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Up-conversion luminescence of $NaY(WO_4)_2$: Yb, Er under 1550 and 980 nm excitation

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ABSTRACT

Er^{3+} single-doped and Er^{3+}, Yb^{3+} co-doped $NaY(WO_4)_2$ phosphors were synthesized at 1100 °C by a solid-state reaction method. The samples were characterized by XRD and emission spectral analysis, and the luminescence properties of the phosphors were studied using different excitation sources. The maximum emission intensity of the phosphor was achieved at 24 mol% of the Er^{3+} ion single-doped under 980 and 1550 nm excitation. The red emission of the phosphor was not changed by increasing Yb^{3+} ion concentrations, and the material exhibited excellent color purity and color stability. When excited by the 1550 nm laser, the fraction of red emission slightly increased compared with that observed under 980 nm excitation but the main bright green emission. The brightness of Yb^{3+}, Er^{3+} co-doped $NaY(WO_4)_2$ is about 4 times more intense than that of conventional Er^{3+} single-doped $NaY(WO_4)_2$. The UCL mechanisms of the phosphor at 980 and 1550 nm are completely different.

1. Introduction

Up-conversion luminescence (UCL) is a radiation process in which two or more low-energy (long wavelength) photons are converted into a high-energy (short wavelength) photon. Fluorescent materials have been investigated extensively because of their important applications in many fields, such as biological labeling, data storage technology, laser anti-counterfeiting, and three-dimensional displays, etc. Selecting an appropriate matrix and activator is an effective method to improve the efficiency of UCL. For example, recent studies have shown that highly efficient UCL can be obtained by using Yb^{3+} as a sensitizer, Er^{3+}, Tm^{3+}, and Ho^{3+} as activators, and oxysulfide and fluoride as the matrix under ~980 nm excitation [1].

In recent years, efforts to improve the efficiency of UCL have required changing the excitation wavelength. For example, when using Nd^{3+} as a sensitizer, an ~980 nm excitation source can be replaced with an ~800 nm one to avoid the thermal effects on tissue damage during biological imaging [2–5]. If an ~1500 nm excitation source is used, the quantum yield of UCL materials is generally much higher than that of some conventional materials under ~980 nm excitation. Such an excitation source may be especially suited for solar capture [6]. At present, few studies on UCL materials under ~1500 nm excitation, such as those on Er^{3+}: ZBLAN glass [7,8], $Er_3Al_5O_{12}$ ceramic [9], CaF_2: RE(RE = Er^{3+}, Yb^{3+}) crystals [10], Yb^{3+}, Er^{3+} co-doped β-$NaYF_4$ microcrystals [11], colloidal $LiYF_4$: Er^{3+} nanocrystals [12], M_2O_2S: Er^{3+} (M = Y, Gd, La) phosphors [13,14] and our group has studied Y_2O_2S: Yb^{3+}, Er^{3+} phosphors [15] and Y_2O_3: Yb^{3+}, Er^{3+} phosphors [16], are available. The oxide matrix presents unique advantages in many applications because of its excellent chemical stability. In the oxide matrix, tungstates such as $NaY(WO_4)_2$: Yb^{3+}, Er^{3+} are highly efficient UCL materials [17–21]. Tungstates can also be applied in X-ray detection and white light LEDs [22,23], Herein, for the first time, we report the UCL of $NaY(WO_4)_2$: Yb^{3+}, Er^{3+} phosphors under 1550 nm excitation. Yb^{3+}, Er^{3+} co-doped $NaY(WO_4)_2$ samples were synthesized by a solid-state reaction method, and the UCL properties of the phosphors are studied under 980 and 1550 nm excitation. The samples present not only highly pure colors but also intense brightness. High-purity green emission is achieved by controlling the doping concentrations of Yb^{3+} and Er^{3+} ions.

2. Experimental

All of the raw materials used in this experiment, including the Na_2CO_3, WO_3, Er_2O_3 (99.99%), Yb_2O_3 (99.99%), and Y_2O_3 (99.99%), were of analytical reagent grade. After the materials were weighed stoichiometrically, they were mixed thoroughly by grinding for 0.5 h. $NaY(WO_4)_2$ samples were obtained by annealing the mixture at 1100 °C for 8 h and then cooling to room temperature naturally [24], The samples were ground and subsequently characterized.

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X-ray powder diffraction was performed at 40 kV and 40 mA using a D/MAX-Ultima X-ray generator with Cu Kα radiation ($\lambda = 0.15406$ nm) over the 2θ range of 10°–80°. UCL spectra (200–900 nm) were recorded by a Hitachi F-4500 fluorescence spectrophotometer (slit width: 1 nm) equipped with a 980 and 1550 nm fiber laser diode (LD). The scanning speed was 1200 nm/min, and the power of the LD was measured by a laser power meter (LPE-type). The brightness of the phosphors was recorded by a CS-100A luminance meter.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Er^{3+} single-doped and Er^{3+}, Yb^{3+} co-doped $NaY(WO_4)_2$ samples. Samples (b) and (c) exhibit diffraction patterns very similar to that in JCPDS Card No. 48-0886. No other impurity peaks were observed, which indicates the Er^{3+} single-doped and Er^{3+},Yb^{3+} co-doped $NaY(WO_4)_2$ present pure phases. The diffraction peaks of both samples shift to the high angle compared with the peaks of the standard card, thus suggesting that the doping ions of Yb^{3+} and Er^{3+} replace Y^{3+} ions in the lattice because the atomic radii of Yb^{3+} (85.8 pm) and Er^{3+} (88.1 pm) are smaller than that of Y^{3+} (89.3 pm). Replacement of Y^{3+} by Yb^{3+} and Er^{3+} ions demonstrates that the rare-earth ions enter the lattice of the matrix.

Fig. 2 shows the UCL spectra of $NaY(WO_4)_2$: 24 mol% Yb^{3+}, 24 mol% Er^{3+} under 1550 and 980 nm excitation. $NaY(WO_4)_2$: Yb^{3+}, Er^{3+} exhibits excellent bright green emission under 1550 and 980 nm excitation. The spectra obtained consist of two emission bands under 980 nm excitation: (1) The strongest peak, which is located at 553 nm, and the third-strongest peak, which is located at 532 nm, can be attributed to Er^{3+} ion $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. (2) The strongest red emission is located at 656 nm and can be attributed to the Er^{3+} ion $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The UCL intensity of the samples first increases and then decreases with increasing Yb^{3+} ion concentration. The maximum UCL intensity is achieved at Yb^{3+} ion concentration of 24 mol%. When excited at 1550 nm, the UCL spectrum of $NaY(WO_4)_2$: Yb^{3+}, Er^{3+} exhibits the same emission peaks but a different intensity ratio of red to green emissions compared with that obtained under 980 nm excitation. The red emission of the phosphor is significantly improved by excitation at 1550 nm. This enhancement is attributed to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. Because of the presence of $WO_4{}^{2-}$ in the sample, which can improve the covalence of the crystal, the rare-earth doping concentration of $NaY(WO_4)_2$ is dramatically increased and exceeds that in other matrices [25], For example, the concentration of the activator is usually lower than 2%–3% in the fluoride and oxysulfide systems. Such doping levels are important to improve UCL efficiency [26].

Red emissions can be enhanced with increasing the Er^{3+} and Yb^{3+} ion concentrations in conventional UCL materials [27]. The distances of Er–Er, Yb–Yb, and Yb–Er can be shortened by increasing of Er^{3+} and Yb^{3+} ions concentrations, leading to enhancement of cross-relaxation and red-emission components. For example, Wang and Liu [28] reported that $NaYF_4$: Yb^{3+}, Er^{3+} with high I_R/I_G ratios can achieved by increasing the Yb^{3+} ion concentration. Wei et al. [29] reported that a single red emission can be achieved by cross-relaxation theory with increasing Er^{3+} and Yb^{3+} ion concentration in the $NaYF_4$ matrix. However, this phenomenon is not observed for the present $NaY(WO_4)_2$ samples. Even though the concentration of co-doped Er^{3+}, Yb^{3+} is as high as 24 mol% in the samples, the color purity of the phosphors remains extremely high. The main reason is that the special crystal structure of tetragonal $NaY(WO_4)_2$ [30], the concentration quenching due to the cross-relaxation process (e.g $^4F_{7/2} \rightarrow {}^4F_{9/2}$ and $^4F_{9/2} \leftarrow {}^4I_{11/2}$) is significant suppressed via energy clustering at the sublattice level [31]. Therefore, concentration of the rare earth ion doping is very high, and the red emission is greatly weaked. While UCL materials such as M_2O_2S: Er^{3+} (M = Y, Gd, La) [13,14] Er^{3+}, Yb^{3+} co-doped Y_2O_2S [15], and Y_2O_3 [16] usually show red emission under 1550 nm excitation, Er^{3+}, Yb^{3+} co-doped $NaY(WO_4)_2$ still exhibits green emission under 1550 nm excitation, thus significantly differing from previous UCL materials (Fig. 3b).

Fig. 3 shows the CIE chromaticity coordinates and digital camera images of $NaY(WO_4)_2$: 24 mol% Yb^{3+}, 24 mol% Er^{3+} under 980 and 1550 nm excitation. The emission color changes gradually with increasing excitation current at 980 nm (Fig. 3a). The green emission slightly changes with the excitation current, thereby indicating the $NaY(WO_4)_2$: Yb^{3+}, Er^{3+} phosphor possesses excellent color stability. Fig. 3b shows that the emission color moves first to the green region and then back to the red region with increasing excitation current at 1550 nm. Despite this shift toward the red region, most of the emission is still concentrated in the green region, which suggests the high color purity of the $NaY(WO_4)_2$: Yb^{3+}, Er^{3+} phosphor.

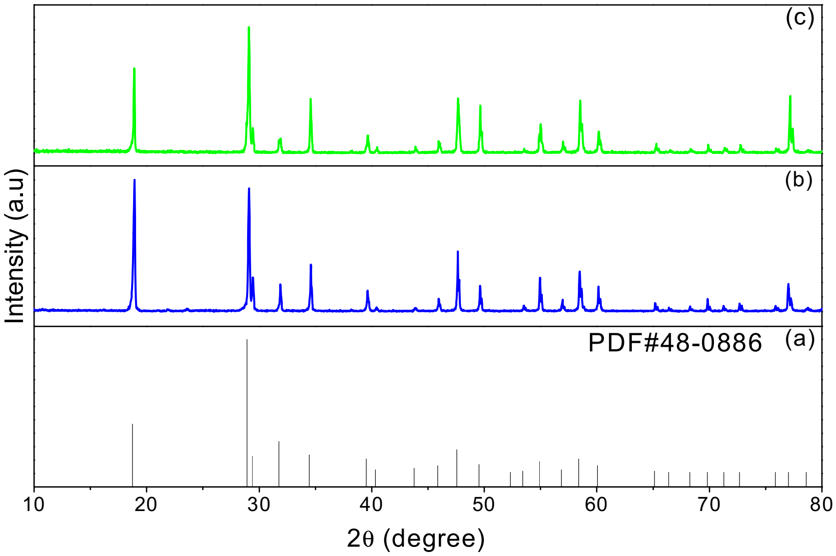

Fig. 1. XRD patterns of $NaY(WO_4)_2$: (a) JCPDS cards 48-0886, (b) $NaY(WO_4)_2$: 24 mol% Er^{3+}, (c) $NaY(WO_4)_2$: 24 mol% Yb^{3+}, 24 mol% Er^{3+}.