



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Influence of Cr^{3+} on upconversion luminescent and magnetic properties of $\text{NaLu}_{0.86-x}\text{Gd}_{0.12}\text{F}_4:\text{Cr}_x^{3+}/\text{Er}_{0.02}^{3+}$ ($0 \leq x \leq 0.24$) material

Zayakhuu Gerelkhuu^a, Bui The Huy^{a,b}, Jong Won Chung^a, The-Long Phan^c, Eric Conte^d, Yong-Ill Lee^{a,*}

^a Department of Chemistry, Changwon National University, Changwon 51140, South Korea

^b Institute of Research and Development, Duy Tan University, K7/25 Quang Trung, Da Nang, Vietnam

^c Department of Physics and Oxide Research Center, Hankuk University of Foreign Studies, Yongin, Gyeonggi 449-791, South Korea

^d Department of Chemistry, Western Kentucky University, 1906 College Heights Blvd., Bowling Green 42101, United States

ARTICLE INFO

Article history:

Received 17 October 2016

Received in revised form

6 January 2017

Accepted 17 February 2017

Available online 20 February 2017

Keywords:

Upconversion luminescence

Chromium (III) ions

Sensitizer

Mechanism

Magnetic-resonant

ABSTRACT

Upconversion phosphors can convert near-infrared light into visible emission by sequentially absorbing multiple photons. In most studies, $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Tm}^{3+}$ ions are used as sensitizer/activator in host materials. In this work, we introduce chromium (Cr^{3+}) ions to $\text{NaLu}_{0.86-x}\text{Gd}_{0.12}\text{F}_4:\text{Cr}_x^{3+}/\text{Er}_{0.02}^{3+}$ (UCCr) material that is instead of ytterbium (Yb^{3+}) ions. The UCCr material with a different concentration of Cr^{3+} ions ($0 \leq x \leq 0.24$) was synthesized by a facile hydrothermal synthesis method. The characterization of the developed UCCr material was performed by photoluminescence (PL), Field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD) and Electron paramagnetic resonance (EPR). The effect of Cr^{3+} ions on the upconversion luminescence and magnetic-resonant properties of UCCr material was investigated in detail. The upconversion mechanism was proposed.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Lanthanide-doped upconversion (UC) materials have attracted attention as next-generation luminescent materials in the fields of biology and material science [1]. UC process is a unique type of photoluminescence in which lower-energy excitation (near-infrared light) is converted into higher-energy emission (visible light) via multi-photon absorption processes [2–5]. Upconversion phosphors (UCPs) are typically composed of an inorganic host lattice and lanthanide dopant ions [6]. Generally, lanthanide (4f), actinide (5f) and transition metal (3d, 4d and, 5d) ions can produce UC fluorescent emission when embedded in solids or inorganic host lattice (sodium rare-earth (RE) fluoride and rare-earth oxide) [7]. Up to now, the trivalent lanthanide ions (Ln^{3+}) are predominantly used in UC materials due to the Ln^{3+} ions have more than one metastable state which makes them best suited for UC processes [8]. The advantages of using lower-energy are as an excitation source including, high resistance to photo-bleaching, no auto-fluorescence interference, and high penetration depth tissue. Luminescent inorganic nanoparticles doped with Ln^{3+} ions are considered as the most efficient systems for upconversion luminescence (UCL), due to their low autofluorescence, a good

chemical, and optical stability, these have been widely employed in photocatalyst [9–11], biomedicine [12–14], bioimaging [15], and analytical chemistry [16–19].

To date, the metal ions doped materials for multifunctional applications have been widely studied. The metal ions may serve as activators, namely lanthanide, transition metal [20]. In recent years, transition metal-codoped UCPs were studied for enhancing upconverted luminescence with pairs of $\text{Yb}^{3+}/\text{Er}^{3+}$ sensitizer/activator. For instance, Dongguang Yin's group had observed the enhancement of UCL properties in $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ by tri-doping with Mo^{3+} ions effect. These UC materials were exhibited excellent paramagnetic behavior. Moreover, the UCL intensities of the green and red emissions of UCPs co-doped with 10 mol% Mo^{3+} ions were enhanced by 6 and 8 times than without Mo^{3+} ions UCPs, respectively [21]. Ramasamy's group reported the enhancement of UCL intensity of Fe^{3+} ions co-doped $\text{NaGdF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanoparticles, where the green and red emissions were enhanced by 34 and 30 times, respectively [2]. Cheng's group doped 7 mol% Li^+ ions in $\text{NaGdF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals and observed enhancement up to 47 and 23 times in the visible green and red upconversion emissions [22]. Wang's group presented the luminescence intensity of $\text{NaErF}_4:\text{Yb},\text{Mn}$ (30%) upconversion nanoparticles with single-band red emission was 2.3 times enhanced of bright emission [23]. Kitaoka's group was reported the energy transition processes of Cr^{3+} ions in the Al_2O_3 . The Cr^{3+} ions with

* Corresponding author.

E-mail address: yilee@changwon.ac.kr (Y.-I. Lee).

$3d^5$ electron configuration exhibit a broad emission band (650–1600 nm) ascribed to the ${}^4T_2 \rightarrow {}^4A_2$ transition, or a narrow emission band (~ 700 nm) due to the ${}^2E \rightarrow {}^4A_2$ radiation, which strongly depends on the crystal-field environment of the host lattices 2E is the lowest excited state [24]. The energy transfer from Cr^{3+} to Nd^{3+} in $Ca_3Ga_2Ge_3O_{12}:Nd,Cr$ was also reported [25]. Therefore, the Cr^{3+} ions can endow for UC process.

Among the fluoride-based host materials, $NaREF_4$, $NaYF_4$, and $NaLuF_4$ materials have been reported as the most efficient UC due to its low phonon energy [26–30]. $Yb^{3+}/Er^{3+}/Gd^{3+}$ or $Yb^{3+}/Tm^{3+}/Gd^{3+}$ co-doped $NaLuF_4$ materials exhibit extreme UCL properties under low-intensity laser excitation [30]. $NaLuF_4$ material exists in two structures with hexagonal (β -phase) and cubic (α -phase) structure. The UCL intensity of hexagonal structure is higher than that of cubic structure. However, UCPs with the hexagonal structure is usually synthesized in organic solvents (oleic acid, oleylamine, octadecene, etc.) under high temperature (~ 300 °C) with complicated steps [30–32]. By doping Gd^{3+} ion, the hexagonal structure of $NaLuF_4$ can be obtained at relative low reaction temperature. Additionally, the Gd^{3+} based UCPs showed an excellent paramagnetic and low toxic property [33–35]. Up to now, most previous reports were used Yb^{3+} ions as a sensitizer for UC process. Therefore, the developing a simple synthesis method for obtaining material with high UCL intensity without using Yb^{3+} is highly desirable.

In this work, we present a facile synthesis of $NaLu_{0.86-x}Gd_{0.12}F_4:Cr_x^{3+}/Er_{0.02}^{3+}$ (UCCr) ($x = 0, 6, 12, 18,$ and 24 mol%) material without doping Yb^{3+} ions by the one-step hydrothermal method. The UCCr material was capped by carboxyl group ($-COOH$) of malonic acid (MA) to bring on the available application in chemistry. We have also proposed a possible upconversion mechanism of UCCr material. The highest upconversion luminescence emission was revealed at UCCr material with $x = 18$ mol% Cr^{3+} ions. The role of Cr^{3+} ions on the upconversion luminescence of UCCr material was investigated in proposed upconversion mechanism. Moreover, the Cr^{3+} ions doped UCCr are discussed paramagnetic property by EPR study.

2. Experimental section

2.1. Reagents and materials

The rare earth oxides, gadolinium oxide (Gd_2O_3 99.99%) was purchased from Acros Organics Co. The lutetium oxide (Lu_2O_3 99.99%) was received from Aladdin Chemical Co. The erbium oxide (Er_2O_3 99.99%), sodium fluoride (NaF), sodium hydroxide (NaOH), concentrated hydrochloric acid (HCl), methanol (CH_4O) and malonic acid ($C_3H_4O_4$), chromium chloride ($CrCl_3$) were received from Sigma-Aldrich. Deionized water was used throughout all the experiments. All other chemical reagents in analytical grade were used directly without further purification.

2.2. Preparation of $RECl_3$ solution precursor

The preparation method for the rare-earth chloride ($RECl_3$) can be described as follows. Typically, $RECl_3$ [$Lu:Gd:Er$], Lu_2O_3 , Gd_2O_3 , and Er_2O_3 were dissolved into HCl solution (20 mL deionized water/10 mL conc. HCl) at 70 °C under water bath. Water was evaporated using the vacuum evaporation at 60 °C, then until 50 mL methanol solution was added to the remaining sample.

2.3. Synthesis of UCCr material

The synthesis of UCCr material was carried out in accordance to an earlier reported procedure [19] it consisted of facile one step. In

a typical synthesis, NaOH (17.5 mmol) was dissolved in deionized water (20 mL), and then malonic acid (19.2 mmol) was added at room temperature to obtain a transparent solution. NaF (4.8 mmol) was added with vigorous stirring for 30 min. Then $RECl_3$ (1.1 mL, 0.6 mmol) and $CrCl_3$ (0, 6, 12, 18 and 24 mol %) were injected into the above solution with vigorous stirring. After stirring for 20 min, the mixture was transferred to a 40 mL Teflon-lined autoclave and heated at 200 °C for 12 h. After cooling to room temperature, the precipitates were separated by centrifugation and washed with deionized water for several times, and then dried under vacuum at 55 °C for 12 h.

2.4. Characterization

Crystal structure measurements were recorded using an X-ray diffractometer X'Pert PW3040/00 from PANalytical (Almelo, Netherlands) using $Cu-K\alpha$ (ratio $K\alpha_2/K\alpha_1=0.5$) radiation. Scans of selected diffraction peaks were carried out in step mode (step size 0.02°, measurement temperature at 25 °C). FE-SEM images were obtained using a CZ/MIRA I LMH FE-SEM microscope. Energy dispersive X-ray (EDS) emission spectra were measured using an EDS X-ray detector located inside a FE-SEM (Mira-II, Tescan, Czech). The electron beam was accelerated at 20 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were performed using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific, Madison, USA). The upconversion photoluminescence emission spectra were recorded with a fluorescence spectrophotometer (Acton Spectra Pro 750-Triplet Grating Monochromator) from CCD detector (Princeton EEV 1024 \times 1024 and PI-Max 133 Controller), using a 980 nm semiconductor CW laser diode as the excitation source, which was placed about at an angle of 45 °C in front of the sample holder. Quantitative analysis of Lu, Gd, Er, and Cr were analyzed by inductively coupled plasma (ICP X-series II, Thermo, USA). Electron paramagnetic resonance (EPR) measurements with 20 mg powdered samples were carried out on a JEOL-JES-TE300 spectrometer operating at 9.21 GHz. All investigations were carried out at room temperature.

3. Results and discussion

3.1. Characterization of morphology and crystal structure

$NaLuF_4$ phosphors have usually two structures, cubic and hexagonal. The according to the experimental conditions, the luminescent properties of hexagonal structure is more efficient than that of cubic structure [36]. Therefore, it is necessary to get the hexagonal structure with the hydrophilic surface at low reaction temperature. For getting hexagonal structure, Gd^{3+} ions can play the role of phase transformation from cubic to hexagonal structure, then shows high efficient luminescence [32,37]. In this work, we used optimized concentration of Gd^{3+} ions were 12 mol%. Fig. 1a shows the XRD patterns of the UCCr material prepared at 200 °C for 12 h. All the diffraction peaks can be indexed to the hexagonal $NaLuF_4$ phosphors (JCPDS 27-0726). It can be seen that the XRD peaks of the concentration of Cr^{3+} ions (6, 12, and 18 mol%) indicate pure hexagonal structure. When exceeding the concentration of Cr^{3+} ions, the impurity peaks Na_3CrF_6 (marked by an asterisk, JCPDS no. 74-1314) were observed due to the Cr^{3+} ions concentration quenching [38]. Moreover, the XRD peak shifted to the low angle as the amount of Cr^{3+} ions were increased from 0 to 24 mol%. The ionic radius of Cr^{3+} ions (0.62 Å) is smaller than Lu^{3+} ions (0.86 Å) [39], therefore Cr^{3+} ions are small enough to enter any crystal site, such as substituting for the Lu^{3+} ions or interstitial sites. As a result, the enlarged area of the main diffraction peak (100) shows that the diffraction peak shifts towards

Download English Version:

<https://daneshyari.com/en/article/5397876>

Download Persian Version:

<https://daneshyari.com/article/5397876>

[Daneshyari.com](https://daneshyari.com)