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Letter

Hydrothermal synthesis of fully crystalline Nd:Lu_2O_3 nanopowders under a low temperature

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ABSTRACT

Fully crystallite Nd^{3+}:Lu_2O_3 nanopowders were synthesized by a facile hydrothermal processing at 220 °C directly without additives such as catalysts or templates. The as-prepared Nd:Lu_2O_3 phosphors satisfied fully crystalline and good luminescence properties without further calcination. It is found that pH value of the hydrothermal environment plays an important role in the controlling of morphology and luminescent properties of the obtained Nd:Lu_2O_3 nanocrystalline phosphors. As-prepared Nd:Lu_2O_3 phosphors under the conditions of pH 14, 220 °C for 22 h possess fully crystallized cubic phase and it exhibits octagonal morphology with the grain size range from 50 nm to 200 nm. The PL spectra demonstrate that the intensity of main emission peak is strongly dependent on crystallinity of Nd:Lu_2O_3 phosphors.

1. Introduction

Hydrothermal technology has been widely utilized as a facile approaching to synthesize rare earth functional materials, focusing on the controlling of the morphologies of products under different environment. Among effective factors, templates and catalysts are commonly applied to synthesize the rare earth compounds with various morphologies [1,2]. Li and his coworkers have successfully synthesized a series of rare earth hydrate compound ($RE(OH)_3$) nanowires, nanosheets, nanotubes, and fullerene-like nanoparticles based on hydrothermal treatment in the range of 120–180 °C [3–5]. Wang fabricated Eu or Tb doped Lu_2O_3 nanoflakes, nanoquadrels, nanorods and squared nanosheets via a similar hydrothermal processing at 140 °C, followed by subsequent thermal decomposition at 900 °C [6,7]. It is obvious that a calcination processing after hydrothermal synthesis seems necessary to achieve the fully crystalline oxide products, which is a time and device consuming drawback.

Lu_2O_3 is a kind of attractive sesquioxide with cubic structure, which favors its applications as promising phosphors, host material for scintillators and laser gain media [8–14]. In this report, we have successfully synthesized fully crystalline Nd:Lu_2O_3 phosphors by a facile hydrothermal approach without any catalysts, templates or subsequent thermal decomposition. The crystallization of Nd:Lu_2O_3 phosphors was optimized by altering the pH value of the hydrothermal environments. The effects of pH values on morphologies and luminescent properties of Nd:Lu_2O_3 phosphors were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), transmission electron microscopy (TEM), and photoluminescence (PL) spectrum.

2. Experimental procedures

The starting materials used were commercial Lu_2O_3 and Nd_2O_3 powders (purity 99.99%, Xiyuan International, Shanghai, China). Basic lutetium carbonate precursor was synthesized by a modified precipitation (NH_4OH to NH_4HCO_3 with 1:4 molar ratio) method based on our previous work [12,15,16]. As-prepared colloidal solution was divided into 3 parts, and the 10 M NaOH solution was used as the mineralizer to adjust the final pH values (pH 10, 12, 14, respectively). Then the white colloid was transferred into a Teflon-lined stainless autoclave (302ACT304, Parr, US), and carried out a hydrothermal processing in an oven at 220 °C for 22 h. The resulting products were then collected by filtration, washed with water and ethanol repeatedly and dried at 80 °C in air.

The phase composition identification of the as-received products was performed by X-ray diffractometer (D\max-2550, Rigaku, Japan) with Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV/200 mA) in the 2θ range from 10° to 80°. FTIR spectroscopy spectra were recorded by an infrared spectrometer (AVATAR 370, Thermo Nicolet, US) on KBr pellets in the region of 4000–500 cm^{-1} under ambient conditions. Microstructure of as-prepared powders was observed by field emission transmission electron microscopy (JEM-2010, JEOL, Japan). The photoluminescence emission spectrum of the specimen pumped by 808 nm LD was recorded by a spectrofluorometer (Fluorolog-3, Jobin Yvon, France) equipped with a Hamamatsu R928 photomultiplier tube at room temperature.

3. Results and discussion

X-ray diffraction (XRD) patterns of the as-prepared products at different pH values (pH 10, 12 and 14) via hydrothermal treatment

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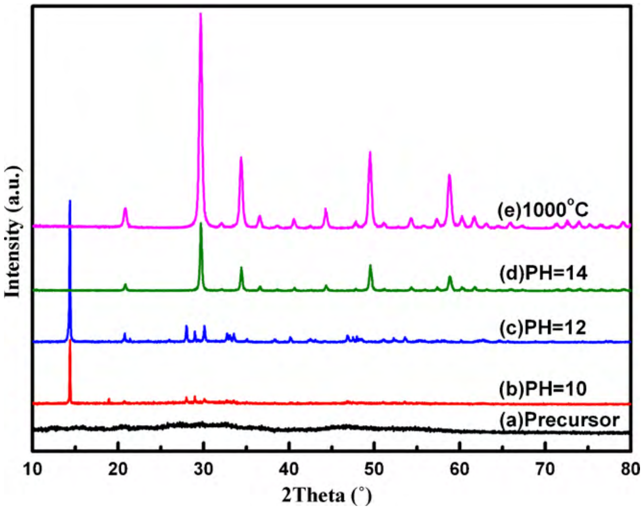

Fig. 1. XRD patterns of as-synthesized lutetium compounds via hydrothermal treatment.

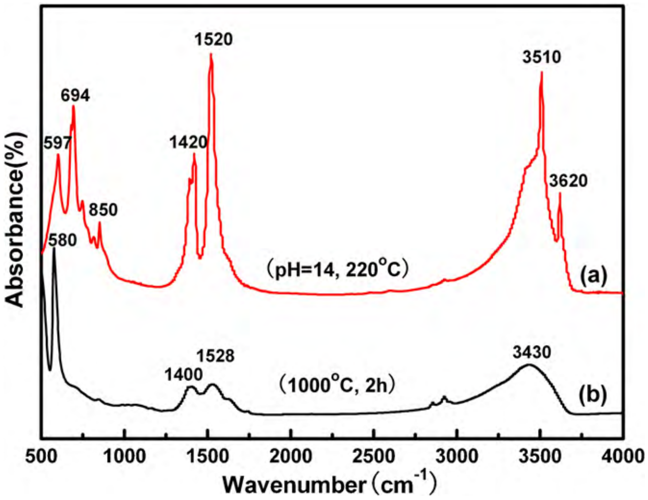

Fig. 2. FTIR spectra of the Nd:Lu_2O_3 powder calcined at 1000 °C for 2 h and hydrothermal synthesized under pH 14, 220 °C.

are shown in Fig. 1. The XRD patterns of the co-precipitation precursor and corresponding oxides calcined at 1000 °C for 2 h are present as contrasts. As shown in curve e in Fig. 1, all of the diffraction peaks could be indexed to the cubic crystalline Lu_2O_3 phase (*JCPDS#65-3172*) and no other phase of Lu-compounds was observed. From the profiles of the patterns (b)–(d), it is demonstrated that the degree of crystallinity of the products was improved greatly as pH values was raised from 10 to 14. For the colloid product, hydrothermal treated under pH 10 or 12, the patterns (b) or (c) cannot be indexed to some lutetium compounds known, suggesting that the amorphous precursor has not transformed into complete crystalline compounds. In the case of pH 14 (curve d in Fig. 1), all the diffraction

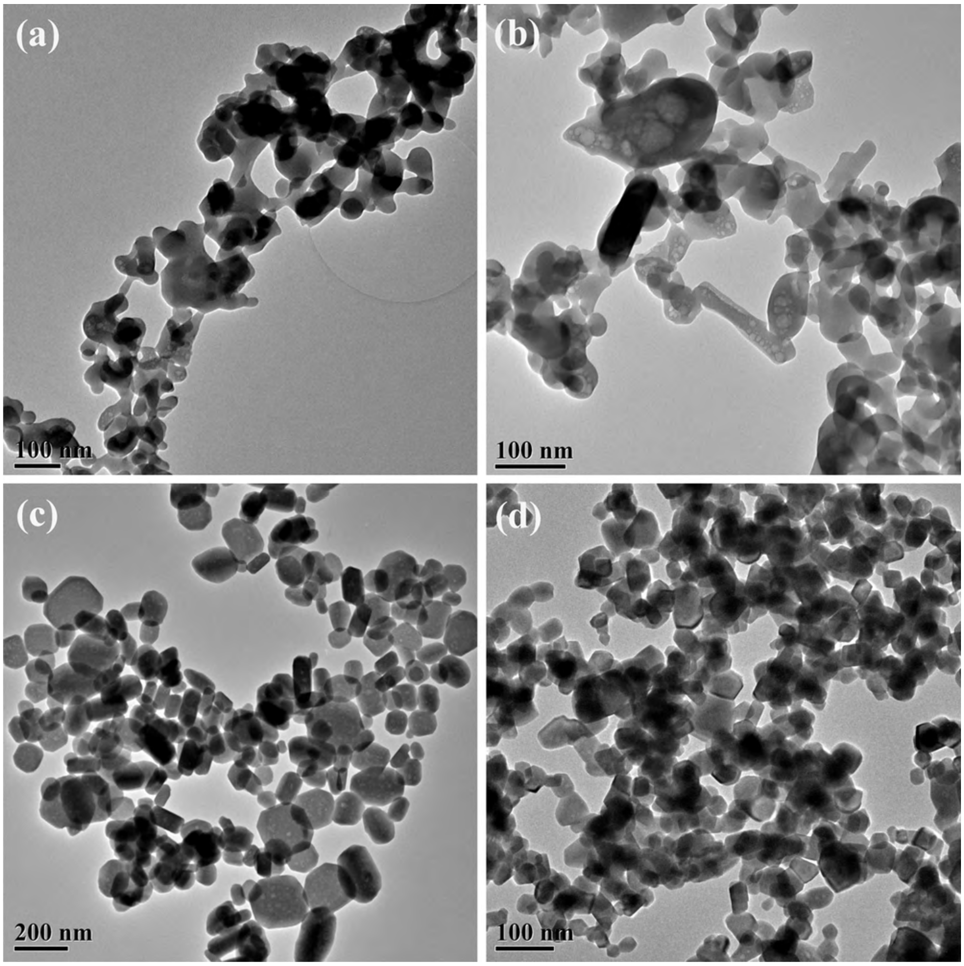

Fig. 3. TEM image of the as-synthesized lutetium compounds at (a) pH 10, (b) pH 12, (c) pH 14 by hydrothermal processing at 220 °C, and (d) calcined at 1000 °C without hydrothermal treatment.

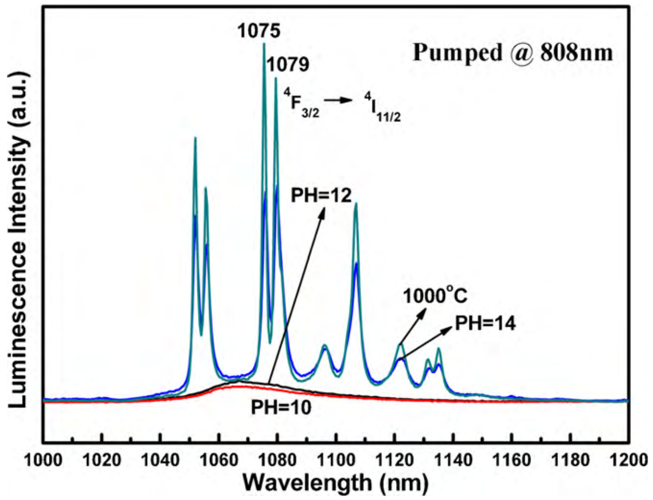

Fig. 4. Fluorescence spectrum of Nd-doped lutetium compounds.

peaks coincide well with standard pattern of Lu_2O_3 (*JCPDS#65-3172*), which indicating that pure phase of Lu_2O_3 powder could be obtained under this condition. However, the diffraction intensity of as-synthesized phosphor (pH 14, 220 °C) is weaker than that of 1000 °C calcined powders. It might contribute to the insufficiency of grain growth at 220 °C during hydrothermal processing.

Fig. 2 shows the FTIR spectra of the hydrothermal synthesized $Nd:Lu_2O_3$ nanoparticles at pH 14, 220 °C and 1000 °C calcined co-precipitation powders. In curve (a), the broad absorption band around 3510 cm^{-1} and 3620 cm^{-1} are attributed to the coupled effects of molecular water and free hydroxyl groups. The two intense peaks at 1520 cm^{-1} and 1420 cm^{-1} are assigned to the asymmetric stretch of the C–O bond in $CO_3{}^{2-}$, corresponding to the vibration located at 1528 cm^{-1} and 1400 cm^{-1} in curve (b). [10,12] The absorption peak at 850 cm^{-1} is due to the symmetric stretch and the deformation vibration of C–O in $CO_3{}^{2-}$, and the peak at 694 cm^{-1} corresponding to the vibration of the residual nitrates. These peaks indicate that the impurity functional groups are hard to be washed out from the hydrothermal synthesized products without high temperature calcination. The spectrum of 1000 °C calcined sample shows the typical absorption band at 580 cm^{-1}, corresponding to the peak at 597 cm^{-1} in hydrothermal product, which is attributed to the stretching of the Lu–O bond [17]. The deflection of the Lu–O peak in hydrothermal product is probably connected with the effect of the impurity.

Transmission electron microscopy (TEM) observation provides further insight into the size and morphology details of Nd-doped lutetium compounds synthesized by hydrothermal processing. Fig. 3(a)–(c) displays TEM micrographs of as-prepared $Nd:Lu_2O_3$ powders at pH 10, 12, and 14, respectively. Fig. 3(d) shows the TEM micrograph of co-precipitant derived $Nd:Lu_2O_3$ powder after being calcined at 1000 °C for 2 h. The similar morphologies of unclear crystalline in grain profiles can be observed in Fig. 3(a) and (b), which indicates that the crystalline transformation is difficult to complete during hydrothermal processing at pH 10 or 12. The results are in good agreement with XRD analysis shown in Fig. 1. While the pH value reaches 14, fully crystalline $Nd:Lu_2O_3$ powders were obtained at 220 °C. As-synthesized powders are well dispersed octagonal morphology with the grain size range from 50 to 200 nm, and it is different from equiaxial hexagon morphology of the 1000 °C calcined Lu_2O_3 powders, as shown in Fig. 3(d).

Fig. 4 shows the fluorescence spectra of as-synthesized $Nd:Lu_2O_3$ nanoparticles pumped at 808 nm wavelength. It demonstrated that the photoluminescence differed remarkably as pH values varied. The products synthesized under pH 10 or 12 show hardly luminescent emission in the range of as-measured wavelength, whereas the luminescence of as-prepared $Nd:Lu_2O_3$ powders obtained at pH 14, 220 °C increased drastically. The as-prepared $Nd:Lu_2O_3$ phosphors (pH 14) and nanopowder calcined at 1000 °C exhibit similar luminescent properties with the main emission bands located at 1075 nm and 1079 nm, corresponding to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions of Nd^{3+} [14].

4. Conclusions

Fully crystalline and well dispersed $Nd:Lu_2O_3$ phosphors have been successfully synthesized by the hydrothermal processing at pH 14, 220 °C for 22 h without subsequent calcination. It is found that pH value plays an important role to prompt the crystalline transformation during the hydrothermal processing. Although the phosphors are prepared under such a low temperature (220 °C, pH 14), the same XRD patterns and the similar luminescent intensity are obtained, compared with the 1000 °C calcined powders by a co-precipitation method without hydrothermal treatment.

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