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Ultra-small niobate based red phosphor showing highly luminescent performance



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ABSTRACT

This work presented a simple hydrothermal route based on polyoxometalate chemistry of niobium to prepare a novel red phosphor, $\text{K}_2\text{GdNb}_5\text{O}_{15}:\text{Eu}^{3+}$, with ultra-small size and high quantum efficiency. The red/orange (I_{612}/I_{594}) ratio of Eu^{3+} emission is 6.8, indicating high color purity and being nearly ideal for the red component in high luminous efficacy white LEDs. The as-measured quantum yield for $\text{K}_2\text{GdNb}_5\text{O}_{15}:\text{Eu}^{3+}$ nanoparticles is as high as 63% at Eu^{3+} concentration $\sim 20\%$.

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1. Introduction

The ever-increasing energy demands and the subsequent global energy crisis have declared a continuous challenge to traditional lighting industry. As an alternative to traditional light sources, solid state lighting devices, especially the white light-emitting-diodes (LEDs), have garnered much research attention due to its low-energy cost, long-lifetime and robust properties [1,2]. Up to date, the development of solid state lighting devices is notably influenced by the discovery of RGB phosphor materials, which have to efficiently absorb in the near UV to blue spectral range. As a key component of the tricolor luminescence, red emitted phosphors currently utilized by industry for GaN LED are Eu^{2+} doped nitridosilicates [3]. Recently, particular attention has focused on the engineering of Eu^{3+} -doped converting materials [4], since these phosphors have the possibility to improve the luminous efficacy and color rendering index for LEDs.

Rare earth niobates and tantalates comprise a large group of metal oxides that exhibit a unique array of characteristics including chemical and electrochemical stability, photocatalytic activity, and luminescence [5]. Eu^{3+} could act as a very efficient activator in many niobates and tantalates for high quantum luminescence emission [6]. From the viewpoint of the unprecedented practical applications, it is urgently necessary to explore novel Eu^{3+} -doped red niobate phosphors with high quantum efficiency. However, their poor solubility and high crystallization temperature limit the opportunities for soft chemical routes other than solid state processing which hinder discovery of the novel phases in nanosizes.

Fortunately, an aqueous synthetic approach based on polyoxometalate chemistry of niobium was developed [7], which is expected to be important for finding novel niobate phosphors.

Though a great number of Eu^{3+} doped nanophosphors have been investigated, there are very few reports on Eu^{3+} doped tetragonal tungsten bronze-type (TTB) structure niobates. Therefore, the present investigation aims at the synthesis and characterization of Eu^{3+} doped TTB structure phosphor as well as its luminescent properties. Herein, we report a novel red phosphor, $\text{K}_2\text{GdNb}_5\text{O}_{15}:\text{Eu}^{3+}$ (named as KGN: Eu^{3+}), prepared via a facile hydrothermal method and discovered an intensive red emission under near UV excitation which shows a promising application of solid state lighting devices and the relevant technologies.

2. Experimental

The typical procedure is described as follows: 0.009 g Eu_2O_3 (99.99%) and 0.168 g Gd_2O_3 (99.99%) were dissolved in diluted nitrate acid on heating while stirring, which was allowed to cool down to room temperature. Then, 0.12 g EDTA was added into the mixed solution while stirring. 1.82 g $\text{K}_7\text{HfNb}_3\text{O}_{19} \cdot 13\text{H}_2\text{O}$ (prepared according to Ref. [7]) was dissolved in 20 ml degassed water and slowly dropped in the abovementioned mixed solution with vigorous stirring. At last, 10 ml of 5 M KOH was added to form an almost clear solution. This solution was sealed in 30 ml Teflon-lined stainless steel autoclaves and reacted at 200 °C for 24 h. The obtained products were washed with distilled water for several times and dried at 80 °C for 3 h. Eu^{3+} doped $\text{K}_2\text{GdNb}_5\text{O}_{15}$ samples with different doping levels were also obtained.

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Phase purities were characterized by X-ray power diffraction (XRD) on a Rigaku DMAX2500 X-ray diffractometer using a copper target. Particle sizes and morphologies were determined using transmission electron microscopy (TEM) on a JEM-2010 apparatus with an acceleration voltage of 200 kV. Optical diffuse reflectance spectra were measured using the integrating sphere of a Lambda 900 UV/VIS Spectrometer in the wavelength region between 200 and 800 nm. BaSO₄ was used as a reference material. Emission and excitation spectra were measured on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with both continuous (450 W) and pulsed xenon lamps. Absolute quantum yield measurement was made by exciting the samples with diffuse light inside an integrating sphere.

3. Results and discussion

Fig. 1a illustrates the transmission electron microscopy (TEM) image of KGN: Eu³⁺ nanoparticles. It is observed that all nanoparticles exhibited highly dispersed property. Its selected-area electron diffraction (SAED) shows distinct ring pattern, revealing the polycrystalline nature of KGN:Eu³⁺ nanoparticles and the particle size of KGN: Eu³⁺ was estimated to be ~1–4 nm. The HRTEM image gave further evidence for the polycrystalline behavior of the as-prepared nanoparticles (inset of Fig. 1b, FFT pattern). As seen in Fig. 1b, the spacing between the adjacent lattice fringes of the as-prepared nanoparticles was 0.391 nm, which is very close to that

of 0.3934 nm for K₂GdNb₅O₁₅. Moreover, EDS data confirmed that the main elemental components are K, Gd, and Nb (Fig. 1c). The signal of C is attributed to the organic surface layers (S1) and Cu from the TEM grid was also detected. EDS maps of KGN: Eu³⁺ nanoparticles indicated that all detected signals dispersed homogeneously (S2). In addition, the atomic ratio of K, Gd and Nb determined by EDS was 7.75:3.69:17.64, which confirmed the formation of K₂GdNb₅O₁₅ compound. Fig. 1d shows the XRD pattern of the KGN: Eu³⁺ nanoparticles. The broadened diffraction peaks were observed, demonstrating the fine nature and ultra-small crystal size. To further confirm the phase structure of as-prepared nanoparticles, KGN: Eu³⁺ nanoparticles were allowed to grow larger and examined by XRD and HRTEM measurements (S3).

The ultra-small size of KGN: Eu³⁺ nanoparticles reduces scattering losses, and the flexibility of the crystal structure enables tailoring optical properties, such as broadening the excitation line width [8], which will predict high quantum efficiency. We first investigated the electronic transitions of KGN: Eu³⁺ nanoparticles. The absorption edges (Fig. 2a) for KGN: Eu³⁺ nanoparticles is located around 310 nm (4.0 eV). Gaussian function fitting indicated that the absorption spectrum consisted of two components, corresponding to the transitions of two types of NbO₆ polyhedra in K₂GdNb₅O₁₅ lattice [9]. The room temperature excitation spectrum of KGN: Eu³⁺ is shown in Fig. 2b. A series of sharp lines appeared in the range of 300–550 nm, which are characteristic of *f–f* transitions of Eu³⁺ ions. The full width at the half maximum (FWHM) of the most intense transition at 394 nm (⁷F₀–⁵L₆) is

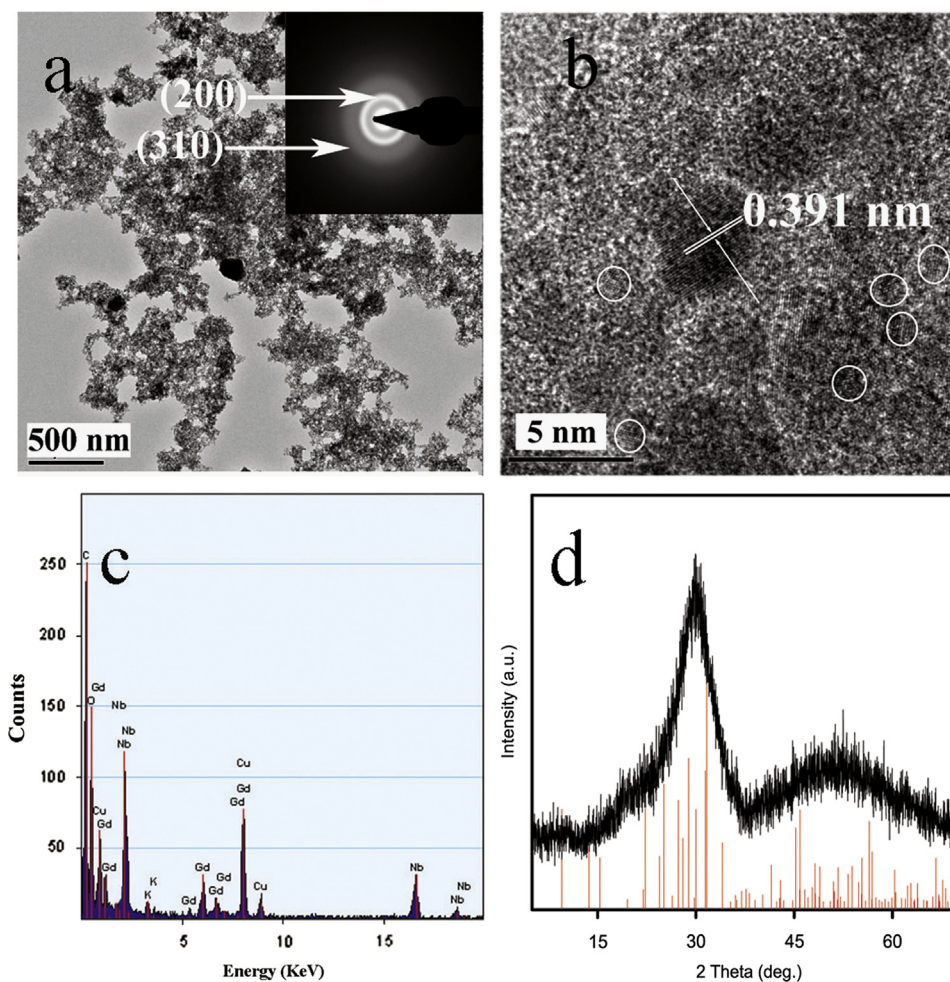


Fig. 1. TEM image (a), HRTEM image (b), EDS data, (c) and XRD pattern (d) of KGN: Eu³⁺ nanoparticles. Inset is the SEAD pattern of KGN: Eu³⁺ nanoparticles.

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