

Synthesis and Characterization of Luminescent Yttrium Oxide Doped with Tm and Yb

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Combustion synthesis was used to obtain nanocrystalline $Y_{(2-x-y)}Tm_xYb_yO_3$ blue-emitting phosphors. From X-ray diffraction (XRD) it was determined that the powders in the as-synthesized state were in a state of high strain. Upon thermal treatment, the strain in the lattice decreased, which resulted in an improvement in the photoluminescence emission intensity of these phosphors. Fourier-transform infrared spectrometry analysis showed that there is a negligible difference in the absorbed impurities with heat-treatment temperature and time. Hence, it was concluded that the surface impurities do not play a role in the increase in luminescence intensity of these phosphors. The optimum activator concentrations were determined to be approximately $x = 0.02$ and $y = 0.01$.

I. Introduction

SEVERAL studies have shown that nanometer-sized phosphor powders exhibit spectroscopic properties that are different from their micrometer-sized counterparts. However, the effect of particle and crystallite size on the luminescence intensity of phosphors is still not completely understood. Specifically, the effect of particle and crystallite size on the brightness of phosphor materials is a matter of great controversy. In addition, the available literature continues to be unclear in regards to the distinction between particle size (i.e., agglomerate size) and crystallite size of phosphor powders. Generally, the observed luminescence in nanocrystalline materials has been explained using two arguments: (1) luminescence is dominated by quantum confinement effects, and (2) luminescence is dominated by defect interactions and chemical species. For the studies that generally fall within the first group, in which it is argued that quantum confinement plays a leading role in luminescence, it has been found that there is a decrease in luminescence with an increase in particle and/or crystallite size. For example, in studies where $Y_2O_3:Eu$ powders were prepared, one study showed that the emission intensity decreased approximately fivefold as the particles increased in size from 10 nm to 6 μm ,¹ while another study showed that the luminescence decreased with an increase in size from 36 to 111 nm.² The particle sizes in both studies were determined using dynamic light scattering, while the crystallite sizes were not determined. Another study, in which $Y_2O_3:Tb$ powders were prepared, showed a decrease in

luminescence efficiency with an increase in crystallite size from 4 to 9 nm.³ The crystallite size of the powders in this latter study was determined using transmission electron microscopy (TEM). As the powders were prepared using a sol-gel technique, in which agglomeration is known to occur quite frequently, the particle size distributions given in the paper are probably not the real particle size, but the crystallite size. As no electron microscopy images are provided in the paper, a determination of the level of agglomeration in the powders cannot be determined. Theoretically, the brightness of a phosphor can be determined using the method presented by Yoo and Lee.⁴ Using this method, it can be verified that the brightness of a phosphor decreases with an increase in particle size, even for particles of micrometer size. It has also been shown theoretically that a small particle size may be much better in the case of low-voltage excitation if the phosphors can be kept at high purity. This may be explained by realizing that smaller particles allow for more of the activators to be located at, or close to, the surface of the powder particles (for the same atomic percent of activators). This allows for a more efficient excitation of the activators. If the powder particles are very large, then some activators will be located deep inside the particle and will not be excited. In field-emission displays this is an acute problem because the energy of the electrons used for excitation is very low and the exciting electrons do not penetrate deep into the phosphor host.

For the studies that generally fall within the second group, in which luminescence is dominated by defect interactions and chemical species, it has been found that there is an increase in luminescence intensity with an increase in crystallite size. Table I lists recent results found in the literature. In reference⁷ the measurements on $Lu_2O_3:Tb$ were not fully quantitative, but differences in the emission intensities were so profound as to leave no doubt that the heat treatment of the powders brought a dramatic improvement in the materials' brightness. The increase in luminescence intensity was attributed to the elimination of dangling OH^- groups on the surface of the powders with heat treatment. Similar results were found in studies on $YAG:Cr$,⁹ where Fourier-transform infrared spectrometry (FTIR) showed that the powders heat treated at 1473 K had much more residual OH^- adsorbed surface groups, as well as NO_3^- and NH_4^+ complexes, as compared with the powders heat treated at 1823 K. Most other studies explained the results by concluding that the increase in crystallite size eliminated the large amount of grain boundaries, with the grain boundaries acting as luminescence quenching centers because of the higher concentration of impurities at those locations. However, as in the studies in which luminescence decreased with an increase in particle and/or crystallite size, none of the studies explicitly and quantitatively determined the impurities in the samples as a whole or at the grain boundaries. Determining these impurities by simply looking at the impurities in the reactants is impossible, because the incorporation of the impurities depends on the preparative technique used.

D. W. Johnson—contributing editor

Manuscript No. 20652. Received June 7, 2005; approved October 20, 2005.

Based in part on the thesis submitted by S. Varma for the M.S. degree in Metallurgical Engineering, University of Nevada-Reno, Reno, NV 89557.

Project supported by the UNR Office of the Vice President for Research, Junior Faculty Research Grant.

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Table I. Phosphor Materials that Exhibit an Increase in Luminescence with Increase in Crystallite Size

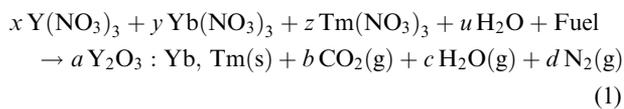
Material	Initial crystallite size (nm)	Final crystallite size	Reference
Y ₂ O ₃ :Eu	5–12	Bulk—microcrystalline	Tessari <i>et al.</i> ⁵
Y ₂ O ₃ :Er	5–20	Bulk—microcrystalline	Copabianco <i>et al.</i> ⁶
Lu ₂ O ₃ :Tb	12	65 nm	Zych ⁷
Y ₃ Al ₅ O ₁₂ :Tb	60	100 nm	McKittrick <i>et al.</i> ⁸
Y ₃ Al ₅ O ₁₂ :Cr	40	80 nm	McKittrick <i>et al.</i> ⁹
Y ₃ Al ₅ O ₁₂ :Ce	35–50	Bulk—microcrystalline	Lu and Jagannathan ¹⁰

In direct contradiction to all the studies mentioned above, some authors have found that there is no difference in the luminescence intensity between nanocrystalline and bulk phosphors.^{11–14} For example, in studies by Zhang *et al.*¹¹ powders of Y₂SiO₅:Eu were prepared by sol-gel and conventional solid-state synthesis. Results show that the sol-gel prepared powders had a crystallite size less than 50 nm. The sample prepared by solid-state synthesis had a crystallite size of ~2 μm. In comparing the nanocrystalline and bulk powders with the same concentration of Eu, it was found that the luminescence spectra exhibited no obvious differences. However, the amount of Eu that could be incorporated into the nanocrystalline powders was much higher before luminescence quenching was observed. The quenching concentration of bulk Y₂SiO₅:Eu is 2 mol%, while for the nanocrystalline powder, concentration quenching emerges until 6 mol%. The luminescence intensity of the nanocrystalline powders with a 6 mol% Eu³⁺ concentration is twice as great as that of bulk powders with a 2 mol% Eu³⁺ concentration, which is where the highest luminescence is observed for bulk powders. Another study that found the same results was for the preparation of Y₂O₃:Eu powders, for which luminescence quenching started at concentrations higher than about 10%, while a concentration of 6%–8% was expected.¹⁵ It was hypothesized¹⁶ that the nanocrystalline powders have fewer impurities that quench the luminescence because of the small size of the particles; hence more Eu³⁺ can be incorporated that allows for higher emission intensity.

The goal of this research effort was to develop a comprehensive understanding of the factors that affect the luminescence behavior of combustion-synthesized Y_(2-x-y)Tm_xYb_yO₃ nanophosphors with crystallite sizes between ~15 nm and several hundred nanometers. The material chosen for this study is a phosphor that exhibits blue luminescence and has applications in upconversion. When considering the importance of these materials for the display market and for other optoelectronic applications, it is absolutely essential that a clear understanding of their behavior be developed.

II. Experimental Procedure

Many different techniques have been used to prepare phosphor powders. In particular, combustion synthesis^{5–8,17–20} has been under development in the last 20 years, and offers many advantages over solid-state reactions. Combustion synthesis is a wet chemical process in which an exothermic reaction between precursor components is utilized. The exothermic reaction occurs between metal nitrates and a carbonaceous fuel in a rapid and self-sustaining manner. The type of fuel and the fuel-to-nitrate ratio are the most important controlling parameters for determining the reaction temperature reached during combustion.^{17,18} In a typical combustion reaction, the precursor mixture, which is diluted in a small amount of water and placed in a low-temperature muffle furnace, dehydrates and ruptures into a flame in less than 5 min. As an example, the reaction shown below for Y_(2-x-y)Tm_xYb_yO₃



is such that the products contain the desired voluminous, foamy material and gases that escape during the reaction. The gaseous products carry heat away from the system, hindering particle growth, and allowing the synthesis of powders with crystallites of nanometer dimensions. The gases increase the surface area of the powders by creating micro- and nano-porous regions within the reaction zone. Computer modeling studies have shown that there are over 100 possible product species that can be formed during the reaction.¹⁹ However, most of the products exist in such small amounts that they can be ignored. The phosphors in this study were synthesized using carbonylhydrazide (CH₆N₄O) as a fuel, as it has two desirable features: (1) it produces a very high reaction temperature, and (2) it complexes with the metal cations thereby increasing their solubility and preventing selective precipitation from occurring as the water is evaporated during the reaction. The carbonylhydrazide molecule has two amine groups, both of which are available to participate in the complexation of metal ions.²⁰

The experimental arrangement for executing a combustion synthesis experiment is exceedingly simple, only requiring a muffle furnace and a Pyrex crystallization dish. Figure 1 illustrates the steps to follow for the synthesis of the powders. In this work, the precursor material, after weighing as per the stoichiometric relation shown in Eq. (1), was mixed thoroughly in a crystallizing dish using de-ionized water. The dish was then placed in the furnace and reacted in less than 5 min. A typical batch of reacted powder consisted of approximately 5 g of material. The amount of Tm and Yb activators that were incorporated into the Y₂O₃ lattice varied between $x = 0.01$ – 0.05 and $y = 0$ – 0.05 in increments of 0.01 for a total of 30 samples, where x and y represent the subscripts in Y_(2-x-y)Tm_xYb_yO₃. Reactions with fuel lean (1:1.2) mixtures were performed because a stoichiometric mixture was found to be too violent. The precursors for the powders were: Y(NO₃)₃·6H₂O 99.99% (Alfa Aesar #11187, Ward Hill, MA), Tm(NO₃)₃·5H₂O 99.99% (Alfa Aesar #11203), Yb(NO₃)₃·5.5H₂O 99.99% (Alfa Aesar #11196), and carbonylhydrazide—(H₂NNH₂)₂C=O 97% (Alfa Aesar #A1145). After the synthesis, the powders were thermally treated in a furnace at 773, 1023, and 1273 K for various times.

After synthesis and thermal treatments, the characterization techniques that were performed on the as-synthesized and annealed phosphors were the following: (a) X-ray diffraction (XRD) (Philips 3100 Diffractometer, Koningklÿke Philips Electronics N.V., Eindhoven, The Netherlands). The phosphor to be examined (as-synthesized or thermally treated) was lightly ground by hand using a porcelain mortar and pestle. The ground powder was then spread evenly on a 2 mm thick aluminum plate with a 20 mm square hole in the center. The experiment was run using CuK α radiation. (b) Transmission electron microscopy (TEM) (JEOL 2010, JEOL Ltd., Tokyo, Japan). The ground powders were diluted in acetone and spread on a formvar grid. The instrument was run using a 200 kV accelerating voltage. (c) Photoluminescence measurements (Hitachi F-4500, Hitachi Ltd., Tokyo, Japan). The photoluminescence measurements were run using a 364 nm excitation wavelength. (d) FTIR (Midac Prospect-IR FTIR spectrometer, Midac Corporation, Costa Mesa, CA). An Attenuated Total Reflectance attachment from Pike Technologies was employed to analyze the powder samples. (e) Dynamic Light Scattering (DLS) (Microtrac Nanotrac 250, Microtrac, Inc., Montgomeryville, PA).

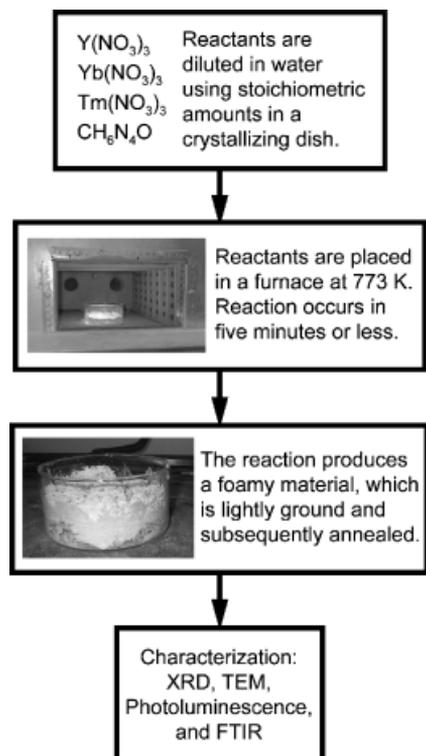


Fig. 1. Flow chart of the synthesis and characterization of powders.

Measurements were made by dispersing the powders with 0.5 g/L of sodium pyrophosphate in de-ionized water. The powders were magnetically stirred and ultrasonicated for 15 min in order to achieve a homogeneous dispersion.

III. Results and Discussion

(1) Morphology of Powders

Figures 2(a) and (b) show the XRD patterns obtained from the as-synthesized and annealed $Y_{1.98}Tm_{0.02}O_3$ powders. The pattern matches PDF #43-1036, which is the stable body-centered

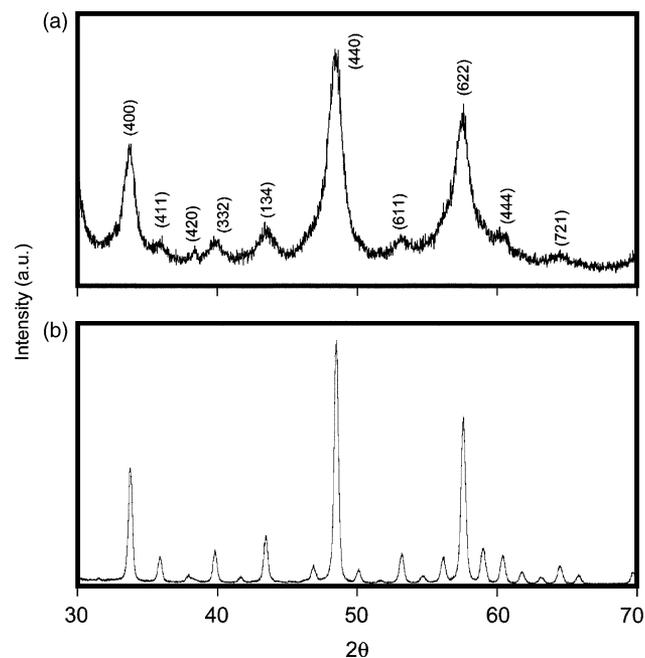


Fig. 2. X-ray diffraction pattern for (a) $Y_{1.98}Tm_{0.02}O_3$ powders in the as-synthesized state, and (b) $Y_{1.98}Tm_{0.02}O_3$ powders annealed for 12 h at 1273 K. All peaks, both labeled and unlabeled, correspond to cubic Y_2O_3 .

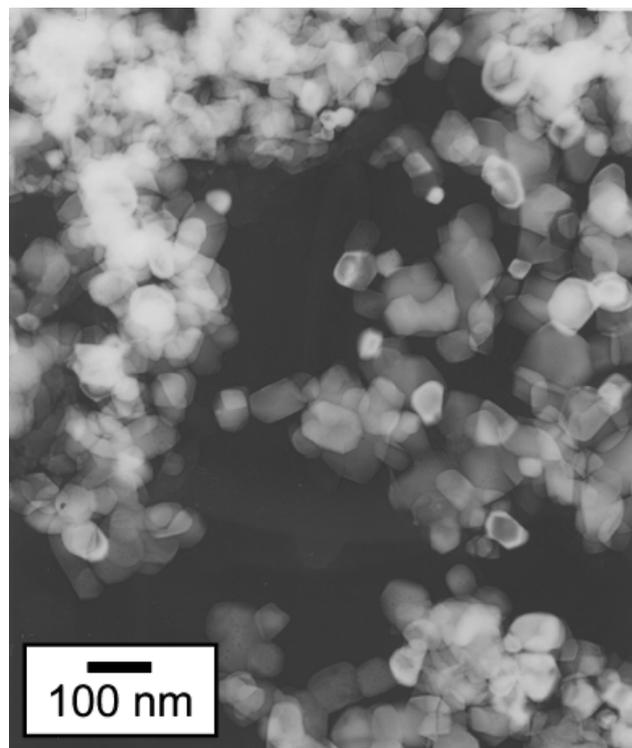


Fig. 3. Transmission electron microscopy image for sample annealed at 1273 K for 6 h.

cubic structure of Y_2O_3 with the Ia3 space group.²¹ The elementary cell contains 16 formula units with 32 cation sites, eight centro-symmetric sites with C_{3i} symmetry, and 24 non centro-symmetric sites with symmetry C_2 , for which the trivalent rare earth activators can substitute. From previous X-ray analysis and spectroscopic studies,²² it is now well-established that the trivalent rare earth ions occupy the two types of sites with approximately equal probability and that the optical transitions for luminescence mostly occur within the ions at the C_2 sites. In addition to phase determination, the diffraction patterns for all samples were used to determine the crystallite size and strain of the powders using the Williamson–Hall technique. As can be seen from the XRD results, the as-synthesized powders have broad peaks, which are diminished upon annealing of the powders at 1273 K. This can be attributed to both growth of the crystals and minimization of the strain in the crystals. These results will be discussed in the next section in connection with photoluminescence measurements. TEM analysis, shown in Fig. 3 for a representative sample treated at 1273 K for 6 h, serves to confirm the results from XRD. As can be seen, the powders are shown to consist of crystallites with dimensions < 100 nm. In addition, the particle size distribution of the powders was measured using dynamic light scattering. As shown in Fig. 4 for powders treated at 1273 K for 2, 6, and 12 h, the particle size of the agglomerated powders does not change with heat-treatment time. All other treatment times and temperatures exhibit the same behavior, that is, heat treatment does not change the particle size distribution of the powders. We attribute this to the lower temperatures used in this study, in which the morphology of the powders changes within the agglomerates (i.e., the crystallite size increases), but not between the agglomerates (i.e., there is no sintering of the agglomerates with each other). Modification of the particle size distribution would require the use of a different fuel-to-oxidizer ratio, which would modify the combustion temperature during synthesis. In summary, the powders in this study consist of nanometric Y_2O_3 crystallites, the sizes of which change with heat-treatment temperature and time, but a constant particle size distribution that does not change with thermal treatment of the powders. Hence, the effect of crystallite size on the photoluminescence of the powders can be deter-

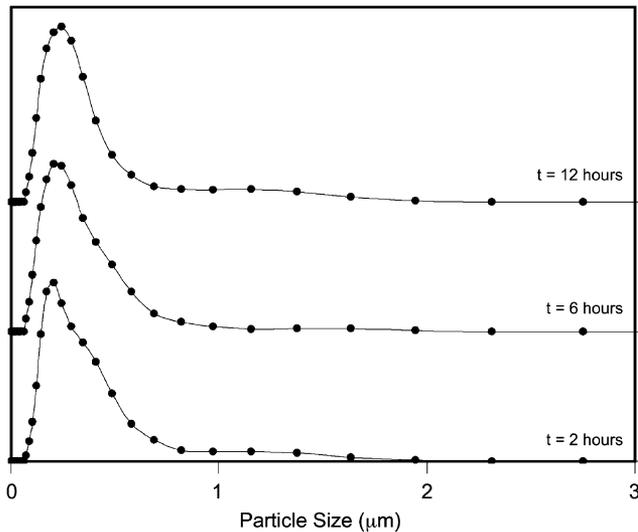


Fig. 4. Particle size distribution for samples annealed at 1273 K for three different times.

mined, while keeping the particle size effects independent of the crystallite size effects.

(2) Photoluminescence

(A) *Effect of Crystallite Size:* The change in photoluminescence intensity of the phosphors with annealing time and temperature, as well as with variations in the amount of activators, was measured for all samples. It was found that the phosphors in the as-synthesized state were not luminescent. However, upon thermal treatment of the samples, emission in the blue portion of the visible spectrum was observed. This is shown in Fig. 5 for a representative $Y_{1.98}Tm_{0.02}O_3$ sample. The spectra show the characteristic ${}^1D_2 - {}^3F_4$ Tm^{3+} transition at 454 nm. When making a comparison between the luminescence intensity and crystallite size (Fig. 6), it is seen that thermal treatments increase the crystallite size, but not the emission intensity of the phosphors. In other words, the samples in the as-synthesized state are not luminescent, but as soon as a thermal treatment is applied, the powders acquire a maximum luminescence intensity, which does not change with either heat-treatment time or crystallite size. It can then be concluded that the crystallite size is not a factor in the ultimate luminescence of these powders. The strain in the lattice, as determined from XRD, exhibits the opposite behavior as the luminescence intensity. That is, in the as-synthesized state, the powders are highly strained. Upon heat treatment, the strain in the lattice reaches a minimum value,

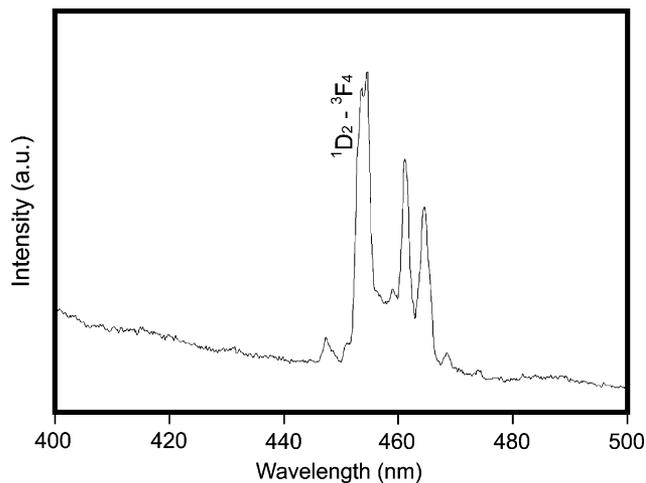


Fig. 5. Representative emission spectrum for $Y_{1.98}Tm_{0.02}O_3$ powders. This particular sample was annealed for 6 h at 1273 K.

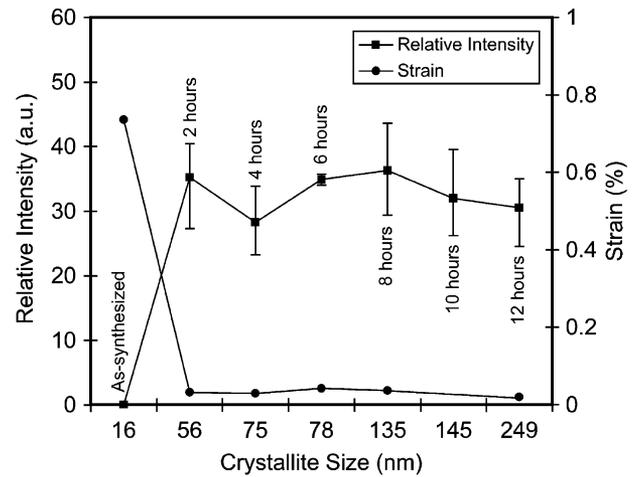


Fig. 6. Change in emission intensity with crystallite size and change in strain with crystallite size for $Y_{1.98}Tm_{0.02}O_3$ samples treated at 1273 K for various times.

which again does not change with either heat-treatment time or crystallite size. From these combined results, we conclude that the powders in the as-synthesized state are not luminescent because of their state of high strain and disorder upon synthesis. The thermal treatment diminishes the strain in the lattice and the powders acquire their maximum luminescence intensity, independent of the crystallite size. Hence, the reasons for the decrease in intensity with increase in particle size in the studies by Sharma *et al.*¹ and Copeland *et al.*² must be related to a different effect, not associated with the crystallite size. Sharma *et al.*, for example, show that the particle size of their $Y_2O_3:Eu$ powders changes with the use of surface modifiers during synthesis. The smallest particle size was obtained using a 10 wt% modifier concentration, which yielded particles of about 10 nm. To corroborate, high-resolution TEM shows crystallites of about 10 nm in size. However, the TEM image shows agglomerates much larger than 10 nm in size in a matrix of an amorphous substance. This can certainly be explained by realizing that the TEM images were taken before removal of the organic modifiers, as described by the authors, which takes place at temperatures of 350°–380°C. The particle size measurements were then taken after the powders were treated at 450°C for 2 h. As only one heat-treatment regime was applied to the powders, it can be assumed that the crystallite size of the powders does not change from sample to sample. The precipitation process used in the study yielded crystallites of around 10 nm in size, which then agglomerated to smaller or larger extents depending on the amount of surface modifier used during synthesis. As quantum confinement is an effect that occurs because of the size of the crystals, not the particles, it is difficult to assess why the powders exhibit higher luminescence intensity with a decrease in the particle size. Presumably, the quantum confinement effect is only occurring because of the 10 nm crystallites, independent of how much they have agglomerated into larger particles. We conclude that, as the powders that exhibit lower luminescence intensity are so agglomerated, the internal surfaces of these powders trap larger amounts of the organic impurities within the agglomerates, which are not removed with the 450°C treatment. These impurities then can act as quenching centers for the luminescence. The study by Copeland *et al.*² describes both measurements of crystallite size and particle size, but does not make clear what their values are for the different samples tested and how they corroborate with each other.

(B) *Effect of Impurities:* Figures 7(a)–(c) show the photoluminescence spectra for the $Y_{1.97}Tm_{0.02}Yb_{0.01}O_3$ sample annealed for (a) 15 min, (b) 2, and (c) 12 h at three different temperatures (773, 1023, and 1273 K). As can be seen, with an increase in heat-treatment temperature, the emission intensity

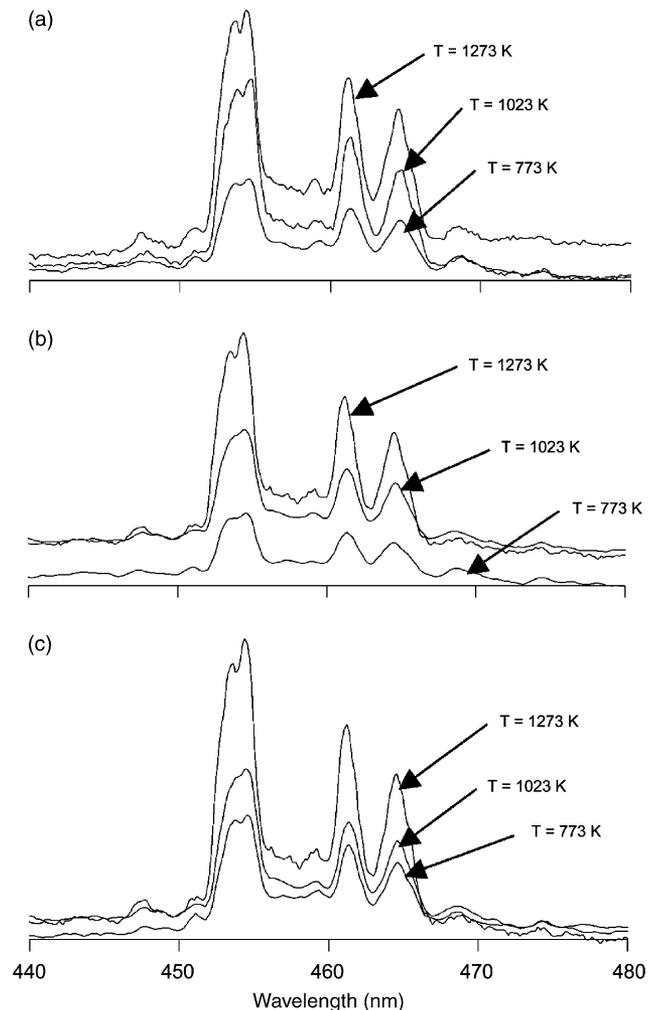


Fig. 7. Emission spectrum of $Y_{1.97}Tm_{0.02}Yb_{0.01}O_3$ annealed for (a) 15 min, (b) 2 and (c) 12 h.

increases. In an effort to determine the reasons for an increase in luminescence with increasing annealing temperature, FTIR experiments were performed and are shown in Fig. 8. The results show that there is a negligible difference in the absorbed impurities with heat-treatment time and temperature. The spectra do exhibit small absorption bands at 3500 and 1500 – 1650 cm^{-1} , which do not change with temperature. These bands are because of vibrations of water molecules. All FTIR spectra are displayed to the same scale but are offset from one another to facilitate comparison. As the particle size of the powders is not changing, we conclude that the removal of water on the surfaces of the powders occurs equally among all powders. Hence, the amount of impurities on the surfaces does not change significantly with treatment temperature and time. This was achieved by a very careful choice of fuel-to-oxidizer ratio, so that no organic impurities were left after the reaction, and by the use of only small amounts of water during the reaction, so that very little water was left on the surfaces of the powders after reaction. Experiments by Zych⁷ and McKittrick *et al.*⁹ showed that impurities consist of OH^- groups (from H_2O), NO_3^- complexes, and NH_4^+ complexes. In particular, Zych analyzed OH^- impurities on $Lu_2O_3:Tb$ powders and showed that there were clear differences in the emission intensity with heat-treatment temperature. Similar results were found in studies on YAG:Cr by McKittrick *et al.*, where FTIR showed that the powders heat treated at 1473 K had much more residual OH^- adsorbed surface groups, as well as NO_3^- and NH_4^+ complexes, as compared with the powders heat treated at 1823 K. The powders in our study were mostly free of such impurities and, in addition, were about the same for all powders. Hence, from the results of FTIR, it can be

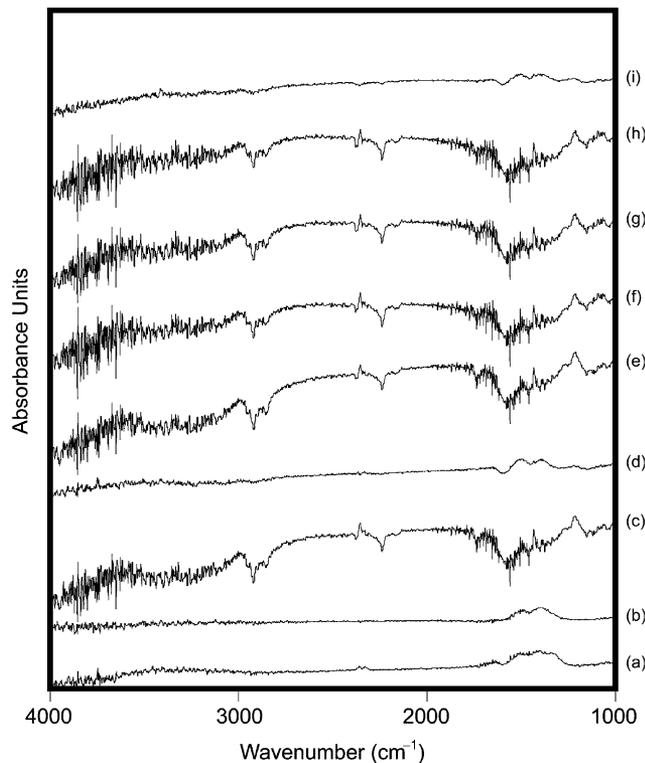


Fig. 8. Fourier-transform infrared spectrometry spectrum of Y_2O_3 powders treated for (a) 15 min at 773 K, (b) 2 h at 773 K, (c) 12 h at 773 K, (d) 15 min at 1023 K, (e) 2 h at 1023 K, (f) 12 h at 1023 K, (g) 15 min at 1273 K, (h) 2 h at 1273 K, and (i) 12 h at 1273 K.

concluded that adsorbed impurities on the surfaces of our powders do not play a role in the increase in luminescence of the phosphors. Thus, we conclude that the high strain of the powders in the as-synthesized state does not allow for a proper chemical and/or electronic environment around the activators, which does not permit the efficient luminescence of the powders. As heat-treatment temperature increases the strain in the lattice is removed more efficiently and, as a consequence, a higher emission is obtained from the powders.

If the maximum emission intensity is plotted for all $Y_{(2-x-y)}Tm_xYb_yO_3$ samples treated at 1273 K (shown in Fig. 9), an approximate determination of the optimum activator concentration for this phosphor can be made. The values of maximum emission intensities, in arbitrary units, were taken for the $^1D_2 \rightarrow ^3F_4$ transition. Figure 9 shows a clear concentration quenching at the higher activator concentrations. The optimum activator concentrations for this particular phosphor were determined to be $x = 0.02$ and $y = 0.01$.

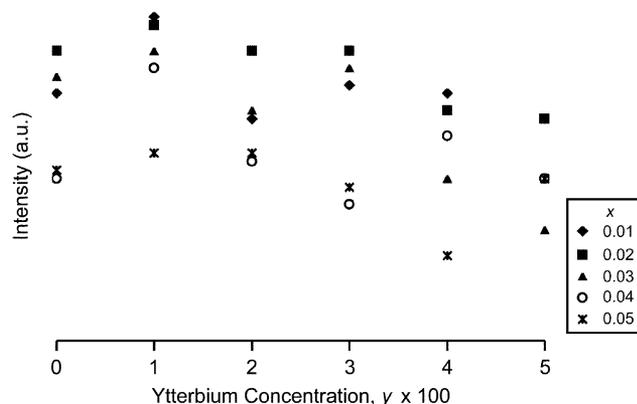


Fig. 9. Change in emission intensity with increasing Tm and Yb concentrations. Quenching of luminescence is clearly seen at the higher activator concentrations.

IV. Conclusions

Combustion synthesis was used to obtain nanocrystalline $Y_{(2-x-y)}Tm_xYb_yO_3$ phosphors using metal nitrates and carbonylhydrazide as precursors. From XRD it was determined that the powders in the as-synthesized state were in a state of high strain, as evidenced from the broad peaks in the XRD pattern. Upon thermal treatment, the XRD peaks became sharper and strain was minimized. Crystallite size from XRD was obtained using the Williamson–Hall technique, which showed that an increase in the crystallite size did not enhance the brightness of the phosphors. Clearly, an increase in crystallite size does not appear to affect luminescence in powders greater than ~ 30 nm. From photoluminescence measurements, it was noted that the phosphors were not luminescent in the as-synthesized state. However, upon annealing, the phosphors became luminescent and the intensity of emission increased with increasing treatment temperature. FTIR analysis showed that there is a negligible difference in the absorbed impurities with heat-treatment temperature. Hence, from the results of FTIR, it can be concluded that the impurities on the powder surfaces do not play a role in the increase in luminescence of these phosphors. Instead, the removal of strain in the lattice, which improves the electronic environment of the activators, can be invoked to explain the improvement in luminescence. A careful distinction between crystallite size and particle size needs to be made. In this study, the particle size (i.e., agglomerate size) was kept constant. Hence, the effect of crystallite size on luminescence intensity was measured. If the particle size is changed, the removal of impurities on the surfaces of the powders will be affected, and as a consequence the luminescence will be affected. The activator concentration is important to achieve maximum brightness. The optimum activator concentrations for this particular phosphor were determined to be approximately $x = 0.02$ and $y = 0.01$. With higher concentrations of the activator, quenching of luminescence was noted.

Acknowledgments

The contributions of Mr. Francisco Ruiz from the Centro de Ciencias de la Materia Condensada of the Universidad Nacional Autónoma de México in the TEM characterization are gratefully acknowledged.

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