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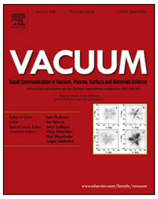

Nearly pure NIR to NIR upconversion luminescence in Tm^{3+}, Yb^{3+} co-doped $ZnO-TiO_2$ composite phosphor powder

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ABSTRACT

Tm^{3+} and Yb^{3+} co-doped $ZnO-TiO_2$ composite system were successfully synthesized via powder-solution mixing method and their upconversion (UC) luminescence characteristics were studied as a function of various ZnO/TiO_2 mixing ratios and dopant concentrations under 980 nm laser excitation. The XRD patterns showed that the product fired at 1300 °C consisted of four phases, Zn_2TiO_4, TiO_2, $RE_2Ti_2O_7$, and RE_2TiO_5 (RE = Tm^{3+} and/or Yb^{3+}). The NIR emission centered at 795 nm wavelength was detected as the strongest emission intensity which it was in accordance with the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ion. The NIR emission intensity of the products was varied by changing $ZnO-TiO_2$ mixing ratios, and Tm^{3+} and Yb^{3+} concentrations. The simple chemical formula equations, for interpreting the site preference of Tm^{3+} and Yb^{3+} ions in the host crystal matrix, were originated by considering the host crystal structure, its crystal arrangement, and the effect of Tm^{3+} and Yb^{3+} ions to the changes in lattice parameters of host crystal. The $1ZnO:1TiO_2$ (in mole) doped with 0.125 mol% Tm^{3+}, 15 mol% Yb^{3+} fired at 1300 °C for 1 h was the best condition that displayed highest NIR emission intensity. The possible UC mechanism was suggested and discussed in detail.

1. Introduction

Trivalent rare earth ions (RE^{3+}) doped near-infrared (NIR) to near-infrared (NIR) upconversion (UC) luminescence materials have received much attention in recent years since the investigations have shown great potential for many applications in biomedical fields, especially biomedical optical bioimaging technologies which they use the NIR biological transparency windows (NIR window, 650–1450 nm) for biological tissues because the traditional visible imaging range (400–750 nm) has limited observation depth due to very low penetration depth caused by the body tissues and water molecules, leading to the attenuation of signal proportional to the depth of the interest targeting [1,2]. To date, the Tm^{3+}-Yb^{3+} system is recognized as one of the most efficient activator-sensitizer pair for generating NIR emission when they are introduced into a suitable host material because the intense NIR emission can be obtained by the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} activator ion. Besides, it has been considered as one of the important and useful choices for fabricating NIR UC phosphors and infrared materials [3–5].

According to many researches regarding UC luminescence materials, the most effective UC host is fluoride based material because fluorides usually exhibit low phonon energies of less than 350 cm^{-1} and high chemical stability [6–8]. However, they are hygroscopic and are of limited use. In comparison, oxide based materials demonstrate higher chemical and thermal durability, therefore, oxides with low phonon energy may have more promising applications [9]. At present, the composite materials have gained much attention due to their properties such as light weight, flexible, high corrosion resistance, and impact strength. Because of these properties, composite materials have been considered as a replacement of classical materials used in the aerospace, construction, and electrical and electronics [10]. Among various oxide based composite materials, $ZnO-TiO_2$ composite is thought of as a promising host material because it is inexpensive, non-toxic, thermally and chemically stable, and environmental friendliness [8]. Additionally, the noteworthy product of $ZnO-TiO_2$ composite is Zn_2TiO_4 that is a

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high thermal stability host material due to its inverse spinel structure. Also, other properties of Zn_2TiO_4 show the great potential for being the good optical host such as high value of refractive index n = 2.1 [11], and low phonon energy around 721 cm^{-1} [12]. Hence, ZnO-TiO_2 composite could be one of the proper hosts for UC luminescence applications.

As far as we know, as of now, a series of reports regarding UC luminescence from ZnO-TiO_2 composite phosphor have shown only the results in the visible region (e.g. green, orange, and red emissions) which were observed from Er^{3+}/Yb^{3+} and Ho^{3+}/Yb^{3+} co-doped ZnO-TiO_2 composites prepared by solid-state reaction method [13–15] and metal-organic decomposition method [16–18]. Until now, there is no any result concerning NIR UC luminescence from ZnO-TiO_2 composite phosphor. Therefore, in this study, we performed a systematic analysis of the NIR to NIR UC luminescence properties of ZnO-TiO_2 composite doped with Tm^{3+} and Yb^{3+} prepared by the new simple method, powder-solution mixing method, to produce the homogeneous UC phosphor powder by using only deionized water as the solvent. The effect of ZnO/TiO_2 mixing ratio, Tm^{3+} and Yb^{3+} doping concentrations, and UC luminescence characteristics were methodically investigated. In addition, the interesting and important results about the site preference of Tm^{3+} and Yb^{3+} in the host crystal matrix was proposed and described in order to comprehend how RE^{3+} ions substitute complex inorganic crystal structure. Lastly, this new preparation method was comparatively discussed with those two methods in detail.

2. Experimental

The Tm^{3+} and Yb^{3+} co-doped with ZnO-TiO_2 composite system were synthesized by powder-solution mixing method using ZnO (NanoTek, ~34 nm, 99%), TiO_2 sol solution (Ishihara Sangyo Kaisha, 39.5 wt.%), $Tm(NO_3)_3 \cdot 5H_2O$ (Aldrich, 99.9%), and $Yb(NO_3)_3 \cdot 5H_2O$ (Aldrich, 99.9%). The raw materials were thoroughly mixed in a beaker with deionized water by constant stirring with a high-power mixer. Each starting material was changed as follows. Various ZnO-TiO_2 composite samples were prepared by different ZnO/TiO_2 mixing ratios, changing ZnO amounts from $x = 0.5$–1.5 mol, while keeping constant TiO_2 (1 mol) and the samples were named as Z*x*T1. The Tm^{3+} and Yb^{3+} concentrations were varied from 0 to 0.15 mol% and 0–18 mol%, respectively. After completely mixed, the sample was dried at 90 °C in drying oven for 12 h and subsequently fired in an air atmosphere at 1300 °C for 1 h. The fired products were crushed by vibration mill for 30 s to obtain the final products in powder form. In order to avoid the surface adsorption of moisture, all samples were kept continuously in a vacuum desiccator over silica gel at room temperature for 6 h before carrying out the optical measurement.

The crystal structure of samples was characterized by X-ray diffraction (XRD), a Shimadzu XRD-6300 instrument with CuKα radiation in the range of $2\theta = 10°$–$80°$. Herein, to describe the crystallization process results, the relative phase contents calculated based on pseudo-quantitative analysis of each specific phase were estimated from the XRD patterns by using equation (1):

$$\text{Relative phase content} = I_{(\text{phase})} / I_{(\text{total})} \qquad (1)$$

where $I_{(\text{phase})}$ is the intensity of selected peak from the peak position that consists of only one phase; $I_{(311)}$ for Zn_2TiO_4, $I_{(110)}$ for TiO_2, $I_{(004)}$ for $RE_2Ti_2O_7$, and $I_{(102)}$ for RE_2TiO_5; and $I_{(\text{total})}$ is the intensity summation of all selected peaks.

The microstructure of phosphor powders was characterized by scanning electron microscopy (SEM), a Hitachi S-3000N instrument. Before SEM measurements, the samples were mounted securely by means of conductive carbon tape. Subsequently, the samples were coated with a thin layer of Pt-Pd (coating time of 90 s, around 5 nm thickness) under vacuum condition (vacuum-argon gas flushing) by ion sputter (Hitachi, E-1030).

The UC emission spectra excited by a 980 nm laser was recorded from 250 to 800 nm spectral range using USB 4000 UV-VIS-NIR fiber optic spectrometer (Ocean optics), having spectral resolution 1.34 nm (FWHM) and slit width 25 μm. The change in the maximum intensity on the laser power (0–200 mW) was measured for considering the potential UC mechanism. All measurements were performed at room temperature.

3. Results and discussion

3.1. Effect of ZnO/TiO_2 mixing ratio on crystalline phase

The XRD patterns of various Z*x*T1 samples doped with 0.125 mol % Tm^{3+} and 15 mol% Yb^{3+} are shown in Fig. 1. The diffraction patterns of the prepared samples can be well indexed with four phases; Zn_2TiO_4 (JCPDS: 25–1164), rutile TiO_2 (JCPDS: 21–1276), $RE_2Ti_2O_7$ ($Tm_2Ti_2O_7$, JCPDS: 23–0590 and/or $Yb_2Ti_2O_7$, JCPDS:17–0454) and RE_2TiO_5 (Tm_2TiO_5 and/or Yb_2TiO_5) [19]. Nevertheless, the information of RE_2TiO_5 phase is ambiguous due to the lack of information of *hkl* planes, therefore, its crystal structure has been still unclear since it was first published [20], causing to the incomplete quantitative phase analysis via Rietveld refinement.

However, the content of each phase can be estimated by using pseudo-quantitative phase analysis in the term of relative phase content (equation (1)) and the calculated results are shown in Fig. 2. It was obvious that most of all samples showed the dominant Zn_2TiO_4 phase. According to the phase diagram of ZnO-TiO_2 system [21], it should be noted that Zn_2TiO_4 phase is a stable phase and easily formed by the reaction between ZnO and TiO_2, even if the system has low amount of ZnO. As shown in Fig. 2, with increasing ZnO amount up to $x = 1.00$, the content of Zn_2TiO_4 phase increased and at the same time, TiO_2, $RE_2Ti_2O_7$, and RE_2TiO_5 contents gradually decreased. Further increase of the ZnO amount $x > 1.00$, the Zn_2TiO_4 content continuously increased and still was the dominant phase, and TiO_2 phase disappeared at $x = 1.25$. As increasing ZnO

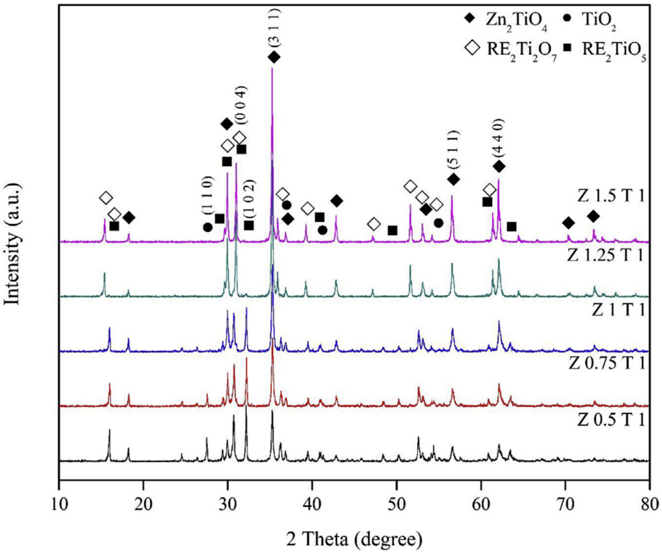

Fig. 1. XRD patterns of various ZnO/TiO_2 mixing ratios doped with 0.125 mol% Tm^{3+} and 15 mol% Yb^{3+}.