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Fabrication of Lu_2O_3:Eu transparent ceramics using powder consisting of mono-dispersed spheres

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Abstract

Mono-dispersed spherical Lu_2O_3:Eu (5 mol%) powders for transparent ceramics fabrication were synthesized by urea-based homogeneous precipitation technique. The effects of the doped-Eu^{3+} on the synthesis of Lu_2O_3:Eu particles were investigated in detail. The results show that the doping of Eu^{3+} ions into Lu system can significantly decrease the particle size of the resultant precursor spheres. Owing to the sequential precipitation in Lu/Eu system, there are compositional gradients within each of the resultant precursor spheres. Well dispersed, homogeneous and spherical/near spherical Lu_2O_3:Eu powders were obtained after calcination at 600–1000 °C for 4 h. The powder calcined at 600 °C shows better sintering behavior and can be densified into transparent ceramic after vacuum sintering at 1700 °C for 5 h. The luminescence properties of the obtained Lu_2O_3:Eu powder and transparent ceramic were also studied.

Keywords: Lu_2O_3:Eu; Homogeneous precipitation; Mono-spheres; Transparent ceramics

1. Introduction

Rare-earth compounds are interesting functional materials with wide applications in various aspects of contemporary science and technology owning to their interesting optical, magnetic, electrical, and catalytic properties [1,2]. Recently, synthesis of submicron/nano-sized spherical powder of lanthanide-doped rare earth oxides for phosphor applications has attracted increased attention, mainly because powder consisting of mono-dispersed spheres offers not only the desired optical properties of rare earth materials but also the merits derived from ordered assembling of monospheres. In deed, a narrow size distribution and spherical shape allow a uniform and denser phosphor layer to be formed through close packing of spherical particles, resulting in improved efficiency of luminescence and brightness of the phosphor panel [3–6]. Moreover, the fabrication of ceramics similarly needs dispersed spherical particles of a sharp size distribution [7,8]. In this case, it is particularly attractive for transparent ceramics production.

As is well known, the materials existed as transparent polycrystalline ceramics are considered more desirable than those in other forms (such as single crystals and phosphors). Compared with single crystals, transparent ceramics have various advantages, for example, lower manufacturing cost, lower fabrication temperatures, feasibility of shape controlling and enhanced doping concentrations. Moreover, it is less scattering of light than dense layers of powder phosphors [9–11]. Among the various investigated compositions, transparent Lu_2O_3:Eu ceramic has been concerned widely by many researchers because of its potential usage as new scintillator material in the field of X-ray and γ-ray detection technologies [12,13]. Lu_2O_3 is isostructural with Y_2O_3 and belongs to cubic structure, which is possible to achieve complete transparency. It has high mass density (~9.42 g/cm^3), high atomic number of Lu (Z=71), good chemical stability, high thermal conductivity, high melting point, wide band gap, low thermal expansion and broad optical transparency from the visible to the NIR regions [14–16]. In addition, it is reported earlier that

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Lu is more favorable cation than Y for many trivalent rare earth dopant emission [17,18]. Because of its refractory nature (melting point: 2467 °C), Lu_2O_3 has been mainly developed in transparent ceramics rather than single crystals [19].

The starting powders were the key to fabricate the transparent ceramics. To obtain the high-quality transparent ceramics, high purity, fine, mono-sized, well-dispersed and spherical powders are of great importance [20–22]. The uniform spherical powders can be beneficial to dense-packing during the powder compaction, leading to a more homogeneous green compact with substantially reduced the number of compaction defects in comparison with compacts fabricated from powders with undefined morphology [23]. Among the available synthesis routes, urea-based homogeneous precipitation (UBHP) has long been established as a relatively simple, inexpensive and effective method to generate mono-dispersed spherical powders of rare-earth oxides with a narrow size distribution [24]. The synthesis of mono-dispersed colloids for single lanthanide [25], and more recently mixed systems of Y/Gd [26], Y/Gd/Eu [27], and Lu/Eu [28], have been extensively and systematically studied. For a mixed lanthanide system, our previous work shows that the precipitation behavior of the host constituent might be intervened with the addition of a second lanthanide ion, in case of Y/Gd binary system, e.g., the addition of Gd steadily decreases average size of the colloidal spheres. Moreover, concentration gradients with regard to Y and Gd within each particle of mixed Y/Gd systems were noticeably observed [26]. This issue turns particularly important while applying the UBHP methodology to synthesize phosphor particles for optical materials applications, since if not treated properly a nonuniform distribution of activators may lead to localized concentration quenching of luminescence and thus a poor luminescent performance. The effects induced by Gd addition in Y/Gd system has been ascribed to slight varied precipitation behaviors for the two elements due to their minute difference in ionic radius ($r_{Y^{3+}} = 0.0900$ nm, $r_{Gd^{3+}} = 0.0938$ nm). According to the lanthanide contraction law, the lanthanide show similar but systematically varied solution chemistry depending on the ionic radius of the elements. Compared with that of Y/Gd system, the large ionic radius difference between Lu^{3+} (0.0848 nm) and Eu^{3+} (0.0950 nm) suggests that introducing Eu element into Lu system might shade a more profound influence on the precipitation. However, until now, the influences of the doped-Eu^{3+} on the synthesis of phosphor particles in Lu/Eu system have not been explicitly discussed yet. Moreover, in search of the literature, it has been found that the fabrication of transparent ceramics using mono-dispersed spherical powders has been quite scare [23].

In this work, urea-based homogeneous precipitation method has been adopted to synthesize mono-dispersed Eu-doped Lu_2O_3 spheres for transparent ceramics production. The purpose of the work is thus two folds: (1) to elucidate the effects of the doped-Eu^{3+} on the synthesis of Lu_2O_3:Eu phosphor particles; (2) to establish a synthesis route for fabricating Lu_2O_3:Eu transparent ceramics using powder consisting of mono-dispersed spherical particles. The doping concentration of the Eu^{3+} ions was 5 mol% with respect to Lu^{3+} ions, which is the best doping concentration to gain the highest luminous intensity in our previous study.

2. Experimental

2.1. Synthesis

The mono-dispersed colloid spheres of lutetium precursor powders and (Lu, Eu) precursor powders were prepared via a homogeneous precipitation method. High-purity Lu_2O_3 (99.995%, Rare-Chem. Hi-Tech. Co., Ltd., Huizhou, China) and Eu_2O_3 (99.99%, Rare-Chem. Hi-Tech. Co., Ltd., Huizhou, China) powders were dissolved in appropriate nitric acid (with purity of A.R., Sinopharm Chemical Reagent Co., Ltd., China), resulting in the formation of colorless transparent solutions of $Lu(NO_3)_3$ and $Eu(NO_3)_3$. Appropriate amounts of the above solutions and urea ($CO(NH_2)_2$, 99%, Sinopharm Chemical Reagent Co., Ltd., China) were dissolved in 1 L deionized water to prepare a clear aqueous solution with total cation and urea concentrations of 0.015 and 0.5 mol L^{-1}, respectively. After homogenizing under magnetic stirring at room temperature for 60 min, the transparent solution was heated to 95 ± 1 °C. After reacting at this temperature for 2–4 h, the resultant suspension was separated by centrifugation, washed thoroughly with deionized water and anhydrous ethanol, and dried in air at 120 °C for 24 h. Afterwards, the obtained precursor was calcined at 600–1200 °C for 4 h to produce oxide particles.

The obtained Lu_2O_3:Eu powders were ball-milled for 6 h and compacted into pellets followed by cold isostatic pressing at about 200 MPa. Then the pellets were sintered under vacuum at 1700 °C for 5 h to obtain Lu_2O_3:Eu transparent ceramics.

2.2. Characterization

Morphologies of the samples were inspected via field emission scanning electron microscopy (FE-SEM, JSM-7001F, JEOL, Tokyo) and transmission electron microscopy (TEM, EM-420, Philips). The average particle size was calculated from at least 200 particles with an image analysis software (WinRoof, Mitani Corporation, Fukui, Japan). X-ray diffraction patterns (XRD, PW3040/60, Philips, Eindhoven) of the samples were conducted under 40 kV/40 mA using nickel filtered Cu Kα radiation. The crystallite size can be estimated following the Scherrer's formula:

$$D_{hkl} = (K\lambda)/(\beta \cos \theta) \quad (1)$$

where K is a constant (0.89), λ is the X-ray wavelength (0.15406 nm), β is the half-width of the diffraction peak, θ stands for the diffraction angle, D_{hkl} denotes the crystallite size. Elemental analyses of Lu and Eu were carried out on inductive coupled plasma (ICP) spectrophotometer (Optima-4300DV, Perkin-Elmer, Shelton). Specific surface area of the samples was measured by the Brunauer–Emmett–Teller (BET, Tri-Star II 3020, Micrometritics Instrument Corp., Norcross, GA) method. The average particle diameter was determined from the following equation:

$$D_{BET} = 6/(\rho S_{BET}) \quad (2)$$

where S_{BET} is the specific surface area, ρ is the theoretical density, and D_{BET} is the average particle size. Densification