Effect of low-density polyethylene on the luminescent properties of thulium-doped yttrium oxide obtained by the polyol technique

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Abstract

In the present work polyethylene is used as a support of yttrium oxide particles doped with thulium atoms and its effect on the luminescent properties is studied. Thulium-doped yttrium oxide was prepared through the polyol method, different values of thulium are explored: 0, 0.5, 1, 1.5, 2.5 and 3.5 at%, as well as different calcinating temperatures: 400, 600, 800 and 1000 °C, are explored in order to determine the synthesis conditions needed for the maximum emission intensity, whose values were 1.5 at% of thulium and 1000 °C. The synthesized powder is dispersed in low-density polyethylene and dispersed as a thin film on glass substrates. The luminescent excitation and emission spectra showed important changes attributed to the influence of the -CH2– chain vibration; in addition, the presence of the polymer had an important influence on the emission decay time: while the powder showed a single emission process with a time of 9.293 μs, the film showed a two decay process with 1.156 μs and 4.086 μs, each.

Introduction

Luminescent or phosphor materials have proven their worth because of their different applications, they are used as sensors, cell markers, light-emitting diodes, and solar cells, among other applications [1–4]. Phosphors can be synthesized as thin films on different substrates, depending on the application, but some of them are synthesized as powders that can be pressed in pellet shape or glued on a surface. Some of the most novel applications require the use of flexible luminescent materials: flexible displays, for example. Unfortunately, since the common luminescent semiconductors are hard ceramics with a fixed internal structure, so they are brittle instead of flexible.

In order to obtain flexible luminescent materials, scientists have made use of polymers, either modifying them so they might emit radiation themselves, or using them as a flexible host of small particles of luminescent ceramics or metals. In both cases, the internal structure consisting of long atomic chains with low interaction forces among them is what gives them the flexibility required. However, on one hand, these polymers can be doped with substitutional monomers or rare-earth atoms that alter the electronic structure of the host polymer and yield either electron donor and acceptor states, or atomic states splitting between which radiative electronic transitions take place, making it a luminescent polymer [5, 6]. On the other hand, radiative materials such as metal nanoparticles, quantum dots or ceramics have been included among the long fibers of the polymer [7–9]; in this case, the polymer has no active participation in the absorption, transmission and reemission of energy carried on by the phosphor. Ideally only the polymer flexibility and high transmittance are used when applied as support; however, the polymer still can have an effect on the luminescent properties. Because of this, research
work is needed in order to study the effect the support has on the luminescent properties and help decide whether it is suitable for such use.

Among many others, polyethylene is one of the simplest polymers that can be used to obtain flexible luminescent materials. Either as support of inorganic materials such as terbium doped alumina [10], as a host to several other monomers like polyethylene glycol, pyrene and 7-hydroxycoumarin [11–13] or supporting CdS quantum dots [14], polyethylene has proven to be an adequate material for luminescent applications. Our group has used it as support of aluminum oxide doped with terbium and europium [15, 16] but, to our knowledge, polyethylene has not been used as a host of luminescent particles of materials such as rare-earth-doped yttrium oxide.

Rare earth-doped yttrium oxide is being studied as a luminescent material because yttrium ions present the same oxidation state (3+) and a quite similar ionic radius (104 pm) as some of the most important luminescent lanthanides: Eu (108.7 pm), Tb (106.3 pm), Tm (102 pm), Yb (100.8 pm), Er (103 pm) and Sm (109.8 pm). This leads to an easy substitution of yttrium ions in the lattice, as well as a small distortion of the lattice itself. Also, chemical stability of the compound and the efficiency it presents makes it one of the most studied.

Based on this, in the present work we aim to study the influence of polyethylene on the luminescent properties of thulium-doped particles, when it is used as support. The luminescent particles were synthesized using the polyl method. Once obtained and characterized the sample with the best characteristics is dispersed in polyethylene and the mixture deposited as a thin film. The crystalline structure and the morphology of the luminescent powders were studied as a function of temperature, and dopant concentration. The optical properties such as infrared absorption, UV–vis transmittance, luminescent emission and decay time are analyzed in both: powder and deposited thin film.

**Experimental**

**Synthesis of luminescent powders**
To synthesize thulium-doped yttrium oxide powders through the polyl method first the main solution, 0.1 M, of yttrium nitrate hexahydrate (Y(NO3)3·6H2O) dissolved in diethylene-glycol was obtained. The solution was divided into 6 portions and thulium chloride hexahydrate (TmCl3·6H2O) was added in different concentrations to each one. In this case Tm/Y atomic percentage ratios of 0.0, 0.5, 1.0, 1.5, 2.5 and 3.5 at%, were prepared.

To achieve the desired reactions the different solutions were undertaken to a series of heating processes. First, the temperature of the solutions was raised to 80 °C for 30 min, aiming to properly dissolve all precursors; then, the temperature was increased to 150 °C for one hour, the solution turned cloudy and got white-colored, indicating the formation of yttrium hydroxides or hydroxinitrates; finally, the temperature was raised once again up to 180 °C for one hour, at this point the solution became a colloid and turned brownish, indicating the formation of small particles.

In order to recover the powders, the colloids were rinsed three times. The process consists of centrifuging for 20 min and redispersing the resulting powders in ethanol. As a final step, the precipitated powders were dried for one hour at 200 °C.

Since some hydroxides and/or hydroxinitrates might have remained in the powders, they were annealed for 4 h at different temperatures: 400, 600, 800 and 1000 °C in order to obtain a pure Y2O3 phase.

**Deposition of luminescent LDPE films**
In order to obtain pristine polyethylene films, low-density polyethylene was dissolved in cyclohexane and heated at 70 °C, later they were dispersed on glass substrates by dip coating. The substrates were properly cleaned in a sonic bath using soapy water, methanol and acetone; then, they were immersed in the polyethylene solution and kept submerged in it for one minute while the temperature was controlled at a temperature of 70 °C. The yttrium oxide sample with the maximum luminescent intensity was dispersed in the polyethylene solution using a magnetic stirrer and was deposited on the substrates in the same way to obtain the luminescent polymer film.

**Samples characterization**
Yttrium oxide powders structure was determined by XRD in a SIEMENS diffractometer D-5000, using the CuKα wavelength (λ = 1.540 Å); while the surface structure was studied by SEM, using a JSM-6390LV from JEOL. The same microscope was used to determine chemical composition of the samples by EDS.

The optical properties of both the powders and the films were studied in an FSS spectrophotometer from Edinburgh Instruments. The fluorimeter was used to obtain transmittance spectra of the film as well as the luminescent characterization, consisting of excitation and emission spectra, quantum yield and decay time. FTIR spectra were obtained for the films using a Perkin Elmer Spectrum One using an ATR configuration.
Results and discussion

Structural properties of Y$_2$O$_3$:Tm$^{3+}$ powders as function of temperature

Figure 1 shows the XRD patterns obtained in a sample doped at 1.5 at%, as an example of the behavior presented by all samples. As can be seen, sample annealed at 400 °C shows broader peaks that could be related to an amorphous phase or too small crystallite sizes. As temperature is raised the intensity of the diffraction peaks was enhanced, indicating an improved crystallinity. Samples annealed at 1000 °C showed very intense reflections that matched appropriately the JCPDS43-1036 diffraction card, correspond to the cubic phase of Y$_2$O$_3$ with a lattice constant of 10.604 Å. Since no other diffraction peaks were observed it can be concluded that no other compounds or phases were found in the samples.

The reduction of the peak width in figure 1 with temperature is indicative of a larger crystallite size ($d$) when applying the Sherrer equation:

$$d = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $\lambda$ is the wavelength used, $\theta$ the diffraction angle and $\beta$ the full width at the half maximum of the more intense peak (222), Samples annealed at 1000 °C showed very intense reflections that matched appropriately the JCPDS43-1036 diffraction card, correspond to the cubic phase of Y$_2$O$_3$ with a lattice constant of 10.604 Å. Since no other diffraction peaks were observed it can be concluded that no other compounds or phases were found in the samples.

The average values measured for the cumuli in the samples are 255 nm (400 °C), 162 nm (600 °C), 96 nm (800 °C) and 66 nm (1000 °C). By comparing these values with those obtained for the crystallite size in XRD (table 1) it can be concluded that the cumuli might consist of several of the crystallites detected in XRD. The demonstration of this assumption is left for further work given the need of an HRSEM to resolve cumuli structure. Such fact can be of importance when studying the luminescent emission, this is due to the presence of unsatisfied boundaries that introduce electronic states in the bandgap that can be used in the relaxation process. Also, the short-range symmetry in grain boundaries modifies the crystal field and in consequence the

| Temperature (°C) | Crystallite size (nm) | Average cumuli size (nm) |
|------------------|-----------------------|-------------------------|
| 600              | 21                    | 162                     |
| 800              | 25                    | 96                      |
| 1000             | 36                    | 66                      |

Figure 1. XRD patterns obtained by samples doped at 1.5 at% and annealed at different temperatures. The sample treated at 1000 °C shows the best crystallinity, while that treated at 400 °C depicted a rather amorphous phase.
electron transition probability. Since samples treated at 1000 °C were more crystalline: showing the largest values of crystallite size and smaller grain size, this temperature will be used in advance to prepare the luminescent films.
Properties of luminescent powders

Figure 3 compares SEM images of samples annealed at 1000 °C with different Tm concentrations. From the measurements carried out, it can be said that the dopant concentration has no influence on the surface morphology of the samples: the cumuli are still present. However, the presence of the rare earth does have an
Influence on the cumuli size, by observing the average grain size values measured: 103.8 nm (0 at%), 59.1 nm (0.5 at%), 74.8 nm (1.5 at%) and 63.3 nm (3.5 at%), it can be observed a shrinkage as large as 40 nm. This might be due to the presence of chlorine atoms in the solution, whose high electronegativity limits the growing speed of grains by including an intermediate solvation step in the reaction process. The first step of the reaction implies the formation of yttrium hydroxide precipitates and nitric acid:

\[ \text{YN}_3 \text{O}_3 + 3\text{H}_2\text{O} \rightarrow \text{Y(OH)}_3 + 3\text{HNO}_3 \]  

These yttrium hydroxides are decomposed when increasing temperature, yielding yttrium oxide and water molecules:

\[ 2\text{Y(OH)}_3 \rightarrow \text{Y}_2\text{O}_3 + 3\text{H}_2\text{O} \]  

However, when including thulium chloride, chlorine ions solvate yttrium ions producing:

\[ \text{YN}_3 \text{O}_3 + 3\text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{Y(OH)}_2\text{Cl} + \text{OH}^- + 3\text{HNO}_3 \]  

Thus, when the annealing temperature increases it is obtained:

\[ 2\text{Y(OH)}_2\text{Cl} \rightarrow \text{Y}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{HCl} \]  

In this case, since chlorine ions have a smaller radius than hydroxide ions it is expected larger dissociation energy and a larger time of crystal formation, thus, the smaller grain size observed.

EDS analysis was performed on samples with different thulium concentration and heat treated at 1000 °C. Figure 4 shows a sample of the spectra obtained from the microscope, while table 2 shows the results of the percentages of yttrium, thulium and oxygen atoms present in the sample, as well as the theoretical percentages of the stoichiometric compound. The values obtained for thulium atoms indicate that its incorporation increases with its concentration in the reaction solution; thus, the incorporation can be properly controlled. The fact that oxygen values remain practically unchanged while yttrium percentages decrease is indicative of substitutional incorporation of thulium atoms in yttrium sites. When analyzing the \( \text{Y} + \frac{\text{Tm}}{\text{O}} \) ratios it is observed that it decreases with yttrium concentration, indicating a larger amount of oxygen that can be incorporated in interstitial sites or that can be indicative of yttrium vacancies.

Table 2. EDS results for chemical composition of samples doped with different thulium concentrations. When compared to the stoichiometric theoretical compound it is observed that oxygen presence increases with the increase of thulium concentration in the start solution.

| Tm\(^{3+}\) at% | O   | Y   | Tm | (Y + Tm)/O |
|-----------------|-----|-----|----|------------|
| Theoretical     | 60  | 40  | 0  | 0.66       |
| 0.0             | 61.70| 38.30| 0.00| 0.62       |
| 0.5             | 64.09| 35.63| 0.28| 0.56       |
| 1.0             | 61.97| 37.68| 0.35| 0.61       |
| 1.5             | 63.08| 36.33| 0.60| 0.58       |
| 2.5             | 63.90| 35.04| 1.82| 0.57       |
| 3.5             | 65.12| 33.44| 1.94| 0.54       |

Figure 4. EDS spectra of the sample treated at 1000 °C, peaks corresponding to yttrium, oxygen and thulium are indicated.
The emission and excitation spectra of samples annealed at 1000 °C are shown in figure 5. In all samples, excited with a wavelength of 362 nm, the characteristic emission of Tm³⁺ ion is observed, corresponding to transitions ¹D₂→³H₄, ¹D₂→³H₅, ¹G₄→³H₆ and, being the more intense, the one corresponding to a transition ¹D₂→³F₄ (figure 5(a)). The inset in figure 5(a) shows the intensity for the last transition versus thulium concentration. As can be seen, the intensity increases with the dopant concentration up to a maximum at a concentration of 1.5 at%. At larger concentrations, the intensity decreases due to the well-known quenching effect. The excitation spectra of the sample doped at 1.5 at%, shown in figure 5(b), presents a global maximum at 362 nm and a second peak at 369 nm, these maxima corresponding to a direct excitation of the Tm³⁺ ions.

The luminescence emission was also recorded for samples doped at 1.5 at% with different annealing temperatures. As can be seen, in figure 6 the sample treated at 1000 °C showed the highest intensity. Such emission can be attributed to the better crystallinity of which we talked in previous sections; this is, that the sample presents fewer grain boundaries where light can be scattered or reabsorbed, and the probability of non-radiative transitions is larger.

**Properties of LDPE films**

IR spectra of pristine polyethylene film and the film with the luminescent powders in it is shown in figure 7. In this figure it is observed the narrow absorption lines corresponding to asymmetric (2916 cm⁻¹) and symmetric (2848 cm⁻¹) vibrations of aliphatic groups. The band at 1463 cm⁻¹, corresponds to an asymmetric deformation of CH₂ or CH₃ groups, and the band at 719 cm⁻¹ is assigned to the rocking vibrations from...
out-of-phase and in-phase ethylene groups of neighbored chains [17]. The sample containing luminescent powders presents the same absorption lines, but adds one more at 562 cm$^{-1}$, that according with file SDBS 40494 is assigned to Y-O stretching vibrations.

Transmittance spectra of both samples were also recorded and are shown in figure 8. Pristine films show a transmittance above 90% in the visible region; while the average transmittance of the sample with the powders decreases to 65%. Such decrement can be attributed to dispersion processes comprising the dispersed powder.

Luminescence tests of the $\text{Y}_2\text{O}_3$:Tm powder and the PE + $\text{Y}_2\text{O}_3$:Tm films are shown in figure 8. It is observed, in the emission region, that the emission intensity at 452 nm decreases, while the emission of the $^3\text{G}_4-^3\text{H}_6$ transition of thulium at 463 nm completely disappears; also, in the excitation region is observed the peak at 361 nm disappeared, while a maximum appeared at 371 nm. Such behavior can be explained according to the work of Nehate et al [18] where they studied luminescence in low-linear-density polyethylene, low-density polyethylene and high-density polyethylene. It turns out that the compound presents a large emission band (from 300 to 500 nm) constituted by three wide bands peaking at 400 nm, the more intense, and at 360 nm and 468 nm, the other two. The emission at 468 nm is attributed to C–H or –CH$_2$ (bending) chain. Since the emission band of the polymer at 360 nm matches with the 362 nm of our excitation wavelength, its energy might be used to excite mostly the polymer vibrations instead of thulium atoms. This leads to the decrease of the
360 nm peak in the excitation spectra, recorded at 452 nm, leaving as a maximum excitation wavelength the one at 371 nm. However, when using the 360 nm to excite the sample, the emission spectra in figure 9 still shows a decreased emission in 452 nm, this indicates that some energy is used to excite thulium ions and some to excite the polymer vibrations, the latter is inferred by the appearance of an emission shoulder at 468 nm. In addition, the disappearance of the emission at 463 nm could be attributed to an absorption of the polymer, since this wavelength is close to the emission band peaked at 468 nm the polymer vibrations might be producing a quenching effect on the emission. In the work of Nehate et al, the excitation wavelength was of 205 nm, since our smallest wavelength is 230 nm we could not reproduce these results.

The emission decay time of both samples was also determined, figure 10 shows the graph of intensity versus time obtained. As can be seen, the powder presents an almost linear decay that can be related to a single radiative process with a decay time of 9.293 μs. The polyethylene sample presents a different behavior, the emission decays in a two-step process, the first one carried on in the first 25 μs with a decay time of 1.156 μs, and the second one after 25 μs, where the behavior is rather similar to that of the powder sample and presents a decay time of 4.086 μs. Such behavior could also be explained based on the work of Nehate et al. Since the polymer chains are being excited by the emitted photons of thulium, some of these might reemit or disperse energy as

![Figure 8.](image) UV–vis spectra of an LDPE film with and without phosphors in it. The average transmittance decays from 92% to 68% due to the dispersion of light from the phosphor particles.

![Figure 9.](image) Comparison of the excitation and emission spectra of the as-synthesized yttrium oxide powder and the same powder supported by the polyethylene film. The loss or decrease of some peaks from the phosphor is indicated, as well as the presence of new small emissions attributed to the polymer.
vibrations through the polymer; in this case, the emission would decay fast: yielding the behavior observed in the first microseconds. Once the emission centers in the polymer are depleted, only the emission centers in the yttrium oxide remain and decay at a smaller rate: yielding the behavior of the decay in the region above 25 μs.

Absolute quantum yield measured for both samples with the integrating sphere module results in low values. In the powder case, the value obtained was 0.46%, while the value obtained for the luminescent polymer is 0.14%. The first value indicates a low efficient absorption-transmission-emission process in the phosphor. The second value is expected due to the absorption of the main emission lines of thulium by the polyethylene. Since quantum yield is defined as the ratio of the emitted to the absorbed energy, in this case, the polyethylene host increased probably the absorption of energy of this system, which was then dispersed through non-radiative processes, leading to a drop in the quantum yield value.

Conclusions

Thulium-doped yttrium oxide powders were synthesized by the polyol method. X-ray diffraction showed an improvement of crystallinity as temperature rised. Such conclusion is correlated by SEM images and a study of average grain and crystallite sizes where grain size decreases with temperature while crystallite size increases. Sample doped with 1.5 at% of thulium presents a grain size of about 63 nm, consisting of crystallites of about 36 nm. The temperature of 1000 °C presents both the best crystallinity and the more intense luminescent emission. EDS studies indicate a larger oxygen atoms percentage in the samples as thulium concentration rises.

The powder synthesized with a concentration of thulium of 1.5 at% and annealed at 1000 °C was successfully hosted on low-density polyethylene and dispersed as a thin film on glass substrates using the dip-coating technique. FTIR spectra of a film with and without the powder showed the typical absorption of the polymer and, in due case, the absorption peaks were attributed to yttrium oxide. UV–vis spectra showed a decrease in average transmittance in the visible region which is due to a dispersion phenomenon provoked by the dispersed particles of the phosphor.

The luminescent emission of the powder is distorted by the polymer presence: while the typical emission of thulium at 452 and 463 nm is present in the powders, the former wavelength is attenuated by the polymer while the latter is completely lost. Also, the appearance of emission at 468 nm, attributed to the polymer, is shown. The excitation spectrum is modified too by the polymer, while three peaks are registered at 358, 362 and 369 nm for the powder, only the wavelength at 369 nm remains as an activator of the emission. The effect of the polymer is also dramatic in the decay time of the luminescent emission. On one hand, the powder presents a typical decay corresponding to a random relaxation of the atoms with a decay time of 9.293 μs; on the other hand, the powder in the polymer showed a two-stage decay behavior. Within the first 25 μs the decay time is attributed to an emission of the polymer with a decay time of 1.156 μs, once this emission is depleted the remnant emission is due to the phosphor with a decay time of 4.086 μs.
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