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Flame synthesis and effects of host materials on Yb^{3+}/Er^{3+} co-doped upconversion nanophosphors

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ABSTRACT

The upconversion nanophosphors (UCNPs) of Yb^{3+}/Er^{3+} co-doped into Y_2O_3, La_2O_3, and Gd_2O_3 were synthesized via the combustion method and characterized by powder X-ray diffractometer (XRD), scanning electron microscopy (SEM) and upconversion fluorescence spectroscopy. The characterization results showed that at the same flame temperature (2705 K) and precursor concentration (0.1 M), pure monoclinic and cubic-phase phosphors were achieved on Gd_2O_3 and Y_2O_3 hosted UCNPs, respectively; while the mixed phases were observed on La_2O_3 hosted UCNPs. Further annealing process at 850 °C produced pure cubic-phase La_2O_3:Yb^{3+},Er^{3+} UCNPs; while there was no phase transition observed on Gd_2O_3:Yb^{3+},Er^{3+} UCNPs. The dependence of upconversion luminescence on precursor concentrations and host materials was then examined. The La_2O_3 and Gd_2O_3 hosts were shown to be the promising alternates for the commonly used Y_2O_3 hosts for rare-earth doped phosphors.

1. Introduction

Rare-earth (RE) doped upconversion nanophosphors (UCNPs), which produce sharp visible luminescence with near-infrared (NIR) excitation, have broad applications spanning from ceramic solid-state lasers, luminescent displays, biolabeling and photodynamic therapy to authentication and security [1–10]. Compared to conventional down-conversion phosphors [11,12], UCNPs benefit from the availability of low cost and high power infrared lasers. In addition, the use of infrared excitation allows deeper tissue penetration and reduces background noise due to the absence of autofluorescence. Furthermore, the UC process has tunable optical properties and simultaneous detection of multiple targets. Therefore, UCNPs have received considerable interest not only from academic researchers, but also from commercial applications.

To prepare oxides hosted UCNPs, several different techniques, such as sol–gel [13], facile hydrothermal and coprecipitation [14], solution combustion synthesis [15], spray pyrolysis [16], and flame spray synthesis [17] have been reported. Among these methods, the flame based combustion synthesis methods have presented great commercialization potential with high production rates, broad temperature controllability, low cost, and synthetic flexibility on choosing host materials. Moreover, they can produce high purity nanoparticles with small primary size and narrow size distributions. For commercial application, besides choosing a suitable synthetic method, another task is to identify the most efficient UC phosphor system. So far, the hexagonal-phase $NaYF_4$ host is reported to be the most efficient for UCNPs, especially at nanoscale [9,10], however, the fluorides based UCNPs have the concerns of toxicity problem due to the fluorine-containing species. Furthermore, the fluoride hosts are impractical for the high temperature synthesis (>1000 °C) under the oxygen atmosphere. To date, the ceramic based oxides, such as Y_2O_3, La_2O_3, and Gd_2O_3 are found to be the most stable and low toxic host concerning the above factors [18]. Exploring deeper into the inside the crystalline structure, some photophysical properties of these oxides hosts are the same as those of fluorides based UCNPs, e.g., low phonon energy, transparent to visual light and in the absence of the low energy levels and interaction between the doped RE activator ions. Therefore, the oxide hosted phosphors have been actively investigated in parallel with those fluorides based phosphors.

Flame synthesis of the Y_2O_3:Yb^{3+},Er^{3+} UCNPs has been reported [17]. However, there is still no work on the flame synthesis of La_2O_3 and Gd_2O_3 hosted UCNPs. Therefore, both the fundamental and experimental investigations exploring their potential applications for UCNPs are still needed. In this paper, two new UCNPs of Yb^{3+}:Er^{3+} co-doped into hosts of Re_2O_3 (Re = La and Gd) were prepared by the FSP synthesis and were characterized.

2. Experimental

Fig. 1 shows the process of FSP method and schematic of the FSP system. The flame nozzle consisted of three concentric stainless steel tubes. By varying the flow rates of all gases, the flame temperature and particle residence time can be controlled. For example, the oxygen nitrogen and methane flow rate was kept constant at 2, 1.23 and 0.6 L/min, respectively, the corresponding adiabatic flame temperature (Tad) was estimated at 2705 K by using CHEMKIN [19].

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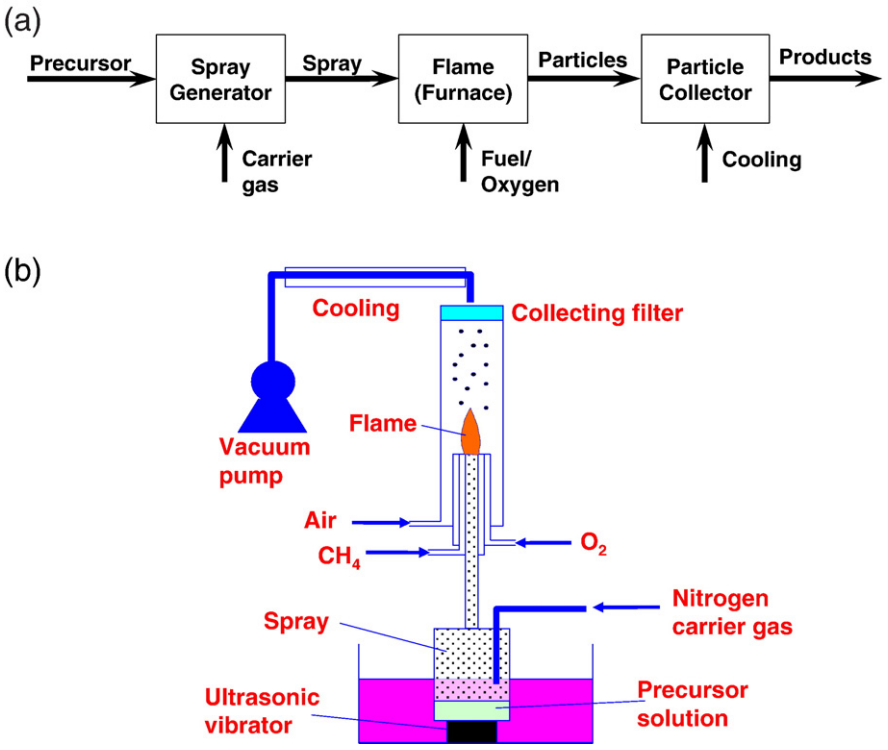

Fig. 1. FSP system: (a) process of combustion synthesis, and (b) experimental setup.

The particles were cooled and collected by using a filter paper. In this work, ethanol was selected as the solvent. The precursor solutions were prepared by dissolving a given amount of nitrates of metals in ethanol. Powder X-ray diffractometry (XRD) was used for the characterization of crystal phase and the estimation of the crystalline size. The morphology and size of particles were examined using a field-emission scanning electron microscope (FE-SEM, Philips XL30). PL spectra were measured with excitation at 980 nm using a NIR laser diode.

3. Results and discussions

In this work, to compare the effects of the hosts on the UC luminescence, the flame temperature was kept at 2705 K. Fig. 2 shows

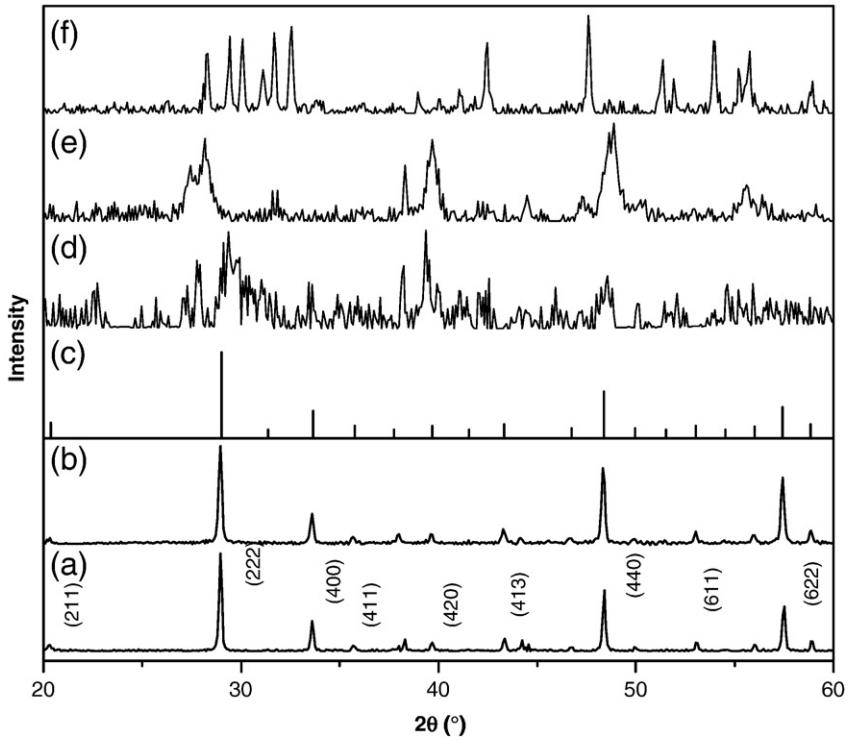

Fig. 2. Powder XRD patterns of (a) Y^{86}:Yb^{8}:Er^{6}, (b) Y^{96}:Yb^{1}:Er^{3}, (c) JCPDS card No. 41-1105, (d) La^{95}:Yb^{1}:Er^{4}, (e) La^{95}:Yb^{1}:Er^{4} after 4 h annealing at 850 °C, and (f) Gd^{95}:Yb^{10}:Er^{8}.