Comparison of luminescent properties of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ and $\text{LaPO}_4\text{:Ce}^{3+}$, Tb^{3+} phosphors prepared by various synthetic methods

S. Lee ^a, J. I. Choi ^b, Y. J. Kim ^b, J. K. Han ^c, J. Ha ^b, E. Novitskaya ^a, J.B. Talbot ^{b,d} and J. McKittrick ^{a,b,*}

^a Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA

^b Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093, USA

^c Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA

^d Department of NanoEngineering, University of California, San Diego, La Jolla, CA 92093, USA

Abstract

The crystallite and particle sizes, morphology and corresponding photoluminescence (PL) properties of nanocrystalline phosphors $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ and $\text{LaPO}_4\text{:Ce}^{3+}$, Tb^{3+} , produced by combustion synthesis, co-precipitation, hydrothermal reaction, sol-gel, spray pyrolysis, and solid-state reaction protocols, are compared. In general, phosphors particles with a relatively large crystallite size with a spherical and agglomerated morphology are favored for emitting the highest PL intensity. However, spray-pyrolyzed particles with a uniform spherical morphology and narrow size distribution produced the lowest PL emission intensity, which is attributed to the small crystallite size. For both compositions, the PL emission intensity increased with increasing crystallite size, but was not dependent on the particle size.

Keywords: phosphor, photoluminescence, crystallite size, particle size, morphology.

* Corresponding author: Phone No.: 1-858-534-5425; Fax No.: 1-858-534-5698; jmckittrick@ucsd.edu

1. Introduction

Understanding and enhancing the luminescence output of nanophosphors is important for applications such as displays, sensors, scintillators and lighting [1-4]. Among the numerous phosphors, europium-activated yttrium oxide ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) has been widely used as a red-emitting phosphor in fluorescent lamps, high resolution projection devices and displays [5,6]. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors show a strong 611 nm red emission from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition and weaker emissions from the $^5\text{D}_0 \rightarrow ^7\text{F}_{1,3}$ transitions of Eu^{3+} [7,8]. Cerium and terbium-activated lanthanum phosphate ($\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$) displays an efficient 543 nm green emission of Tb^{3+} under deep UV radiation, which are widely used as a green-emitting phosphors in fluorescent lamps [9]. UV excitation of Ce^{3+} occurs through a $4\text{f}^1 \rightarrow 4\text{f}^0 5\text{d}^1$ transition and then energy transfer from Ce^{3+} to Tb^{3+} arises, resulting in a Tb^{3+} emission from the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 0-6$) relaxation.

$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ have been synthesized through various methods such as spray pyrolysis [10,11], microemulsion [12,13], combustion [14,15], sol gel [16,17], hydrothermal [18,19], homogeneous precipitation [20,21], and co-precipitation [22,23]. The microstructure and physical properties are largely dependent on the characteristics of the precursors in the controlled synthesis and thermal decomposition conditions. These conditions may have an effect on the morphology, crystallite and particle size, and photoluminescence (PL) emission intensity of the resulting phosphors. A crystallite is the smallest detectable single crystal and its size is usually estimated from X-ray diffraction line broadening analysis based on the Scherrer's formula or from transmission electron microscope studies. A particle consists of multiple crystallites that are strongly bound together. These sizes are measured by scanning electron microscopy (SEM) or from light scattering methods. Agglomerates are a number of particles that are weakly or strongly held together and their size can be measured using SEM or

light scattering methods. Optimal phosphors for any application are sub-micron sized, spherically shaped powders with a non-agglomerated narrow size distribution.

There have been studies that report the effects of crystallite and particle size on PL emission intensity for numerous phosphors, each synthesized by a sole method. An increase in PL intensity has been observed with an increase in crystallite size [11,24-29]. With smaller crystallites, the probability for non-radioactive recombination becomes more probable due to the increased number of atoms in grain boundaries and on the surface, lowering the light generation efficiency compared to larger crystallites. There are only a few reports on the effect of particle size. Wang et al. [30] prepared submicron phosphors of different crystallite and particle sizes through by varying the synthesis temperatures. They observed an increase in PL emission intensity when particle size was increased from 200 to 500 nm with a constant crystallite size, but PL emission intensity leveled when the particle size was ≥ 500 nm. It was concluded that the crystallite size had a more important role in affecting PL emission intensity than the particle size. Jung et al. [31] studied the effects of particle size and crystallite size on PL emission intensity for phosphors prepared by spray pyrolysis and found the emission intensity increased for particles up to ~ 3 μm in size and leveled off for particle sizes of 4 μm to 12 μm , similar to results of Wang et al. [30], although the leveling off occurred at a larger particle size. From these two reports, it appears that as the particle size increases, the PL emission intensity increases up to a certain size and then remains constant beyond that size. The initial increase in intensity with increasing particle size may be due to increased light scattering.

There have been some studies that compare the effect of different synthesis methods on PL emission intensity [26,27,32-36], with most comparing a chemical synthesis method with a solid-state reacted material. If volatile elements such as Li are present, methods that require a lower

synthesis temperature were found to be optimal [35]. In one study, a single phosphor composition was synthesized by different methods had emission intensities in the order: combustion > hydrothermal > sol-gel > solid-state. The high PL intensity for the combustion synthesized powders was attributed to the uniform, spherical morphology [33]. There is no consensus about the best method to produce phosphors, which is likely dependent on the host composition.

There are no direct comparisons of the luminescence properties of phosphors synthesized by a large variety of methods and their relationship to the crystallite and particle sizes and morphology. In this report, a red-emitting simple oxide, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, and a green-emitting phosphate, $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$, were synthesized by various methods to investigate the effect of powder morphology, crystallite and particle sizes on the PL emission intensity.

2. Experimental

The starting materials were yttrium(III) nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich), europium(III) oxide (Eu_2O_3 , Alfa Aesar), citric acid (CA, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, EMD Chemicals), ethylene glycol ($\text{C}_2\text{H}_6\text{OH}$, Fischer Scientific), polyethylene glycol (PEG, $(\text{C}_2\text{H}_4\text{O})_n\text{H}_2\text{O}$, Sigma Aldrich), nitric acid (68 – 70%, EM Science), ammonium hydroxide (NH_4OH , Puritan Products), urea ($\text{CH}_4\text{N}_2\text{O}$, Fisher Scientific), terbium (III) nitrate hexahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich), cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Alfa Aesar), and lanthanum (III) nitrate pentahydrate ($\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Sigma Aldrich). All materials were used without further purification. The starting powders for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ consisted of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Eu_2O_3 (molar ratio $\text{Y}/\text{Eu} = 0.95/0.05$) and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ consisted of La_2O_3 , Tb_4O_7 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ (molar ratio $\text{La}/\text{Tb}/\text{Ce}/\text{P} = 0.9/0.025/0.075/1$). Solutions for both compositions were made with a 1:1 volume ratio of water and nitric acid and stirred for 30 min until a clear

solution was observed. The starting solutions for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ will be named solution A (Y molar amount = 0.95) and B (La molar amount = 0.9), respectively.

2.1. Sol-gel/Pechini method

CA (0.93 g), which acts as chelating agent for the metal ions, and 2.5 g of PEG, which acts as a cross-linking agent, were added to solution A. To solution B, 0.90 g of CA and 2.0 g of PEG were added. The solutions were continually stirred for 10 h at 80°C to form a transparent gel. The gels were preheated at 350°C for 1 h in air to evaporate residual water until a black powder remained. The powders from solution A was annealed at 800°C for 1 h, and from solution B was annealed at 1000°C for 1 h to remove organic materials, resulting in white phosphor powders.

2.2. Combustion method

Urea was added as fuel in the amount of 0.88 g for solution A and 1.28 g for solution B. After the addition of urea, the beakers were directly placed inside a preheated furnace at 500°C until the mixture started to boil and subsequently produced a flame that was sustained for a few seconds. The beakers were taken out of the furnace and allowed to cool to room temperature. The resulting powders were collected and transferred to ceramic crucibles. Powders from solution A were heated at 800°C for 1 h in air, and powders from solution B were heated at 1000°C for 1 h in air to produce phosphors.

2.3. Hydrothermal method

Solution A was heated at 100°C for 10 h until all residual acid was evaporated from the solution and a transparent solid was obtained. Water (25 ml) was added to the solid under stirring conditions until the entire solid dissolved. To produce the precipitate, NH_4OH was added

dropwise until the pH was ~6. The slurry was then transferred into a closed Teflon pressure vessel and thermally treated at 130°C for 24 h. The resulting solution was then filtered, dried at room temperature, and annealed at 800°C for 1 h in air to further crystallize the powders. For solution B, NH₄OH was added drop-wise until the pH was 5-6. The slurry was then transferred to the Teflon pressure vessel and treated at 130°C for 24 h. The heated solution was then filtered, dried at room temperature for 10 h, and annealed at 1000°C for 1 h for further crystallization of the phosphor powders.

2.4. Co-precipitation method

To create precipitates for solutions A and B, the same steps were taken up to control the pH as in the hydrothermal method. Instead of annealing in the pressure vessel, both solutions were filtered and dried at room temperature for 10 h. The resulting powders from solution A were annealed at 800°C for 1 h in air, and those from solution B were annealed at 1000°C for 1 h in air.

2.5. Spray-pyrolysis method

Mists were generated from solution A by a single 2.4 MHz ultrasonic nebulizer (Sonaer Ultrasonics, Farmingdale, NY) which was then directed into a tube furnace operating at 800°C using argon as carrier gas. The flow rate was set to a range of 0.1 - 0.5 Lmin⁻¹ to control the residence time of the mist in the heating zone to 5-10 s. After passing a heat sink, the particles were collected from a charged plate at the end of the tube. The same process was used for solution B with the tube furnace operating at 1000°C.

2.6 Solid-state method

Solutions of A or B containing ethanol instead of the water and nitric acid solution were milled for 12 h, which resulted in a grey colored mixture. The solutions were then filtered, dried at room temperature to evaporate the residual ethanol, and annealed at 1500°C for 10 h in air.

2.7. Characterization

All particles were slightly ground using a mortar and pestle before analysis. The crystallite sizes were determined from X-ray diffraction (XRD) peak broadening analysis. The particles were examined using a field emission scanning electron microscope (SEM) (FEI-XL30, FEI Company, Hillsboro, OR). The particle sizes were determined using the intercept method, measuring at least 50 particle diameters. PL emission spectra were taken using a Jobin-Yvon Triax 180 monochromator and SpectrumOne charge-coupled device detection system, which was shared with the PL system that uses a 450 W Xe lamp as the excitation source. An excitation wavelength of 276 nm was used for $\text{LaPO}_4\text{:Ce}^{3+}$, Tb^{3+} and 253 nm for $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$. These excitation wavelengths were chosen as they produced the highest PL emission intensity.

3. Results and Discussion

Figure 1 shows the XRD patterns of the $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ powders produced using various methods, each post-annealed at 800°C in air, 1500°C for solid-state. All the diffraction peaks can be indexed to $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ compatible with JCPDS No. 43-1036 for Y_2O_3 with a cubic structure (lattice parameter $a = 1.059$ nm [37]). The peak positions for all synthetic methods are nearly the same, indicating the same Eu^{3+} content. Eu^{3+} substitutes for Y^{3+} and has a larger ionic radius, which would shift the XRD peaks if the Eu^{3+} concentration were not the same. No impurity phases were detected. For the spray pyrolyzed powders, the intensity of the peaks is lowest and

they are broadest with the peaks slightly shifted to lower 2θ values, indicating that the crystallites are smaller, the structure more disordered and have a slightly higher Eu concentration compared to the other samples. The sol gel synthesized powders also have a somewhat lower intensity compared to the other samples, with the peaks shifted to larger 2θ values, suggesting that the Eu concentration may be slightly smaller than for the other samples.

Figure 2 shows the XRD patterns of the $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} particles prepared by various methods, each post-annealed at 1000°C in air, 1500°C for solid-state. LaPO_4 has a monoclinic crystal system with lattice parameters $a = 0.683$ nm, $b = 0.707$ nm, $c = 0.650$ nm, $\beta = 103.3^\circ$ [38]. All six samples exhibit the characteristic diffraction peaks of the monoclinic structure of LaPO_4 (JCPDS No. 32-0493), with the peak positions the same, except for the spray pyrolyzed powders. Similar to the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders, these peaks are less intense, broader and are at lower 2θ values. No traces of impurity phases were observed in the patterns.

It is clear from the XRD patterns that there are different magnitudes of peak broadening, showing that the crystallite size varied with each synthesis method. The crystallite size was calculated using the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where $\lambda = 0.154$ nm (x-ray wavelength), β is the line broadening at full-width half-maximum intensity, θ is the Bragg angle, and D is the mean size of the crystallites. The results are shown in Table 1. The crystallite sizes of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ range from 13.2 nm (spray-pyrolysis) to 28.2 nm (co-precipitation). The crystallite size of solid-state reacted $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders provided by OSRAM-Sylvania powders was 51.2 nm, which was the largest crystallite size (not shown in the XRD patterns). For $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} particles, the crystallite sizes were slightly larger and ranged from 14.1 nm (spray-pyrolysis) to 41.7 nm (sol-gel).

Each synthesis method produced different particle sizes and morphologies unique to the method, as shown in Figures 3 and 4. Figure 3a shows a SEM micrograph of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ particles prepared by co-precipitation, which were slightly agglomerated with particle diameters of $\sim 0.2\ \mu\text{m}$. The morphology is significantly different for the particles prepared by the hydrothermal method (Figure 3b), which also involves precipitation of the precursor phase. Most of the particles are not spherical, but exhibit a needle-like morphology of $0.9\ \mu\text{m}$ in length and $40\text{-}50\ \text{nm}$ in width. In Figure 3c the sol-gel particles have irregular shape and are agglomerates of spherical particles with an average agglomerate size of $2.2\ \mu\text{m}$. In Figure 3d the particles prepared by combustion synthesis also have an irregular, agglomerated shape with an average size of $1.6\ \mu\text{m}$. Figure 3e shows the spray-pyrolysis particles with a uniform, spherical morphology with a narrow size distribution with diameters between $0.3\text{-}0.6\ \mu\text{m}$. Figure 3f shows the solid-state powders with irregular, agglomerated morphology with an average particle size of $2.15\ \mu\text{m}$. Standard powders provided by OSRAM-Sylvania (solid-state reacted) are shown in Figure 3g and have shapes resembling various platonic solids and have the largest average particle size of $2.62\ \mu\text{m}$.

Figure 4 shows the SEM images for $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} particles prepared by the various methods. In Figure 4a and b, co-precipitation and hydrothermal powders, both forming precipitates under solution, are shown to have nearly spherical morphology, however being severely agglomerated. The average particle sizes from both hydrothermal and co-precipitation methods were $0.3\ \mu\text{m}$. The morphology is similar to the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders produced by these methods. In Figure 4c, sol-gel particles show a nearly spherical morphology (diameters of $1.4\text{-}2.3\ \mu\text{m}$) with less agglomeration compared to the particles by hydrothermal and co-precipitation methods, and less agglomeration than the sol-gel synthesized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. In Figure 4d, the

combustion-synthesized particles have an irregular shape with a particle size 2.3-3.1 μm , similar to the morphology of the combustion synthesized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The particle size of spray-pyrolyzed powders (Figure 4e) averaged 0.5 μm with a spherical morphology, similar to the spray pyrolyzed $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The solid-state synthesized powders (Figure 4f) show very irregular, agglomerated powders with an average particle size of 1.4 μm .

It can be concluded that the particle sizes and morphologies are similar between $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} under the same synthesis condition. Spray pyrolysis produces powders with the most uniform particles, having a spherical morphology and narrow size distribution. Combustion synthesized powders show the poorest morphologies, with large agglomerates and non-uniform particle sizes. Sol gel, co-precipitated and hydrothermal powders have uniform, small sizes but are agglomerated.

Different crystallite and particle sizes may affect the luminescence properties due to different surface-volume ratios and non-uniform surfaces [39]. Figure 5 shows the PL emission spectra (excitation wavelength, $\lambda_{\text{ex}} = 253 \text{ nm}$) of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders prepared by the different synthesis methods along with the OSRAM-Sylvania standard powders. Amongst the powders produced, the sol-gel method produced the highest emission intensity, though it is two times lower than the OSRAM-Sylvania powder, but also has half the crystallite size. Compared to the other chemically synthesized powders, the higher PL emission intensity of the sol gel powders can be attributed to the larger crystallite and particle size. Combustion, hydrothermal and co-precipitated powders have intermediate PL emission intensities. The low emission intensity of the solid-state reacted powders may be due to the relative low annealing temperature (1500°C); typically, solid-state reacted materials have high emission intensities. The spray pyrolyzed powders have the weakest emission intensity, which can be attributed to the smallest crystallite

size. The powder morphology appears not to be related to the intensity, which is in contrast with Wang et al. [40] who found the highest PL emission intensity for spherical powders of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ compared to rods or flakes.

Figure 6 shows the PL emission spectra ($\lambda_{\text{ex}} = 276 \text{ nm}$) of $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} powders prepared by various methods. The co-precipitated powders produced the highest intensity, which can be attributed to the relatively large crystallite size. The hydrothermal and sol gel powders had the next highest emission intensities, followed by combustion and solid-state reacted powders. As with the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders, the solid-state reacted and spray pyrolyzed powders had the lowest emission intensity.

Although all the chemically synthesized powders were all post-annealed after synthesis for the same time and temperature, there are obvious differences in the PL emission intensities. The sol gel powders generally show larger crystallite sizes. This may be linked to better atomic mixing in the precursor stage that results in shorter diffusion lengths for crystallization, compared to the other methods. On the other hand, spray pyrolyzed powders are formed in a tube furnace, in which evaporation of the solvent and then nucleation and growth of the crystalline phase must occur in sequence, that results in a weakly crystalline material.

Figure 7 show the influence of the crystallite size on the normalized PL emission intensity for both powder compositions. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders were normalized to the sol-gel powder peak intensity (the highest at 611 nm) while the $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} intensities were normalized to the co-precipitated powder peak intensity (the highest at 543 nm). From this plot, it can be concluded that increasing the crystallite size increases the emission intensity, in corroboration with other researchers [11,24-29]. The dotted line on Figure 7 is a best-fit line between crystallite size and normalized intensity. In general, sol-gel, co-precipitated and combustion synthesized

powders have high PL emission intensity and the spray pyrolyzed powders have the lowest emission intensity. The increase in PL emission intensity with increasing crystallite size may arise from several factors: (1) less lattice distortion as evidenced by the narrowing of the XRD peaks [41,42] and (2) more uniform activator distribution across the crystallite [43-47].

The crystallite sizes for spray pyrolysis, hydrothermal, co-precipitation and solid-state synthesized powders are nearly the same for $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ and $\text{LaPO}_4\text{:Ce}^{3+}$, Tb^{3+} , despite Y_2O_3 having three times the unit cell volume of LaPO_4 . The combustion synthesis methods produced two times larger crystallite sizes for $\text{LaPO}_4\text{:Ce}^{3+}$, Tb^{3+} than for $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$, which may be due to the rapid, exothermic reaction that could inhibit the formation and growth of crystallites of the larger unit cell sized Y_2O_3 .

Figure 8 is a plot of the normalized PL emission intensity (as in Figure 7) as a function of particle size $\pm$ standard deviation. The dotted line shows a linear regression of the average sizes. For both compositions, co-precipitation, hydrothermal and spray pyrolysis methods produced the smallest particle sizes, but resulted in a wide range of normalized intensities from ~ 0.3 to 1.0 . Sol gel and combustion methods produced the largest particle sizes, with the normalized intensities between ~ 0.4 to 1.0 . There appears to be no correlation between particle size and PL emission intensity, in contrast to other reports that find a positive particle size dependence on emission intensity [30,31]. It has been reported that dangling bonds [48] or absorbed molecular or atomic species [49,50] at the surface can act as luminescence traps, suggesting that the PL emission intensity would decrease for smaller particles. Additionally, Mie scattering scales with the square of the inverse radius and is larger for smaller particles [51]. However none of the above appears to affect the present results.

Conclusions

This is the first study comparing the crystallite and particle sizes and morphology with the photoluminescence (PL) emission intensity of two phosphor powders synthesized by six methods. The main findings are:

- Red-emitting $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and green-emitting $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} powders were successfully prepared by combustion reaction, co-precipitation, hydrothermal, sol-gel, spray pyrolysis and solid-state synthesis methods.
- For $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, the sol-gel and spray pyrolysis methods showed the highest and lowest PL emission intensities, respectively. For $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} , the co-precipitation method and spray pyrolysis methods had the highest and lowest PL emission intensities, respectively.
- In general, co-precipitation produced high PL emission powders with nearly spherical morphologies and a narrow size distribution.
- The most uniform, spherical powders with a narrow size distribution were produced by spray pyrolysis. Combustion synthesized powders show the poorest morphologies, with large agglomerates and non-uniform particle sizes.
- The crystallite sizes are nearly identical for spray pyrolysis, hydrothermal, co-precipitation and solid-state reacted powder of both compositions.
- The particle sizes and morphologies are similar under the same synthesis conditions for both compositions.
- The PL emission intensity increases with increasing crystallite size, however no correlation was found between PL emission intensity particle size.

Acknowledgements

This work is supported by the National Science Foundation Ceramics Program Grant DMR 1411192 and the U.S. Department of Energy Grant, DE-EE0002003.

References

1. H. Chandler, "Development of nanophosphors – A review," *Mater. Sci. Eng. R*, 49, 113-155 (2005).
2. F. Monti, E. Pavoni, N. Armaroli, "Nanomaterials for lighting and solar energy conversion," in *Nano-Structures for Optics and Photonics*, B. Di Bartolo (ed.), NATO Science for Peace and Security Series B: Physics and Biophysics, Springer Science+Business Media, Dordrecht, 2015, pp. 373-414.
3. B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, M. Kinnan, S. Hoppe, S. Thoma, K.M. Hattar, F.P. Doty, "Size effects on the properties of high z scintillator materials," *Proc. SPIE*, 8509, 85090G-1-G6 (2012).
4. P.K. Sharma, A.C. Pandey, "Rare-earth based insulating nanocrystals: Improved luminescent nanophosphors for plasma display panels," in *Intelligent Nanomaterials: Processes, Properties, and Applications* (eds A. Tiwari, A. K. Mishra, H. Kobayashi and A.P.F. Turner), John Wiley & Sons, Inc., Hoboken, NJ, USA (2012), 89-148.
5. C.R. Ronda, "Phosphors for lamps and displays: an applicational view," *J. Alloys Comp.*, 225, 534-538 (1995).
6. C. He, Y. Guan, L. Yao, W. Cai, X. Li, Z. Yao, "Synthesis and photoluminescence of nano- $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ phosphors," *Mater. Res. Bull.*, 38(6), 973-979 (2003).
7. C.R. Ronda, "Recent achievements in research on phosphors for lamps and displays," *J. Lumin.* 72, 49-54 (1997).
8. G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer-Verlag (1994).
9. H. Meyssamy, K. Riwotzki, A. Kornowski, S. Naused, M. Haase, "Wet-chemical synthesis of doped colloidal nanomaterials: particles and fibers of $\text{LaPO}_4\text{:Eu}$, $\text{LaPO}_4\text{:Ce}$, and $\text{LaPO}_4\text{:Ce, Tb}$," *Adv. Mat.*, 11, 840-844 (1999).
10. K. Y. Jung, Y. C. Kang, Y. K. Park, "DMF effect on the morphology and the luminescence properties of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ red phosphor prepared by spray pyrolysis," *J. Ind. Eng. Chem.*, 14, 244-229 (2008).
11. I.W. Lenggoro, B. Xia, H. Mizushima, K. Okuyama, N. Kijima, "Synthesis of $\text{LaPO}_4\text{:Ce, Tb}$ phosphor particles by spray pyrolysis," *Mat. Lett.*, 50, 92-96 (2001).
12. Q. Pang, J. Shi, Y. Liu, D. Xing, M. Gong, N. Su, "A novel approach for preparation of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ nanoparticles by microemulsion-microwave heating," *Mat. Sci. Eng.*, 103, 57-61 (2003).
13. R. Chai, H. Lian, P. Yang, Y. Fan, Z. Hou, X. Kang, J. Lin, "In situ preparation and luminescent properties of $\text{LaPO}_4\text{:Ce}^{3+}$, Tb^{3+} nanoparticles and transparent $\text{LaPO}_4\text{:Ce}^{3+}$, Tb^{3+} /PMMA nanocomposite," *J. Coll. & Interface Science.*, 336, 46-50 (2009).
14. C. Waite, R. Mann, A. L. Diaz, "Measurement of host-to-activator transfer efficiency in nano-crystalline $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ under VUV excitation," *J. Solid State Chem.*, 198, 357-363 (2013).

15. N. Arul Dhas, K. Patil, "Synthesis of AlPO_4 , LaPO_4 , and KTiOPO_4 by flash combustion," *J. Alloys & Comp.*, 202 137-141 (1993).
16. R.P. Rao, "Preparation and characterization of fine grain yttrium based phosphors by sol gel process," *J. Electrochem. Soc.*, 143, 189-197 (1996).
17. M. Yu, J. Lin, J. Fu, Y. Han, "Sol-gel fabrication, patterning and photoluminescent properties of $\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$ nanocrystalline thin films," *Chem. Phys. Lett.*, 371, 178-183 (2003).
18. P. Tanner, L. Fu, "Morphology of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ prepared by hydrothermal synthesis," *Chem. Phys. Lett.*, 470, 75-79 (2009).
19. H. Dong, Y. Liu, P. Yang, W. Wang, J. Lin, "Controlled synthesis and characterization of LaPO_4 , $\text{LaPO}_4\text{Ce}^{3+}$ and $\text{LaPO}_4\text{Ce}^{3+}, \text{Tb}^{3+}$ by EDTA assisted hydrothermal method," *Sol. Stat. Sci.*, 9, 1652-1660 (2010).
20. C. Wang, Y. Li, W. Zhang, M. Yin, "Effect of acidity of microstructure and spectroscopic properties of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ powders and ceramics," *Spect. Act.*, 75, 8-13 (2010).
21. N. Nunez, S. Liviano, M. Ocana, "Citrate mediated synthesis of uniform monazite LnPO_4 ($\text{Ln} = \text{La}, \text{Ce}$) and Ln:LaPO_4 ($\text{Ln} = \text{Eu}, \text{Ce}, \text{Ce+Tb}$) spheres and their photoluminescence," *J. Coll. & Interface Sci.*, 349, 484-491 (2010).
22. R. Yavetskiy, V. Baumer, M. Danylenko, A. Doroshenko, I. Ogorodnikov, I. Petrusha, A. Tolmachev, V. Turkevich, "Transformation-assisted consolidation of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ nanospheres as a concept to optical nanograin ceramics," *Ceram. Int.*, 40, 3561-3569 (2013).
23. X. Hu, S. Yan, L. Ma, G. Wan, J. Hu, "Preparation of $\text{LaPO}_4\text{:Ce,Tb}$ phosphor with different morphologies and their fluorescence properties," *Powder Tech.*, 192, 27-32 (2009).
24. O.A. Graeve, S. Varma, G. Rojas-George, D.R. Brown, E.A. Lopez, "Synthesis and characterization of luminescent yttrium oxide doped with Tm and Yb," *J. Am. Ceram. Soc.*, 89, 926-931 (2006).
25. A. Boukerika, L. Guerbous, "Annealing effects on structural and luminescence properties of red Eu^{3+} -doped Y_2O_3 nanophosphors prepared by sol-gel method," *J. Lumin.*, 145, 148-153 (2014).
26. N. Lakshminarasimhan, U. Varadaraju, "Role of crystallite size on the photoluminescence properties of $\text{SrIn}_2\text{O}_4\text{:Eu}^{3+}$ phosphors synthesized by different methods," *J. Solid State Chem.*, 181, 2418-2423 (2008).
27. L.S. Chi, R.S. Liu, B.J. Lee, "Synthesis of $\text{Y}_2\text{O}_3\text{:Eu}, \text{Bi}$ red phosphors by homogeneous coprecipitation and their photoluminescence behaviors," *J. Electrochem. Soc.*, 152, J93-J98 (2005).
28. K.Y. Jung, C.H. Lee, Y.C. Kang, "Effect of surface area and crystallite size on luminescent intensity of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ phosphor prepared by spray pyrolysis," *Mater. Lett.*,

- 59, 2451-2456 (2005).
29. J. K. Han, M. E. Hannah, A. Piquette, J. B. Talbot, K. C. Mishra, J. McKittrick, "Sol-gel synthesis of single phase, high quantum efficiency $\text{LiCaPO}_4\text{:Eu}^{2+}$ phosphors," ECS J. Solid State Sci. & Tech., 1, R37-R40 (2012).
 30. W. Wang, W. Widiyastuti, T. Ogi, I. Lenggono, K. Okuyama, "Correlations between crystallite/particle size and photoluminescence properties of submicrometer phosphors," Chem. Mater., 19, 1723-1730 (2007).
 31. K. Jung, D. Lee, Y. Kang, S. Park, "Size-dependent luminescent properties of hollow and dense $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ blue phosphor particles prepared by spray pyrolysis," Korean J. Chem. Eng., 21, 1072-1080 (2004).
 32. J.K. Han, M.E. Hannah, A. Piquette, G.A. Hirata, J.B. Talbot, K.C. Mishra, J. McKittrick, "Structure dependent luminescence characterization of green-yellow emitting $\text{Sr}_2\text{SiO}_4\text{:Eu}^{2+}$ phosphors for near UV LEDs," J. Lumin., 132, 106-109 (2012).
 33. H.N. Luitel, R. Chand, T. Torikai, M. Yada and T. Watari, "Rare earth free $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor with controlled microstructure and its photocatalytic activity," Intl. J. Photoenergy, 2013, Article ID 410613 (2013).
 34. T. Ye, S. Li, X. Wu, M. Xu, X. Wei, K. Wang, H. Bao, J. Wang and J. Chen, "Sol-gel preparation of efficient red phosphor $\text{Mg}_2\text{TiO}_4\text{:Mn}^{4+}$ and XAFS investigation on the substitution of Mn^{4+} for Ti^{4+} ," J. Mater. Chem. C, 1, 4327-4333 (2013).
 35. H. He, R. Fu, H. Wang, X. Song, Z. Pan, X. Zhao, X. Zhang and Y. Cao, " $\text{Li}_2\text{SrSiO}_4\text{:Eu}^{2+}$ phosphor prepared by the Pechini method and its application in white light emitting diode," J. Mater. Res., 23, 3288-3294 (2008).
 36. Y. Li, D. He, Y. Want, M. Fu, Y. Wu, F. Miao, "Luminescence properties of nano-crystalline $\text{Ba}_3\text{MgSi}_2\text{O}_8\text{:Eu}^{2+}$, Mn^{2+} phosphors," J. Nanosci. Nanotech., 11, 9829-9832 (2011).
 37. S. Som and S.K. Sharma, " $\text{Eu}^{3+}/\text{Tb}^{3+}$ -codoped Y_2O_3 nanophosphors: Rietveld refinement, bandgap and photoluminescence optimization," J. Phys. D: Appl. Phys., 45, 415102 (11pp) (2012).
 38. S. Phadke, J.C. Nino, M.S. Islam, "Structural and defect properties of the LaPO_4 and $\text{LaP}_5\text{O}_{14}$ -based proton conductors," J. Mater. Chem., 22, 25388-25394 (2012).
 39. J. McKittrick, M.E. Hannah, A. Piquette, J.K. Han, J.I. Choi, M. Anc, M. Galvez, H. Lugauer, J.B. Talbot, K.C. Mishra, "Phosphor selection considerations for near-UV LED solid state lighting," ECS J. Solid State Sci. Technol., 2, R3119-R3131 (2013).
 40. L.S. Wang, Y.H. Zhou, Z.W. Quan, J. Lin, "Formation mechanisms and morphology dependent luminescence properties of $\text{Y}_2\text{O}_3\text{:Eu}$ phosphors prepared by spray pyrolysis process," Mater. Lett., 59, 1130-1133 (2005).
 41. L.A. Diaz-Torres, E. De la Rosa, P. Salas, H. Desirena, "Enhanced cooperative absorption and upconversion in Yb^{3+} doped YAG nanophosphors" Opt. Mater., 27, 1305-1310 (2005).

- 42 Q. Ju, Y. Liu, R. Li, L. Liu, W. Luo, X. Chen, "Optical spectroscopy of Eu^{3+} -doped BaFCl nanocrystals", *J. Phys. Chem. C*, 113, 2309–2315 (2009).
- 43 W. Zhao, S. Anghel, C. Mancini, D. Amans, G. Boulon, T. Epicier, Y. Shi, X.Q. Feng, Y.B. Pan, V. Chani, A. Yoshikawa, " Ce^{3+} dopant segregation in $\text{Y}_3\text{Al}_5\text{O}_{12}$ optical ceramics", *Opt. Mater.* 33 684-687 (2011).
- 44 H.J. Byun, J.U. Kim, H. Yang, "Blue, green, and red emission from undoped and doped ZnGa_2O_4 colloidal nanocrystals", *Nanotech.*, 20, 495602-495607 (2009).
- 45 Y.V. Yermolayeva, A.V. Tolmachev, T.I. Korshikova, R.P. Yavetskiy, M.V. Dobrotvorskaya, N.I. Danylenko, D. S. Sofronov, "Spherical core-shell structured nanophosphors on the basis of europium-doped lutetium compounds," *Nanotech.*, 20, 325601-325610 (2009).
- 46 X. Ye, W. Zhuang, Y. Hu, T. He, X. Huang, C. Liao, S. Zhong, Z. Xu, H. Nie, G. Deng, "Preparation, characterization, and optical properties of nano and submicron-sized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors", *J. Appl. Phys.* 105, 064302-064306 (2009).
- 47 X.C. Jiang, C.H. Yan, L.D. Sun, Z.G. Wei, C.S. Liao, "Hydrothermal homogeneous urea precipitation of hexagonal $\text{YBO}_3:\text{Eu}^{3+}$ nanocrystals with improved luminescent properties", *J. Solid. State. Chem.*, 175, 245–251 (2003).
- 47 E. Zych, C. Brecher, J. Glodo, "Kinetics of cerium emission in a YAG:Ce single crystal: the role of traps", *J. Phys.: Condens. Matter*, 12, 1947–1958 (2000).
- 49 H. Zhou, H. Alves, D.M. Hofmann, W. Kriegseis, B. K. Meyer, G. Kaczmarczyk, A. Hoffmann, "Behind the weak excitonic emission of ZnO quantum dots: $\text{ZnO}/\text{Zn}(\text{OH})_2$ core-shell structure", *Appl. Phys. Lett.*, 80, 210-212 (2002).
- 50 G. Xiong, U. Pal, J. Garcia Serrano, "Correlations among size, defects, and photoluminescence in ZnO nanoparticles", *J. Appl. Phys.*, 101, 024317-024322 (2007).
51. H.K. Park, J.H. Oh, Y.R. Do, "Toward scatter-free phosphors in white phosphor-converted light-emitting diodes,"

List of Table and Figure Captions

Table

- 1 Crystallite and particle sizes and normalized photoluminescence emission intensity for each synthesis method. PL for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ was normalized to the sol gel (SG) peak intensity at 611 nm (highest) and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ was normalized to the co-precipitated (CP) peak intensity at 543 nm (highest).

Figures

- 1 X-ray diffraction patterns of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ prepared by spray pyrolysis, sol gel, co-precipitation combustion, hydrothermal and solid-state reaction, compared with JCPDS card #43-1036 for cubic Y_2O_3 .
- 2 X-ray diffraction patterns of $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ prepared by spray pyrolysis, co-precipitation, solid-state reaction, hydrothermal, combustion and sol gel methods compared with JCPDS card #32-0493 for monoclinic LaPO_4 .
- 3 Scanning electron micrographs of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders produced by: (a) co-precipitation; (b) hydrothermal; (c) sol-gel; (d) combustion; (e) spray pyrolysis; (f) solid-state; (g) OSRAM-Sylvania sample. Bar = 2 μm .
- 4 Scanning electron micrographs of $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ powders produced by: (a) co-precipitation; (b) hydrothermal; (c) sol-gel; (d) combustion; (e) spray-pyrolysis; (f) solid-state reaction. Bar = 2 μm .
- 5 Photoluminescence emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders produced by different synthesis methods compared with a OSRAM-Sylvania powder..
- 6 Photoluminescence emission spectra of $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ powders produced by different synthesis methods.
- 7 Normalized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (red circles) and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ (green squares) photoluminescence emission intensity as a function of crystallite size. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is normalized to the sol gel intensity (highest intensity at 611 nm) and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ is normalized to the co-precipitated intensity (highest intensity at 543 nm).
- 8 Normalized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (red dashed) and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ (green solid) photoluminescence emission intensity as a function of particle size for different synthesis methods. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is normalized to the sol gel intensity (highest intensity at 611 nm) and $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ is normalized to the co-precipitated intensity (highest intensity at 543 nm).

Table 1. Crystallite and particle sizes and normalized photoluminescence emission intensity for each synthesis method. PL for $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ was normalized to the sol gel (SG) peak intensity at 611 nm (highest) and $\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$ was normalized to the co-precipitated (CP) peak intensity at 543 nm (highest).

	$\text{Y}_2\text{O}_3\text{:Eu}^{3+}$			$\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$		
Method	Crystallite size (nm)	Particle size (μm)	I/I_{SG}	Crystallite size (nm)	Particle size (μm)	I/I_{CP}
Combustion	18.0	1.64 ± 0.57	0.89	39.8	2.74 ± 0.45	0.78
Co-precipitation	28.2	0.32 ± 0.15	0.64	32.8	0.33 ± 0.07	1.00
Hydrothermal	23.7	0.95 ± 0.08	0.59	22.3	0.31 ± 0.10	0.94
Sol gel	26.3	2.19 ± 0.54	1.00	41.7	1.56 ± 0.52	0.89
Spray-pyrolysis	13.2	0.56 ± 0.18	0.29	14.1	0.76 ± 0.05	0.43
Solid-state reaction	17.5	2.15 ± 0.47	0.41	19.1	1.38 ± 0.24	0.62
OSRAM-Sylvania	51.2	2.62 ± 0.39				

Figure(s)
Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

(c)

(d)

(e)

(f)

Figure 5

Figure 6

Figure 7

Figure 8