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Photoluminescence of Eu^{3+}: Y_2O_3 as an indication of crystal structure and particle size in nanoparticles synthesized by flame spray pyrolysis

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Dedicated to the 70th birthday of Professor Daniel E. Rosner

Abstract

Nanoparticles of europium-doped yttrium oxide (Eu: Y_2O_3) were synthesized by flame spray pyrolysis. The nanoparticles were separated by centrifugation into two size groups (5–60 nm and 50–200 nm), each characterized by laser induced fluorescence spectroscopy, Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD). The fluorescence spectra, the electron diffraction pattern, and the XRD pattern of the large particles were typical of the stable cubic (Mn_2O_3 type) phase of bulk Y_2O_3 while those of small particles were quite different and indicated the possible presence of higher density metastable mixed phases—including monoclinic with some indication of a face-centered cubic phase. The size dependence of the particle properties could be attributable to the effect of surface free energy that elevated the internal particle pressure as size decreased. Doping with the lanthanide ion provided a new and useful diagnostic method for determining the crystal structure of flame-synthesized materials.

Keywords: Nanoparticles; Yttrium; Europium; Fluorescence; Spray pyrolysis

1. Introduction

Gas processing of nanostructured materials offers significant advantages over liquid phase chemistry. The process is scalable to high production rates; it can yield material of high purity; a wide range of materials can be formed; and the process can be designed to be both environmentally benign, with no toxic by-products, and energetically efficient. The important characteristics of the product include the particle size distribution, composition and morphology. Rosner, McGraw, and Tandon (2003) and Rosner and Pyykonen (2002) have recognized the importance of multiple variables in the design and operation of gas phase synthesis processes and have developed an appropriate formalism for treating this problem numerically. Crystal structure may ultimately be predictable with such methods, and in some materials and applications, such as yttrium oxide (yttria), the crystal phase may be an important process variable.

Yttrium oxide (Y_2O_3) has often been used as a host material for phosphors and other optical applications and is conventionally processed from micron-sized powders that almost always contain small amounts of impurities. While

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the size and quality of micron-sized powders may be adequate for conventional technologies, durability, mechanical strength, and infrared transparency (in the window from 3 to 5 μm and beyond) is sought in refractory ceramics like yttria for missile and aerodynamic applications. Realization of these critical properties is highly dependent on the ability to reproducibly synthesize nanometer sized ceramic powders of single phases.

The doping of lanthanides into yttria provides additional functionalities for this material. Lanthanide-doped nanoparticles have attracted a great deal of interest because of their high fluorescent intensity, large Stokes shift and long fluorescence lifetime (Bhargava, 1996; Tissue, 1998). They are used in the display industry (Wakefield, Holland, Dobson, & Hutchison, 2001) and show promise in sensor applications (Feng et al., 2003). This type of application requires a method for the production of nanopowders (ultra-fine particles with diameters below 100 nm) with high production rates (grams per hour range), at low cost, and with the ability to obtain materials with different photoluminescent spectra.

Yttrium oxide (Y_2O_3) is one of the best hosts for lanthanide ions (Hao, Studenikin, & Cocivera, 2001; Yang et al., 1999) because its ionic radius and crystal structure are very similar to many lanthanide oxides. Doping with a variety of lanthanide ions (Eu for red, Tb for green, Dy for yellow, Tm for blue) (Hao et al., 2001; Vetrone, Boyer, Capobianco, Speghini, & Bettinelli, 2004) can yield materials with different fluorescent spectra. The doping concentration of lanthanide ions into Y_2O_3 is of key importance in determining the efficiency of fluorescence emission of these materials (Bazzi et al., 2003; Kang, Park, Lenggoro, & Okuyama, 1999).

A wide variety of synthesis techniques have been developed for the production of pure and doped nanopowders, including wet chemical methods (Bazzi et al., 2003), laser ablation (Eilers & Tissue, 1996; Jones, Kumar, Singh, & Holloway, 1997) and combustion techniques (Hao et al., 2001; Kang, Roh, & Park, 2000; Kang, Roh, Park, & Park, 2002). Different sets of parameters for each synthesis method determine the structural and optical properties of the final products. The ability to measure and control these properties with good reproducibility is an important characteristic for any method of synthesis. In fact, it is very desirable to have an analytical method that may provide an online process control so that flow rates, temperatures, and feedstock can be adjusted to yield the desired product.

In general, the physical characterization of nanoparticles for luminescent applications is performed by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) or scanning electron microscopy (SEM) (Tissue, 1998). These techniques provide crystallographic characterization and enable evaluation of the particle size distribution, degree of aggregation and morphology. However, they are slow and require expensive equipment. Optical methods may provide a useful alternative in some cases.

A number of optical methods have been used for the in situ characterization of combustion-generated nanoparticles. Elastic light scattering (Xing, Rosner, Koylu, & Tandon, 1997; Xing, Koylu, & Rosner, 1996, 1999) has been used to infer particle size and the fractal dimension of aggregates. Laser-induced incandescence has been used to obtain size characteristics of carbonaceous materials such as carbon nanotubes (Vander Wal, Berger, Ticich, & Patel, 2002). The presence of trace metals in aerosols can be measured with laser breakdown spectroscopy (Vander Wal, Ticich, West, & Householder, 1999). Arabi-Katbi, Pratsinis, Morrison, and Megaridis (2001) used FTIR spectroscopy to measure in situ flame and particle temperatures in the synthesis of anastase and rutile TiO_2 nanoparticles—the crystallinity and phase were determined by ex situ thermophoretic sampling and XRD analysis. Spectroscopy has not been explored as a possible method for the rapid, and ideally in situ, determination of crystallinity and phase. Lanthanide-doped nanophosphors may offer the potential for a diagnostic of this type.

Lanthanide atoms can occupy different crystallographic sites in the host crystal lattice. Different sites give rise to unique fluorescent spectra. As a characterization technique, optical studies of the lanthanide emission spectra are very sensitive probes of the crystal structure (Chen, Stump, Haire, & Peterson, 1992). This makes it possible to use laser-induced fluorescence (LIF) to study the crystal structure of the nanoparticles—so called site-selective optical spectroscopy (Eilers & Tissue, 1996; Williams, Yuan, & Tissue, 1999). The structural properties of Eu-doped Y_2O_3 (Eu: Y_2O_3) nanoparticles and their fluorescent spectra have been found to depend on the particle size in the case of material obtained by laser ablation followed by condensation (Tissue & Yuan, 2003). These changes arise from alteration to the crystal structure.

Several crystal structures of Y_2O_3 are possible. A cubic (Mn_2O_3 type) crystal lattice is the stable equilibrium form for lanthanide oxides under standard state conditions. However, a monoclinic, high-density phase can be obtained during high pressure synthesis (Hoekstra & Gingerich, 1964).

We have employed a conventional flame spray pyrolysis technique to produce europium-doped yttrium oxide (Eu: Y_2O_3) nanoparticles with the ultimate purpose to use them as luminescent labels in bioassays. Our