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Effects of hydroxy propyl cellulose (HPC) surfactant on fabrication, microstructure and optical properties of Ce^{3+}:$Lu_3Al_5O_{12}$ (Ce:LuAG) transparent ceramics

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ABSTRACT

Nanosized Ce^{3+} doped $Lu_3Al_5O_{12}$ (Ce:LuAG) powder with narrow particle size distribution and high sinterability were successfully synthesized via a modified co-precipitation method using hydroxy propyl cellulose (HPC) as surfactant. It was suggested that a polymer layer was formed by HPC wrapping on the Ce:LuAG precursors instead of free water during precipitation and drying processes owing to its typical property of lower critical solution temperature (LCST), which could reduce the agglomeration among the particles. The green compact shaped by the powders exhibited a superior linear thermal shrinkage (19.7%) from room temperature to 1500 °C and could be subsequently densified into high optical quality Ce:LuAG transparent ceramics at 1750 °C for 10 h under vacuum sintering without any sintering aids. The in-line optical transmittance of the Ce:LuAG ceramic reached 73.48% at the wavelength of 550 nm without observable micro-pores and secondary phases at grain boundaries or within grains.

1. Introduction

Transparent ceramics have attracted great interests owing to their lower fabrication temperature, uniform doping concentration and lower production cost compared with the corresponding single crystals. Besides widely used in solid-state laser fields [1–3], they are also playing an important role as scintillation materials in high energy physics, oil well logging and nuclear medical imaging [4–6]. Scintillators convert high energy ionizing radiation (e.g. γ-ray, β-ray and X-ray) into near ultraviolet to visible light, which can be applied to analyze interior characteristics of different substances [4]. Recently, many ceramic scintillators have been investigated to obtain high scintillation performance (high light yield and fast decay time), such as Ce^{3+} or Pr^{3+} doped $Lu_3Al_5O_{12}$ (LuAG) transparent ceramics [7–10].

In order to fabricate transparent ceramics with high optical quality, well dispersed and low-agglomerated nano-sized powders are of great importance. Ultrafine particle size (about 100 nm) and spherical particle shape are the two important requirements for this objective, which enable particles to close contact during the sintering process, and thus give rise to sufficient densification of polycrystalline ceramics [11]. The main synthetic processing to obtain such ultrafine powders can be generally classified into two routes. One is solid-state reaction method and the other is wet chemical method. Synthesis of LuAG powders by direct solid-state reaction with mixed lutecia and alumina powders normally requires a temperature higher than 1400 °C with a prolonged heating period [7]. Meanwhile, the as-fabricated powders usually possess submicron particle size with strong agglomeration, which is not beneficial to consolidate the ceramic green compacts into transparent ceramics. Therefore, sintering aids such as MgO or tetraethyl-ortho-silicate (TEOS) are often adopted to lower the sintering temperature and promote the densification process [7,10]. However, sintering aids segregated as secondary phases at grain boundaries can form defects deteriorating the scintillation properties of transparent ceramics [10].

On the other hand, wet chemical method is an effective way to resolve this problem due to the absence of sintering aids during ceramic sintering. In recent years, various wet chemical methods have been successfully developed to synthesize LuAG nano-sized powders such as co-precipitation method [8,12], sol–gel method [13,14] and solvothermal method [15,16]. These methods result in reactants mixing on a molecular level and reduction of the crystallization temperature of powders, which is usually 400–500 °C lower than that using solid-state reaction method [7,8,12–14].

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Among these methods, co-precipitation method is a commonly used and promising technique since the particles can be prepared on a large scale in aqueous solution rather than in organic chemicals without using complicated apparatus. Recently, some groups have prepared LuAG nano-sized powders by co-precipitation method, however, the agglomeration state of the as-synthesized powders was frustrated [8,17]. In order to achieve highly dispersed LuAG powders, appropriate surfactants such as cationic surfactant (e.g. cetyl trimethyl ammonium bromide (CTAB)), anionic surfactant (e.g. sodium octylphenol polyoxyethylenated ethylsulfonate (OPS)) and nonionic surfactant (e.g. polyethylene glycol (PEG)) are usually adopted to alleviate agglomeration state of the powder [18,19].

In our previous work [20], we used hydroxyl propyl cellulose (HPC) as nonionic surfactant during co-precipitation process to alleviate the agglomeration state of the as-synthesized Ce:LuAG powders. It was found that the low-agglomerated nano-sized Ce: LuAG powders could be fully densified into high quality Ce:LuAG transparent ceramics at relative low sintering temperature owing to their improved sinterability. In this paper, we further illuminate the function and wrapping mechanism of HPC especially its typical property of lower critical solution temperature (LCST) nicely performed during the preparation process. Effects of HPC surfactant on the morphology and sintering behavior of Ce:LuAG powders as well as the microstructure of Ce:LuAG transparent ceramics are investigated in detail.

2. Experimental

2.1. Preparation process

Polycrystalline nano-sized Ce:LuAG powders were synthesized by a reverse-strike co-precipitation method (adding the cationic salt solution into the precipitant solution). We used commercial Lu_2O_3 (>99.99%, Xiyuan International, Shanghai, China), $Ce(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (analytical grade) as starting materials. NH_4HCO_3 of analytical grade was used as precipitant. Aqueous nitrate solution of Lu^{3+} was prepared by dissolving Lu_2O_3 in HNO_3 solution (12 M) under stirring and heating. $Al(NO_3)_3$ and $Ce(NO_3)_3$ solutions were obtained by dissolving $Al(NO_3){\cdot}9H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ in deionized water, respectively. The mixed nitrate solution containing Lu^{3+}, Al^{3+} and Ce^{3+} according to $(Ce_{0.005}Lu_{0.995})_3Al_5O_{12}$ was added at a speed of 2 ml/min into 2 M NH_4HCO_3 solution under vigorously stirring at room temperature (RT). 0.8 wt% of HPC (>99% Aldrich) was added in NH_4HCO_3 solution as surfactant. After being aged for 24 h, the precipitated slurry was filtered using suction filtration, followed by washing with deionized water and anhydrous alcohol (analytical grade) for several times, and then dried at 80 °C for 36 h. The dried precursors were crushed with an alumina pestle, sieved by a mesh and calcined at 1000 °C for 2 h. The as-calcined powders were ball milled by high purity ZrO_2 ceramic balls with anhydrous alcohol for 8 h, then compacted to form a ceramic green body (Φ18 mm × (3–4) mm) under uniaxial press of 5 MPa and cold isostatic press (CIP) of 200 MPa. The green body was finally sintered at 1750 °C for 10 h in vacuum without sintering aids.

2.2. Characterization

Fourier transform infrared spectroscopy (FT-IR) of the Ce:LuAG powders was recorded by an infrared spectrometer (1725X, Perkin Elmer, Waltham, MA) on KBr pellets in the region of 400–4000 cm^{-1} with 4 cm^{-1} resolution under ambient conditions. X-ray diffraction (XRD) patterns of the Ce:LuAG powder and ceramics were acquired through a XRD diffractometer (D\max-2550, Rigaku, Japan), utilizing nickel filtered Cu K_α radiation (1.5406 Å). The morphology of the as-fabricated Ce:LuAG powders and microstructure of the as-sintered Ce:LuAG ceramics were observed by transmission electronic microscope (TEM, JEM-200CX and JEM-2010F, JEOL, Japan) and field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan), respectively. The specific surface area (S_{BET}) of Ce:LuAG nano-sized powders was measured by a multipoint Brunauer–Emmett–Teller (Tristar 3000, Micromeritics, USA). Particle size distribution was determined using dynamic light scattering (DLS) method (Zetasizer 3000HS, Malvern, UK). In order to evaluate the sinterability of as-fabricated Ce:LuAG powders, green compacts with dimension of Φ18 mm × 8 mm were formed by dry-pressing under 5 MPa in a stainless steel die and a cold isostatic pressing under 200 MPa. Then linear thermal shrinkage curves of the green compacts were measured by a thermal expansion analyzer (TOM-AC, DLR, Germany) with a VIS–NIR detector ranging from RT to 1500 °C at a heating rate of 10 °C/min in a 95% Ar and 5% H_2 atmosphere. The in-line optical transmittance of Ce:LuAG ceramics was measured by an UV–VIS spectrometer (UV-2501PC, SHIMADZU, Japan). Photoluminescence excitation (PLE) and Photoluminescence (PL) spectra of Ce:LuAG ceramics were performed on a fluorescence spectrophotometer (RF-5301PC, Shimadzu, Japan). All measurements were carried out at RT except the linear thermal shrinkage measurement.

3. Results and discussion

3.1. Role of HPC in co-precipitation process

FT-IR spectra of the precipitate Ce:LuAG precursors with and without HPC are illustrated in Fig. 1. The FT-IR pattern of pure HPC is also plotted as a reference to expatiate its wrapping mechanism. The broad absorption band at 3440 cm^{-1} is attributed to the coupled effect of molecular water and aluminum/lutetium hydroxyl groups (–OH) [21]. The two intense bands at 1532 and 1400 cm^{-1} are assigned to the asymmetric stretch of C–O bond in CO_3^{2-}, and the bands at 1093 and 850 cm^{-1} are originated from the symmetric stretch and deformation vibration of C–O bond in CO_3^{2-}, respectively [22]. No typical bond-stretching modes of N–O bond and NH_4^+ ions are observed in the Ce:LuAG precursors which demonstrates that the superfluous NH_4^+ and NO_3^- ions are totally removed after washing with deionized water and anhydrous

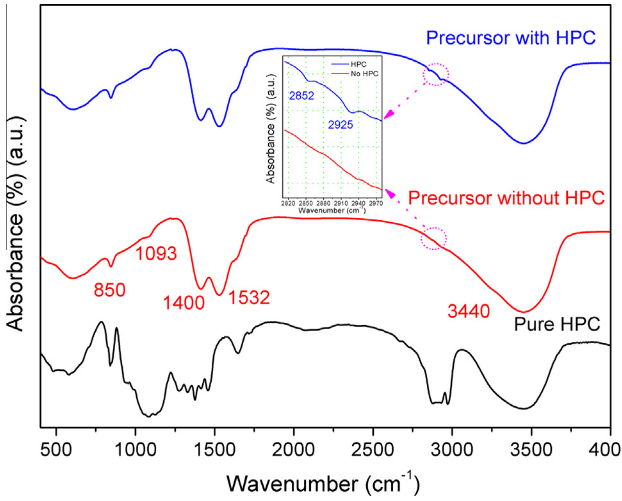

Fig. 1. Fourier transform infrared (FT-IR) spectra of the Ce:LuAG precipitate precursors with and without 0.8 wt% HPC (pure HPC plotted as a reference).