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Invited paper

Luminescence and crystallinity of flame-made Y_2O_3:Eu^{3+} nanoparticles

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Abstract—Cubic and/or monoclinic Y_2O_3:Eu^{3+} nanoparticles (10–50 nm) were made continuously without post-processing by single-step, flame spray pyrolysis (FSP). These particles were characterized by X-ray diffraction, nitrogen adsorption and transmission electron microscopy. Photoluminescence (PL) emission and time-resolved PL intensity decay were measured from these powders. The influence of particle size on PL was examined by annealing (at 700–1300°C for 10 h) as-prepared, initially monoclinic Y_2O_3:Eu^{3+} nanoparticles resulting in larger 0.025–1 μm, cubic Y_2O_3:Eu^{3+}. The influence of europium (Eu^{3+}) content (1–10 wt%) on sintering dynamics as well as optical properties of the resulting powders was investigated. Longer high-temperature particle residence time during FSP resulted in cubic nanoparticles with lower maximum PL intensity than measured by commercial micron-sized bulk Y_2O_3:Eu^{3+} phosphor powder. After annealing as-prepared 5 wt% Eu-doped Y_2O_3 particles at 900, 1100 and 1300°C for 10 h, the PL intensity increased as particle size increased and finally (at 1300°C) showed similar PL intensity as that of commercially available, bulk Y_2O_3:Eu^{3+} (5 μm particle size). Eu doping stabilized the monoclinic Y_2O_3 and shifted the monoclinic to cubic transition towards higher temperatures.

Keywords: Flame spray pyrolysis; nanoparticle; yttria; europium; phosphor.

1. INTRODUCTION

Eu^{3+}-doped yttrium oxide (Y_2O_3:Eu^{3+}) is a red-emitting phosphor commonly used in lighting (e.g. fluorescent lamps) and display applications (e.g. plasma displays) [1, 2]. For enhanced display luminescence and resolution, phosphor particles with controlled morphology and smaller sizes are needed. Even though its bulk

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properties are known [1], new approaches are necessary to make submicron-sized phosphors. In addition, the use of nanosized particles/phosphors as luminescent labels of bio-assays has the potential to widen the field of applications [3, 4]. Moreover, weakly or, better, non-agglomerated particles are required for stable slurries in manufacturing of displays [5]. Rare-earth-containing phosphors showed promising properties such as stability in vacuum and corrosion-free gas emission under electron bombardment in cathode ray tube applications [6]. Furthermore, these materials have high damage resistance and high reflectance in light-emitting diodes and high-power pulsed ultraviolet lasers [6]. However, few nano-phosphors based on Y_2O_3:Eu^{3+} with luminescence brightness as high as commercial bulk phosphors have been reported to date [5]. In recent years several studies investigated the physical, electronic and optical property changes of nanosized Y_2O_3:Eu^{3+} compared to bulk materials [7–10]. Optical properties such as the shift of the charge transfer band, phonon relaxation and spontaneous transition rates were reported to vary with nanosized phosphors [11]. The higher surface-to-volume ratio of nanoparticles and increased surface defects were suggested to result in quenched luminescence [12].

Nanosized Y_2O_3:Eu^{3+} has been made by the sol-gel processes [13], microemulsions (ME) [14], combustion synthesis (CS) [15–17], and gas-phase processes such as laser ablation [18], chemical vapor deposition [19], spray pyrolysis (SP) in tubular, hot-wall reactors [5, 7, 8, 20, 21] and flame-assisted SP (FASP) [22–24]. Recently, combustion of an appropriate, organometallic liquid precursor spray [25] was used to make solid Y_2O_3:Eu^{3+} nanoparticles of controlled size and monoclinic or cubic crystallinity without any post-processing. Controlling the high-temperature particle residence time allowed synthesis of either monoclinic or cubic Y_2O_3:Eu^{3+} nanoparticles.

According to the Y–O equilibrium phase diagram [26] (at ambient pressure) the cubic phase of yttria is stable up to 2325°C; at higher temperatures it is transformed into the polymorph, hexagonal phase. It was also reported that the melting point of Y_2O_3 is reached at temperatures of 2430°C [26]. The meta-stable monoclinic phase was only obtained when high pressures (25 kbar) at relatively high temperature (1000°C) followed by fast quenching were applied [27]. Above 1000°C the monoclinic phase was formed at even lower pressures [28]. In the synthesis of yttria nanoparticles by flame-assisted processes the temperatures can easily exceed these critical temperatures and might form either monoclinic or cubic-phased particles depending on the maximum flame temperature and cooling rates [22, 23, 25].

Here, synthesis of Y_2O_3:Eu^{3+} phosphors by scalable flame SP (FSP) is investigated in detail, and compared to particle growth, crystallinity and morphology evolution in hot-wall reactors [5, 7, 8, 20, 21] and FASP [22–24]. For better understanding of the photoluminescence (PL) of flame-made Y_2O_3:Eu^{3+} phosphors, as-prepared particles are annealed systematically focusing on the phase transition of monoclinic to cubic Y_2O_3 and the influence of Eu content on PL and grain growth.