of Ce^{3+} excitation bands, which potentially can lead to an increased Ce^{3+} emission intensity when the sample is heated up. However, this transition has been shown to occur and early saturate at very low temperatures, between 30 and 70 K (Bartosiewicz et al. 2015) with no significant changes at higher temperatures. Our earlier work (Venetsev et al. 2017) has also shown that in the range from 90 to 400 K (where significant portion of NTQ of Ce^{3+} emission takes place) there is no change in the intensity of left-over Gd^{3+} lines.

An alternative explanation is that upon cooling the localization of charge carriers on traps is occurring more efficiently due to a decrease in the mobility of carriers and increase of their lifetime on traps (Zych et al. 2000).

Experimental methods

All tested samples were prepared at the Philips Research Eindhoven facility in the form of ceramic disks 2 mm thick and 15 mm in diameter. To study the influence of Ga content on the NTQ, a set of ceramics with the composition $\text{Y}_2\text{Gd}_1\text{Ga}_x\text{Al}_{5-x}\text{O}_{12}:\text{Ce}^{3+}$ ($x = 2.0, 2.5, \text{ and } 3.0$) was used. Three other samples of $\text{Lu}_x\text{Gd}_{3-x}\text{Ga}_2\text{Al}_3\text{O}_{12}:\text{Ce}^{3+}$ ($x = 0.0, 0.3, \text{ and } 1.0$) were used to study the impact of Lu content on the temperature quenching under X-ray irradiation. Additional two samples included ceramics of $\text{Lu}_{0.33}\text{Gd}_{2.67}\text{Ga}_{2.5}\text{Al}_{2.5}\text{O}_{12}:\text{Ce}^{3+}$ annealed in wet forming gas (FG) and air (O_2).

Radioluminescence (RL) spectra were measured under continuous excitation using an X-ray tube with tungsten anode. The tube voltage and current were 40 kV and 10 mA, respectively. Emission was detected by an MDR-2 monochromator coupled to a Hamamatsu H8259-01 photon counting head. Samples were positioned in reflection geometry (Potapov et al. 2004).

Temperature-dependent measurements were carried out using a vacuum cryostat. A copper sample holder and silver glue (Leitsilber 200) were used for better thermal conductivity. The temperature dependence of RL intensity for each sample was measured at a fixed wavelength corresponding to the maximum of Ce^{3+} emission.

Thermally stimulated luminescence (TSL) measurements were performed in a following way: samples were irradiated with X-rays for 300 s at 77–80 K (using the same X-ray tube), followed by a 600s waiting time to diminish the influence of thermally active traps; then measurements of TSL intensity were carried out under a constant heating rate of 0.25 K/s using the Hamamatsu H8259 photon counting head in the integration mode. The temperature lag at such speed did not exceed 5 K, a value comparable to the overall error of the temperature measurements.

Results and discussion

To reveal a correlation between negative thermal quenching and charge localization processes we performed series of RL and TSL measurements. Temperature dependence of Ce^{3+} emission for a set of three ceramic samples of $\text{Y}_2\text{Gd}_1\text{Ga}_x\text{Al}_{5-x}\text{O}_{12}:\text{Ce}$ with Ga content of $x = 2.0, 2.5 \text{ and } 3.0$ is shown in Fig.1a (normalized at maximum). All three ceramic samples contain the usual high-temperature thermal quenching region as well as the negative thermal quenching region. The position of emission maximum changes with Ga content and is 320, 250 and 210 K for $x = 2.0, 2.5, \text{ and } 3.0$, respectively.

It has been shown in multiple works (Ogieglo et al. 2013; Ueda et al. 2015) that at high temperatures the decrease in Ce^{3+} emission intensity is attributed to thermal ionization of an electron from Ce^{3+} excited states. The fact that with the increase of Ga content we observe a low temperature shift in the position of the high-temperature quenching region indicates the lowering of the bottom of the conduction band (CB).

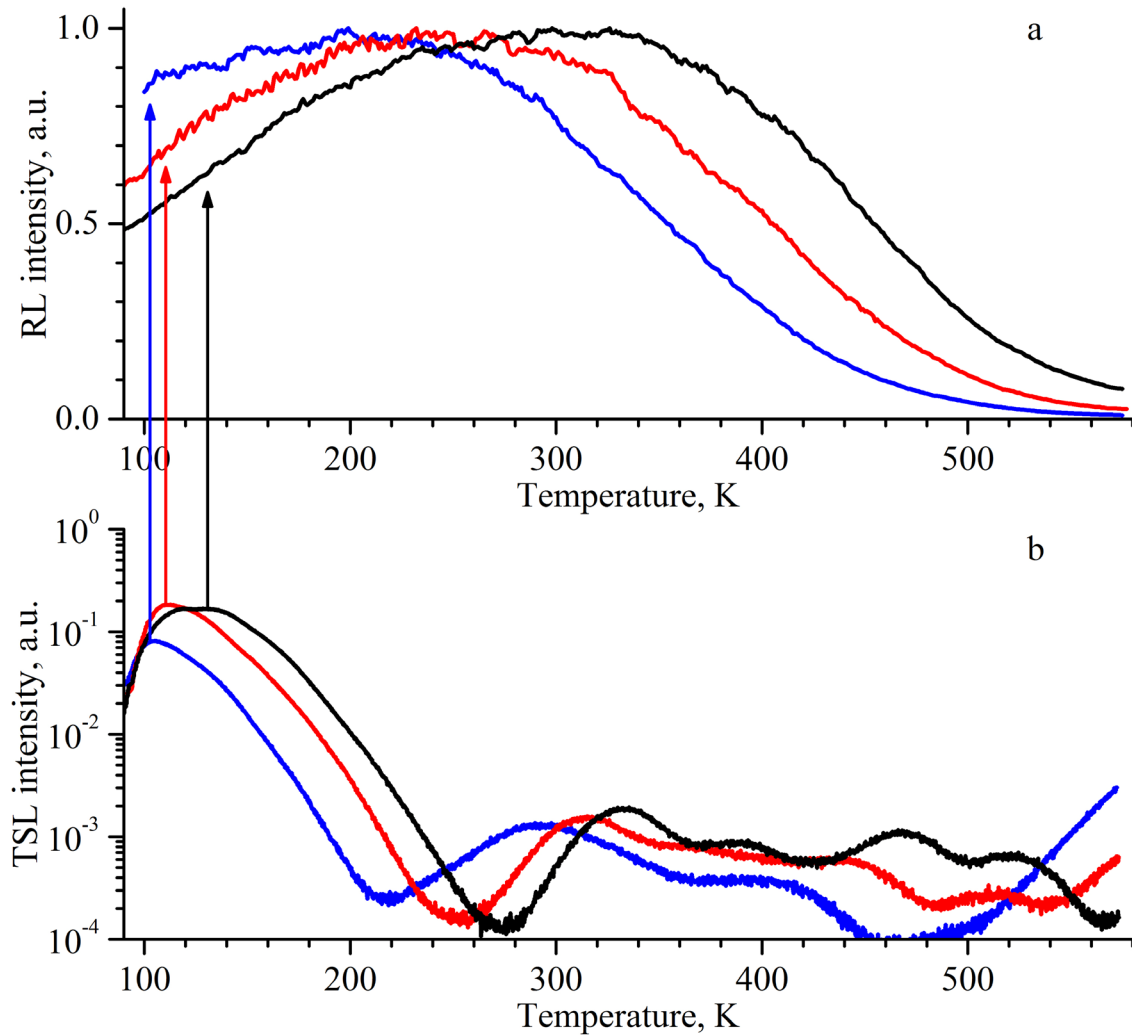


Fig. 1. Temperature dependences of RL intensity (a) and thermally stimulated luminescence (b) of $\text{Y}_2\text{Gd}_1\text{Ga}_x\text{Al}_{5-x}\text{O}_{12}:\text{Ce}^{3+}$ ceramics with $x = 2.0$ (black line), 2.5 (red line) and 3.0 (blue line)

NTQ in these samples takes place in the range from 90 to 300, 220 and 200 for ceramics with $X = 2.0$, 2.5 , and 3.0 , respectively. Furthermore, the slope of the negative thermal quenching region clearly decreases. Such behavior can be explained with the use of TSL measurements which are meant to point at the presence of thermally active traps at a certain temperature and, in some cases, to estimate the trap depth. TSL curves are shown in Fig. 1b in the same temperature range. Every curve consists of a large peak around 90–220 K, which could also be the combination of several unresolved peaks, and a set of smaller peaks at higher temperature. It is known that the latter can be attributed to various rare-earth and transition metal impurities, such as Yb, Eu, Cr, V, etc. (Dorenbos et al. 2015a; Khanin et al. 2017). The low-temperature TSL structure is usually attributed to various intrinsic defects, such as antisites or vacancies (Fasoli et al. 2011). Changes in garnet composition led to either a decrease or increase in the depth of related traps relative to the bottom of the conduction band and, consequently, to a shift of the peak maxima at the temperature scale.

In Fig. 1b, we can clearly see that positions of the largest peaks at low temperature correlate with the shape of the NTQ in Fig. 1a. For example, in $\text{Y}_2\text{Gd}_1\text{Ga}_2\text{Al}_3\text{O}_{12}:\text{Ce}$ ceramics the TSL peak is located around 90–240 K, and the corresponding NTQ range is approximately the same. In $\text{Y}_2\text{Gd}_1\text{Ga}_2\text{Al}_3\text{O}_{12}:\text{Ce}$, this peak has a lower intensity and is shifted to 90–180 K range while the corresponding NTQ curve has a flatter slope and also spans over the same range of temperatures.

Fig. 2a demonstrates temperature dependence of Ce^{3+} emission intensity in $\text{Lu}_x\text{Gd}_{3-x}\text{Ga}_2\text{Al}_3\text{O}_{12}:\text{Ce}^{3+}$ ($x = 0.0, 0.3, \text{ and } 1.0$). In this case, we did not observe the shift in the thermal ionization process,

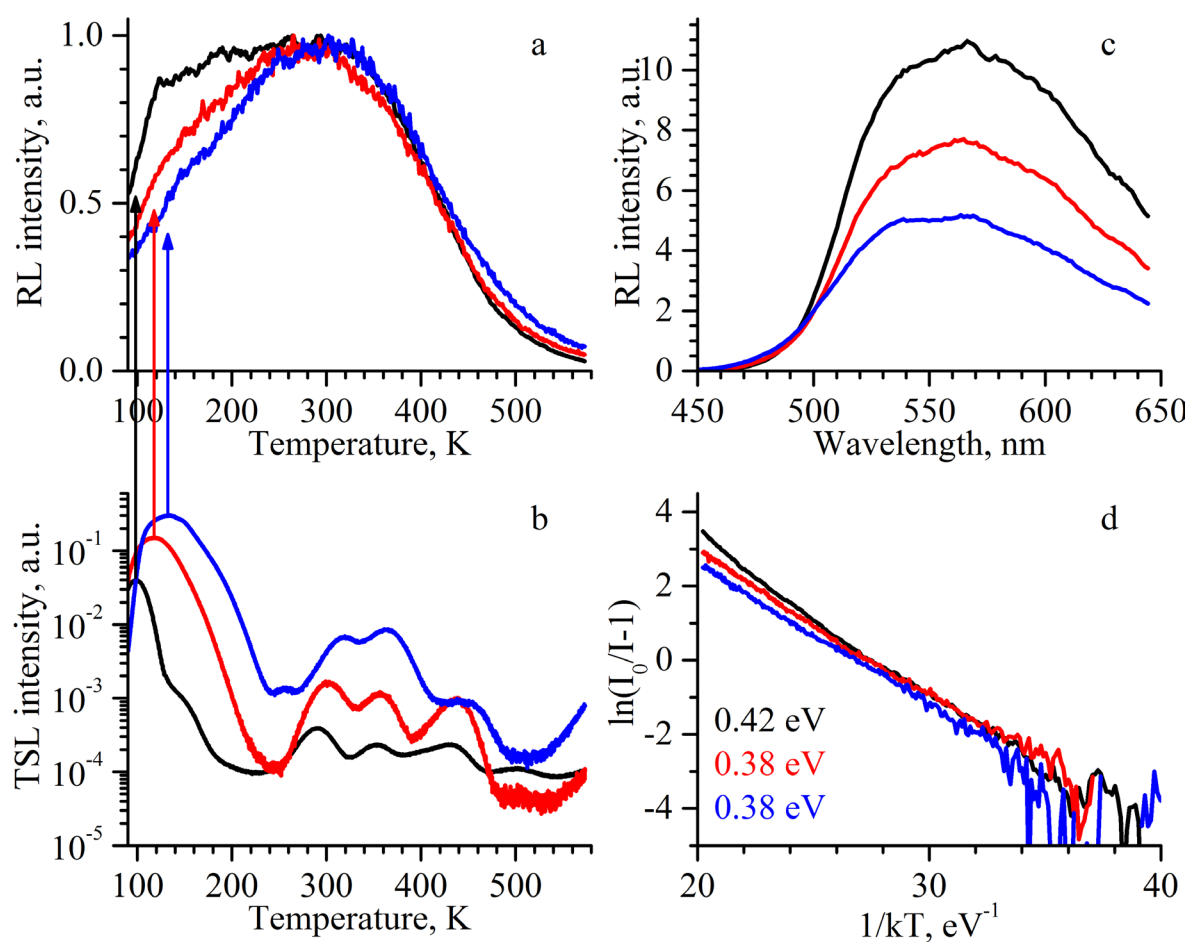


Fig. 2. Properties of $\text{Lu}_x\text{Gd}_{3-x}\text{Ga}_2\text{Al}_3\text{O}_{12}:\text{Ce}^{3+}$ ceramics with $x = 0.0$ (black line), 0.3 (red line) and 1.0 (blue line), where a—temperature dependence of RL intensity, b—thermally stimulated luminescence curves, c—RL spectra at room temperature, d—Arrhenius plots of RL temperature dependence

except for the slight change in the shape of the slope at higher temperatures. The emission maximum is located at 300 K for all samples, which ensures the best thermal stability for room temperature applications. Below 300 K, the ceramic samples behave differently. In case no Lu is present, we observe a slow decrease in intensity in the range from 300 to ~ 125 K followed by a sharp drop in intensity in the range from 125 to 90 K. The samples which contain Lu have an overall steeper slope with no sharp drop. At 90 K, ceramics with $x = 1$ has the lowest emission intensity.

TSL curves of the samples are shown in Fig. 2b. The peak structure is similar to what was observed in Fig. 1b. In this case, we can find the same patterns: at Lu $x = 1.0$, the NTQ spans from 90 to 240 K, while the first TSL peak has the range from 90 to around 230 K; at Lu $x = 0.3$, the NTQ has a slightly flatter slope and spans up to around 200 K, while the corresponding TSL peak has a decreased intensity and a range from 90 to 190 K. The most interesting picture is observed for the ceramic sample with Lu $x = 0.0$: in the range from ~ 115 to 190 K, it has a significantly smaller TSL intensity than the other samples and, at the same time, the intensity of Ce emission barely changes in that region; but at lower temperature (from 115 to 90 K) there is still an intensive TSL peak that, most probably, corresponds to traps which are responsible for the sudden drop in intensity.

We also made an attempt to determine the activation energy of thermal ionization process. This is illustrated by the Arrhenius plot in Fig. 2d. The plot corresponds to the range from 290 to 580 K. As these curves were measured at Ce^{3+} emission maximum (Fig. 2c), their shape is determined only by the processes related to energy transfer to Ce ions. The linear shape indicates that there is a single thermally activated process. The activation energy can be determined by the linear approximation where the slope is the desired value (also shown in Fig. 2d). It is clearly seen that the addition of Lu has only a slight effect on the activation energy. Since Ce 4f ground state position in the energy diagram does not

depend on the composition (Dorenbos 2013) and since the distances from the ground to the excited state and from the excited state to the bottom of the CB also stay almost the same, we can conclude that the position of the CB bottom does not significantly change upon addition of Lu up to $x = 1$. Therefore, changes in the shape of the TSL and, consequently, of the NTQ are due to the change in the concentration of traps. This is most probably explained by the absence of Lu in $\text{Gd}_3\text{Ga}_2\text{Al}_3\text{O}_{12}:\text{Ce}^{3+}$ which led to disappearance of certain types of antisites.

To further investigate the influence of trap concentration on the shape of the NTQ, we used two $\text{Lu}_{0.33}\text{Gd}_{2.67}\text{Ga}_{2.5}\text{Al}_{2.5}\text{O}_{12}:\text{Ce}^{3+}$ ceramic samples prepared under exactly the same conditions but annealed in different atmospheres—i.e., wet FG and O_2 . It is known that treatment in an oxidizing atmosphere can improve luminescence properties of multicomponent garnets and decrease their afterglow and TSL intensity (Boka et al. 2015). In our study, the intensity of Ce^{3+} luminescence of O_2 annealed ceramic (Fig. 3c) is around 40% lower than that of wet FG annealed sample. On the other hand, Fig. 3b shows that the improvement of the TSL response does take place. Both samples have a similar shape of the TSL curve with the main peak around 90–200 K, but the sample which was treated in O_2 has around 1000 times lower intensity. At the same time, temperature dependence of the RL intensity of that sample (Fig. 3a) has a much less pronounced NTQ region. Such correlation is another indirect evidence that NTQ occurs as a result of localization of charge electrons on traps.

The visible two-slope behavior of the luminescence intensity in the high temperature region in Fig. 3a is a notable aspect of these samples. One of the two components located at higher temperature has an activation energy $E_i = 0.38$ eV and basically corresponds to the thermal depth of the $\text{Ce}^{3+} 5d_1$ excited state relative to the conduction band (the approximation is shown in Fig. 3d), while the other one (between 120 and 300 K) can be attributed to the process of thermally activated transfer of an electron to a nearby trap (Grigorjeva et al. 2018).

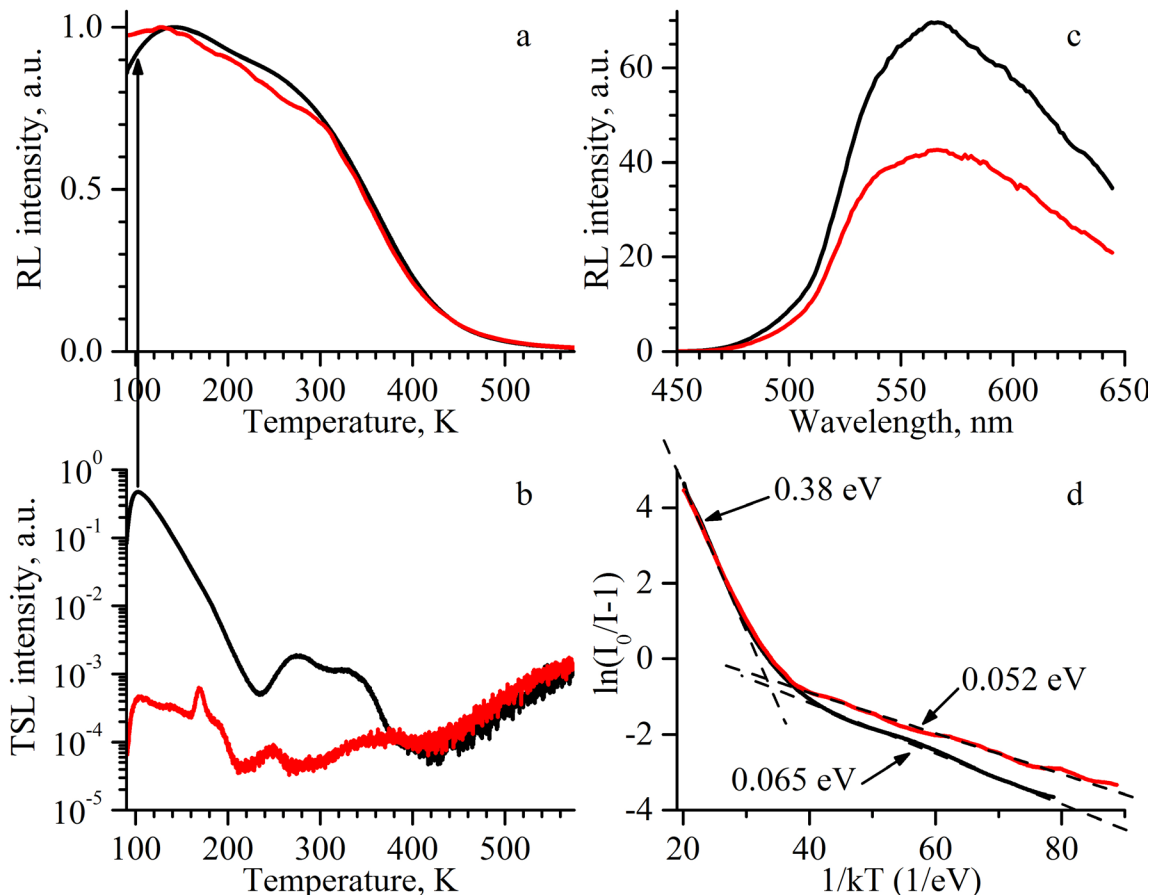


Fig. 3. Properties of $\text{Lu}_{0.33}\text{Gd}_{2.67}\text{Ga}_{2.5}\text{Al}_{2.5}\text{O}_{12}:\text{Ce}^{3+}$ ceramics annealed in wet FG (black line) and O_2 (red line), where a—temperature dependence of RL intensity, b—thermally stimulated luminescence curves, c—RL spectra at room temperature, d—Arrhenius plots of RL temperature dependence

Conclusion

Our studies have shown several instances of negative thermal quenching in Ce-doped complex garnets. In all the instances, there was a distinct correlation between the position of low-temperature TSL peaks and the location of the NTQ in the corresponding RL temperature dependence. Changes in the TSL intensity also affected the slope of the NTQ by making it steeper where the corresponding peak is higher and vice versa. Additionally, a different temperature behavior was observed in two ceramic samples which had the same composition and, therefore, were expected to display only a minimal difference between energy transfer processes. These observations have led us to a conclusion that the negative thermal quenching of Ce³⁺ radioluminescence in complex garnet compounds can be attributed to the localization of charge carriers on traps at low temperatures.

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