Effects of composition and transparency on photo and radioluminescence of \( \text{Y}_2\text{O}_3:\text{Eu} \) complexes

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A solid state-based method using a hot reaction chamber is applied to the synthesis of \( \text{Y}_2\text{O}_3:\text{Eu} \) particles containing Eu from 0 to 5 mol%. The produced powders are studied using X-ray diffraction (XRD), scanning electron microscopy and transmission electron microscopy (TEM), as well as photoluminescence (PL) and radioluminescence tests. TEM and XRD results revealed the powder to be mono-disperse and in the form of a solid solution. The PL of \( \text{Y}_2\text{O}_3:\text{Eu} \) powder depends on both the concentration quenching effect (due to an excess of Eu concentration) and the surface luminescence effect (depicted by a higher surface area induced by the large phosphor concentration in the solution or smaller particle sizes). A \( ^{22}\text{Na} \) gamma source is used to compare the recorded count rates for four \( \text{Y}_2\text{O}_3:\text{Eu} \) scintillator materials with different concentrations of Eu. Each scintillator composition is examined in four forms: solid pellets with a high volume porosity and three aqueous solutions of \( \text{Y}_2\text{O}_3:\text{Eu} \) particles of the different scintillator materials at concentrations of 25, 50 and 100 mg/mL. The radioluminescence results indicated that increasing the transparency and/or the amount of Eu mol% of the scintillators increases the net average counts.

**Keywords:** photoluminescence; gamma radiation; radioluminescence; nanoparticles; X-ray

1. Introduction

Red-emitting phosphor, europium-doped yttrium oxide (\( \text{Y}_2\text{O}_3:\text{Eu} \)) has been the subject of growing interest for use in conventional applications such as fluorescent lamps, high-definition and projection TVs and low-voltage displays such as plasma display panels and field emission displays. The wide use of red-emission phosphors in these new generation displays has been attributed to their high efficiency under a low electron accelerating voltage compared with the conventional cathode ray tube, as well as their established long-term chemical stability (1–4). Furthermore, \( \text{Y}_2\text{O}_3:\text{Eu} \) can attain a quantum efficiency close to the perfect 100\% (5). As an oxide, it is far more stable than sulfur-containing phosphors, which undergo changes in their surface chemistry when interacting...
with an electron beam, seriously degrading their cathodoluminescent brightness and releasing gases that can poison the field-emitting tips (6). Moreover, Y₂O₃:Eu is a thermographic phosphor whose luminescent properties are temperature-sensitive and thus can be used to measure surface temperatures by applying a thin coat to a substrate surface and observing its luminescence when illuminated with UV light. Being photosensitive at high temperatures, Y₂O₃:Eu could potentially be used in high-temperature environments and applications such as gas turbines, chemical rockets, jet engines and nuclear reactors (7, 8). In addition, a Y₂O₃:Eu phosphor combined with silicon has been utilized as a detector in medical imaging applications based on the observed high X-ray luminescence efficiency (at 30 kVp X-ray tube voltage). As such, these materials could be good candidates as detectors in digital mammography applications (9–11).

Despite its potentially numerous emerging radiographical applications, to the best of our knowledge there is no literature citing the use of Y₂O₃:Eu as a scintillator for other high-energy particles (e.g. gamma and neutrons). Important requirements for scintillator crystals include high light output, high gamma-ray stopping efficiency, good radiation hardness and efficiency for converting incident ionizing radiation to emitted light, fast response, low cost, good proportionality and minimal afterglow. The first results obtained in the experiments with complex oxide scintillators turned out to be rather encouraging. For example, the dependence of light emission intensity on nanograin sizes in yttrium–aluminum garnet with a europium activator demonstrated a distinct maximum for a 90 nm diameter. This maximum is about four times higher than the effectiveness of single crystals of the same chemical compositions (12). The most promising result is a manifold decrease in the scintillation rise time (it became less than 0.1 ns). Both experimental results were obtained for nanograins with mean sizes of 70–100 nm.

Various methods have been implemented to synthesize Y₂O₃:Eu, such as co-precipitation (13, 14), emulsion (15), spray pyrolysis (16, 17), sol–gel (18, 19), alkalide reduction (6), combustion (20, 21), surface diffusion (22), electrostatic-assisted chemical vapor deposition (8) and microwave plasma torch (23). Each method results in different morphologies and particle sizes that affect the luminescence properties. However, different precursor sources, experimental conditions and other factors make it difficult to compare the efficiency and the advantages and disadvantages of the different methods. The plethora of different synthesis techniques also made it feasible to synthesize this phosphor into nanoparticles, nanotubes, microscale particles and thin films.

This work investigated the photoluminescence (PL) and the gamma ray-induced radioluminescence behavior of sub-micron size Y₂O₃:Eu phosphors prepared by the wet chemistry method with different Eu contents (0, 1, 3 and 5 mol%). X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to investigate the effect of the concentration and the Eu mol% on the luminescence behavior of both dry and aqueous solutions of the produced phosphor powder.

2. Experimental

2.1. Materials and synthesis

We implemented wet chemistry methods starting with nitride compounds to synthesize the Y₂O₃:Eu phosphor. A lower processing temperature, higher controllability and insignificant corrosiveness of the chamber are the primary advantages of using nitrides. Yttrium nitrate hexahydrate (99.9%, Sigma-Aldrich) and europium (III) nitrate hydrate (99.99%, Sigma-Aldrich) were dissolved in ethanol in different compositions of 0, 1, 3 and 5 mol%. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to investigate the effect of the concentration and the Eu mol% on the luminescence behavior of both dry and aqueous solutions of the produced phosphor powder.

(2 − 2x)[Y(NO₃)₃ · 6H₂O] + 2x[Eu(NO₃)₃ · 6H₂O] ⇌ Y_{2−2x}Eu₂xO₃ + by products (gas).
Four different samples of the phosphor were produced by adjusting the Eu to 0, 1, 3 and 5 mol%, respectively. The resultant transparent solutions were furnace-dried at 50°C and then crushed into microscale powder and fed to the hot reaction chamber. In the reaction chamber, the precursor powders are exposed to 40 mL/min gas flow of argon (99%) in a crucible. Then, the chamber temperature is rapidly increased to 800°C and kept steady for 5 min, followed by a cooling to ambient conditions. The burst-like reaction of the precursors in the chamber resulted in uniformly distributed fine particles. To better investigate the effect of the average particle size on the luminescence properties, the white powders produced were separately hand-crushed and ball-milled and then characterized using XRD, SEM and TEM. A spectrophotometer and a photomultiplier tube (PMT) were used to characterize the PL and radioluminescence of different samples of tablets made from the dry phosphor powder and an aqueous solution of the powder.

2.2. Characterization and measurements

XRD with Cu Kα radiation was used to identify the phases and examine the crystallinity of the samples. The particle size and morphology in the samples were investigated using both a Hitachi S-5200 SEM and a JEOL 2010 high-resolution transmission electron microscope. In addition, a Cary Eclipse R3896 fluorescence spectrophotometer was used to investigate the PL properties of the samples. For PL measurements of Y₂O₃:Eu phosphors, zero-order emission spectra were measured independent of the exciting wavelength so that the emission intensity variation with respect to Eu mol% and the phosphor concentration could be observed (24).

The radioluminescence measurements employed a ²²Na gamma source, and the recorded count rates for samples of four different compositions of the Y₂O₃:Eu scintillator materials were compared. The four scintillator materials used were: (a) Y₂O₃ without any Eu, (b) Y₂O₃ with 1% Eu, (c) Y₂O₃ with 3 mol% Eu and (d) Y₂O₃ with 5 mol% Eu. The samples were in the form of porous solid pellets (Figure 1(a)) as well as aqueous solutions with three different concentrations of nanoparticles of each of the above scintillator materials: 100, 50 and 25 mg/mL (Figure 1(b)). In all, 12 samples were used to measure the net average counts upon exposure to the ²²Na gamma source. The pellets, with an average diameter of ~1.2 cm and an average density of ~2.42 g/cm³, were ~0.30 cm thick. Incorporating the Y₂O₃:Eu powder in deionized (DI) water-based solutions effectively increased the transparency of the samples, and thus was expected to lower the scattering and increase the transfer of the luminescent photons to the PMT.

Figure 2 presents a line schematic of the setup used in this work to measure the light photons emitted by the different Y₂O₃:Eu scintillators. The dashed lines represent power connections, while the solid arrows represent the output signals. In addition to turning off all lights in the room,

Figure 1. (a) Y₂O₃:Eu solid pellet, (b) spectrophotometer cuvette with DI water, 100 mg/mL, and 50 mg/mL Y₂O₃:Eu solutions.
the PMT, scintillator sample and $^{22}\text{Na}$ radiation source were enclosed within a black box, so as to minimize background light and reduce background counts. A Bicron 3 (x3 NaI(Tl)) scintillation detector was used to test and calibrate the electronic hardware and the multi channel analyzer (MCA). The Bicron 3 (x3 NaI(Tl)) was then replaced by Hamamatsu 13 mm diameter PMT. The PMT was fitted to the scintillator sample, and then wrapped with a light reflecting tape. The single channel analyzer (SCA) was set with a lower-level discriminator (LLD) of 0.25 V and an upper-level discriminator (ULD) to a maximum value of 10 V. The applied voltage was slowly increased to establish an operating voltage of 1000 V. The measurement system was left for 150 seconds to reach a steady condition before recording the count rate.

A set of background counts were taken at a duration of 1 s each, at $\sim 15$ s apart. The same counting process was repeated using the $^{22}\text{Na}$ gamma source. In order to ensure the dependability of the measurements the processes were repeated, and three separate data sets were taken for the background and $^{22}\text{Na}$ gamma source. Note that after completing a set of measurements, the electrical power was turned off for 5 min to cool down the electronics.

$^{22}\text{Na}$ gamma source used in the present investigation emits two distinct gamma photons with two characteristic energies of 511 and 1275 keV. Figure 3(a) shows the decay scheme of $^{22}\text{Na}$, and the measured emission spectrum using the NaI calibration detector is shown in Figure 3(b). The $^{22}\text{Na}$ atoms undergo a positron ($\beta^+$) decay into an excited $^{22}\text{Ne}$ state, which in turn decays with a high-energy gamma (1.275 MeV) and a positron. The positron interacts with the source atoms causing a positron–electron annihilation, releasing two 511 keV annihilation gamma photons. The high-energy gamma photons (1.275 MeV) and the annihilation photons (511 keV) can be seen as
two distinct peaks on a scintillation detector, as shown in Figure 3(b), and are spread out over the energy range used for the calibration of the MCA.

In the present measurements for the Y$_2$O$_3$:Eu, because of the low intensity of the emitted photons by the Y$_2$O$_3$ scintillator samples (3–5 photons/s), it was not possible to detect the distinct emission characteristics of the $^{22}$Na source shown in Figure 3(b). The low emission intensity of the light photons reaching the PMT results in very small signals in the mV range. Thus, in order to increase the number of counts recorded, while keeping the background counts relatively low, the detected signal is amplified by increasing the gain in the PMT to 500.

3. Results and discussion

Figure 4 shows the XRD results of the differently prepared samples. It can be seen that Eu is doped proportionally in the yttrium positions of the Y$_2$O$_3$ crystalline structure in the form of a solid solution rather than a shell–core structure. The XRD patterns of the three different Y$_2$O$_3$:Eu samples are fairly consistent with those of the Joint Committee on Powder Diffraction Standards No. 25-1011 and this confirms that our samples are almost cubic in structure.

The obtained XRD patterns indicate that the samples with 3 mol% Eu and 1 mol% Eu exhibit a higher degree of crystallinity compared with the single-phase Y$_2$O$_3$. The presence of Eu is depicted with four extra peaks that were not observed for the single-phase Y$_2$O$_3$. Small peaks near 2$\theta$ = 29°, 33°, 48° and 57° were also observed, indicating that most of the dissolving Y (NO$_3$)$_3$ and Eu (NO$_3$)$_3$ were converted to Y$_2$O$_3$:Eu phosphor. A single phase of Y$_2$O$_3$ was obtained, with Eu$_2$O$_3$ entering the Y$_2$O$_3$ crystal lattice. The strong intensities relative to the background signal indicate the high purity of the Y$_2$O$_3$:Eu phosphor phase of the prepared samples, though a significant line broadening between 1, 2 and 5 mol% Eu samples and the particle size seems to be consistent according to the Scherer formula.

The TEM micrographs also show the prepared powder to be of a solid solution (Figure 5). At higher magnifications, the nanoparticles in the samples display lattice fringes, indicating a high crystallinity. The inconsistent crystal lattice planes seen on nanocrystals indicate that the elongated particles are composed of agglomerated smaller particles. Furthermore, at the upper
right edge, the existence of an amorphous surface layer with a number of defects and strained regions is visible. Such a surface-damaged region can be expected to have a detrimental effect on phosphor efficiency at low electron penetration depths. This surface damage can be attributed to the hand-crushing and ball-milling procedures used.

The arbitrary morphology of the samples can be concluded from SEM micrographs. Figure 6, for instance, shows different effects on the morphology of Y₂O₃:3 mol% Eu particles. Figure 6(a) reveals the effect of a methanol expulsion such as evaporation, during the reaction in the chamber, which appears as sharp edges, holes and secondary-bounded small particles over the surface of larger ones. On the other hand, Figure 6(b) illustrates that further milling using the ball mill reduces the particle size distribution and results in more equiaxed particles, with blunt edges and a relatively smooth surface. The sharp edges, rough surface and irregularly shaped-particles cause a non-radiative transition center, which can decrease the luminescence efficiency (25). Figure 7 further contrasts the particle size differences between the ball-milled and hand-crushed samples using TEM micrographs.

Figure 8 shows the effects of the Eu concentration and the particle size on the room-temperature PL spectra as a function of the concentration of the Y₂O₃:Eu phosphor in the solution. The results are presented in terms of the intensity of the zero-order emission spectra. The samples were prepared in three different concentrations by dispersing 25, 50 and 100 mg of the ball-milled powder into 1 mL of DI water. In order to increase the reliability of the obtained results, all samples were sonicated sufficiently in a water bath and then poured in a standard quartz vial. In addition, to reveal the effect of the solution, 1 g of powder was compacted to form a disc ~10 mm
Figure 7. TEM micrograph showing the effects on particle size of Y$_2$O$_3$:5% Eu sample (a) ball-milled and (b) hand-crushed.

Figure 8. The emission spectra of (a) 5%, (b) 3%, (c) 1% and (d) 0% Eu samples for both hand-crushed and ball-milled powder in different concentrations.

in diameter. The PL spectra of the dry samples were determined and normalized with respect to their corresponding densities.

The strong emission intensities observed in Figure 8 are indicative of the presence of Eu$^{3+}$ in a highly crystalline cubic Y$_2$O$_3$. The spectra are recognized by the well-known ($5D^0 \rightarrow 7F^J$, $J = 0, 1, 2, \ldots$) line emission of the Eu$^{3+}$ ion. The line positions are unchanged for the different phosphor concentrations. For the two samples with a 25 mg/mL concentration, the ball-milled sample exhibited a higher PL intensity compared to the hand-crushed sample. This is mostly due to the increase in the surface area through the reduction in particle size. It is well known that the
PL intensity of a phosphor increases as the surface area increases; this is referred to as the surface luminescence effect (26). It can be seen that the 25 mg/mL (ball-milled) samples have the highest PL intensity, whereas those with 100 mg/mL had the lowest PL, although both samples had the same particle size. This is true for the samples of 3 and 5 mol% Eu concentration. The samples with 1 mol% Eu showed better PL emission at 100 mg/mL. This anomaly can be explained better by studying the effect of Eu mol% on the PL.

Figure 9 shows the PL spectra of the Y2O3:Eu specimens with various Eu concentrations. The PL emission spectra present similar characteristics for all concentrations. As the Eu concentration increased from 0 to 3 mol%, the PL intensity of the Y2O3:Eu phosphor increased. Beyond 3 mol% Eu, the PL intensity decreased; for example, at 5 mol% Eu. It may be hypothesized that higher Eu concentrations quench the PL intensity. The present results are in good agreement with those reported by several other research groups (27–29), concluding that higher Eu concentrations (>5 mol%) in nanoparticles lead to a quenching of the PL intensity. Based on the results delineated in Figures 8 and 9, the PL intensity of Y2O3:Eu increased by increasing the surface area (through increasing the phosphor concentration) while maintaining a low Eu mol%. The same effect was observed by decreasing the surface area (via lowering the concentration of Y2O3:Eu, e.g. 25 mg/mL) and maintaining a high Eu mol% (5%, for example). Thus, one can conclude that the influence on the PL of Y2O3:Eu powder is caused not by the concentration quenching effect (due to an excess of Eu concentration) or the increased surface area (depicted by higher phosphor
Figure 10. Raw counting using 25 mg/mL liquid solution of Y$_2$O$_3$:5%Eu.

Figure 11. Average counts for the different samples of Y$_2$O$_3$:Eu scintillators with different Eu wt% and transparencies.

concentration in the solution or smaller particles size) leading to surface luminescence, but rather by their combined effects.

Upon exposing the different Y$_2$O$_3$:Eu scintillator samples to a $^{22}$Na gamma source, the emitted photons were counted. A sample of the measured count rates, including background, is presented in Figure 10. The recorded fluctuations in the count rates are within <5%. Statistical averages of the raw data that include the total count rate and that of the background are indicated by the horizontal solid lines in Figure 10. The average net count rate is the total rate minus the background (Figure 10). The obtained values of the average net count rates of the different scintillators investigated in this work are shown in Figure 11 (versus an arbitrary transparency). A transparency of 1 is assigned to the solid pellets and transparencies of 2, 3 and 4 is assigned to the aqueous solutions of the scintillators of Y$_2$O$_3$:Eu with concentrations of 100, 50 and 25 mg/mL, respectively.

Figure 11 shows that Y$_2$O$_3$ without Eu addition consistently gives the lowest count rates of 574 ± 34 counts/s, compared with 620 ± 34 and 769 ± 40 counts/s for the Y$_2$O$_3$ nanoparticle aqueous solutions of 50 and 25 mg/mL with no Eu addition, respectively. Despite the decrease in the concentration of the Y$_2$O$_3$ scintillator materials with increased transparency, the increase in the average net count rates suggests that the reduced opacity of the scintillator materials, and
hence the self-absorption of emitted light photons, increases the net number of photons detected by the attached PMT.

The results in Figure 11 also show that the increase in the number of emitted light photons as the amount of Eu in the samples increases, rather than the density of the scintillator materials, significantly increases the number of photons counted or the count rate. For example, the net average count for the solid pellet with no Eu is $582 \pm 34$, compared with $856 \pm 41$ with 1 mol% Eu, $1086 \pm 54$ with 3 mol% Eu and with the highest value of $1575 \pm 60$ with 5 mol% Eu.

A similar trend can be seen at all other transparency levels with an increasing amount of the Eu dopant in the Y$_2$O$_3$ nanoparticles in aqueous solutions (Figure 11). The results delineated and compared in this figure clearly indicate that increased transparency and the amount of Eu dopant consistently increase the net average counts measured. For example, considering the Y$_2$O$_3$:Eu scintillator with 5 mol% Eu, the measured net average counts increased from $1575 \pm 60$ for the solid pellet (transparency of 1) to $1619 \pm 61$, $1698 \pm 63$ and $1999 \pm 66$ for the aqueous solutions with Y$_2$O$_3$:Eu concentrations of 100 mg/mL (transparency of 2), 50 mg/mL (transparency of 3) and 25 mg/mL (transparency of 4), respectively.

The relative effects of increasing both the mol% Eu and the transparency on the measured counts are better shown in Figure 12(a) and (b). In this figure, the net average counts are normalized to those of the Y$_2$O$_3$ scintillators with 0% Eu (Figure 12(a)) and to that of the solid pellets (Figure 12(b)). Figure 12(a) clearly shows that increasing the amount of Eu dopant from 0 to

![Figure 12](image-url)

Figure 12. Relative effect of Eu wt% and transparency of the Y$_2$O$_3$:Eu scintillators on the measured net average counts.
5 mol% increased the net average count rate 2–3-fold. The relative comparison in Figure 12(b) shows that increasing the transparency also increases the measured net average count rate.

The results presented in Figures 10–12 suggest that the high opacity of the Y\textsubscript{2}O\textsubscript{3}:Eu solid pellets cause high scattering and trapping of the photons produced by the luminescent Y\textsubscript{2}O\textsubscript{3}:Eu phosphor. For the same active area of scintillators attached to the PMT in the current measurements, the solid pellet with a density of \( \sim 2.42 \text{ g/cm}^3 \), compared with 25 mg/cm\(^3\) in the 25 mg/mL aqueous solution, has a higher luminescence. However, the net average count for the 25 mg/mL acqueous solution of the Y\textsubscript{2}O\textsubscript{3} powder is \( \sim 1.3 \) times higher than that of the solid pellet with the same content of the Eu dopant in the particles.

4. Summary and conclusions

Using yttrium nitrate hexahydrate and europium nitrate hexahydrate as starting materials, Y\textsubscript{2}O\textsubscript{3}:Eu powders have been synthesized successfully using wet chemistry. The mol% of Eu was adjusted by controlling the stoichiometry. XRD analysis of the produced samples revealed the successful penetration of the Eu\textsubscript{2}O\textsubscript{3} in the Y\textsubscript{2}O\textsubscript{3} cubic crystal. Particle sizes were reduced by applying hand-crushing and ball-milling techniques. Additionally, we synthesized powder with different Eu doping percentages both in dry tablets and in DI water-based solutions. The emission results of Y\textsubscript{2}O\textsubscript{3}:Eu both in dry pellets and in DI water-based solutions under the visible light spectra suggest that the best configuration is that using a low concentration solution (e.g. 25 mg/mL) of particles with 3 mol% Eu dopant.

The results suggest that the PL of Y\textsubscript{2}O\textsubscript{3}:Eu powder is caused not by the concentration quenching effect (due to an excess of Eu concentration) and the increased surface area effect (depicted by higher phosphor concentration in the solution or smaller particles size) leading to surface luminescence, but rather by their combined effects.

The recorded count rates using a \(^{22}\text{Na}\) gamma source are compared for four different compositions of the Y\textsubscript{2}O\textsubscript{3}:Eu scintillator materials with different concentrations of Eu: 0, 1, 3 and 5 mol%. Each scintillator composition is examined in four forms: solid pellets with a high volume porosity (>50%) and three aqueous solutions of the Y\textsubscript{2}O\textsubscript{3}:Eu particles of the different scintillator materials at the three concentrations of 25, 50 and 100 mg/mL, respectively. The results indicated that increasing the transparency and/or the amount of Eu doping in the scintillators increased the measured net average count rates. The Y\textsubscript{2}O\textsubscript{3}:Eu scintillator materials fabricated and tested in this work are relatively inexpensive, easy to manufacture and possess excellent handling properties. Because of the opacity of the Y\textsubscript{2}O\textsubscript{3} scintillators, the number of light photons emitted and the produced counts are relatively low (3–5 photons/s). These materials could not, therefore, be used to obtain the emission spectra of gamma sources or be used in nuclear forensics testing of suspected radioactive sources.

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