Local structure and time-resolved photoluminescence of emulsion prepared YAG nanoparticles

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1. Introduction

Solid state lighting based on the blue light emitting diode (LED) [1] is slated to replace incandescent and fluorescent lighting. Most commercially available white LEDs use an InGaN blue emitter with an emission peak at 460 nm in combination with a Y3Al5O12:Ce3+ (YAG:Ce) yellow phosphor, absorbing strongly in the blue and re-emitting at ~530 nm [2,3]. Recently, there have been studies that suggest the use of phosphors with a diameter of a few hundred nanometers would significantly reduce back-scattering of the blue photons and improve the overall performance [4,5]. The correlation between the size of the phosphor particles and the luminescence efficiency for lamp phosphors has been well documented by Wang et al. [6] and references therein. It is a common problem that the conditions required for high downconversion efficiency are not compatible with nanoparticle synthesis. Several recent reports have applied chimie douche methods to the preparation of YAG:Ce. Chatterjee et al. prepared ~10 µm spheres of YAG using an inverse emulsion of sorbitan monooleate and cyclohexane [7]. Caponetti et al. used a water/cetyl trimethylammonium bromide/1-butanol/n-heptane emulsion to produce YAG:Nd particles ~20 nm in size [8]. Inverse emulsion synthesis using surfactants to stabilize aqueous droplets in a non-polar phase has been well treated in the literature for both polymer and inorganic systems [9–14]. Preparations of YAG:Ce nanoparticles have also been reported by microwave synthesis [15], sonochemistry [16], sol–gel [17,18], salted sol–gel [5], co-precipitation [19], and solvothermal [20] methods. The as-prepared particles are usually amorphous or of very low crystallinity and require further calcination for photoluminescence. However, the degree to which the particles sinter together during this calcination, while critical to gaining the benefits of using nanoparticles, is often not addressed.

The absorption and emission transitions of the active center Ce3+ in YAG:Ce involve the 5d and 4f levels. These are parity-allowed processes with broad, intense bands. The participation of the 5d energy levels makes the transitions sensitive to the crystal field environment [21] and to the site symmetry [22] of the host lattice. A recent study by Su et al. of YAG:Ce nanoparticles proposed that the incomplete garnet structure at the surface, observed in HRTEM, provided traps for the excited 5d electrons lost to the host lattice and thus quenched radiative emission [23]. Jacobson et al. described a change in the radiative lifetime of the Ce3+ ion in Ce2SiO5:Ce due to the perturbed electric field at the surface of nanoparticles [24]. Zych et al. [25] proposed that lattice discontinuities at the interface can modify the energy of the conduction band of the host lattice, quenching the cerium emission by photonization. Jia et al. reported that the intensity of the
photoluminescent emission increased as the nanoparticle phosphor calcination temperature was raised [26]. The change in efficiency was ascribed to higher crystallinity and subsequent elimination of emission quenching defects. Similarly, the low photoluminescent intensity observed in nanoscale samples by Wang et al. [6] was attributed to defects on the crystallite surface and the presence of amorphous phases.

In this contribution we compare the structural and luminescent properties of emulsion prepared YAG:Ce nanoparticles with bulk ceramic preparations. Rietveld and pair distribution function analyses of synchrotron powder diffraction data reveal decreased long range order in lower temperature preparations and unexpected amounts of impurity phases. Decay lifetime measurements show that the nanoparticles had a higher ratio of non-radiative recombination pathways, likely associated with the impurity phases and disorder.

2. Experimental

Powder samples were prepared by emulsion synthesis and calcined at various temperatures to obtain the garnet phase. All agents were of high purity and obtained from Sigma–Aldrich Chemical Co. The aqueous phase was prepared by dissolving Y(NO3)3·x(H2O), Al(NO3)3·x(H2O), and Ce(NO3)3·x(H2O) in stoichiometric ratios to form a 0.1 M solution. The pH of the solution was raised to ~3 using ammonium hydroxide. The continuous phase consisted of a 20:1 volume ratio of cyclohexane and sorbitan monooleate. The two solutions were combined and placed in an ultrasonic bath for 90 min, forming a white, milky emulsion. The emulsion was then refluxed in air at 90 °C while stirring for 48 h. Particles were hydrolyzed by the addition of tetraethyl ammonium hydroxide under vigorous stirring until the pH reached ~11. A color change from white to yellow was also observable when the hydrolysis was complete. At this point, the particles were still suspended, but readily separated by centrifugation at 3000 rpm for 15 min. They were washed several times with H2O and ethanol to remove any unreacted starting materials and remaining solvent, followed by drying under vacuum at room temperature. The products were then calcined in air at various temperatures for 2 h. The non-polar phase solvent, ratio of surfactant to solvent, reflux time to remove any unreacted starting materials and remaining solvent, and measured using a Keithley 195 digital multimeter.

The purity of the samples was initially characterized with laboratory powder X-ray diffraction using CuKα radiation. Data were recorded from 10° to 75° 2θ with a step size of 0.017°. Synchrotron powder diffraction data were collected in transmission mode on beamline 11-ID-B of the Advanced Photon Source, Argonne National Laboratory, at room temperature. Powder samples were loaded into polyaniline tubes, sealed with glass wool and placed vertically in a sample holder in the path of the beam at room temperature, with an experimental set-up similar to that described by Chupas et al. [27]. Scattering data were collected with an image plate system (MAR345) and sample-to-detector distances of 970 mm and 305 mm using high energy X-rays (~90 keV). Data for Rietveld analysis (970 mm) were collected using single 30–100 s exposures, and data for PDF analysis (305 mm) were collected in three exposures of 10–60 s. The image plate data were processed using the program FIT2D [28]. The Rietveld method [29] was used to refine the structures and for quantitative phase analysis using the programs XND [30] and the GSAS-EXPGUI [31,32] suite. The PDF, \( G(r) = 4\pi r \rho(r) - \rho_0 \) [33,34], was extracted with the program PDFGetX2 [35], using a maximum momentum transfer of \( Q = 20 \text{ Å}^{-1} \). Full structure profile refinements with the PDF data were carried out in the program PDFFIT2 and PDFgui [36]. A bulk cubic CeO2 standard provided an effective wavelength of \( \lambda = 0.1368 \text{ Å} \) for refinements as well as instrument parameters for PDF analysis.

Scanning electron microscopy (SEM) images were obtained using a JEOL 6340F FESEM. Photoluminescence measurements were carried out at room temperature using a Perkin Elmer LS55 UV/Visible spectrometer.

Fluorescence lifetime measurements were performed using the time correlated single photon counting (TCSPC) technique [37]. Excitation pulses of approximately 100 fs with a wavelength tunable from 360 to 470 nm were generated using a frequency doubling β-barium borate crystal in combination with a Spectra-Physics Tsunami mode-locked Ti–sapphire laser. The laser repetition rate was reduced to 2 MHz using an acousto-optical pulse picker to avoid chromophore saturation. The TCSPC system was equipped with a Hamamatsu R3805U-51 ultrafast microchannel plate photomultiplier tube detector and a Becker & Hickl SPC-630 counting module, providing a response time <50 ps. The triggering signal for the TCSPC board was generated by sending a fraction of the laser beam to a Si photodiode. The fluorescence spectrum was monitored using a Roper Scientific PIXIS-400B CCD camera equipped with an Acton Research SP300 monochromator and an ALP longpass filter. Fluorescence transients were not deconvolved from the instrument response function since their characteristic time constants were much longer than the width of the system response to the excitation pulse. Variable temperature measurements were performed using a liquid nitrogen cryostat with temperature controller down to 77 K or a heating stage up to 500 K.

Emission quantum efficiency (QE) measurements in solid samples were performed using a Labsphere integrating sphere with excitation light from a Spectraphysics Beamlock 2065 Ar-ion laser at 363 nm or 457 nm. The experimental setup is similar to the one described in a paper by Greenham et al. [38]. The light exiting the sphere passed through appropriate colored glass or interference filters. Emission was detected using a Newport UV-818 calibrated Si photodiode, amplified with a Stanford Research Systems SR570 and measured using a Keithley 195 digital multimeter.

3. Results and discussion

A YAG:Ce precursor was prepared as described and heated to 700 °C, 1000 °C, or 1300 °C for 2 h to follow the effect of calcination temperature on luminescent intensity. Scanning electron micrographs of these samples are shown in Fig. 1. An increase in particle size and sintering can be seen as the temperature was increased. The 1300 °C sample showed bright yellow luminescence under UV illumination at 365 nm, while the 1000 °C sample was a weaker yellow. The 700 °C sample did not luminesce. The nanoparticles show the characteristic 2F → 2D transitions of Ce3+ with excitation in the blue region around 460 nm and a broad emission in the yellow region centered at 530 nm. The relative emission intensity at \( \lambda_{ex} = 460 \text{ nm} \) light was quantified by photoluminescence spectroscopy and is shown in Fig. 2. The spectra show a direct correlation between calcination temperature and brightness, increasing from no intensity after heating to 700 °C to a strong intensity from the 1300 °C and bulk samples. Quantum efficiency was measured for the 1300 °C and bulk samples, which showed 42% and 74% conversion, respectively. Powder X-ray diffraction data collected after the three calcinations are shown in the top of Fig. 3. The lowest temperature sample remained amorphous while the 1300 °C calcination product appeared to be a crystalline yttrium...
aluminum garnet phase (Y₃Al₅O₁₂) with the cubic space group Ia₃d. 1000 °C corresponded to an X-ray diffraction pattern matching the garnet phase seen at 1300 °C but with broader peaks, as would be expected for nanoparticles.

The synchrotron data for the samples in the study are shown in the bottom of Fig. 3 along with Rietveld refinement fits to the data for the 1000 °C, 1300 °C, and bulk samples. All of the data sets revealed impurity phase scattering not detected with laboratory diffraction. For the bulk sample, a CeO₂ impurity phase was identified along with another very small impurity which was visible, but not significant enough to index to any known composition, and the data was modeled as a 2 phase refinement with a 1% ceria contribution. For the sample annealed at 1000 °C, an 11% fraction of a monoclinic phase impurity and 10% impurity of a hexagonal perovskite phase were identified in a three phase refinement. The monoclinic phase corresponds to Y₄Al₂O₉, in spacegroup P2₁/c [39] and the hexagonal phase corresponds to YAO₃ in space group P6₃/mmc [40]. The refinement for the sample calcined at 1300 °C showed 13% monoclinic phase and 1% ceria phase impurities. Relative phase amounts determined from Rietveld analysis are given in Table 1 and show an increase in the YAG phase percentage with increasing calcination temperature.

An inverse relationship between the cubic lattice parameter a and calcination temperature is also seen. The absence of crystallinity in the 700 °C samples prevented any refinement or phase analysis.

The experimentally determined G(r)’s are given in Fig. 4 along with PDF refinement of the 1300 °C sample. In the PDF refinements, impurity phases were included as fractions (determined via Rietveld analysis) and their parameters were not refined. For the cubic YAG phase refinements, the lattice parameter a, the isotropic atomic displacement parameter (constrained for each element to be equivalent among all the phases), and the x, y, and z oxygen positions of the cubic phase were refined. In addition, a scale factor refinement and a peak broadening parameter Qₐ accounting for correlated motion were applied. In the top of Fig. 4, the length of the structural coherence can be seen to be similar for the bulk and 1300 °C samples, shorter for the 1000 °C preparation and significantly reduced in the 700 °C sample. The plot in the bottom of Fig. 4 of the bulk, 1300 °C, and 1000 °C PDF at low r reveals the metal–oxygen distances are more poorly fit than the metal–metal distances. Results from the PDF fits and calculated bond lengths are given in Table 2. Fig. 5 shows that the isotropic atomic displacement parameter (Uiso) increased for Y and O at lower calcination temperatures. The isotropic atomic displacement for the yttrium increases by 8% and 64% at 1300 °C and 1000 °C respectively with respect to the bulk sample, while the isotropic atomic displacement for the oxygen increased by a very similar 9% and 55% for the same values, suggesting an increasingly disordered lattice.

Time-resolved luminescent measurements allowed us to follow the intensity of the emission of the phosphor after a laser excitation pulse. When only one kind of process is involved, the emission intensity decreases monoexponentially according to

\[ I_t = I_0 e^{-\tau} \]  

where \( I_t \) and \( I_0 \) are the intensities of the emission at time \( t \) and at initial time, respectively, and \( \tau \) is the lifetime of the luminescence.
The lifetime $\tau$ is the time when the population of the excited state has decreased to $1/e$ ($\sim 37\%$). If there is more than one process involved, the emission intensity can also decrease biexponentially according to:

\[
\text{Counts} = \begin{cases} 
0.2 & \lambda = 1.5406 \text{ Å} \\
0.4 & \lambda = 0.1368 \text{ Å}
\end{cases}
\]

**Table 1**

<table>
<thead>
<tr>
<th>Sample ($^\circ$C)</th>
<th>Phase</th>
<th>Contribution (%)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>YAG</td>
<td>99</td>
<td>11.9989 (3)</td>
</tr>
<tr>
<td>1300</td>
<td>CeO$_2$</td>
<td>1</td>
<td>12.0013 (4)</td>
</tr>
<tr>
<td></td>
<td>YAG</td>
<td>86</td>
<td>12.0209 (7)</td>
</tr>
<tr>
<td></td>
<td>Y$_4$Al$_2$O$_9$</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CeO$_2$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>YAG</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Y$_4$Al$_2$O$_9$</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YAlO$_3$</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

The refined lattice parameter is given for the YAG phase.

**Fig. 3.** Top: Laboratory X-ray diffraction patterns ($\lambda = 1.5406$ Å) of the same emulsion prepared precursor heated to 1300 °C, 1000 °C, and 700 °C. Bottom: Synchrotron diffractograms ($\lambda = 0.1368$ Å) and multi-phase Rietveld refinement for the same samples (700 °C not refined). Plotted in $1/d$.

**Fig. 4.** Top: Experimental pair distribution functions extracted from synchrotron diffraction data. Bottom: Detail of the PDF functions (circles) and fits (lines) at low $r$ with difference curves offset below. Al–O bonds are indicated by green triangles, Y–O bonds by red triangles, and metal–metal bonds by blue circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
where $I_1$ and $I_2$ are the intensities of the emissions of the different processes at initial time, respectively, and can give the contribution of each process to the total deactivation. $\tau_1$ and $\tau_2$ are the lifetimes of each process.

The top of Fig. 6 shows the intensity decay measured for the emission of the bulk YAG:Ce preparation and for the YAG:Ce nanoparticles at room temperature after a 450 nm laser excitation pulse. The best fit model to the data was a biexponential, allowing us to determine the corresponding lifetimes of each decay. The fast process, $\tau_1$, was 6.29 ns for the bulk and 5.18 ns in the 1300 °C nanoparticles. The slow process, $\tau_2$, was 58.07 ns for the bulk and 53.36 ns in the nanoparticles. For the bulk YAG:Ce sample the contribution of the fast process is small (~5%) and the lifetime of the slow process is very close to the 67 ns previously reported by Zych et al. [41], while for the nanoparticles the contribution of the fast process becomes more significant, around 20%.

The fast process is likely due to the quenching of the cerium by defects at the surface, increased lattice distortion, or the presence of impurity phases. In our YAG:Ce nanoparticles, the increased contribution to the fast decay part of the biexponential reduces the absolute quantum efficiency from 74% for the bulk preparation to 42% for the 1300 °C nanoparticles.

We have performed time-resolved experiments at different temperatures to establish the effect of thermal quenching on lifetime and quantum efficiency. As the intensity at initial time $I_0$ is proportional to the quantum efficiency, we were able to determine the temperature dependence using measurements at initial time $I_0$.

The center of Fig. 6 shows that the quantum efficiency for the bulk YAG:Ce diminishes from 74% at room temperature to 56% at 473 K. A similar behavior can be observed for the YAG:Ce nanoparticles in the same temperature range, its quantum efficiency diminishing from 42% to 34%.

The lifetimes of each process measured by the biexponential fitting at different temperatures for these samples are shown in the bottom of Fig. 6. It can be seen that the behaviors are very similar for the lifetime of the fast component $\tau_1$. In the case of the slow process, the lifetime of the YAG:Ce nanoparticles drops slightly over 350 K.

### 4. Summary

The emulsion method has been successfully applied to obtain nanoscale spheres of oxide phosphors. Relatively high efficiency was obtained by emulsion-templating with a calcination temperature 300 °C lower than the bulk oxide preparation and in a single
heating step, which represents a large energy savings on its own. Unfortunately it seems that the calcination conditions required for highly efficient luminescence also lead to sintering of the particles.

Two important conclusions were reached by Rietveld and PDF refinement with synchrotron powder diffraction data in combination with the quantum efficiency and lifetime measurements. First, the high resolution synchrotron X-ray data revealed that additional phases, not detected with laboratory X-rays, are present in the nanoparticle samples calcined at 1000°C and 1300°C. These additional phases no doubt account in part for the loss of photoluminescent efficiency. Second, the PDF results indicate that the order within the structures of the 1000°C and 1300°C nanoparticle samples is lower than in the bulk sample. In fact, the increases in the atomic displacement parameters at 1000°C and 1300°C (compared to the bulk sample) correlate well with the lower luminescent efficiencies of these samples, as shown in Fig. 2. Since this is not a surface effect, it appears that defects in the body of the nanoparticle samples may be partly responsible for rapid, non-radiative decay pathways in the phosphor nanoparticles.

References