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A novel co-precipitation synthesis of a new phosphor Lu_2O_3:Eu^{3+}

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Abstract

Europium-doped Lu_2O_3 phosphors were prepared via a co-precipitation process. The influence of precipitants on morphology and dispersibility of the obtained Lu_2O_3 powders were investigated. Precipitation was performed with three different precipitants, namely ammonium hydroxide ($NH_3{\cdot}H_2O$), ammonium hydrogen carbonate (NH_4HCO_3), and the mixture of $NH_3{\cdot}H_2O$ and NH_4HCO_3. Ultrafine, nearly monodispersed, weakly agglomerated and near-spherical lutetia powders could be obtained with mixed $NH_3{\cdot}H_2O$ and NH_4HCO_3 as the precipitant. The precipitate precursor with the mixed precipitant was believed to possess a basic carbonate composition and its thermal decomposition and phase evolution processes were investigated. Photoluminescence characteristics of Lu_2O_3:Eu^{3+} phosphors obtained by this modified precipitation method were also studied.

Keywords: Optical properties; Lu_2O_3; Precipitation; Phosphors

1. Introduction

Lutetium-based materials have attracted considerable attention as host crystals during the last 2 decades, among which Ce-doped Lu_2SiO_5 and $LuAlO_3$ have become the most competitive candidates to replace $Bi_4Ge_3O_{12}$ in positron emission tomography (PET) cameras.[1] The crystallographic structure of Lu_2O_3 is of the same type as cubic Y_2O_3.[2] In contrast, lutetium could be a more favorable cation than yttrium for lanthanide dopant emission.[3] Due to its high density (~9.42 g/cm^3) and high Z-number of lutetium, Lu_2O_3 can serve as a promising host material for some novel applications in electrooptics field. The crystal field of lutetia ceramics favors their uses as a host material in ceramic lasers or scintillators. Lutetia doped with Nd or Yb is a promising ceramic laser material,[4,5] while europium-doped Lu_2O_3 ceramic scintillator can find its application in the field of X-ray imaging technology.[6]

Different synthesis methods lead to different particle morphologies and specific surface areas, which, in turn, determine the particle properties. Preparation of lutetia-doped with Eu^{3+} by the conventional ceramic powder processing is not favorable, as it employs a solid-state reaction of the oxides at high temperatures with sequential grinding and firing steps. It has been long recognized that wet-chemical process offers considerable advantages of good mixing of the starting material and excellent chemical homogeneity of the final product. As Robinson described,[7] the secret to improve a ceramic material is the control of the structure at very small length scales in an early stage of fabrication; chemistry might be the way to achieve this goal. Many chemical methods have been adopted to fabricate ultrafine lutetia powders. For example, Zych adopted combustion synthesis method to prepare nanostructured Lu_2O_3:Eu^{3+} phosphors,[8] moreover, oxalate precipitation[6] and a molten salts route[9] were employed by Lempicki and Trojan-Piegza to prepare Lu_2O_3:Eu^{3+} phosphors, respectively.

Co-precipitation has been verified its feasibility for fabricating ceramic powders with favorable characteristics. However, for rare earth oxides, two commonly used precipitants, oxalic acid and urea, were not adopted due to some of their disadvantages. For example, the relative high values of the solubility constants (K_{sp}) of the rare earth oxalates will cause rapid and thorough reaction of the precipitation, thus resulting in a fast growing rate and uncontrolled severe agglomeration of the resultant crystallites; the considerably low hydrolization rate of

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urea limits the yield of homogeneous precipitation process. The aim of the present work is to synthesize nanostructured Eu^{3+}-doped Lu_2O_3 phosphors with favorable characteristics using an improved co-precipitation method. The mixture of ammonium hydroxide ($NH_3{\cdot}H_2O$) and ammonium hydrogen carbonate (NH_4HCO_3) is used as a mixed precipitant. Lu_2O_3:Eu^{3+} phosphors obtained by this modified co-precipitation processing show uniform and nanosized grains and its photoluminescence properties were also investigated.

2. Experimental

Lutetium and europium nitrate solution were prepared with corresponding oxide (purity > 99.9%, Rare Earth Products Ltd., Hongkong, China) dissolved in slightly excess nitric acid. The concentration of the Eu_2O_3 dopant was set at 5 mol% and compensated by an equivalent decrease of the lutetium oxide. Analytical grade ammonium hydroxide and ammonium hydrogen carbonate were mixed to act as a mixed precipitant. For the purpose of comparison, $NH_3{\cdot}H_2O$ and NH_4HCO_3 were also used individually. The precursor precipitate was produced by adding 250 ml of the precipitant solution (~2.5 M) at a speed of 3 ml/min into 1000 ml of the mother solution (~0.06 M for Lu^{3+}) under mild stirring. The resultant suspension, after aged for 24 h, was filtered using a suction filter, washed four times with deionized water, and then twice with ethyl alcohol, and followed by drying at 100 °C for 24 h. The dried precursor was crushed with an alumina pestle and mortar and calcined at 550 °C, 650 °C, 750 °C, 850 °C and 1000 °C for 2 h, respectively. Fig. 1 gives a flow chart describing relevant details of the co-precipitation processing.

Phase structure identification was performed with X-ray diffractometer (D/max 2550 V, Rigaku, Japan) utilizing nickel filtered Cu Kα radiation (1.5406 Å) in the range of $2\theta = 10$–$70°$. IR absorbance spectra were recorded using a Thermo Nicolet Nexus Fourier Transform infrared spectrometer with KBr pellets. TG-DTA-MS measurements were conducted using a NETZSCH-STA 449C apparatus. Powder morphology and microstructure were observed by field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan). Specimens for the transmission electron microscopy (TEM, JEM2010 JEOL, Japan) study were ultrasonically dispersed into methanol, and the suspension was spread on the surface of silicon plate. Photoluminescence measurements were carried out on a fluorescence spectrometer (Fluorolog-3, Jobin Yvon, France) at room temperature.

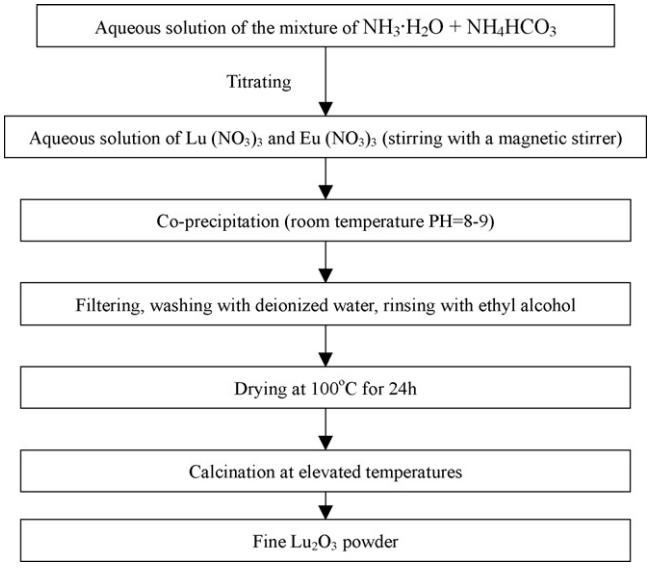

Fig. 1. Flow chart illustrating sequence used in the precipitation experiments.

3. Results and discussion

Fig. 2 shows the Fourier transform infrared (FTIR) absorption spectra of the dried precursor powders in the range 4000–400 cm^{-1}. In the case of $NH_3{\cdot}H_2O$ precipitant alone, though after many times of water washing and ethyl alcohol rinsing, residual NO_3^- and NH_4^+ still exists. The intense absorption band at around 1380 cm^{-1} and the peak locating at 1540 cm^{-1} indicate the existences of NO_3^- and NH_4^+, respec-

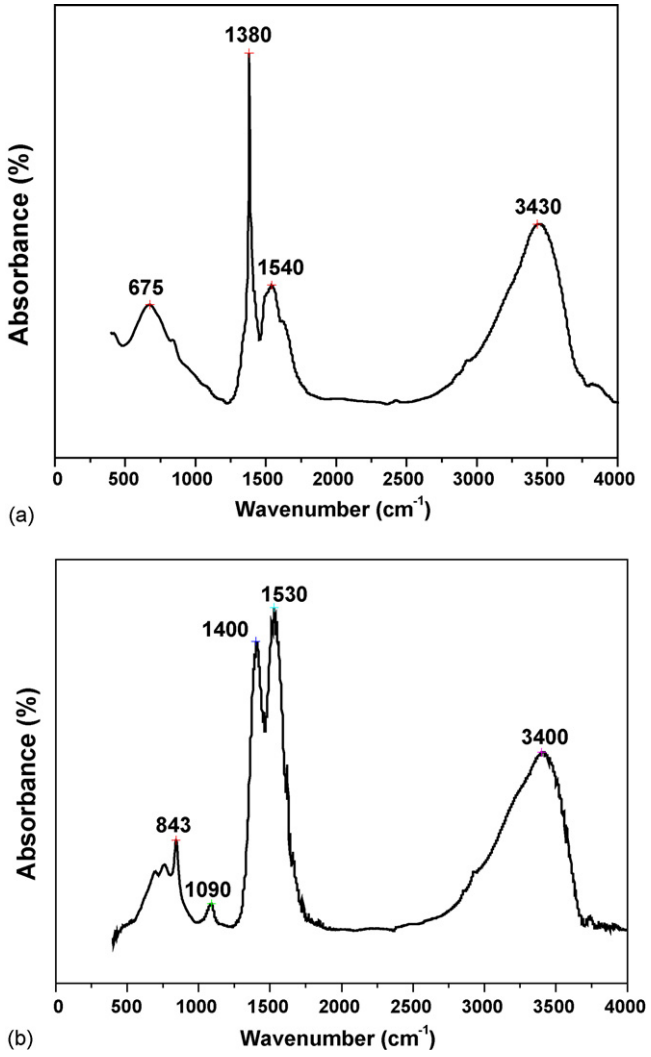

Fig. 2. FT-IR of the precursors prepared with: (a) $NH_3{\cdot}H_2O$, (b) NH_4HCO_3 or $NH_3{\cdot}H_2O + NH_4HCO_3$ as the precipitants.

tively. IR spectra of the two precursors prepared with single NH_4HCO_3 and with $NH_3{\cdot}H_2O + NH_4HCO_3$ mixture are almost identical. The peak at around 750 cm^{-1} results from deformation of O–H band. The broad absorption band at 3410 cm^{-1} is assigned to O–H stretching. The two intense peaks at 1530 cm^{-1} and 1400 cm^{-1} are assigned to the asymmetric stretch of C–O in CO_3^{2-}, while the absorption peaks at 1090 cm^{-1} and 840 cm^{-1} are due to the symmetric stretch of C–O band and deformation vibration of C–O in CO_3^{2-}, respectively. These absorption peaks indicate the presence of carbonate groups.

TEM morphologies of the precipitate precursors obtained by the three precipitants are shown in Fig. 3(a), (b) and (c). The resultant powders from $NH_3{\cdot}H_2O$ are severely agglomerated. The primary particles are aggregated together and almost no discrete particles can be seen from the photographs. Severe agglomeration of the $NH_3{\cdot}H_2O$ method was due to the bridging of the adjacent particles with water by hydrogen bonding and the huge capillary force generated during drying.[10] Readey[11] proposed that this hydroxide process involves hydrogen bonding of surface hydroxyl groups on the hydroxide precipitate, and the water molecules can bridge the surface hydroxyl groups of neighbouring precipitates, thus bonding adjacent particles. Powders synthesized by the NH_4HCO_3 method, though apparently agglomerated, show a lower agglomeration degree than that of

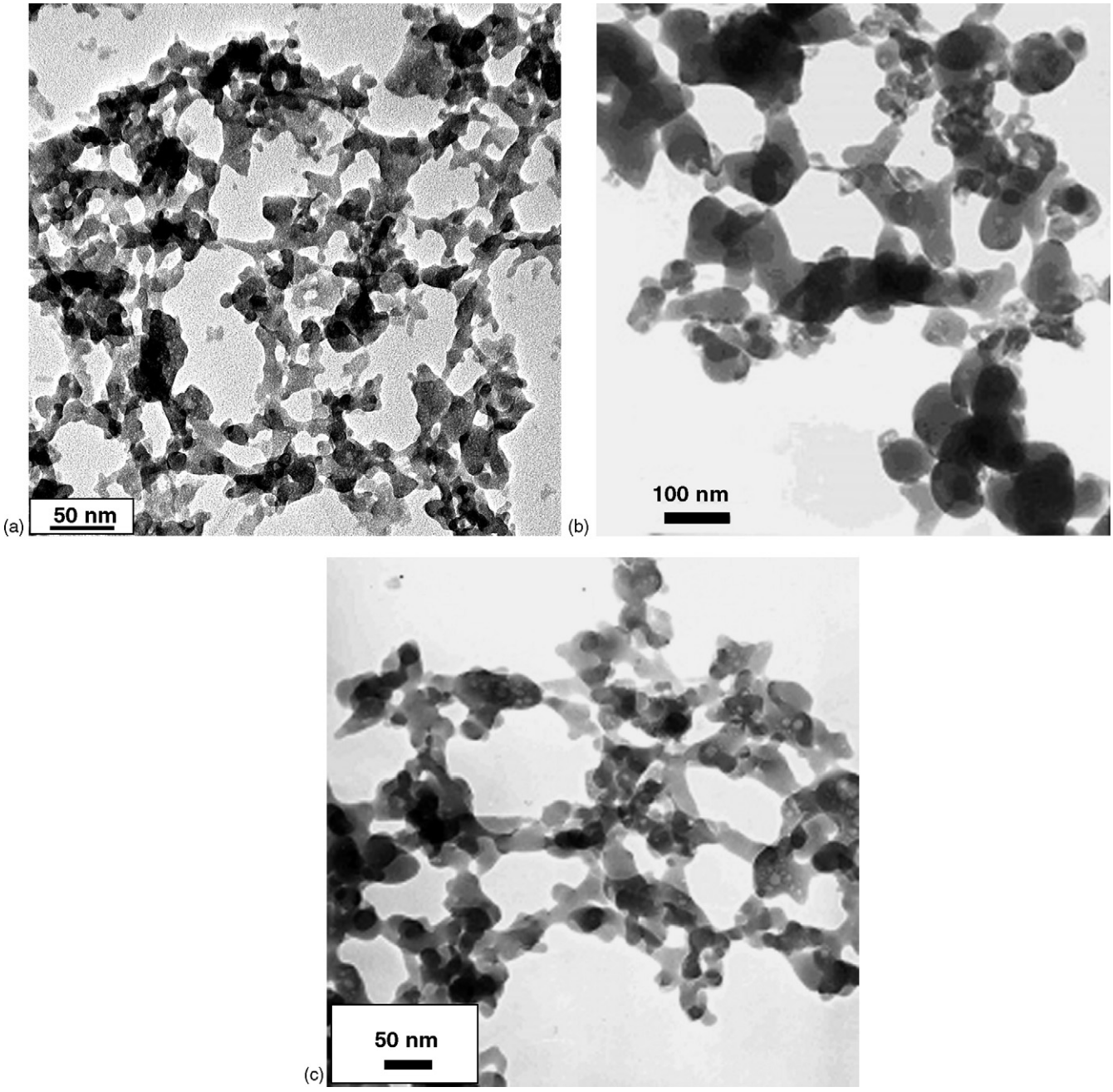

Fig. 3. TEM photographs of the precipitate precursors prepared with: (a) $NH_3{\cdot}H_2O$, (b) NH_4HCO_3 and (c) $NH_3{\cdot}H_2O + NH_4HCO_3$ as the precipitants.

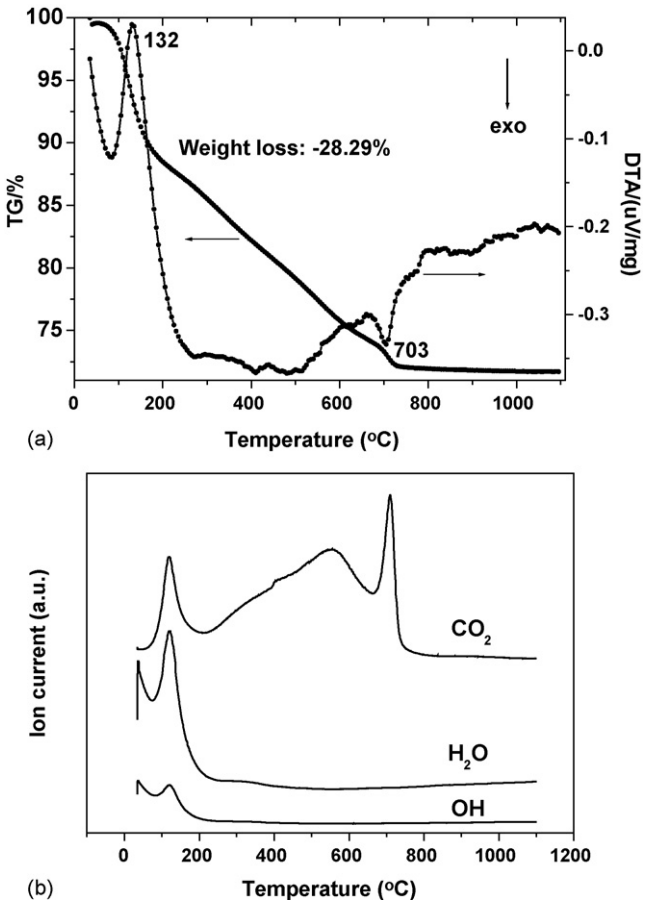

Fig. 4. (a) TG-DTA and (b) MS curves of the precursors prepared with $NH_3{\cdot}H_2O + NH_4HCO_3$ as the precipitant.

the hydroxide-derived powders. The basic carbonate precipitates precursor from the mixed precipitant method show better dispersibility and weaker agglomeration. Relatively discrete, spherical particles only slightly link together. The precursor morphology favors the creation of well-dispersed oxide powders after calcination.

TG-DTA curves of the precursor produced by the mixed precipitant method are given in Fig. 4(a). The TG curve displays a relatively continuous weight loss to near 800 °C. The total weight loss is around 28.3%. The DTA curve shows an endothermal peak at about 132 °C corresponding to the release of water of hydration and OH, and the exothermic peak at about 703 °C due to the chemical decomposition of the carbonate or dioxycarbonate, which is indicated by the MS curves shown in Fig. 4(b). The weight loss of the sample between 100 °C and 800 °C is apparently a consequence of the thermal decomposition of Lu(OH)CO_3H_2O into Lu_2O_3, according to the following equation:

$$\mathrm{Lu(OH)\,CO_3H_2O} \xrightarrow{\approx 120^\circ\mathrm{C}} \mathrm{Lu_2(CO_3)_3\ or\ (Lu_2O_2CO_3)} \xrightarrow{\approx 710^\circ\mathrm{C}} \mathrm{Lu_2O_3}$$

The precipitation process is somewhat similar to that of urea homogeneous precipitation. The homogeneous decomposition of urea and subsequent dissociation of the reaction products will yield OH^- and CO_3^{2-}.[12] Composition of the precursor obtained by the mixed precipitant technique will be the result of the competition between OH^- and the carbonate species to form precipitates with Lu^{3+} as characterized by the following chemical reactions:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4HCO_3 \rightleftharpoons NH_4^+ + HCO_3^-$$

$$OH^- + HCO_3^- \rightleftharpoons H_2O + CO_3^{2-}$$

$$Lu^{3+} + OH^- + CO_3^{2-} + H_2O \rightarrow Lu(OH)CO_3H_2O$$

XRD patterns of the precursor prepared with $NH_3{\cdot}H_2O + NH_4HCO_3$ and Lu_2O_3 powders calcined at various temperatures from 550 °C to 1000 °C are illustrated in Fig. 5. The as-precipitated powder is amorphous with no XRD peaks. The crystallization process of the precipitate precursor with subsequent heat-treatment can be clearly seen. Calcination at 550 °C is not adequate for the precursor to crystallize. After calcined at 650 °C for 2 h, the precursor transforms to cubic Lu_2O_3 phase. The diffraction peaks intensity enhance and also the full-width at half-maximum (FWHM) reduce due to the improvement of crystallinity and grain growth upon further heating to 850 °C and 1000 °C.

Fig. 6(a)–(c) show the SEM morphologies of the lutetia powders by calcining the precipitates at 1000 °C for 2 h with $NH_3{\cdot}H_2O$, NH_4HCO_3 and $NH_3{\cdot}H_2O + NH_4HCO_3$ mixture as precipitants, respectively. The lutetia powders obtained from the mixed precipitant are much better dispersed than those from $NH_3{\cdot}H_2O$ and NH_4HCO_3 as precipitants. Narrowly distributed in size, weakly agglomerated and fine spherical powders can be obtained by the mixed precipitant method after calcined at 1000 °C for 2 h. The average crystallites sizes of lutetia powders prepared with $NH_3{\cdot}H_2O + NH_4HCO_3$ method calcined at

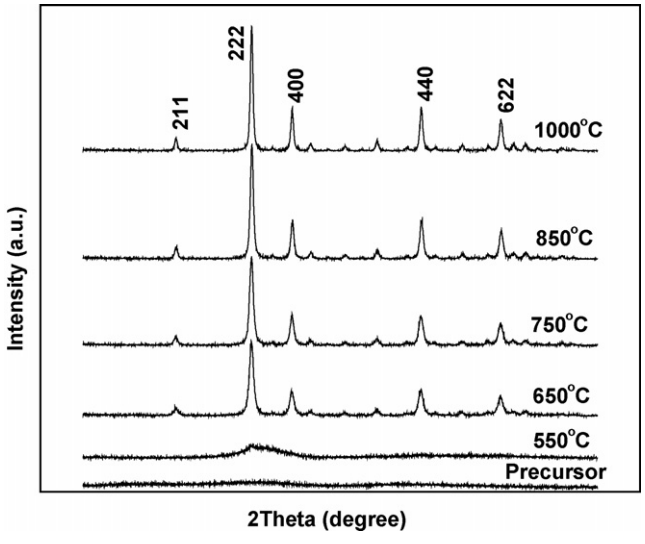

Fig. 5. XRD patterns of the precursor prepared with $NH_3{\cdot}H_2O + NH_4HCO_3$ as the precipitant.

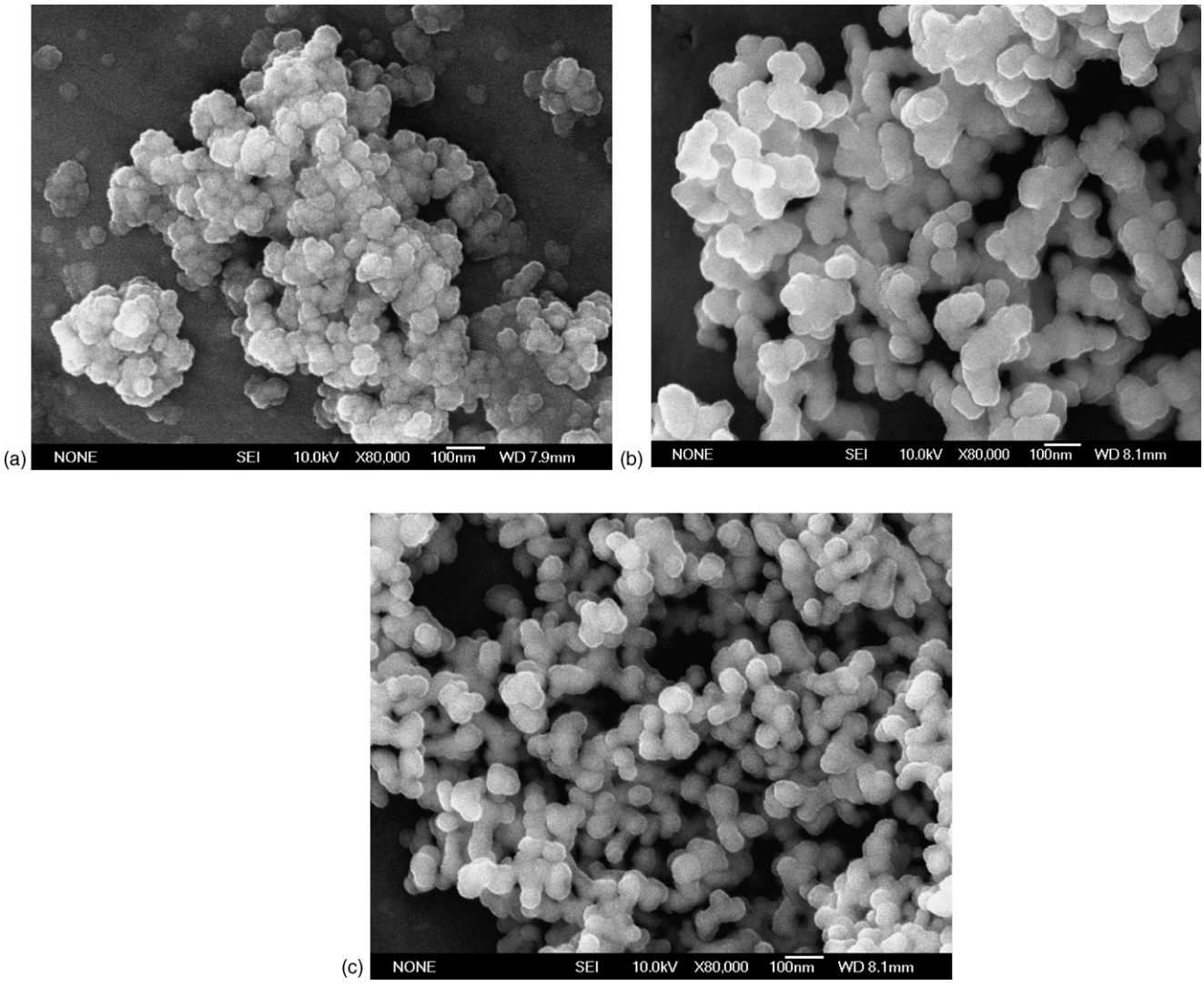

Fig. 6. SEM morphologies of powders calcined at 1000 °C for 2 h with: (a) $NH_3{\cdot}H_2O$, (b) NH_4HCO_3 and (c) $NH_3{\cdot}H_2O + NH_4HCO_3$ as the precipitants.

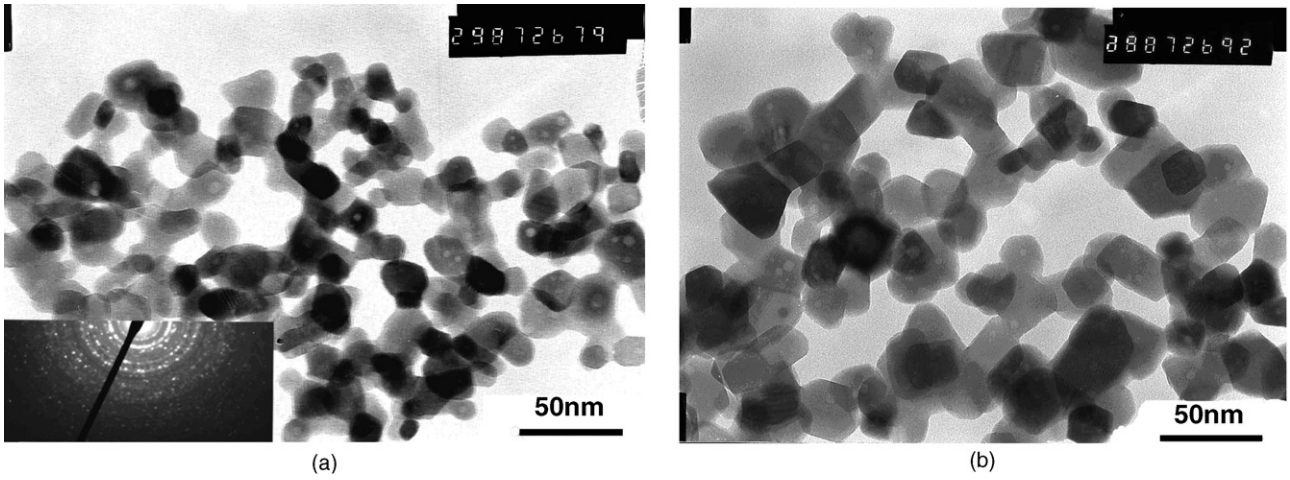

Fig. 7. TEM micrographs of lutetia powders prepared with $NH_3{\cdot}H_2O + NH_4HCO_3$ calcined at: (a) 850 °C for 2 h (SAED inset) and (b) 1000 °C for 2 h.

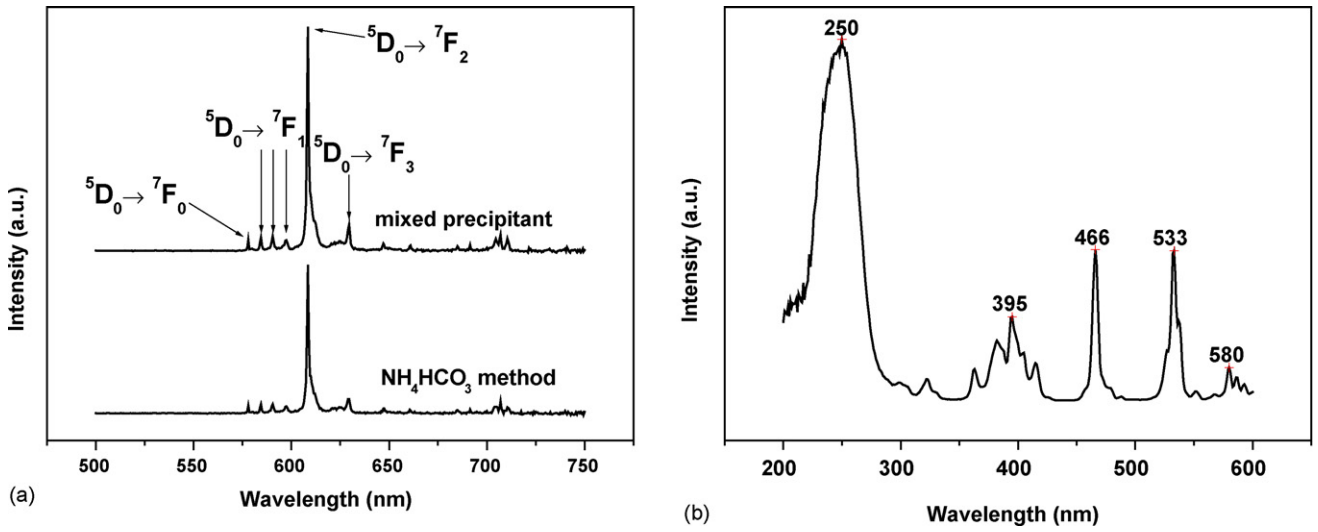

Fig. 8. (a) Emission (λ_{ex} = 394 nm) spectra of the phosphors from NH_4HCO_3 and the mixed $NH_3{\cdot}H_2O + NH_4HCO_3$ precipitants; (b) excitation (λ_{em} = 610 nm) spectrum of the phosphors from mixed $NH_3{\cdot}H_2O + NH_4HCO_3$ precipitant.

850 °C and 1000 °C for 2 h are about 20 nm and 40 nm, respectively, which were revealed by TEM micrographs as shown in Fig. 7(a) and (b). Selected area electron diffraction (SAED) of the powders calcined at 850 °C indicates complete crystallization. The Lu_2O_3 powder obtained at 1000 °C experiences significant grain growth. From the powder morphology comparison, it is suggested that the introduction of CO_3^{2-} is essential to obtain less agglomerated and uniformly dispersed powders. The release of CO_2 during the decomposition of the carbonate will prevent the particles from severe agglomerating with each other, thus resulting in well-dispersed nanopowders.

Fig. 8(a) shows the emission (λ_{ex} = 394nm) spectra of the phosphors obtained from NH_4HCO_3 and the mixed precipitant techniques. We choose the two phosphor samples for comparison purpose because they have similar powder characters such as grain size, particle morphology and surface state. The emission spectra demonstrate the well-known $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2 . . .) transition of Eu^{3+} ions. The energy level diagram of Eu^{3+} in Lu_2O_3 host is shown in Fig. 9. The irradiation with ultraviolet (UV) light of nanocrystalline Lu_2O_3:Eu^{3+} into the charge transfer band, which yields intense red emission at 610 nm dominated by $^5D_0 \rightarrow {}^7F_2$ transition. It has been proposed that phosphors materials with fine crystallite size, narrow size distribution, non-agglomerated feature, and spherical morphology have good luminescent properties.[13] Lu_2O_3:Eu^{3+} phosphors obtained by the mixed precipitant processing show enhanced photoluminescence compared with that from the NH_4HCO_3 method. This is probably due to the near-spherical particle morphology and relatively good particle dispersion with high particle size uniformity from the mixed precipitant technique. Fig. 8(b) shows the excitation (λ_{em} = 610 nm) spectrum of the phosphors obtained from $NH_3{\cdot}H_2O + NH_4HCO_3$ method. The broad excitation band in the region between 220 nm and 280 nm is known to result from the charge-transfer (CT) transitions between O^{2-} and Eu^{3+} ions, which corresponds to the electronic transition from the 2*p* orbital of O^{2-} to the 4*f* orbital of Eu^{3+}.[14] The narrow lines in visible and near UV part of the excitation spectrum reflect the intraconfigurational partially forbidden 4f → 4f transitions within the Eu^{3+} ion.[15]

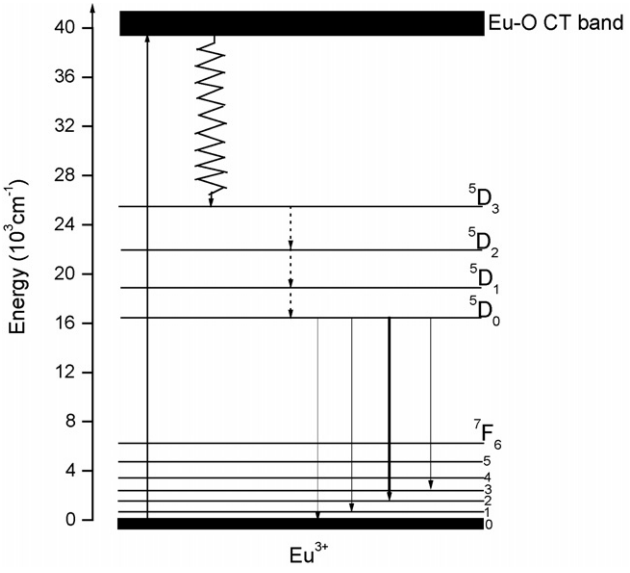

Fig. 9. Energy level diagram of Eu^{3+} in Lu_2O_3 host lattice.

4. Conclusions

Europium-doped lutetium oxide phosphors have been prepared by a novel co-precipitation method, with $NH_3{\cdot}H_2O + NH_4HCO_3$ mixture as the precipitant. Ultrafine, nearly monodispersed, weakly agglomerated and spherical powders can be obtained. The combined analysis results of IR, TG-DTA and MS characterizations reveal that the precursor has a basic carbonate composition and its thermal decomposition process includes the removals of hydration water, OH^- and CO_3^{2-} ions during heating-up. Phosphors obtained by this mixed precipitant technique present enhanced photoluminescence due to its favorable powder characteristics.

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