Abstract

Four samples of \((Y_{1-x}Ce_x)\frac{3}{2}(Al_{1-y}Ga_y)\frac{5}{2}O_{12}\) (where \(x=0.01, 0.02\) and \(y=0, 0.5\)) were synthesized via the simple, efficient combustion synthesis method in order to determine the effect of substituting Ga\(^{3+}\) for Al\(^{3+}\) on the temperature-dependent fluorescent lifetime. X-ray diffraction (XRD) data show that the average crystallite size is 20-30nm and that the gallium-doped samples have longer lattice constants and smaller average crystallite sizes relative to the single-doped samples. Transmission electron images confirms the average crystallite size from XRD data and reveal large agglomerates composed of nanocrystalline particles. Photoluminescence data reveals that the addition of gallium into the YAG:Ce matrix induces a red shift in the absorption spectra and a blue-shift in the emission spectra. The emission spectra of the gallium-doped samples shows an intense broad-band emission centered at approximately 520nm and a low-intensity, broad-band emission centered at 700nm. The laser-induced fluorescent lifetime was determined as a function of temperature over the range of 0-125°\(^\circ\)C using red and green emission filters. Increasing the amount of dopant ultimately results in a decrease of the fluorescent lifetime. The quenching temperatures for the Ga-doped samples were lower than the samples without gallium. The lowest quenching temperatures were observed when using the red emission filter. The results of this work show that a simple, inexpensive combustion synthesis reaction is viable method for making highly luminescent, nanocrystalline TGP's. In addition, we have shown that the quenching temperature of YAG:Ce can be altered by substituting ions which alter the location of the charge transfer state and by collecting emission at a longer wavelengths.

Introduction

Cerium-doped yttrium aluminum garnet (\(Y_3Al_5O_{12}:Ce\), YAG:Ce) is used in several applications such as solid state lighting, displays, scintillators, and thermographic phosphors [19], [4], [17]. The Ce\(^{3+}\) ion is responsible for nanosecond decay time and an intense visible emission wavelength. In cathode ray tubes, Al\(^{3+}\) is often replaced with Ga\(^{3+}\) in YAG:Ce because of the similarity in cation size and because the addition of Ga\(^{3+}\) induces changes in the photoluminescence spectra. In fact, Wu et al.[18] have shown that increasing the amount of Ga\(^{3+}\) in
YAG:Ce blue-shifts the emission due to lattice distortions around the rare-earth ion. These results are useful to the development of red phosphors for solid state lighting devices.

We are interested in how the addition of Ga\(^{3+}\) in YAG:Ce effects the performance of the material as a thermographic phosphor (TGP). Thermographic phosphors are a special class of materials commonly used as non-contact thermometers because the fluorescent decay lifetime is temperature dependent [4]. The luminescent properties of doped nanocrystals are attracting great interest now because the fluorescent characteristics of nanocrystalline phosphor materials do not scale with micron-sized materials. For example, the decay time of bulk YAG:Ce particles is temperature dependent between 150-300°C. However, Allison et al. showed that nanocrystalline YAG:Ce exhibits temperature dependency between 7-77°C [5]. The shift in temperature dependency is observed as function of size and has also been observed in Y\(_2\)O\(_3\):Eu nanocrystals. The size effect is likely due to increasing lattice distortions in smaller particles [13]. Similarly, the quenching temperature of bulk yttrium aluminum garnet, where Ga\(^{3+}\) is substituted for Al\(^{3+}\) and Ce\(^{3+}\) is substituted for Y\(^{3+}\)(YAGG:Ce), is approximately 100°C and shows microsecond decay times [3]. However, there are no studies which determine the temperature dependency of nanoparticles of YAGG:Ce.

In this work, we have synthesized nanocrystalline particles of YAGG:Ce in order to determine how gallium effects the temperature dependent fluorescent properties of YAG:Ce. We have determined the fluorescent lifetime as function of temperature and analyzed the results in relation to crystal structure and the location of the charge transfer state. In addition, we compare our results to fluorescent temperature data obtained with micron-sized particles of YAGG:Ce. The results of this study show how nanocrystalline features can be exploited to design other phosphors for use as TGPs. To the best of our knowledge, there has been no study that compares the performance of YAG:Ce and YAGG:Ce in relation to crystal structure and particle size for use as a thermographic phosphor.

3 Experimental

Samples of \((Y_{1-x}Ce_x)_{3}(Al_{1-y}Ga_y)_{5}O_{12}\) where \(x=0.01, 0.02\) and \(y=0, 0.50\), were made by preparing an aqueous solution containing appropriate molar ratios of Y(NO\(_3\))\(_3\) (anhy), Al(NO\(_3\))\(_3\)*9H\(_2\)O, Ce(NO\(_3\))\(_3\)*6H\(_2\)O, and Ga(NO\(_3\))\(_3\)*H\(_2\)O. The fuel used to initiate the combustion reaction was urea (CO(NH\(_2\))\(_2\)) and the oxidant-to-reductant ratio was stiochiometric. Each sample was placed in a muffle furnace at 500°C to evaporate the water, after which the auto-combustion process began with the evolution of a white gas. Immediately following the auto-combustion, a voluminous, porous yellow powder formed. Unreacted carbon was driven off by calcining the synthesized powders at 1000°C for 5 hours.

The x-ray powder diffraction patterns were measured at room temperature with a Scintag XRD with CuK\(\alpha\) (\(\lambda = 1.5405\)Å) radiation. The average crystallite size was determined according to Scherrer’s equation: \(D_{ac} = k\lambda/\beta \cos \theta\), where \(k\) is Scherrer’s constant equal to 0.89, \(\beta\) is the full width at half-maximum (FWHM), and \(\theta\) is the diffraction angle. Preliminary TEM images were taken on a Hitachi 3300 with 100kV beam. Room temperature photoluminescence measurements were taken using a QuantaMaster-14/2005 with a 150W Xenon lamp excitation source. The emission spectra were recorded using a Quadrascopic monochromator.
Figure 1: Fluorescent Temperature Dependent Experimental Setup

and photomultiplier tube.

The temperature dependence was determined by using the configuration shown in Figure 1. The excitation source was a nitrogen laser (Laser Science Corporation, model VSL-337ND) with $\lambda_{\text{ex}}=337\text{nm}$ and an excitation band width of 0.1nm. The pulse width was 4ns at a characteristic energy of 300$\mu$J. The excitation pulse was conveyed to the sample via a 1mm optical fiber. An identical fibre collected and transmitted the emitted signal to a photomultiplier tube which served as the detector. Each phosphor sample was placed in the bottom of the plastic capsule which covered the excitation and detector fiber. The capsule/fiber was placed in an oil bath and slowly heated at a rate of 1°C/min. A k-type bare wire thermocouple (Omega Engineering 871) which was placed near the capsule, monitored the temperature of the phosphor. Bandpass filters centered at 540nm and 700nm were used to collect the emitted signal. A waveform processing oscilloscope with 350Hz bandwidth displayed, digitized, and stored the data.

4 Results

4.1 Structure

The X-ray diffraction (XRD) spectra of $(Y_{1-x}Ce_x)_{3} (Al_{1-y}Ga_y)_{5}O_{12}$ is shown in Figure 2. All samples were calcined for 5 hours at 1000°C, which is well above the reported crystallization temperature of 900°C [19], [12]. The average crystallite size was approximated using Scherrer’s equation and the lattice constant was determined using the relationship

$$a = d \sqrt{h^2 + k^2 + l^2}$$

where $d$ is the inter-planar spacing (determined using Bragg’s relationship) and $h, k$ and $l$ are the Miller indices of the plane. All peaks approximately match the cubic $Y_3Al_5O_{12}$ phase (JCPDS file 33-40 [1]). The presence of gallium in the YAG matrix shifts the peak positions to lower diffraction angles due in part to the fact that the radii of Ga$^{3+}$ and Al$^{3+}$ ions are 125pm and 120pm, respectively [16]. Since Ga$^{3+}$ is larger than the host site, the inter-planar spacing
will decrease and the lattice constant will increase due to the increased repulsion between adjacent atoms (Table 1).

Transmission electron microscopy images of the calcined 1%Ce and 0%Ga (x=0.01 and y=0.5) are shown in Figure 3. The material is composed of micron-sized agglomerates composed of ~30nm crystallites. In addition, the crystallites are embedded in amorphous material. The source of the amorphous material is most likely due to inhomogeneous temperature distribution of the flame during the synthesis. Future work will use energy dispersive spectroscopy techniques to identify and quantify the amorphous components of each sample.

4.2 Photoluminescence

Photoluminescence spectra are shown in Figure 4 and corresponding data are given in Table 1. The emission spectra reveal an absorption band centered at 344nm which is due to crystal field splitting of the 5d orbitals. There is an additional absorption band centered at 485nm (not shown) which is the absorption of the $^2E_g$ orbital [18]. The emission spectra show that all samples exhibit an intense broad-band emission centered between 520-540nm, which is due to electronic transitions from the $^2D_j$ excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground states of the luminescent Ce$^{3+}$ ion [10]. The shouldering observed in the emission peak (~630nm) is due to the doublet ground state of the Ce$^{3+}$ ion. The addition of gallium into YAG:Ce red-shifts the absorption peak approximately 8nm while the emission peak is blue-shifted approximately 15nm. The blue-shift of the emission wavelength correlates well with other studies and has been attributed to a tetragonal distortion of the oxygen atoms surrounding the Ce$^{3+}$ ion.
Table 1: Structural and spectroscopic properties of $\left(Y_{1-x}Ce_x\right)_3\left(Al_{1-y}Ga_y\right)_5O_{12}$

<table>
<thead>
<tr>
<th>x (%Ce)</th>
<th>y (%Ga)</th>
<th>a (Å)</th>
<th>Average Crystallite Size (nm)</th>
<th>$\lambda_{exc}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0</td>
<td>12.0866</td>
<td>37.112</td>
<td>343</td>
<td>537</td>
</tr>
<tr>
<td>0.01</td>
<td>0.5</td>
<td>12.2207</td>
<td>27.069</td>
<td>351</td>
<td>514</td>
</tr>
<tr>
<td>0.02</td>
<td>0</td>
<td>12.1012</td>
<td>32.437</td>
<td>343</td>
<td>539</td>
</tr>
<tr>
<td>0.02</td>
<td>0.5</td>
<td>12.2658</td>
<td>27.279</td>
<td>351</td>
<td>517</td>
</tr>
</tbody>
</table>

brought about by the substitution of $Al^{3+}$ for $Ga^{3+}$ [18] [7]. The inset of Figure 4 shows a portion of the emission spectra using $\lambda_{exc}=485$nm to excite the sample. Using this excitation wavelength, a small, novel, low-intensity emission was observed at 700nm. There are no known emission peaks for $Ce^{3+}$ in the red region. Trivalent chromium is known to absorb in the blue region and emit around 700nm due to the $^4T_2 \rightarrow ^4A_2$ and $^2E \rightarrow ^4A_2$ transitions [15]. It is highly likely that this anomalous emission is due to $Cr^{3+}$ contamination because the doublet shape, multiexponential decay curves, and emission lifetime are very similar to known emission spectra of YAG:Cr [2]. As shown below, this unexpected emission was very useful in demonstrating the effect of Ga-substitution on the quenching temperature. In the future, atomic absorption spectroscopy will be used to verify $Cr^{3+}$ contamination.

4.3 Fluorescence Temperature Dependency

Two bandpass filters centered at 540nm and 700nm were used to determine the temperature dependency. These emission filters were chosen because of emission signals given in the PL data. A 700nm filter was chosen because spectral data showed a low-intensity, broad-band emission in the red region. Figure 5 shows the fluorescent decay lifetime as a function of tem-
Figure 4: Excitation and emission spectra of calcination treated \((Y_{1-x}Ce_x)_{3}(Al_{1-y}Ga_y)_{5}O_{12}\) for \(\lambda_{em}=344\text{nm}\) and \(\lambda_{exc}=540\text{nm}\). Inset: Portion of emission spectra for \(\lambda_{em}=485\text{nm}\).

Temperature using both emission filters. Quenching temperatures and lifetime ranges are shown in Table 2. The quenching temperature, \(T_{\text{quench}}\), is the temperature at which fluorescence begins to decrease due thermal effects within the lattice and \(\tau_{\text{range}}\) is the range of the decay lifetime for which \(\tau\) is inversely proportional to temperature. For comparison, data for micron-sized particles of similar materials are also given. In addition, the lifetimes of the nanocrystals were approximately 60ns which correlates well with observed lifetimes in both micron and nanosized Ce-doped phosphors [5] [6]. It was interesting to observe that lower quenching temperature were observed when using a red emission filter.

| Table 2: Quenching Temperatures For \((Y_{1-x}Ce_x)_{3}(Al_{1-y}Ga_y)_{5}O_{12}\) |
|-----------------------------------|-----|-----|-----|
| \(x\) (%Ce) | \(y\) (%Ga) | \(540\text{nm Filter} T_{\text{quench}}\) (°C) | \(700\text{nm Filter} T_{\text{quench}}\) (°C) |
| 0.01       | 0   | 0   | 0   |
| 0.02       | 0   | 0   | \(\sim45\) |
| Bulk YAG:Ce [5] | 150 | -   |
| 0.01       | 0.5 | 90  | 19  |
| 0.02       | 0.5 | 45  | 14  |
| Bulk YAGG:Ce [3] | 100 | -   |
Figure 5: Decay Time vs. Temperature of $(Y_{1-x}Ce_x)3(Al_{1-y}Ga_y)5O_{12}$ using different emission filter

5 Discussion

5.1 Overall Lifetime

In this work, we are interested in determining the temperature dependent fluorescent lifetime for YAG doped with Ce$^{3+}$ and Ga$^{3+}$. From the data presented in Figure 5, two important conclusion can be drawn about the radiative lifetime: i) increasing the amount of dopant (whether Ce$^{3+}$ or Ga$^{3+}$ or both) decreases the radiative lifetime, and ii) quenching temperatures for the samples with Ga$^{3+}$ are easily identified at lower temperatures compared to the samples without Ga$^{3+}$.

The total fluorescent lifetime is the sum of radiative and non-radiative transition rates

$$\tau_{total} = \left( W_{rad} + W_{nr} \right)^{-1}$$  \hspace{1cm} (2)

where $W_{rad}$ and $W_{nr}$ are the rate of radiative and non-radiative transitions between the ground and relative excited state, respectively. The fluorescent decay lifetime is $\tau$. Non-radiative transitions are temperature dependent and can occur by several pathways such as tunneling to nearly resonant vibrational states, energy transfer between higher level excited states, and multi-phonon emission [4]. Non-radiative transitions also occur as a result of defects within the host lattice. Defects within the crystal lattice can occur as missing atoms, size-mismatch from dopants, or dislocations. Temperature-dependence measurements of the luminescence of YAG:Ce have shown that energy trapped at defect centers can be released thermally which leads to competition for radiative emission between activator and defect centers [14]. Thus, the number of pathways available for non-radiative transitions increases when more defects, such as dopants, are introduced into the crystal. Likewise, Figure 5 shows that as the molar amount of dopant increases, the overall lifetime decreases. Furthermore, Table 1 shows that the average crystallite size decreases as the molar amount of dopant increases. Consequently, the number of defects per unit volume is proportional to the molar amount of dopant in the

```math
\tau_{total} = \left( W_{rad} + W_{nr} \right)^{-1}
```
crystal. This is why a decrease in overall lifetime is observed as the dopant amount increases and as the average crystallite size decreases. Peng et al. has shown a similar effect. In their work, Eu-doped Y$_2$O$_3$ nanocrystals have shorter lifetimes compared micron-poly crystalline particles. The increase in non-radiative transitions was attributed to the surface defects of the nanocrystals [13].

The exception to the trend described above is the sample with 1%Ce and 50%Ga (x=0.01 and y=0.5). This sample has a lower overall lifetime compared to the sample with 2%Ce and 50%Ga. It is not clear why this occurs however, the fact that the overall lifetime is longer for the 2% Ce sample indicates that more pathways are available for radiative emission in the 2%Ce sample (x=0.02 and y=0.5). This may occur because the luminescent Ce$^{3+}$ ions are closer together and therefore energy transfer between luminescent centers is more efficient for 2%Ce doping. Katelnikovas et al. [9] has shown that concentration quenching does not occur for YAG:Ce until the sample is doped with 4 mol % Ce . Because the Ce-dopant level in this experiment is below that of 4%, the overall lifetime of the 2%Ce-50%Ga sample is longer than the 1%Ce-50%Ga because of an increase in energy transfer between Ce$^{3+}$ ions due to the increase in Ce-dopant concentration.

5.2 Quenching Temperature

While the lifetime does decrease with temperature for the samples without Ga$^{3+}$, it is not clear at what temperature quenching effects begin. For the x=0.01 and y=0 sample, the variation in $\tau$ over the experimental temperature range is only a few nanoseconds. It is possible that the crystallite size is too large to observe strong temperature dependence in the range of 0-120°C. In this case, the temperature dependent behavior of this material is similar to bulk YAG:Ce where the quenching temperature is 150°C. When x=0.02 and y=0, the variation in lifetime is greater than the when x=0.01 and y=0, but it is not obvious exactly where thermal effects begin to influence the fluorescent lifetime. Possibly, the quenching temperature occurs at approximately 45°C because the greatest variation in the lifetime occurs roughly between 45-120°C.

In contrast, the quenching temperature is obvious for the Ga-doped samples. In addition, our results show that the presence of Ga$^{3+}$ decreases the quenching temperature of YAG:Ce. If the quenching temperature shifts to lower temperatures, the relative location of the charge transfer state is at a lower energy when Ga$^{3+}$ is present as opposed to when only Al$^{3+}$ is present. Thermal quenching of radiative emission can arise from the presence of charge transfer states (CTS) which offer non-radiative pathways that become energetically favorable at higher temperatures [4]. When the CTS is at a lower energy, lower temperatures are required to make this state energetically favorable. Thus, in order to understand the observed reduction in the quenching temperature we must compare the chemical nature of the O-Ce bond with and without the presence of Ga$^{3+}$.

That the CTS is at a lower energy when Ga$^{3+}$ is present can be explained by considering the lattice structure of the YAG matrix in relation to the covalency of Ga-O bond versus the Al-O bond. The garnet structure is cubic and the general chemical formula of garnets is C$_3$A$_2$D$_3$O$_{12}$ where C represents a large ion located in a dodecahedral site with a coordination number(CN) of 8, A is a medium-sized ion in a octahedral site with CN=6, and D is comparatively small ion
in a tetrahedral site with CN=4. In Y₃Al₅O₁₂, Y³⁺ or Ce³⁺ ions are in the C site and Al³⁺ ions are in the A and D sites. The bonds in the dodecahedral site can be visualized as a distorted cube in which half of the 8 bonds are longer than the other half. These bonds are directly affected by the spatial arrangement of atoms in the tetrahedral and octahedral sites. Nakatsuka et al. reported that Ga³⁺ ions preferentially occupy the tetrahedral site. The strong covalency of the Ga-O bond introduces shielding effects by electrons which reduce cation-cation repulsive forces and stabilize the crystal matrix [11]. As a result of the shielding effects, the repulsion between the octahedrons on either side of the tetrahedron is reduced and the octahedrons will move closer together. Because the octahedrons are closer, the electronic interaction between the Ce³⁺ and the octahedral oxygen atom will decrease. Likewise, the covalency of the Ce-O bond will increase. Consequently, the electronegativity difference between cerium and oxygen is less, so that the charge-transfer transitions between these ions shift to lower energy [8]. Since the charge transfer state is at lower energy when Ga³⁺ is present, transitions to this state become energetically favorable at lower energies and hence at lower temperatures.

5.3 Collecting Emission with 700nm Filter

Finally, the quenching temperatures are considerably lower when observing the lower energy transition (collecting emission at 700nm). Table 2 compares the quenching temperatures for the Ga-doped samples at the two emission wavelengths. It is highly likely that the red emission occurs as a result of Cr³⁺ contamination. The decay curve for the 700 nm emission showed multiexponential decay and showed low temperature T_q values. Although this emission is unexpected, the effect of Ga-doping lowering the CTS (described above) is observed for this lower energy transition. This is interesting because Cr³⁺ ions will substitute in the octahedral or tetrahedral sites instead of the dodecahedral sites. It is not clear at this point if Ga³⁺ is lowering the CTS for the Cr-O transition or an energy transfer is occurring between the two dopant ions, however, it is clear that Ga³⁺ significantly lowers the quenching temperature.

6 Conclusions

We have investigated the fluorescent lifetime of (Y₁₋ₓCeₓ)₃(Al₁₋ₚGaₚ)₅O₁₂ as a function of temperature between 0-120°C. X-ray diffraction measurements revealed that increasing the amount of dopants in the garnet matrix decreased the average crystallite size. This decrease in crystallite size indicates that the number of surface defects per unit volume also increased. The radiative lifetime of bulk YAG:Ce and YAGG:Ce is longer than the radiative lifetime of nanocrystals because decreasing the average crystallite size decreases introduces more defect centers in the phosphor. The results of this work show that nanocrystals of YAGG:Ce synthesized via the simple combustion synthesis technique can be used as thermographic phosphors for low temperature non-contact remote-sensing thermometry. The quenching temperatures of Ga-doped samples were lower than the samples with no gallium because the CTS is lower in the Ga-doped samples. The relation of the crystal structure to the environment of the Ce³⁺ ion gives a qualitative explanation of the shift in quenching temperature when dopants are added to different crystallographic sites in the YAG matrix. Ultimately, we have shown that
the presence of dopants such as Ga$^{3+}$, collecting emission from different energy states, and defects within the host lattice are possible mechanisms by which to alter the quenching temperature of Ce-doped garnets. These results may be useful in the design and implementation of thermographic phosphors and also phosphors used in solid-state lighting, display, or light emitting diodes.

References


