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Observation of green emission from Ce^{3+}-doped gadolinium oxide nanoparticles

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ABSTRACT

Green emission at around 500 nm is observed in $Gd_2O_3:Ce^{3+}$ nanoparticles and the intensity is highly dependent on the concentration of Ce^{3+} in the nanoparticles. The luminescence of this emission displays both picosecond (ps) and millisecond (ms) lifetimes. The ms lifetime is over four orders of magnitude longer than typical luminescence lifetimes (10–40 ns) of Ce^{3+} in traditional Ce^{3+} doped phosphors and therefore likely originates from defect states. The picosecond lifetime is shorter than the typical Ce^{3+} value and is also likely due to defect or surface states. When the samples are annealed at 700 °C, this emission disappears possibly due to changes in the defect moieties or concentration. In addition, a blue emission at around 430 nm is observed in freshly prepared Gd_2O_3 undoped nanoparticles, which is attributed to the stabilizer, polyethylene glycol biscarboxymethyl ether. On aging, the undoped particles show similar emission to the doped particles with similar luminescence lifetimes. When Eu^{3+} ions are co-doped in Gd_2O_3:Ce nanoparticles, both the green emission and the emission at 612 nm from Eu^{3+} are observed.

1. Introduction

Radiation detection is an important area with many applications, including medical imaging, diagnosis and therapeutics [1]. In addition, radiation detection is crucial for homeland security. The potential for terrorist activities within the United States has focused attention on the ability to detect nuclear weapons and radiological dispersal devices (dirty bombs). For radiation detection, sensitivity, response time and energy resolution are important. To perform optimally, a scintillator must have a high luminescence quantum efficiency, a short luminescence decay time and high stopping power, as well as a high carrier mobility-lifetime product [2]. Radiation detectors have traditionally been made with inorganic scintillators, single-crystal materials that generate visible or UV light when traversed by gamma ray photons. Such materials must also be highly transparent to the wavelengths generated. Ce^{3+} doped scintillators have been investigated extensively since the allowed 5d–4f transition has a high luminescence quantum efficiency with a short lifetime in the 10–40 ns range [3–7]. Ce^{3+} is a great activator exhibiting a very fast response in radiation detectors of medical imaging systems employed in diagnostic radiology. Currently, Ce^{3+} doped scintillators meet most of the requirements and are popular scintillators for radiation detection [3,4,6,7]. However, most Ce^{3+}-doped scintillators reported have emissions in the UV–blue range except for Ce^{3+}-doped yttrium aluminum garnet (YAG:Ce^{3+}), which has green emission [8,9].

Luminescence nanoparticles have many potential applications, including solid state lighting, medical labeling, imaging, photodynamic activation and radiation detection [10–13,29,30]. Recent progress in nanocomposites offers a means to combine properties of a wider choice of materials and the ability to control properties at the molecular level [10,14,15]. As the size of a particle is reduced to near the exciton Bohr diameter, its electronic structure and optical properties undergo drastic changes [16–18]. Scintillating nanoparticles have been shown in research to possess a three times higher luminescence efficiency and doubled energy resolution compared to those of bulk crystal scintillators [19,20]. For these Ce^{3+} doped scintillators, the emission in the UV–blue range has some limitations for radiation detection as UV–blue emissions are absorbed strongly by water and polymers, which limit their applications. Here we report the observation of green emission in $Gd_2O_3:Ce^{3+}$ nanoparticles and discuss its potential applications for radiation detection and solid-state lighting.

2. Experimental

2.1. Sample preparation

The procedure to prepare nanopowder samples is as follows: 0.65 g (1.42 mmole) of gadolinium acetylacetonate hydrate powder was dissolved in 40 ml ethanol with the help of ultra-sonification.

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Next 2 ml deionized (DI) water was added to the mixture followed by 0.679 g of polyethylene glycol biscarboxymethyl ether (PEG-COOH). The prepared solution was then placed into a flask that was connected to a water condenser. This solution was heated to the boiling point of ethanol (~80 °C) under vigorous magnetic stirring. A solution of 0.2 g NaOH pellets (5 mmole) dissolved in 40 ml ethanol kept at about 0 °C was then added to the heated solution. A white precipitate was observed and the heated solution became cloudy. After a heating time of 30 min, the solution was separated from the solid by filtration. The precipitate was washed with cold deionized water and acetone and then left to dry in ambient conditions for several days before being subjected to heat treatment at 700 °C for 4 h.

2.2. Characterization

The identity and crystalline structure, size and shape of the nanoparticles were observed by X-ray diffraction (XRD) and a high-resolution transmission electron microscope (HRTEM). XRD was obtained from a Siemens Kristalloflex 810 D-500 X-ray diffractometer under an operating mode of 40 kV and 30 mA with $\lambda=1.5406$ Å radiation. The nanopowder samples were brought onto holey carbon covered copper grids for HRTEM observations. The HRTEM images of the particles were obtained with a JEOL JEM-2100 electron microscope with an accelerating voltage of 200 kV. The emission and excitation spectra were measured using a Shimadzu RF-5301PC fluorometer. The absorption spectra were recorded using a Shimadzu UV-2450 UV–vis spectrophotometer. Picosecond luminescence lifetimes were collected using the frequency-doubled output of a synchronously pumped picosecond (ps) dye laser operating at 570 nm. The doubled output was focused onto the samples and emission collected at right angle to the input. The emission was spectrally filtered and the lifetime measured using time-correlated single photon counting. The instrument resolution was determined to be about 50 ps FWHM using a standard scattering material. Lifetimes longer than 50 ps were collected using the output of a nanosecond optical parametric oscillator/amplifier (Spectra-Physics MOPO-730) operating at a 10 Hz repetition rate and tunable between 440 and 1800 nm. The output of the MOPO system was frequency doubled in a BBO crystal and directed onto the particles. Emission was collected at right angles to the excitation and focused into a 1/8 m monochromator equipped with a standard photomultiplier tube. The output of the photomultiplier tube was delivered to a digital oscilloscope to record the luminescence decay curves. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows a TEM image of the Gd_2O_3:Ce^{3+} nanoparticles. The average size of the Gd_2O_3 nanoparticles was found to be 3–5 nm. The nanoparticles appear with regular crystalline lattices with a lattice spacing of $D_{222}=3.2$ A°, which is in agreement with results reported by Bazzi et al. [21] and Mahajan and Dickerson [22]. The X-ray diffraction (XRD) patterns of Gd_2O_3:Ce^{3+} and Gd_2O_3:Ce^{3+}, Eu^{3+} are shown in Fig. 2. The XRD peak signatures of all annealed samples match well with those for gadolinium oxide (ICSD card ♯033652) with cubic features and body-centered lattice. No impurities were observed in the XRD measurements. In addition, no Ce X-ray photoelectron spectroscopy (XPS) signals could be measured from these samples, indicating that Ce is likely doped into the nanoparticle lattice.

Green emission is observed from the Gd_2O_3:Ce nanoparticles. To reveal the origin of the green emission, Gd_2O_3:Ce nanoparticles with different concentrations of Ce^{3+} were synthesized and their excitation and emission spectra recorded (Fig. 3). All of these samples with different concentrations of Ce^{3+} have similar excitation and emission spectra; however, their luminescence intensities are different. From 1.1 to 3.3% doping, the emission intensity increases. Above 3.3% doping, the intensity decreases gradually likely due to concentration quenching. The optimal concentration for the maximum intensity is 3.3 wt%. Pure Gd_2O_3 nanoparticles prepared in the same conditions and coated with the same stabilizer (PEG-COOH) have negligible green luminescence as prepared. Instead, Gd_2O_3 nanoparticles show weak blue emission at around 423 nm as displayed in Fig. 4. The weak emission in Gd_2O_3 is likely from the PEG-COOH stabilizer as the emission spectra are similar (Fig. 4). We note that with aging the undoped Gd_2O_3 particle emission shifts to 500 nm and is virtually identical to the emission from the Ce^{3+}-doped particles. This change could be due to changes in defect species or concentration or could be from oxidation of the surface ligands. The Gd_2O_3:Ce nanoparticle excitation spectra (emission at 500 nm) display a shoulder at around 352 nm and a pronounced peak at 378 nm. Through comparison with the excitation spectra of PEG-COOH and PEG-COOH coated Gd_2O_3 nanoparticles, it is clear that the shoulder at 352 nm is from the PEG-COOH stabilizer, and the main peak at 378 nm originates from Gd_2O_3:Ce nanoparticles.

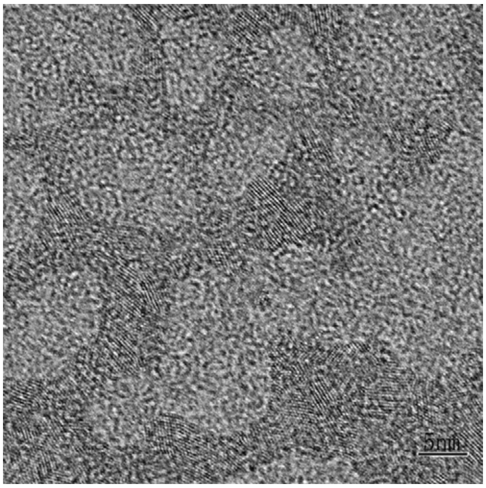

Fig. 1. Transmission electron microscope image of the Gd_2O_3:Ce nanoparticles.

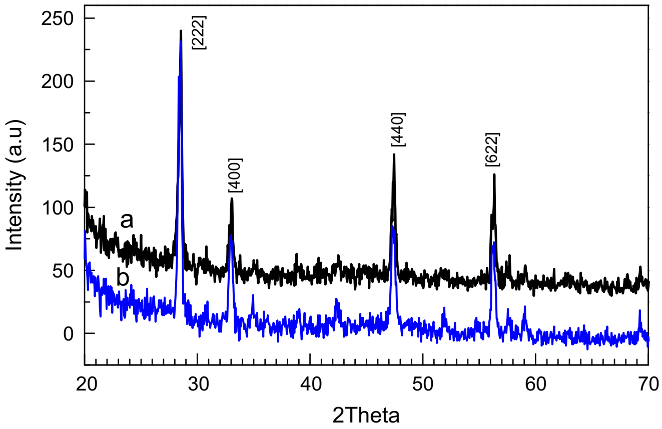

Fig. 2. X-ray diffraction patterns for (a) gadolinium oxide nanopowder and (b) Gd_2O_3:Ce^{3+}.