Quantum efficiency of europium emission from nanocrystalline powders of Lu$_2$O$_3$:Eu

Quantum efficiency of europium emission from nanocrystalline powders of Lu_2O_3:Eu

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Abstract
Three series of nanocrystalline powders of Lu_2O_3:Eu with Eu concentration
varying from 0.05 to 13% were prepared. All specimens were obtained through
combustion synthesis using urea or glycine as the fuel. The powders of the first
series consisted of materials with crystallites about 13 nm in size and were
prepared with urea. For the next series of powders, made with glycine, the
crystallites were about 30 nm in size. The powders of the third series differed
from those of the second one in that they were co-doped with 1% of Ca. For the
series made with urea the quantum efficiency was highest for 3% of Eu and never
exceeded about 30%. For glycine-prepared specimens the highest quantum
efficiency was about 90%. Without the Ca co-doping such a value could be
obtained for specimens doped with 5% of Eu, while in the series co-doped with
Ca 85–90% quantum efficiency could be maintained for all concentrations in
the range 3–10%. A significant number of OH groups were proved to be left
in the final product obtained with urea. The low quantum efficiency of these
powders is attributed to this effect. The results prove that properly prepared
nanocrystalline phosphors can produce luminescence efficiently.

1. Introduction

There is observably a growing interest in the manufacturing and investigation of the properties
of nanostructured materials. These are characterized by particle sizes smaller than 100 nm
at least in one direction. Properties of nanoparticulate materials usually differ, sometimes
significantly, from those of their bulk counterparts. The differences may arise from the much
higher surface-to-volume ratio and/or the quantum confinement of the charge carriers as well
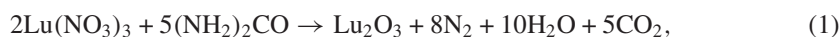as the geometrical confinement of the lattice phonons [1–5]. In insulating materials, such

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as the title compound Lu_2O_3, quantum confinement can, however, be expected only for very small crystallites, probably well below 10 nm.

In recent years we have investigated the properties of both nanocrystalline powders and sintered ceramics of Lu_2O_3 doped with various rare earths [6–11]. In our previous papers we reported on, for example, optimal preparation conditions for making fully crystalline nanoparticulate Lu_2O_3:Eu using a combustion procedure [12–14] and urea or glycine as the organic fuel. We found that the preparation conditions can greatly influence both the crystallinity and the luminescent properties of the products [7, 8, 11, 15]. We also showed that properly synthesized Eu-doped Lu_2O_3 can be an efficiently luminescent material, both under optical and x-ray stimulation. The glycine fuel was found to be more appropriate for producing lutetia-based luminophors showing efficient emission. For the glycine-prepared samples concentration quenching, as deduced from the shortening of the luminescence lifetime, appeared for specimens with Eu content exceeding about 10%, while for urea-prepared samples an analogous effect became visible above 3% content of the dopant [15]. In either case the radiative lifetime of the Eu emission was longer ($\sim$1.6 ms) than in sintered materials ($\sim$1.1 ms) consisting of micron-sized particles. The observations encouraged us to perform a detailed analysis of the quantum efficiency of Eu emission in nanocrystalline powders of Lu_2O_3:Eu. This appears especially interesting as some researchers have reported a significant increase of emission intensity induced by reduction of crystallites size to the nanometre range [16, 17]. In [16] a fivefold increase of luminescence intensity was claimed for nanosized Y_2O_3:Eu compared to its classical analogue. These results were afterwards critically analysed by van Dijken [18], who noted that such a result would imply 450% quantum efficiency for nanometric Eu-doped yttria. In view of this, research on the quantum efficiency of our nanoparticulate Lu_2O_3:Eu appeared especially interesting.

2. Materials, experiments, and calculation procedure

Three series of nanocrystalline powders of Lu_2O_3:Eu, henceforth denoted as series A, B, C, were prepared by means of combustion synthesis. Each series consisted of specimens doped with 0.05, 0.2, 1, 3, 5, 7, 10, 13% of Eu with respect to Lu. Urea, $CO(NH_2)_2$, or glycine, NH_2CH_2COOH, was used as the organic fuel. In a typical synthesis, 1.5 g of $Lu(NO_3)_3 \cdot 5H_2O$ (the appropriate part of which was replaced with the equivalent amount of $Eu(NO_3)_3 \cdot 6H_2O$) and 0.5 g of urea (series A of materials) or 0.42 g of glycine (series B) were dissolved in about 1 cm^3 of water in a 150 cm^3 beaker. Materials of series C were also prepared with glycine as the fuel, but additionally 0.01 g of $Ca(NO_3)_2 \cdot 4H_2O$ was dissolved together with other ingredients. Each of the solutions was dried out by heating up to about 140 °C; the solid residues were kept at this temperature for a few hours. At this point we got a uniform, atomic scale mixture of the nitrates and the fuel. The beaker with the solid residue was put in a furnace preheated to 650 °C; this temperature had previously been found to be the most suitable for the synthesis [8, 9]. Within 5–10 s a vigorous but not explosive reaction began, during which a copious amount of gas was produced and a significant amount of heat was liberated. Independently of the fuel used, the reactions ended within about 30 s. The reaction stoichiometries can be described as follows:

$$2Lu(NO_3)_3 + 5(NH_2)_2CO \rightarrow Lu_2O_3 + 8N_2 + 10H_2O + 5CO_2, \qquad (1)$$

$$6Lu(NO_3)_3 + 10NH_2CH_2COOH \rightarrow 3Lu_2O_3 + 14N_2 + 25H_2O + 20CO_2. \qquad (2)$$

In the actual processes some nitrogen oxides are also created (especially in the case of the reaction with urea), which should be taken into account by the experimenter. The products

were left in the furnace for 30 min to allow the organic residues to burn out completely. The commercial Y_2O_3:5% Eu used in our experiments was supplied by Philips.

Emission, excitation, and reflection spectra were measured on a SPEX Fluorolog spectrophotometer, model F2002, equipped with two double-grating SPEX 1680 monochromators of 0.22 m focal length. A 300 W Xe lamp was used as an excitation source. The excitation spectra were corrected for the incident light intensity. For the measurements the powders were put in a sample holder made of aluminium. It was a 50 mm × 50 mm plate, 5 mm thick, in a middle of which there was a hollow 3 mm wide, 12 mm high, and 1.5 mm deep. The hollow was filled with a measured amount of powder, whose surface was flattened with a plate of glass. Each sample prepared in such a way was put in the spectrophotometer chamber. Hence, the configurations of the measurements were practically identical for all experiments. $BaSO_4$ was used as the standard of reflectivity ($R(BaSO_4) = 0.91$).

X-ray diffraction (XRD) patterns were taken with a DRON-1 diffractometer, using Cu Kα radiation ($\lambda = 1.5418$ Å). The diffractograms were recorded with $0.1°$ steps for 2Θ between $10°$ and $120°$. The crystallite sizes were estimated from Scherrer's formula [19]:

$$D = \frac{0.9\lambda}{\cos\theta\sqrt{\beta^2 - \beta_0^2}},$$ (3)

where D denotes the average size of the crystallites, β is the observed full width at half-maximum of a diffraction line located at θ, β_0 represents the scan aperture of the diffractometer, and λ stands for the x-ray radiation wavelength.

IR transmission spectra of the powders were taken with a Brüker FTIR IFS 113 V spectrometer using Merck's poly(chlorotrifluoroethylene) or Nujol oil.

The quantum efficiencies of the Lu_2O_3:Eu powders investigated were calculated assuming that the value for the commercial Y_2O_3:Eu phosphor supplied by Philips is 90%. This value comes from the phosphor's technical specification, but in older literature we find the efficiency quoted as 80% [20]. The following formula was applied in the calculations:

$$q_X = \frac{1 - R_{ST}}{1 - R_X}\frac{\Phi_X}{\Phi_{ST}}q_{ST},$$ (4)

where q_X and q_{ST} are the quantum efficiencies of the specimen investigated and the standard (commercial Y_2O_3:Eu) material, R_X and R_{ST} are the reflectances of the specimen and the standard, and Φ_X and Φ_{ST} are the total measured luminescence efficiency (the integrated area under the emission spectrum) of the specimen and the standard, respectively.

The reflectances R_X and R_{ST}, respectively, of the Lu_2O_3:Eu and Y_2O_3:Eu investigated were calculated from the formula

$$R_N = \frac{A_{RN}}{A_{RB}} \times 0.91,$$ (5)

where R_N stands for a sample reflectance ($N = X$ and ST for lutetia powders and the Y_2O_3:Eu standard, respectively), and A_{RN} and A_{RB} are total areas under the measured reflection spectra for the sample investigated and the $BaSO_4$, respectively. In this formula the number 0.91 represents the reflectance of the $BaSO_4$ powder.

3. Results and discussion

In figure 1 we show XRD patterns for two powders of Lu_2O_3:Eu (series A, B) and of the commercial Y_2O_3:Eu. All samples contain 5% of Eu. The pattern for the sample of series C is not presented since it is practically the same as that for series B. The results confirm that all the Eu-doped lutetia and yttria specimens are isostructural and crystallize in cubic structure.
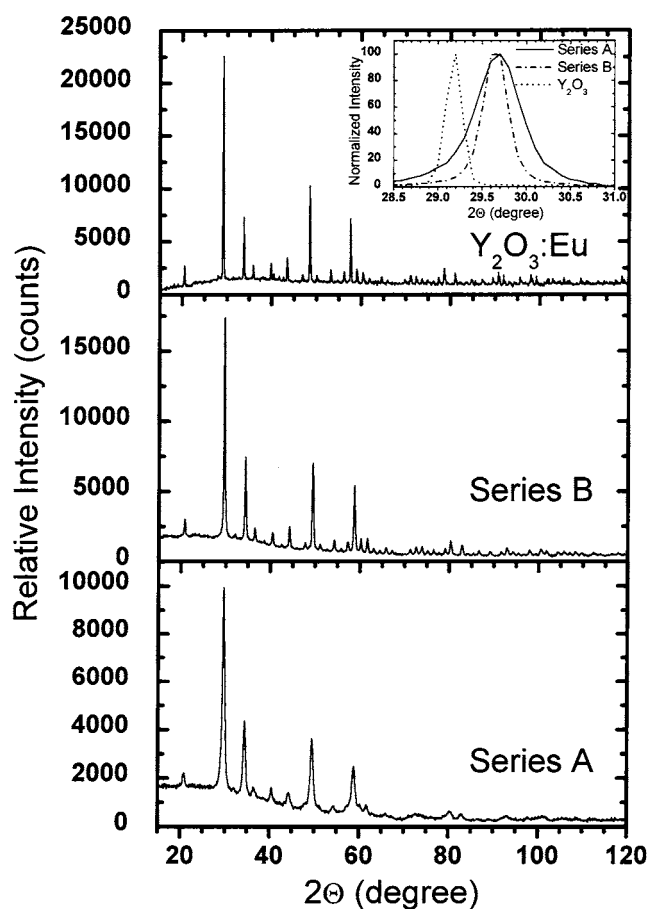
Figure 1. XRD patterns of the commercial Y_2O_3:5% Eu prepared with urea (series A) and with glycine (series B). The result for analogous specimens of series C is indistinguishable from that for specimens of series B. The inset shows the slightly different position of the most intense line for yttrium oxide due to the larger value of its lattice cell size. The other lines shift accordingly.

We can see a small variation in the location of the diffraction lines for yttria in comparison with lutetia (see the inset in figure 1), which reflects the slightly larger unit-cell size of the former (10.604 Å for Y_2O_3 versus 10.391 Å for Lu_2O_3) [21–23] due to the bigger ionic radius of Y^{3+} (0.900 Å) in comparison with Lu^{3+} (0.861 Å) [24]. There is, however, a much more profound and important difference between the XRD patterns. It is immediately seen that the widths of the lines vary strongly from sample to sample. This, according to Scherrer's formula [19], reflects varying average sizes of the crystallites making up the four materials investigated. The broadest XRD lines are seen for the urea-prepared powders and the narrowest for the commercial Y_2O_3:Eu. This is exactly what should be expected, since for the commercial phosphor the size of the crystallites is in the range of micrometres and in such a case the diffraction lines must be narrow, as formula (3) indicates. For materials whose crystallites are smaller than about 100 nm, a significant broadening of the diffraction lines occurs. Using Scherrer's formula we find that the urea-prepared powders (A) consist of crystallites whose sizes are about 13 nm, while crystallites of both series of glycine-prepared powders (B and C) are about 30 nm in size. Thus, the calcium addition—this is what distinguishes series C from
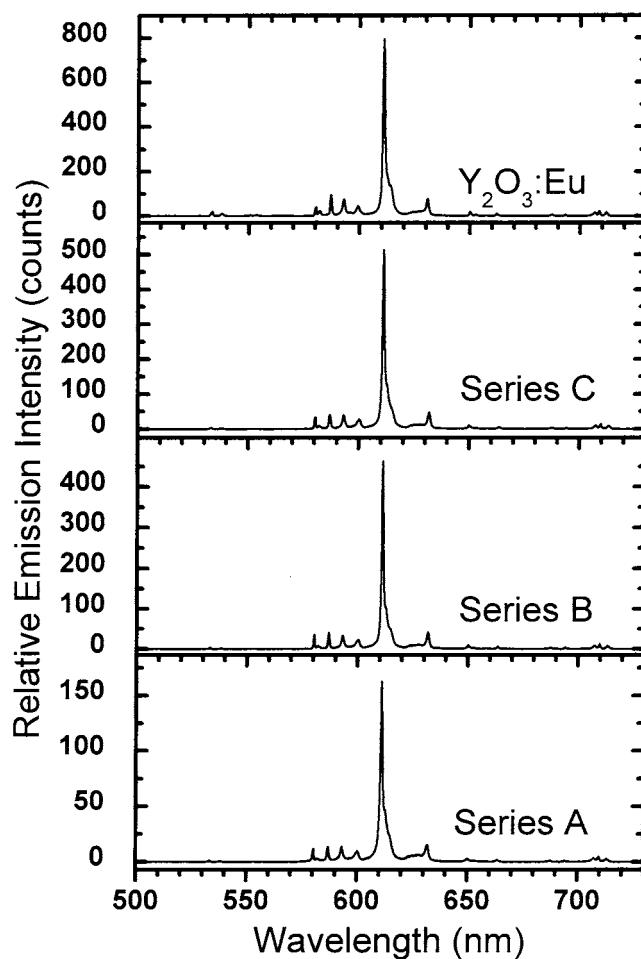
Figure 2. 255 nm excited emission spectra of the three series of Lu_2O_3:5% Eu and the commercial Y_2O_3:5% Eu.

series B—does not influence the process of crystallite growth during combustion with glycine fuel. The integrated intensities of the relevant diffraction peaks do not change among the series. This indicates that all the combustion-prepared specimens are fully crystalline materials. Yet, let us note that the sizes of the crystallites agree nicely with those which we found previously with transmission electron microscopy [9, 15]. Those analyses showed additionally that the urea-derived specimens are strongly agglomerated, while those made with glycine are only slightly agglomerated.

Figure 2 compares emission spectra of the three lutetia specimens doped with 5% of Eu as well as that of the commercial Y_2O_3:Eu. All phosphors are doped with 5% of Eu. It is immediately seen that the luminescence spectra of all specimens are very similar. The emission line locations are almost the same and the lines mostly result from the radiative relaxation of the $^5D_0$ level. For the urea-derived specimen the linewidths are slightly larger. Also, we can note some changes in the branching ratio for some transitions among the series. Hence, for all Lu_2O_3-based phosphors the line around 582.5 nm is weaker than that for the commercial phosphor of Y_2O_3:Eu. The line has been identified [25–28] as arising from a

slow emission from europium ions located in S_6 sites of the host lattice, while almost all the other lines result from the emission of Eu ions residing in C_2 sites. As the concentration of activator increases, the mean distance between the ions of Eu decreases and this makes energy migration between ions of the dopant more probable. Since the levels of Eu^{3+} in the S_6 sites are located slightly above those in C_2 sites, the interaction between such ions leads to energy transfer from Eu^{3+} in S_6 sites to Eu^{3+} in C_2 sites [28, 29]. Lines located around 530 nm arise from the emission from the higher-lying $^5D_1$ level of Eu^{3+}. These lines are also noticeably weaker for all the Lu_2O_3:5% Eu materials as compared to Y_2O_3:5% Eu commercial phosphor, and they systematically weaken with rising Eu concentration. This may result from the slightly stronger interaction between the Eu ions in the lutetia host comparing to those in yttria, since the inter-ionic distances are shorter for Lu_2O_3.

The comparison of the luminescence spectra of the Lu_2O_3-based phosphors with the emission of the commercial Y_2O_3:Eu convinces us that the latter can serve as a very convenient reference material against which the emission efficiency of our nanocrystalline powders of Lu_2O_3:Eu can be judged. Since the emissions of all materials investigated fall within exactly the same spectral region, there is no need to correct the emission spectra for the photomultiplier response to make a reasonable calculation of the quantum efficiencies of the emissions of the various Lu_2O_3:Eu powders.

In figure 3 we show excitation spectra of the same four specimens doped with 5% of Eu. As expected, there is not much difference between the spectra of the lutetia-based nanopowders and the commercial yttria, although again for the urea-prepared specimen (series A) the lines are slightly broader as is the intense band due to the charge-transfer (CT) absorption [30] located below about 290 nm. On the basis of the spectra, we decided that for the measurements of the quantum efficiencies of the three series of specimens of Lu_2O_3:Eu, the most convenient excitation wavelength would be 255 nm. It fits nicely into the broad band of CT absorption and also coincides with the most efficient excitation line of the Hg light sources used in many commercial applications.

Reliable judgment of the real efficiencies of the emissions from the various specimens requires an accurate determination of the amount of light absorbed by each of the phosphors investigated. This is especially important in our case, since the various specimens are characterized by strongly different microstructures and the activator concentration varies by a factor of about 250. To compare the amount of light absorbed by an actual specimen, we measured reflection spectra for each of them and related them to the reflectivity of our standard commercial phosphor of Y_2O_3:Eu and to the reflectivity of $BaSO_4$. Equation (5) shows the relationship between the reflectance of the specimen investigated and the reflectance of the standard powder $BaSO_4$. In figure 4(a) we show reflection spectra for the commercial Y_2O_3:Eu and all the Lu_2O_3:Eu samples doped with 5% of Eu, together with the spectrum of $BaSO_4$. The results leave no doubt that, for reliable estimation of the quantum efficiency of an emission, it is definitely not enough to compare just the luminescence efficiency—it is also necessary to take into account the variations in the amounts of light absorbed by each of the samples. Despite the fact that all the Eu-doped specimens presented in figure 4(a) contain 5% of the activator, their capabilities for reflecting the incident light vary strongly. Thus the amount of light accessible for absorption by the Eu^{3+} ions (able to excite the phosphor) must also alter.

The variations are especially significant when we go from the nanocrystalline powders of Lu_2O_3:Eu to the commercial phosphor Y_2O_3:Eu. Nevertheless, even the nanopowders of lutetia exhibit a varying capability to reflect the incoming light. Figure 4(b) presents how the reflectivity of the incident light varies with Eu concentration for the three series of Lu_2O_3:Eu specimens. Generally, as expected, with rising Eu content less and less light is being reflected, which means that a still increasing amount of the light is being absorbed by the phosphor
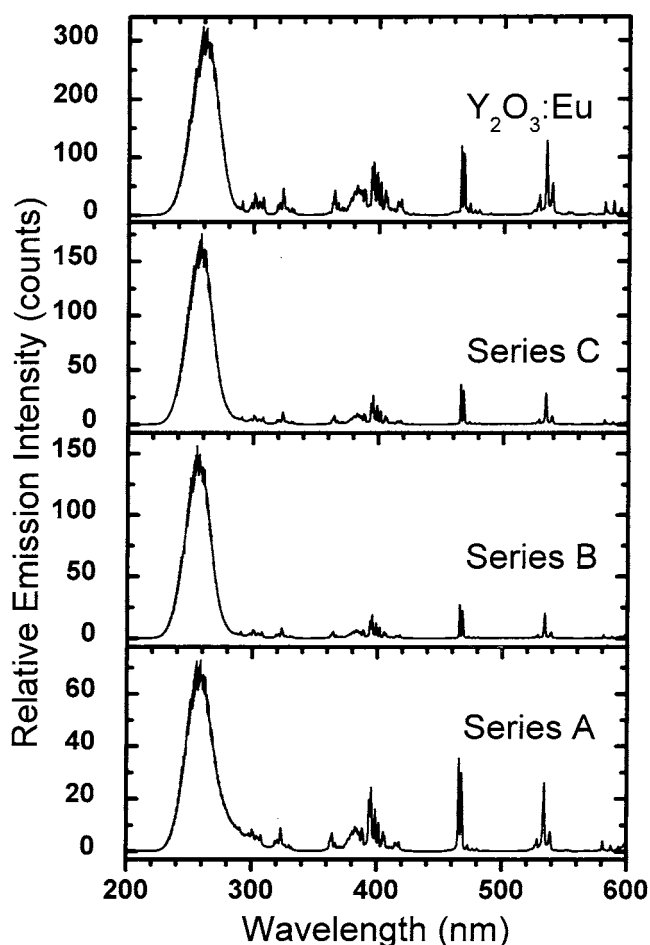
Figure 3. Excitation spectra of the 611.3 nm emission for the three series of Lu_2O_3:5% Eu and the commercial Y_2O_3:5% Eu.

powder. However, for the series A (urea-prepared) specimens the amount of reflected light is almost unchanged when the dopant content changes from 1 to 13%. For the glycine-prepared specimens of series B and C the situation is very different. However, for these two series also the intensity of the reflected light changes irregularly with concentration. These observations again point to the necessity of calculating and taking into account the actual amount of incident light absorbed by the specimens investigated if the quantum efficiencies of their emissions are to be determined reliably.

Figure 5 presents the resulting quantum efficiencies (QEFF) for the three series of nanocrystalline Lu_2O_3:Eu phosphors investigated calculated according to equation (4). There is a significant difference apparent between the quantum efficiencies of the urea-prepared powders of series A and the two series of materials made with glycine. Neither of the samples of series A has a quantum efficiency that exceeds 30%. On the other hand, the efficiencies of samples of series B and especially of series C reach, for some concentrations, the value 90%, which is equal to the quantum efficiency of the Y_2O_3:Eu commercial phosphor.

To some extent the concentration dependence of the QEFF is similar for all three series. The maximum value of QEFF is achieved for specimens containing a few mol% of the activator.
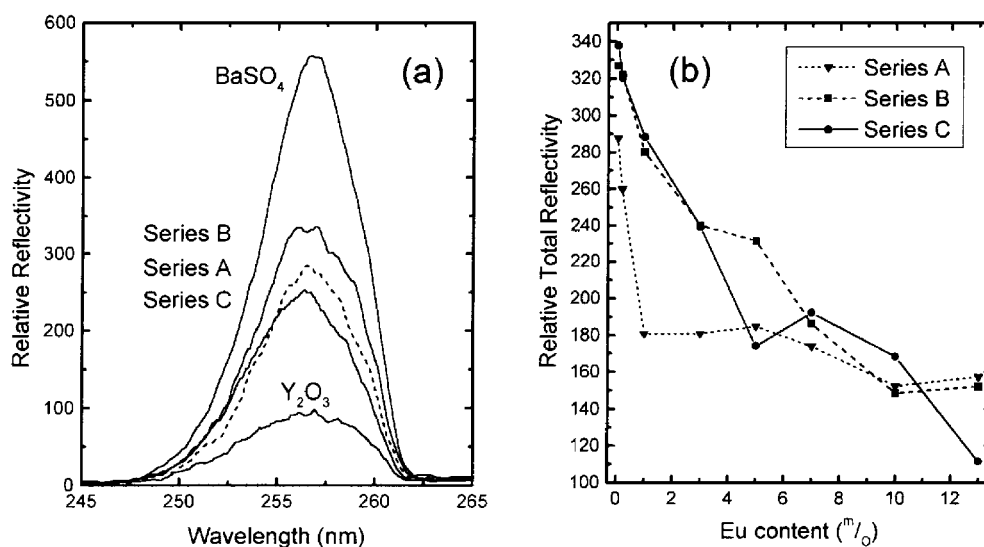
Figure 4. Reflection spectra of the three series of Lu_2O_3:5% Eu, the commercial Y_2O_3:5% Eu, and a $BaSO_4$ powder (a); and the Eu concentration dependence of the total reflectivity of the lutetia-based phosphors (b).
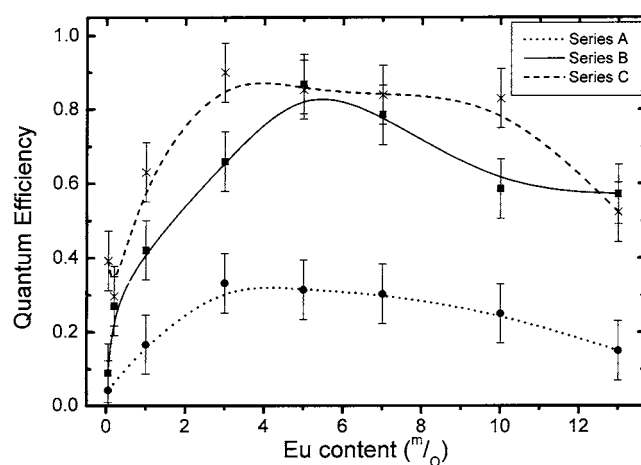
Figure 5. Concentration dependences of the Eu emission quantum efficiencies for the three series of Lu_2O_3:Eu. The curves are drawn to guide the eye.

In the case of series A (urea-prepared), the QEFF is the highest for the specimen containing 3% of the activator and above this concentration the efficiency systematically, although slowly, decreases. For the series B, the highest QEFF of almost 90% is reached for 5% dopant concentration. For concentrations higher than 7% the QEFF decreases noticeably in this series. The addition of calcium (this is what distinguishes the samples of series C and series B) seems to have a beneficial influence on the QEFF of the Lu_2O_3:Eu emission. The results show that in such a case the QEFF stays at practically the same high level of 80–90% over the range 3–10% of Eu concentration. Thus the Ca addition allows a rather broad variation of activator concentration without having a harmful influence on the quantum efficiency of the emission of
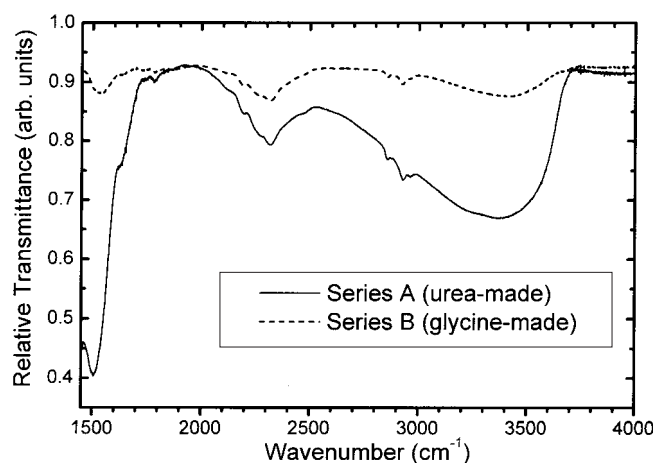
Figure 6. Typical infrared transmission spectra of Lu_2O_3:Eu prepared with urea (series A) and with glycine (series B). The spectra of specimens of series C are practically identical to that shown for series B. The ratios of intensities were found from spectra taken using Nujol, where the fundamental vibrations of the lutetia host are seen at 580 cm^{-1} (see the text).

Lu_2O_3:Eu nanopowders. This effect may be related to the reduction of the amount of extrinsic oxygen in the lattice. Lempicki [31] noted that prolonged heating of sintered Lu_2O_3:Eu in air also significantly reduced the Eu luminescence efficiency. Hence, our result can be considered as consistent with his finding.

We can note that for all three series the QEFF drops drastically for specimens with Eu content lower than about 3%. Such an effect could reflect the presence in the lightly doped materials of competitive absorption centres in the excitation region (~255 nm), which do not contribute to the Eu emission. Such centres would be able to absorb the incident light but would not contribute to any emission, nor would they transfer the acquired energy to Eu ions. Instead, the centres would dissipate the energy gained in non-radiative processes. For higher Eu concentrations the centres could no longer efficiently compete with Eu ions for the incident radiation, since the absorption coefficient of Eu^{3+}, through its CT absorption band, would be so high that it would surpass any competitive absorbing features. It could also be the case that, for some reason, the population of the postulated defect centres systematically decreases with rising Eu concentration. We tried to verify this suggestion by measuring differential absorption spectra of specimens of various Eu concentrations. Unfortunately, while we did indeed observed indications that such an erratic weak absorption band does exist below ~330 nm, a very high scattering coefficient in the UV spectral region prevented us from reaching any definitive conclusions on this matter.

The huge discrepancy between quantum efficiency of emission found for the samples made with urea and those obtained with glycine (either series B or series C) encouraged us to run additional experiments, which could unveil the reasons for such behaviour. Thus we recorded IR spectra of these materials and found, as seen in figure 6, that they are noticeably different. Let us comment here that the spectra in figure 6 were taken using poly(chlorotrifluoroethylene) oil, which lacks any strong lines in the region of OH vibrations. However, these spectra were normalized according to the intensities seen for measurements made using Nujol oil. The latter measurements allowed observation of the fundamental host-lattice vibrations at 580 cm^{-1} and made it possible to relate the intensities of other features accordingly. We believe that the error should not exceed about 15%. The most important difference between the spectra are the changes in the intensity of the characteristic vibrations of OH groups seen as a broad band

located around 3400 cm^{-1} and a doublet situated around 1500–1600 cm^{-1}. It is immediately seen that the intensities of both these bands in the case of the glycine-prepared specimens is much lower than in the case of urea-prepared specimens. The presence of vibrations of such high energy in the materials can be, obviously, deleterious to radiative processes within the Eu^{3+} ion, since the energy gap between the main emitting level, $^5D_0$, and the nearest terminal level, $^7F_6$, hardly exceeds 12 000 cm^{-1} [32]. In such a case, if high-energy vibrations of OH groups are easily accessible to the excited ion, the non-radiative multiphonon relaxation becomes progressively more probable with rising intensity of the vibrations. We trust that this is the main reason, though not necessarily the only one, for the urea-prepared powders of series A being unable to perform more efficiently. On the other hand, the vestiges of OH groups still present in the glycine-prepared powders evidently do not have any significant influence on the performance of the powders. Thus, these may just be resulting from a trace of water absorbed on the top surface of the powder.

There seems to be yet another possible reason for the very low efficiency of the urea-prepared powders—namely, we have some indications, mostly from EPR spectra of Gd- or Tb-doped specimens, that in the urea-prepared nanocrystallites the distribution of the dopant within the host lattice is strongly non-uniform. This effect, however, needs more investigation, and a detailed analysis will be published elsewhere [33].

4. Conclusions

Nanoparticulate powders of Eu-doped Lu$_2$O$_3$ with different compositions and microstructures were prepared via combustion routes. It was found that the synthesis conditions influence the microstructures of the final products, and affects the phosphor spectroscopic properties. Specimens prepared with urea as the organic fuel proved to be rather poor emitters, with the highest quantum efficiency reaching only about 30% for doping with about 3% of Eu. In contrast, the specimens prepared with glycine as the organic fuel performed surprisingly efficiently. Their emission quantum efficiency reached about 90%—exactly what is seen for the commercial phosphor Y$_2$O$_3$:Eu. This result was achieved despite the presence of some residual OH groups in the phosphors—an effect of using water as the solvent during the synthesis. Glycine-prepared specimens co-doped with Ca maintained the high quantum efficiency of 85–90% over the range 3–10% of Eu concentration. All nanoparticulate powders were shown to reflect more of the incident light than the commercial powder of Y$_2$O$_3$:Eu. This makes their observed luminescence less intense as compared to the commercial Eu-doped yttria despite the high QEFF value. This also indicates that a simple comparison of just the luminescence efficiencies of various specimens is not enough for making a reasonable judgment of the real relationship of their actual emission efficiencies.

Acknowledgments

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