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Low-Temperature Luminescence of Lu_2O_3:Eu Ceramics upon Excitation with Synchrotron Radiation in the Vicinity of Band Gap Energy

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Synchrotron radiation has been used to characterize the low-temperature (10 K) spectroscopic properties of Lu_2O_3:Eu phosphors containing varying amount of the dopant. Upon excitation at energies in the vicinity of the band gap, the nominally undoped specimen produced three different emissions. The highest energy luminescence, located at 260 nm, was attributed to direct recombination of electrons and holes. We also found a broad band emission at 380 nm, which we attribute to self-trapped excitons (STEs) on the basis of the excitation spectra of the various emissions. Finally, in doped specimens, we also recorded emission produced by the Eu^{3+} activator. We found that the e−h recombination luminescence at 260 nm was severely quenched in the presence of Eu, disappearing completely at a concentration of 0.1 atom %. The 380 nm STE luminescence intensity decreased much more slowly with increasing Eu content, until at 5 atom % it too disappeared, leaving only the Eu^{3+} emission. This emission became gradually more and more intense with increasing activator content. We found that while excitons carry more than enough excitation energy, they prefer to annihilate radiatively without passing their energy to Eu^{3+} ions. Hence, we concluded that the only efficient channel of energy transfer from the excited host to the activator is through sequential trapping and subsequent recombination of free electrons and holes.

Introduction

Lu_2O_3:Eu materials, both as sintered ceramics and powders (including nanocrystalline), have been subjected to intense research in recent years. The growing interest in such material stems from its very high density of 9.42 g/cm[1−3] and its resultant high absorption coefficient for X-ray and γ radiation. The discovery that ceramic samples of Lu_2O_3:Eu efficiently convert the energy conveyed by X-ray photons into red light made this material highly attractive for real-time planar digital medical imaging with charge-coupled device (CCD) readout.[1,3−6] Indeed, the cited papers reported that Lu_2O_3:Eu containing 5% of the activator emits about 35 000 photons of red light for each MeV of excitation energy. Because the emission from Lu_2O_3:Eu falls within the region of highest quantum efficiency of CCDs, a detector combining this phosphor with CCD electronics clearly has great potential for practical usage.

At the present time, however, the published literature on the spectroscopic properties of Lu_2O_3:Eu does not provide detailed and reliable information on the various processes that occur when the energy of the excitation is close to that of the band gap. Because an understanding of such processes can provide valuable insight into the mechanism of host-to-activator energy transfer that is essential to efficient scintillation, we have undertaken the research that we are reporting here. Also, synchrotron radiation is an ideal tool for such research.

Materials and Methods

Sintered ceramics of undoped Lu_2O_3 and Lu_2O_3:Eu containing 0.05, 0.1, 0.5, 1, 3, and 5 atom % of the activator were prepared from powders by firing at 1700 °C for 5 h in a vacuum. The starting powders were obtained by precipitating the oxalates and decomposing them by heating at 1000 °C for 1 h. Before sintering, the powders were cold-pressed under 9 tons of load into pellets 12 mm in diameter. The luminescence and luminescence excitation spectra were recorded as excited by synchrotron radiation at the Superlumi station of Hasylab, Germany,[7] in two consecutive pulses separated by 200 ns. For the excitation spectra the accessible range of wavelengths was 50−334 nm, and the results were corrected for the variations in light intensity and grating characteristics over this range. Luminescence spectra were similarly corrected for any variations in the characteristics of the measurement instrumentation, such as the sensitivity of the detector (photomultiplier tube/CCD)

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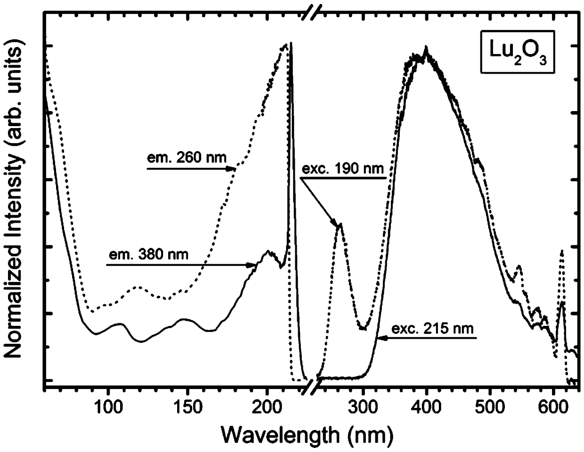

Figure 1. Excitation spectra of 260 nm (e−h recombination) and 380 nm (STE) emissions and luminescence spectra excited at 190 nm (band-to-band transition) and 215 nm (FE formation). Note the shift between peaks of both excitation curves (representing the FE stabilization energy) as well as the disappearance of the e−h recombination luminescence upon 215 nm stimulation. In this and subsequent figures, all measurements were performed at 10 K.

and the grating efficiency. The measurements were performed at 10 K in a cryostat equipped with a turbomolecular pump to ensure vacuum on the order of 10^{-9} hPa. Time-resolved emission spectra were taken in two time windows with different delays after each excitation pulse: The fast component was integrated for 50 ns beginning 3 ns after the excitation pulse (to skip the excitation light scattered from the sample), while the slow constituent was recorded by integrating the signal for 70 ns starting 120 ns after the excitation pulse. For emission spectra, since all the important luminescent features were broad, the resolution was only about 10 nm, and for excitation spectra it was about 2.5 nm.

Results and Discussion

First let us examine the nominally undoped ceramic sample of Lu_2O_3. In Figure 1 we present emission spectra excited at 190 and 215 nm, together with the excitation spectra of the characteristic luminescent bands peaking at 260 and 380 nm. In emission spectra we can distinguish three main features: a band peaking around 260 nm, a broader and stronger band with a peak around 380−400 nm (hereafter referred to as 380 nm luminescence), and a few line-type emissions of very low intensity, the strongest of which appears at 612 nm. The line emissions, as will become evident shortly, are clearly related to the Eu^{3+} ion, traces of which are present even in the nominally undoped sample. As revealed by their excitation spectra, however, the two broadband emissions must be of quite different origin, not only from the lines but also from each other. For the luminescence peaking around 380 nm we see two main features in its excitation: One is a prominent sharp component at 215 nm, whose shape is characteristic for the formation of a free exciton (FE).[8−11] This is accompanied by a broader and less intense mound on its short-wavelength side, which is clearly related to the fundamental valence-to-conduction band absorption of the host lattice. A similar feature with the same origin is seen more clearly in the excitation spectrum of the 260 nm luminescence. This excitation spectrum is much simpler, containing only one band, which climbs gradually from 160 nm to a maximum at about 212−212.5 nm and then falls off sharply to the baseline in the next 4 nm. From the location of the peak and the previously found position of the FE excitation we can estimate the binding energy of the FE as 0.06−0.08 eV, which is a reasonable although somewhat low value for oxides.[11] We should note that there are also other features in the excitation spectra of both the 260 and the 380 nm luminescence bands at even higher energies. These begin at around 90 nm and probably extend well below 50 nm, the short wavelength limit of our experiments. This broad high-energy component has previously been found in Y_2O_3, the isostructural analogue of lutetia, and attributed to the creation of two e−h pairs or one e−h pair and a secondary exciton by a single excitation photon.[9] Such an assignment is reasonable because multiple elevation of electrons from valence to conduction band by one incoming high-energy photon is ruled by the 2.3 factor of energy loss.[2,12] Because we have already located the absorption edge at about 212 nm, we estimate the energy gap in Lu_2O_3 to be 5.8 eV; consequently, the creation of two e−h pairs by a single excitation photon requires that it carry at least $5.8 \times 2.3 = 13.35$ eV of energy. This translates into a wavelength of about 93 nm, almost perfectly matching the onset of the aforementioned high-energy excitation band, clearly supporting our analysis and assignment.

Excitation into the FE line at 215 nm generates only one prominent luminescence feature, a broad band located around 380 nm. This emission, however, does not have the shape characteristic for a FE but rather that for a self-trapped exciton (STE). This is in fact a typical situation in oxides,[9−11] and an effect similar to what we see here has already been reported for Y_2O_3, a structural analogue of lutetia.[13] Thus although irradiation with 215 nm creates FEs, these become self-trapped almost immediately so that only STE entities remain, which then annihilate radiatively to create the broad emission band peaking around 380 nm. This luminescence also appears upon excitation with shorter wavelengths (below 212 nm), characteristic for band-to-band absorption. Thus even an electron elevated all the way into the conduction band can rapidly find a hole left in the valence band to form a STE, whose ultimate annihilation produces the characteristic STE luminescence around 380 nm. Whether this process proceeds directly, through sequential trapping of free carriers, or involves the intermediate formation of FEs we cannot ascertain; it is simply too fast for us to measure.

However, band-to-band excitation (190 nm) gives rise to another more energetic emission, at around 260 nm, that is

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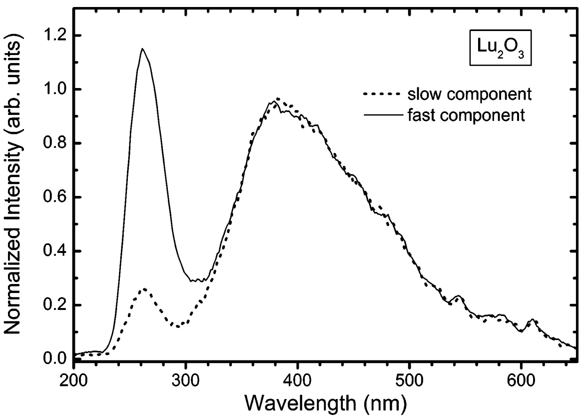

Figure 2. Time-resolved luminescence spectra excited with 190 nm light, showing that the e−h recombination emission at 260 nm is significantly faster than the STE luminescence at 380 nm. The time window for the fast component was 3−53 ns, and for the slow component it was 120−190 ns after the excitation pulse. See also Figure 3.

not generated by excitation into the FE line. From the excitation spectrum of this emission it is clear that its appearance requires elevation of an electron from the valence band all the way up to the conduction band, thereby creating free electrons and holes (e−h). Hence, we assign this luminescence to a direct recombination of e−h pairs. Both the 260 and the 380 nm emission bands are very similar to those reported by Cook et al.[14] for undoped Lu_2O_3 irradiated with X-ray radiation at low temperature. These researchers, however, assigned the two emissions quite differently, ascribing the higher-energy component (which they located at 255 nm) to an STE emission and the band around 380 nm to a self-trapped hole luminescence. This is inconsistent with our results which, as we have seen, are strongly supported by the excitation spectra. This demonstrates the power of synchrotron radiation experiments in analyzing the various spectroscopic processes that take place when materials are excited in the vicinity of their band gaps.

Further proof of the different origins of the 260 and 380 nm emissions can be found in time-resolved luminescence measurements, whose results are presented in Figure 2. Clearly, the luminescence that appears immediately after the excitation pulse contains a quite prominent high-energy component, peaking around 260 nm, that is generated by e−h recombination. In contrast, when the luminescence is recorded with a significant delay after the excitation pulse the dominant emission is that from the STE, whereas the e−h recombination emission, while still present, is greatly diminished. The different kinetics can be readily seen in the decay traces of the two emissions, as shown in Figure 3. Although neither of these emissions decays as a pure exponential, the e−h emission is faster by far, dropping by more than 1 order of magnitude over the accessible 200 ns time span while the intensity of the STE luminescence hardly changes at all.

Now let us consider the Eu^{3+} luminescence. The appearance of such luminescence in even the nominally undoped specimen should not be surprising, because the red emission of Eu in such oxidic hosts is so efficient as to allow the ion to be detected at levels below 100 ppm. As we have already seen in Figure 1, the Eu^{3+} luminescence is noticeably stronger for the shorter wavelength excitation of 190 nm than for the longer at 215 nm. This indicates that the transfer of energy to the activator by recombination of sequentially captured mobile electrons and holes may be more efficient than the capture and recombination of a FE. Indeed, as we shall see later, the appearance of the weak Eu^{3+} emission lines upon excitation with 215 nm photons may arise not from exciton-to-Eu^{3+} energy transfer at all but rather from direct excitation of Eu^{3+} ions into their charge-transfer (CT) state, whose absorption is also located in this range of wavelengths. This will become more evident from results for samples intentionally activated with Eu^{3+} ions, to which we now proceed.

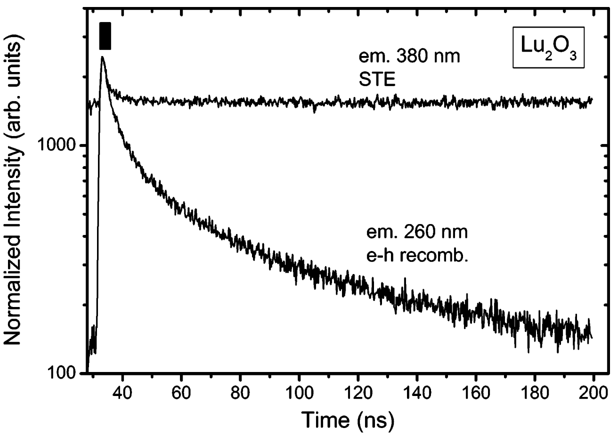

Figure 3. Luminescence decay kinetics, demonstrating that the 260 nm e−h recombination luminescence is much faster than the 380 nm STE emission. The bar at the top left corner represents the duration of the excitation pulse. Compare with Figure 2.

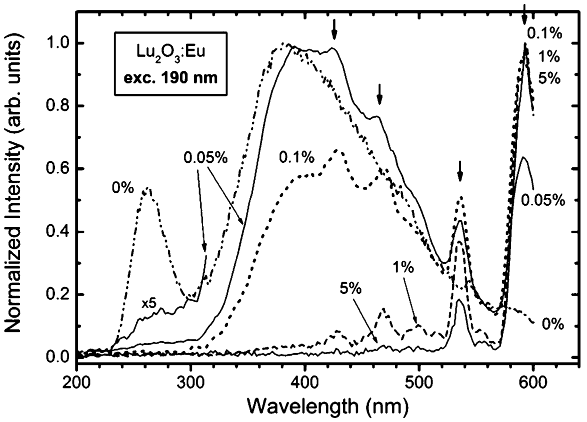

Figure 4. Variations of luminescence spectra with Eu content upon 190 nm excitation. Note that only a trace of the e−h recombination luminescence (260 nm) remains in the 0.05% specimens and disappears completely in the 0.1% samples. The 380 nm STE emission is still well-developed in the 0.1% material and remains detectable even in the 1% sample. Only in the 5% material is the luminescence totally quenched. The Eu^{3+} luminescence becomes progressively stronger with increasing content of the dopant, but luminescent transitions from the levels located above the $^5D_0$ state are hardly observed for the highest Eu concentration, leaving only the peak (actually three unresolved lines) at 590 nm. In this figure we intentionally omit the still stronger Eu^{3+} emission located at 612 nm, which would be well off the vertical scale. Arrows point to Eu^{3+} luminescent lines. Luminescence from higher levels disappears for higher Eu contents due to an increasing efficiency of cross-relaxation.

In Figure 4 we present a set of emission spectra for samples containing progressively increasing levels of Eu, as

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generated by 190 nm excitation, which we already showed to result in elevation of electrons up to the conduction band, leaving holes in the valence band. These spectra, normalized with respect to the strongest emission in each case, reveal how the progressive increase in Eu^{3+} content makes the activator more and more effective in competing with other entities for the energy stored in and conveyed by such mobile carriers. Consequently, the emission from excited Eu^{3+} ions becomes the dominant feature of the spectrum, while emission from other sources becomes completely quenched.

However, a closer look at the spectra reveals that the 260 nm e−h recombination luminescence is much more sensitive to the presence of Eu^{3+} than is the STE emission at 380 nm. The former peak has significant intensity only in the nominally undoped sample. When the Eu content is raised even to the very low level of 0.05%, the 260 nm luminescence dwindles to only a trace and disappears entirely when the Eu content is doubled to 0.1%. The 380 nm emission, in contrast, is considerably more persistent; while its intensity also decreases with rising Eu content it is still quite strong in the 0.1% sample, and vestiges remain even when the Eu concentration reaches 1%. Thus, we see that Eu^{3+} ions compete quite efficiently for the energy of electrons excited to the conduction band of the Lu_2O_3 host and that recombination of e−h pairs through Eu^{3+} ions is the preferred relaxation path. If, however, before reaching a Eu^{3+} site, an electron in the conduction band happens to pair with a hole in the valence band (to form a STE), this entity is much less effective in transmitting its energy to the dopant and may annihilate radiatively even when the lattice contains a substantial amount of Eu^{3+}. Only when the Eu content reaches 5% is there enough to intercept virtually all of the electrons and preclude any significant degree of exciton formation. In such case the relaxation of virtually all of the e−h pairs occurs only through Eu^{3+} ions, and consequently only the red luminescence of Eu^{3+} is observed.

At first, the relatively inefficient quenching of the STE luminescence by Eu^{3+} ions may appear surprising. The STE emission overlaps nicely with a number of Eu^{3+} excited levels of the 4f configuration, especially those located around 350−420 and 460 nm,[3,5,15,16] which is generally considered to be a favorable condition for both radiative and nonradiative energy transfer from STE to dopant.[17,18] However, neither of these mechanisms appears to be very efficient, possibly because the Eu^{3+} ion is such an efficient scavenger of electrons that excitons can form only at too great a distance for efficient STE−Eu^{3+} interaction. Thus an increase in Eu content necessarily reduces the volume in which STEs can form, ensuring that more and more free electrons and holes recombine directly on the activator ions without formation of an intermediate exciton state. In other words, the excitonic luminescence appears upon the band-to-band excitation only if the concentration of Eu^{3+} ions is too low to be able to intercept all the free carriers created before part of them form STEs. This is a typical situation when two centers compete for the same excitation energy.

Figure 4 also gives us information about how the relaxation processes that occur within Eu^{3+} ions change as the concentration of these ions increases and thus as their mutual interaction intensifies. We note that with an increase of Eu content the intensity of the 535 nm emission relative to that at 590 nm systematically decreases. The line at 590 nm is due to $^5D_0 \rightarrow {}^7F_1$ radiative relaxation of Eu^{3+}, and the 535 nm luminescence results from $^5D_1 \rightarrow {}^7F_1$ transitions.[15,16] Clearly, when the Eu concentration increases the nonradiative relaxation from the $^5D_1$ down to the $^5D_0$ level becomes more efficient, and emission from the latter becomes more significant compared to that from $^5D_1$. This effect becomes progressively greater as the Eu content increases from 0.05 up to 5%. Such an increasing efficacy of the $^5D_1 \rightarrow {}^5D_0$ *nonradiative* relaxation with growing Eu content is attributed to cross-relaxation[19] between two neighboring Eu^{3+} ions, as has been discussed elsewhere.[20] The same holds true for still higher-energy lines located at 428, 468, and 498 nm. Their intensities are very low for all concentrations, and they overlap with the stronger STE emission, which make them hard to investigate. From results published by Karbowiak and co-workers[16] it becomes clear that the cross-relaxation between two Eu^{3+} ions is indeed possible. The energy separations between the $^5L_6$, $^5D_3$, $^5D_2$, $^5D_1$, and finally $^5D_0$ excited levels are such that the energy may be used to excite an electron from the ground $^7F_0$ state to the $^7F_3$ or $^7F_4$ level of the nearby located unexcited Eu^{3+} ion. The host lattice offers two different symmetry sites for metal ions. One is centrosymmetric, S_6, and one is noncentrosymmetric, C_2. For the S_6 site the electronic transitions from $^7F_0$ to $^7F_3$ or to $^7F_4$ are totally forbidden.[16] Therefore, Eu in the S_6 site cannot be the ion which receives the energy from the nearby located excited Eu^{3+} ion. However, Eu in both S_6 and C_2 may be the excited ion which passes some of its energy to the nearby placed Eu ion in the ground state through the cross-ralaxation mechanism. Measurements allowing a deeper analysis of this reasoning could bring fascinating results indeed. This, however, does not belong to the subject of present paper.

In Figure 4 yet another effect may be noted. Namely, the STE band is clearly red shifted for samples doped with Eu comparing to the pure material. At present we cannot offer any reasonable explanation of this phenomenon. Maybe excitation spectra recorded for tails of the luminescence band, somewhere around 340 and 510 nm, would be helpful for deeper analysis. Still, the effect may be interesting and worthy of further investigation to understand the physics standing behind it. What is clear is that the CT absorption of Eu^{3+}, which we shall see in Figure 5, does not overlap with the STE emission so it cannot directly deform, reabsorbing the high-energy tail of the STE luminescence.

Further information about the process of energy transfer to the Eu ions is provided by the excitation spectra presented in Figure 5. Here we see that at low concentrations of Eu^{3+}

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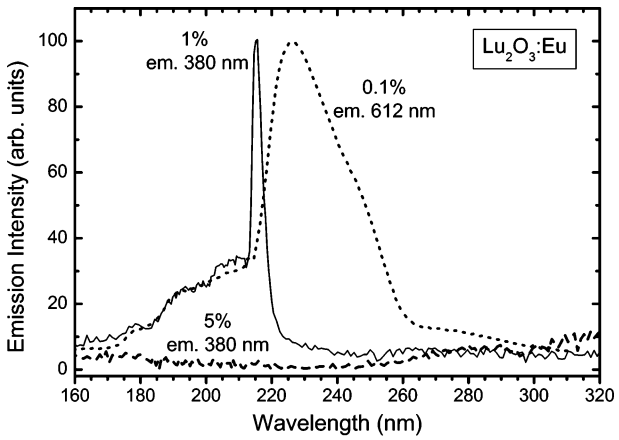

Figure 5. Excitation spectra of various emissions observed in Lu_2O_3:Eu. Note that the CT absorption band of Eu^{3+} (peaking around 227 nm) overlaps with the narrow line representing FE creation (215 nm). This overlap makes it impossible to excite the excitonic emission in Eu-containing materials without simultaneous stimulation of the dopant. However, the Eu^{3+} excitation shows no trace of the sharp peak characteristic of FE formation, indicating the absence of any significant energy transfer from exciton to Eu^{3+}. The absence of any excitation line for the 380 nm luminescence in the 5% specimen demonstrates that high Eu content prevents the formation of excitons.

(0.1%) the ion receives its energy largely through the broad CT band between about 215 and 260 nm, clearly unrelated to the excitation patterns of the emissions from either the direct e−h recombination (260 nm) or the STE annihilation (380 nm). Indeed, as stated earlier, no sign of the former is seen at all. The broad shoulder extending to about 180 nm on the short-wavelength (high-energy) side may merely reflect some unassigned complexity in the CT band; we note, however, that it has just the shape and location that one would expect for the now nonexistent (completely quenched) e−h recombination luminescence, a further indication that the free electrons and holes are now recombining at Eu^{3+} sites.

In contrast, the STE luminescence at 380 nm is still visible upon the excitation with 190 nm light even when the dopant concentration reaches 1%. Although considerably weaker than it was at lower Eu concentrations, the excitation spectrum is readily measurable. This is especially striking in view of the strong Eu absorption in the very wavelength range where FE is formed (around 215 nm), which must necessarily intercept a significant portion of the excitation energy that would otherwise go to FE creation. This may well be the underlying reason for the absence of any detectable STE emission from the 5% sample: it is not that the emission is quenched through energy transfer to the Eu^{3+} ion but rather that the STE entities are not formed in the first place. The CT absorption is so strong that practically all the excitation is being captured *directly and only* by Eu^{3+}.

Another noteworthy point is that while it is perfectly conceivable that the Eu^{3+} ion could receive some excitation energy through the migration of FEs, there is no evidence that this actually takes place to a significant degree under short pulse conditions. Specifically, in the excitation spectrum of the 612 nm luminescence at any concentration of Eu^{3+}, we do not see any sign of the sharp component at around 215 nm that is so characteristic of FE formation. Consequently we conclude that excitons formed with 215 nm light simply do not transfer their energy to Eu^{3+} ions and that the only efficient channel for energy transfer from the excited host to the activator is by means of the recombination of free electrons and holes at the Eu^{3+} sites. When the activator content exceeds 1% any competitive *radiative* relaxation of electrons and holes becomes insignificant. This conclusion does not exclude the possibility of nonradiative energy dissipation by the carriers, but these are simply not efficient enough to play a significant role. Thus, all our results form a consistent and coherent picture of the excitation process.

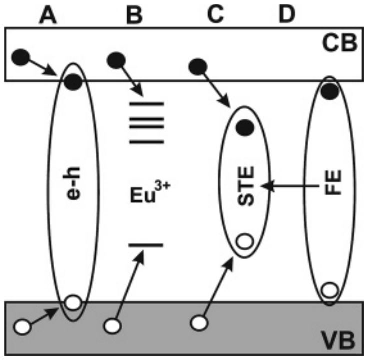

Figure 6. Summary of the various spectroscopic processes taking place in Lu_2O_3. In the absence of Eu free electrons and holes recombine directly (A) or form a STE which annihilates radiatively (C). STE may also be created through intermediate creation of a FE (D). In the presence of Eu^{3+} ions recombination of free carriers occurs mostly through the dopant (B), which quenches other emissions: e−h recombination and STE annihilation.

All the findings presented and discussed above are summarized in Figure 6 presenting a scheme of the main spectroscopic processes occurring when undoped or Eu-doped lutetia is excited in the vicinity of band gap energy. Excitation of electrons up to the conduction band leads to e−h recombination luminescence (A). However, when Eu is introduced to the Lu_2O_3 host the free carriers, instead of such a direct recombination, prefer to recombine with the use of Eu^{3+} ions (B), whose emission appears at the expense of the process A. The free carriers may yet combine and form a STE (C), which annihilates sending off a luminescent photon characteristic for this entity. This process is also diminished by addition of Eu^{3+} ions but to a much lower degree; it persists up to the concentration of 1%. Finally, absorption of a light photon whose energy is just a little bit smaller than the band gap creates FE, which quickly becomes self-trapped (D) and, eventually, annihilates radiatively (D). Also this process is systematically quenched, at least partially, by addition of Eu because FE absorption coincides with the strong CT absorption of Eu^{3+}.

Conclusions

The use of synchrotron radiation has enabled us to determine the exact separation of the valence and conduction bands, whose corresponding absorption we found at 212−212.5 nm. In the undoped material at 10 K, light of higher energy (190 nm) raises electrons into the conduction band, which subsequently recombine with valence band holes to generate a rapidly decaying high-energy emission located around 260 nm. When irradiation is performed by somewhat less energetic light (215 nm), only FEs can be formed; these entities quickly become self-trapped, and upon annihilation create a slowly decaying broad-band luminescence peaking around 380 nm.

The picture is altered by the presence of Eu^{3+}, which even at relatively low concentrations provides a more favorable alternative mechanism for e−h recombination, effectively quenching the 260 nm emission. However, the excitons, once created, do not transfer their acquired energy to Eu^{3+} to any significant extent. Consequently, their emission is much less sensitive to the presence of europium, so that independent emissions from both entities can be observed even at Eu concentrations exceeding 1%.

It is noteworthy that the host-to-activator energy transfer is quite efficient even at the very low temperature of 10 K, when the mobility of the carriers (especially holes), which requires assistance of phonons,[2,21] must necessarily be quite low. Hence, we can conclude that the Lu_2O_3 host and Eu^{3+} activator create a system where conditions are favorable for radiative recombination of e−h pairs through the activator especially when its content exceeds 1%. Our findings are consistent with the already cited literature reporting that the highest efficiency under ionizing excitation is achieved at Eu concentrations in the range of 3−5%. For such concentrations the recombination of electrons and holes through Eu^{3+} is the only efficient pathway for their relaxation.

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