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Slow light enhanced near infrared luminescence in CeO₂: Er^{3+} , Yb³⁺ inverse opal photonic crystals

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Zhengwen Yang*, Hangjun Wu, Jun Li, Bo Shao, Jianbei Qiu, Zhiguo Song

College of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

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ABSTRACT

The surface plasmon resonances of metal nanoparticles and energy transfer between rare earth ions were used widely to enhance the near infrared emission of rare earth ions. In this paper, a new method for near infrared emission enhancement of rare-earth is reported. The CeO₂: Er^{3+} , Yb³⁺ inverse opals with the photonic band gaps at the 500 and 450 nm were prepared by using polystyrene colloidal crystal as templates, and their near infrared emission properties were investigated. The results show that the near infrared emission property of the CeO₂: Er^{3+} , Yb³⁺ inverse opals depends on the overlapped extend between the excited light and photonic band gap. The near infrared emission located at the 1540 nm of the CeO₂: $Er³⁺$, Yb³⁺ inverse opals have been enhanced obviously when the wavelength of the excitation light overlapped with photonic band gaps edge, which is attributed to the slow light effect of photonic crystals. The enhancement of near infrared emission may be important for the development of infrared laser and amplifiers for optical communication.

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1. Introduction

Luminescent materials doped with rare earth ions have been attracting much interest as phosphors in displays, lamps, optical telecommunication components, and as the active materials in lasers [\[1–3\]](#page--1-0). Among various rare earth ions doped luminescent materials, near-infrared luminescence of $Er³⁺$ ions at about $1.5 \mu m$ is very important, which have shown great potential applications in laser sources, optical communications and other datatransmitting services $[4-6]$. The near infrared luminescence of the Er^{3+} ions comes from its parity forbidden intra-4f transitions, resulting in low absorption cross-section and emission efficiency. Therefore, to enhance the excited and emission efficiency of the $Er³⁺$ ions is very important for its practical application. At present, various methods have been developed to enhance the near infrared luminescence properties of Er^{3+} , such as energy transfer through co-doping other ions and surface plasmon resonance of metal nanoparticles [\[7,8\]](#page--1-0).

Photonic crystals are multi-dimensional periodic dielectric structures in which the distribution of refractive index varies regularly on the visible wavelength scale [\[9,10\].](#page--1-0) The refractive index periodicity variety of the photonic crystals may result in the formation of a photonic band gap. Based on the photonic band gap, we can not only construct many new photonic devices such as the low-loss waveguides, high efficiency light-emitting diodes, tunable filters and sensors, but also modify the photo-physics process in the luminescent materials $[11-13]$. In addition, the photonic crystals can be used to enhance the interaction between excitation light and optical materials (slow light effect), leading to the improvement of the luminescence property of materials [\[14–16\].](#page--1-0) Therefore, the photonic crystals provide an effective way to solve the low excited efficiency of rare earth ions. At present, the luminescence enhancement of visible emissions from active centers has been extensively reported by the slow light effect of the photonic crystals [\[14,15\].](#page--1-0) However, as far as we know, the near infrared emission enhancement from rare earth ions has not been reported by the slow light effect of the inverse opal photonic crystals.

Cerium dioxide ($CeO₂$) with a cubic crystal structure has potential applications as an optical coating and ion-conducting layers because of its optical transparency, high refractive index, thermal and chemical stability $[17,18]$. The CeO₂ is a rare earth oxide, and high content doping of rare earth ions in the $CeO₂$ host could be obtained due to the nearness of ion radius between rear earth ions and Ce^{4+} ions [\[19\].](#page--1-0) At present, visible luminescence from the $CeO₂$ doped with rare earth ions was extensively investigated [\[19,20\].](#page--1-0) In addition, upconversion emission in the rare earth ions doped $CeO₂$ host was observed due to its lower phonon energy [\[21\]](#page--1-0). However, few works were carried out on the near infrared luminescence of

[⇑] Corresponding author. Tel./fax: +86 871 6518 8856. E-mail address: yangzw@kmust.edu.cn (Z. Yang).

CeO₂ doped with rare-earth ions. In this paper, the CeO₂: Er^{3+} , Yb^{3+} inverse opals with various photonic band gaps were designed and prepared, and their near infrared emission properties were investigated. Significant enhancement of the near infrared emission at the 1540 nm was observed when the wavelength of the excitation laser overlapped the edge of the photonic band gap.

2. Experimental

The 350 nm and 400 nm polystyrene (PS) microspheres were used to fabricate opal templates on quartz substrates using self-assembly technique as described elsewhere $[21]$. The CeO₂: $0.01E^{3+}$, $0.01Yb^{3+}$ precursor solution was prepared by using CeO₂, Er₂O₃ and Yb₂O₃ as raw materials, similar to previous work [\[21\].](#page--1-0) The prepared CeO₂: Er^{3+} , Yb³⁺ precursor solution was infiltrated into the voids of the opal templates. Subsequently, the PS microspheres were removed by sintering the samples at 950 °C for 5 h, and the CeO₂: Er^{3+} , Yb³⁺ inverse opals were obtained.

The morphologies of the opal templates and inverse opals were characterized by a scanning electron microscopy (SEM). The X-ray diffraction (XRD) patterns of the inverse opals were obtained with a D8 ADVANCE. The transmittance spectra of inverse opals were measured by the HITACHIU-4100 spectrophotometer. The near infrared luminescence spectra of the inverse opals under a 532 nm laser excitation with a power of 2W were measured with omni- λ 300 spectrophotometer. The near infrared luminescence spectra of all the samples were collected along the normal direction of the photonic crystals surfaces.

3. Results and discussions

For the self-assembled process of PS microspheres, cleaned quartz substrates were vertically placed into the PS microspheres suspensions. A meniscus region is formed on the quartz substrate because of wetting by the solution, and a constant solution influx occurs due to the evaporation of the solvent out of the meniscus. During the solvent evaporation, the PS microspheres assemble into the face-centered cubic (fcc) periodic arrays (opals) because Gibbs free energy is minimum in this structure. Fig. 1(a) and (b) shows the SEM images of opal templates prepared by PS microspheres with the diameter of 400 nm and 350 nm, respectively. As is shown in the SEM images, highly ordered fcc templates with (111) plane parallel to the surface of quartz substrate were obtained. This type of ordered templates was applied to the fabrication of $CeO₂$: $Er³⁺$, Yb^{3+} inverse opals. Fig. 1(d) and (e) shows SEM images of CeO₂: $Er³⁺$, Yb³⁺ inverse opals prepared by ordered templates constructed with PS microspheres 400 nm and 350 nm in diameter, respectively. Long-range ordered hexagonal arrangement can be clearly observed in two kinds of inverse opals. The light parts in the SEM images of inverse opals were considered as the crystals of $CeO₂$, while the dark parts were considered as the air holes which were occupied by the PS microspheres before calcination. The $CeO₂$: Er³⁺, Yb³⁺ inverse opals prepared by 400 nm and 350 nm opal templates were denoted as the IPC-1 and IPC-2, respectively. The center-to-center distance between the air holes in the IPC-1 and the IPC-2 was about 310 nm and 280 nm, respectively, which is about 20% smaller than the original size of the PS microspheres owing to the shrinkage during calcination. Two kinds of mixed PS microspheres with the diameter of 220 nm and 400 nm were used to prepare disordered template, as shown in Fig. $1(c)$. For comparison, the completely disordered CeO₂: Er^{3+} , Yb³⁺ reference sample was prepared by using disordered opal template, as shown in Fig. 1(f), which was denoted as the RS.

The crystal structures of the inverse opal samples were also characterized. [Fig. 2](#page--1-0) shows the XRD patterns of the IPC-1 and the IPC-2 on the quartz substrate. The broad band ranging from 17° to 25° in the XRD pattern is attributed to the diffraction of quartz substrate. It can be seen that the XRD pattern of each inverse opal exhibits diffraction peaks, which agree well with the corresponding standard card (No. 01-0800) of cubic phase $CeO₂$ crystal. No other peaks appear, implying that all the $CeO₂$ inverse opals are in the pure cubic phase.

[Fig. 3](#page--1-0) shows the transmittance spectra of the IPC-1 and IPC-2 at different angles of incidence (0-40°). Angles of incidence were measured with respect to the normal direction of the (111) plane, the spectra were recorded consecutively per 10° increment. For the normal incidence, it could be seen that the photonic band gap for the IPC-1 and the IPC-2 were located at the 500 and 450 nm, respectively. The position of photonic band-gap shows a clear blue shift with increasing the angle of incident light, as shown in [Fig. 3\(](#page--1-0)c). With the increasing of angle from 0° to 40° , the photonic band gap of the IPC-1 shifts from the 500 nm to 465 nm, while the photonic band gap of the IPC-2 shifts from the 450 nm to 415 nm. The photonic band gap property of the inverse opals can also be expressed theoretically according to Bragg's law combined with Snell's law.

Fig. 1. The SEM image of the opals template constructed with PS microspheres with diameter of 400 nm (a) and 350 nm (b), the disordered template made of mixing PS microspheres with the diameter of 220 nm and 400 nm (c), the IPC-1 sample (d), the IPC-2 sample (e) and the RS sample (f).

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