Synthesis and upconversion luminescence properties of ZnO–TiO₂ containing Ho³⁺ and Yb³⁺

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Key-words : Upconversion, ZnO–TiO₂ composite, Holmium, Ytterbium

Ho³⁺ and Yb³⁺ co-doped ZnO–TiO₂ composites were prepared by conventional solid-state reaction method and their upconversion (UC) luminescence characteristics were evaluated. The effects of ZnO/TiO₂ mixing ratio, and Ho³⁺ and Yb³⁺ concentrations were investigated. The ZnO–TiO₂ composite products fired at 1200°C consisted of Zn₂TiO₄, TiO₂, RE₂Ti₂O₇, and RE₂TiO₅ (RE = Ho³⁺ and/or Yb³⁺) phases. Bright UC emission peaks centered at 542 and 670 nm wavelengths from the Ho³⁺ ions were observed. The UC emission intensity of the product was changed by varying ZnO/TiO₂ mixing ratios, Ho³⁺ and Yb³⁺ concentrations. The optimum condition for the brightest UC emission was 1ZnO:1TiO₂ doped with 0.05 mol % Ho³⁺, 9 mol % Yb³⁺ fired at 1200°C for 4 h. The pump power dependent studies demonstrated that UC emissions related to the two-photon process and UC mechanisms were suggested and discussed in detail.

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1. Introduction

Photon upconversion (UC) involves the absorption of two or more photons of low energy with subsequent emission of higher energy photon. Due to the discrete energy states of the rare earth ions, rare-earth doped upconverters exhibit superior infrared to visible UC performance.¹,² Since its discovery in the 1960s, the lanthanide-based UC luminescence materials have been researched by many researchers for advancement in new applications and technologies, such as in the fabrication of electronic and optical communication devices (e.g., displays, lasers),³–⁵ UVC-emitting antimicrobial surface,⁶ and medical diagnostic.⁷

There are two kinds of lanthanide ions doped in the UC luminescence materials. One is employed as the luminescent center, which emits the radiation and is called an activator, and the other ion harvest the excited energy efficiently and transfer to the activator and is called a sensitizer. As activator ions, Er³⁺, Ho³⁺, and Tm³⁺ are the most widely used due to their plentiful electronic energy levels to adapt UC luminescence.⁸–¹⁰ Besides, the most of emission colors including white can be generated by the combination of three main emission colors; red, green, and blue. Hence, the proper choices of dopant lanthanide ion are Er³⁺, Ho³⁺, and Tm³⁺ because the red, green, and blue UC emission can be obtained from Er³⁺, Ho³⁺, and Tm³⁺ doped material, and UC emission of other colors is produced by co-doping the mixture of these ions and tuning the concentration ratio.¹¹

The ytterbium ion (Yb³⁺) is generally co-doped because it has large absorption cross-section around 980 nm.¹² The Yb³⁺ ions play a significant role to pump excited photons, transfer the energies to the adjacent activator ions through multiple photon processes into the excited state productively.¹³,¹⁴ The holmium ion (Ho³⁺) as an activator is a good candidate doped ions to generate short wavelength emission, green light (495 to 550 nm) and red light (620 to 750 nm).¹⁵,¹⁶ With these possible emission colors, Ho³⁺/Yb³⁺ co-doped host materials have been investigated by many researchers for employing in various applications, such as full-color range display,¹⁷ biomedical,¹⁸ and optical temperature sensing.¹⁹

The host materials are also important for UC luminescence. Theoretically, the most significant point for selecting the efficient UC host material to obtain high performance UC luminescence is the phonon energy. It is well established that UC host materials should have low phonon energy because phonons (related to lattice vibration) provide non-radiative decay ways to suppress radiative emission, leading to low UC luminescence.¹⁷ Even though, some host materials such as halides and sulfides exhibit low phonon energies, but they have many disadvantages such as poor chemical resistance, thermal unsteadiness, and high cost, therefore, difficult to use in the practical applications.¹⁷,²⁰–²² So far, the most investigated UC host materials are oxides and fluorides because they show low phonon energy and high chemical stability.²³,²⁴

Nowadays, many new applications and technologies require variety of properties of the materials which traditional materials have limited applicability. The composite materials, which consist of the combination of two phases or more with different physical and chemical properties, have attracted much attention in recent years because these materials are 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.²⁵ The ZnO–TiO₂ composite is considered as a promising host material due to their good properties such as low cost, thermal and chemical stability, and environmental friendliness.²⁶ Additionally, the noteworthy product of

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ZnO–TiO₂ composite is Zn₂TiO₄ phase that is a high thermal stability host due to its inverse spinel structure. With these properties, many researches have been conducted and studied for applying in various applications, such as nanofiber photocathode,²⁰ and photocatalysis.²⁷ Also, other properties of Zn₂TiO₄ show the great potential for obtaining the good optical host such as high value of refractive index n = 2.1,²⁸ and low phonon energy around 721 cm⁻¹.²⁹ Recently, our group has reported strong UC luminescence and color tunability in the ZnO–TiO₂ composite doped with Er³⁺ and Yb³⁺.³⁰ As discussed in this report, ZnO–TiO₂ as host material in the form of Zn₂TiO₄ was suitable for using in the field of UC luminescence when the system consisted of mixed phases Zn₂TiO₄, TiO₂, and RE₂Ti₃O₇ (RE = Er³⁺ and/or Yb³⁺). Besides, excess Ti⁴⁺ in the system affected to vacancies generation, leading to higher solubility of RE³⁺ ion into host material. Thus, in this following research, the ZnO–TiO₂ composite doped with Ho³⁺ and Yb³⁺ was examined by the simple solid-state reaction method. The effects of ZnO/ TiO₂ mixing ratio, Ho³⁺ and Yb³⁺ doping concentrations and their ratios on the crystal phase and UC luminescence were methodically investigated.

2. Experimental

The ZnO–TiO₂ composites doped with Ho³⁺ and Yb³⁺ were prepared by solid-state reaction method using zinc oxide (ZnO; Aldrich, AR purity), titanium dioxide (TiO₂; Aldrich, AR purity), holmium oxide (Ho₂O₃; Aldrich, 99.99+%), and ytterbium oxide (Yb₂O₃; Aldrich, 99.99+%). The raw powders were thoroughly mixed by mortar and pestle using ethanol. Various ZnO–TiO₂ composite samples with different ZnO/TiO₂ mixing ratios were made by changing ZnO moles while keeping constant TiO₂ (1 mole). The ZnO/TiO₂ mixing ratios were varied from 0.5, 0.75, 1, 1.25, 1.5, to 2 and named as ZxT1. The Ho³⁺ and Yb³⁺ concentrations were varied from 0.005 to 2 and 3 to 12 mol% based on TiO₂, respectively. The mixed powder was molded to the pellet (Φ 13 mm × 3 mm) by two axial press and fired in an air atmosphere at 1200°C for 4 h. Then, the resulting pellets were finely grounded in vibration mill before characterization and UC emission analysis.

The crystal phase was identified using X-ray diffraction (XRD), a Shimadzu XRD-6300 instrument with Cu Kα radiation in the range of 2θ = 10 to 80°. In order to explain crystallization processes, the relative phase content by pseudo-quantitative analysis of a specific phase was estimated from the measured XRD patterns by using Eq. (1):

Relative phase content = \( \frac{I_{\text{phase}}}{I_{\text{total}}} \) \( \text{(1)} \)

where \( I_{\text{phase}} \) is the intensity of selected peak from the peak position that consists of only one phase; \( I_{101} \) (for Zn₂TiO₄), \( I_{100} \) (for TiO₂), \( I_{004} \) (for RE₂Ti₂O₇), and \( I_{020} \) (for RE₂Ti₃O₇) and \( I_{\text{total}} \) is the intensity summation of all selected peaks.

The UC emission behavior excited by a 980 nm laser was recorded from 250 to 800 nm spectral range using USB 4000 UV–Vis–NIR miniature fiber optic spectrometer (Ocean optics) having spectral resolution 1.34 nm (FWHM) and slit width 25 µm. All samples were measured at room temperature.

3. Results and discussion

The XRD patterns of ZxT1 samples of different x values are shown in Fig. 1. In the case of the lowest amount of ZnO (x = 0.5), Zn₂TiO₄ (JCPDS: 25-1164), rutile TiO₂ (JCPDS: 21-1276), RE₂Ti₃O₇ (Ho₂Ti₃O₇, JCPDS: 23-0283 and/or Yb₂Ti₃O₇, JCPDS: 17-0454) and RE₂Ti₂O₇ (Ho₂Ti₂O₇ and/or Yb₂Ti₂O₇) phases were observed. According to the phase diagram of ZnO–TiO₂ system, Zn₂TiO₄ is a stable phase and easily formed by the reaction between ZnO and TiO₂ even the system has lower amount of ZnO than ZnO/TiO₂ = 2. The effect of ZnO–TiO₂ composition on the relative phase contents of the product is shown in Fig. 2. With the increase of ZnO amount up to \( x = 1.25 \), the Zn₂TiO₄ content increased and at the same time the TiO₂, RE₂Ti₃O₇, and RE₂Ti₂O₇ contents gradually decreased. Subsequently, at \( x = 1.25 \), TiO₂ phase disappeared. And, at above \( x = 1.25 \), the Zn₂TiO₄ phase remained unchanged and was still the dominant phase. The RE₂Ti₂O₇ content primarily increased but RE₂Ti₃O₇ content disappeared when increasing the ZnO amount above \( x = 1.25 \). These phase changes can be explained as follows. The Zn₂TiO₄ phase is formed from the reaction between 2 mole of ZnO and 1 mole of TiO₂. In this study, as increasing ZnO amount from 0.5 to 2 (the stoichiometric composition for Zn₂TiO₄), the Zn₂TiO₄ content increased. Here, the remained TiO₂ react with RE₂O₃ and form RE₂Ti₃O₇ and RE₂Ti₂O₇ phases owing to the negative formation energies of the RE₂Ti₂O₇ (−3.8 eV) and RE₂Ti₃O₇ (−3.79 eV) phases compared to the Zn₂TiO₄ phase (−2.88 eV). These
formation reactions are competitive ones. Up to \( x = 1.25 \), the Zn\(_2\)TiO\(_4\) content increase, that means the amount of RE\(^{3+}\) ions in the crystal increase, leading to the decrease in RE\(_2\)Ti\(_2\)O\(_7\) and RE\(_2\)TiO\(_5\) contents.

The UC luminescence spectra of various ZnO–TiO\(_2\) products doped with 0.05 mol \% Ho\(^{3+}\) and 9 mol \% Yb\(^{3+}\) are shown in Fig. 3. The emission spectrum consisted of the two strong emission bands, a green emission band from 537 to 557 nm and a red emission band from 639 to 675 nm. Corresponding the emission photographs are inserted in Fig. 3 either. The photographs showed that color of the UC luminescence changed green to reddish with increasing ZnO amount. The color of the Z0.5T1 and Z1T1 is green because the green emission band is equal or higher than red emission band. Further, the color of the Z2T1 becomes reddish because the red emission band is higher than green emission band. The central area of the sample (Z0.5T1 and Z1T1) seems to be white, which is caused by the strong emission.

In general, the emission can occur by the incorporation of RE\(^{3+}\) ions in the host material at high temperature. As discussed by Luitel et al. in the ZnO–TiO\(_2\) composite doped with Er\(^{2+}\) and Yb\(^{3+}\), \(^{30}\) Zn\(_2\)TiO\(_4\) has an AB\(_2\)O\(_4\) type inverse spinel structure, where Zn atoms occupy the A-sites (tetrahedral) and B-sites (octahedral) are occupied by randomly arranged Zn and Ti atoms. For this occupant behavior, Zn\(^{2+}\) sites are 4-fold (ionic radius = 0.060 nm) and 6-fold (ionic radius = 0.074 nm), and Ti\(^{2+}\) site is 6-fold (ionic radius = 0.061 nm). In addition, when the system has excess Ti\(^{4+}\) which has tendency to occupy octahedral site, the vacancies are created (presumably in tetrahedral sites) to compensate the charge. Therefore, Ho\(^{3+}\) (ionic radius = 0.090 nm, 6-fold) and Yb\(^{3+}\) (ionic radius = 0.087 nm, 6-fold) should get into vacancies sites in position of Zn\(^{2+}\) sites (4-fold) in Zn\(_2\)TiO\(_4\) crystal more easily than direct occupying the Zn\(^{2+}\) and Ti\(^{4+}\) because ionic radii of RE\(^{3+}\) ions are much larger than Zn\(^{2+}\) and Ti\(^{4+}\), including the valence mismatch of these three ions.

The maximum emission intensity (at 542 nm) of ZnO–TiO\(_2\) composite doped with 0.05 mol \% Ho\(^{3+}\) and 9 mol \% Yb\(^{3+}\) with various ZnO/TiO\(_2\) mixing ratios is shown in Fig. 4. In the lower \( x \) value (\( x < 1.00 \)), the emission intensity increased as the increase of ZnO amount. In the case of \( x > 1.00 \), with the increase of ZnO amount, the emission intensities decreased.

These behaviors are explained by considering XRD analyzes that were carried out for these compositions and showed in Fig. 2. When emission intensity increased (\( x = 0.5, 0.75, \) and 1), there were four phases; Zn\(_2\)TiO\(_4\), TiO\(_2\), RE\(_2\)TiO\(_2\), and RE\(_2\)TiO\(_3\). Further, when emission intensity initially decreased (\( x = 1.25 \)), there were three phases; Zn\(_2\)TiO\(_4\), RE\(_2\)TiO\(_2\), and RE\(_2\)TiO\(_3\) without TiO\(_2\) phase. At \( x = 1.5 \) and 2, the emission intensity decreased continuously and there were only two phases; Zn\(_2\)TiO\(_4\) and RE\(_2\)TiO\(_3\). Therefore, the difference between three ranges of ZnO amount is the existence of TiO\(_2\) phase whose solubility in Zn\(_2\)TiO\(_4\) may affect the UC intensity. In addition, in this study (ZnO–TiO\(_2\):Ho\(^{3+}\)/Yb\(^{3+}\) system) and our previous work (ZnO–TiO\(_2\):Er\(^{3+}\)/Yb\(^{3+}\) system) we prepared under the same environmental conditions, the results showed that the brightest UC luminescence on green and red bands for both systems was observed with optimal mixing ratio ZnO:TiO\(_2\) \( = 1:1 \) (in mole) in the same manner.

The green (542 nm) and red (670 nm) emission intensities of the ZnO–TiO\(_2\) (Z1T1) doped with various mol \% Ho\(^{3+}\) and 9 mol \% Yb\(^{3+}\) are shown in Fig. 5. The inset in graph attached is the photograph of the emission of selected sample irradiated with 980 nm laser.
emission intensity increased because the Ho³⁺ activator concentration in the Zn₂TiO₄ phase increased. In the second part, with the increase of Ho³⁺ concentration up to 0.3 mol%, the emission intensity sharply decreased because of the concentration quenching. In the third part, with the Ho³⁺ concentration more than 0.3 mol%, slow and the continuous decrease in the UC intensity was observed. At higher Ho³⁺ concentration (0.3 to 2 mol%), the emission intensity was very low. This must be due to the saturation of Ho³⁺ solid solution in Zn₂TiO₄ phase.

Figure 6 shows the Yb³⁺ concentration influenced on the emission intensities of the products by keeping Ho³⁺ concentration at 0.05 mol%. With the increase of Yb³⁺ concentration from 3 to 9 mol%, the emission intensity increased, reached maximum at 9 mol% Yb³⁺ doping concentration and then decreased on higher concentration. The increased emission intensity is due to the higher concentration of dissolved Yb³⁺ into the Zn₂TiO₄ phase, which increase the photon absorption and hence the excited Ho³⁺ ions. The decreased emission intensity at higher Yb³⁺ concentration agreed with the concentration quenching. Thus, the optimum Ho³⁺ and Yb³⁺ concentrations for the brightest UC emission were 0.05 and 9 mol%, respectively.

Due to the very low concentration of Ho³⁺ ions, relating to the optimum concentration of Ho³⁺ ions in ZnO–TiO₂:Ho³⁺/Yb³⁺/ZnO–TiO₂:Ho³⁺/Yb³⁺/TiO₂ composite system, the incorporation of Ho³⁺ ions, including Yb³⁺ ions, in this system is the significant point which can be simply explained by considering the XRD patterns of controlled variables based on the best condition for emitting brightest UC emission, consisting of un-doped ZT1, 0.05 mol% Ho³⁺ doped ZT1, 9 mol% Yb³⁺ doped ZT1, and 0.05 mol% Ho³⁺/9 mol% Yb³⁺ co-doped ZT1. As shown in Fig. 7(a), the results showed that when the system consisted of single RE³⁺ ion doping, RE₂TiO₅ and RE₂TiO₇ phases appeared. Hence, Ho³⁺ and Yb³⁺ ions existed in the form of RE titane compounds even the system had very low amount of RE³⁺ ions. Further, the XRD peaks were found to shift to higher angle with increasing RE³⁺ ion compositions. As shown in Fig. 7(b), the magnified XRD patterns of Fig. 7(a) around 2θ = 35.2° (main peak position of Zn₂TiO₄ phase) showed the single peak with a shift toward higher angles. The shift in the positions of diffraction peak confirmed the substitution effects and designated a structural modification due to the lattice distortion caused by the RE³⁺ ions doping. Thus, the Ho³⁺ and Yb³⁺ ions also introduced in the lattice of Zn₂TiO₄ host.

In order to comprehend the UC mechanism of ZnO–TiO₂ composite doped with 0.05 mol% Ho³⁺ and 9 mol% Yb³⁺, the UC emission intensity I were measured as a function of the pump power P. In the UC process, I is proportional to the n power of P, I ∝ Pⁿ, where n is the number of the pumped photons per the emitted photon. As shown in Fig. 8, the plotting of log(I) versus log(P) yielded a straight line, resulting the n values of 1.29 and 1.16 (P = 15 to 196 mW) for the green and red emissions, respectively. Typically, the n value, related to UC mechanism, is lower than the theoretical n value; two-photon process (1 < n ≤ 2) or three-photon process (2 < n ≤ 3), because, in the realistic systems, the population mechanism is more complex than basic mechanism models. The obtained small n values by our results should be indicated that, in the Ho³⁺/Yb³⁺ co-doped ZnO–TiO₂ composite system, the competition between linear decays (in form of radiative and non-radiative transitions) is affected by energy transfer to impurity defect, multi-phonon relaxation, cross-relaxation, or other addition processes, causing to the lack of energy in the intermediate excited states of Ho³⁺ and Yb³⁺ ions which may cause a decrease of the slope.

Figure 9 shows the simplified energy levels diagram of Ho³⁺ and Yb³⁺ ions, and the probable mechanism of energy transfer (ET) that excited by 980 nm laser. First the Yb³⁺ is excited from ²F⁵/₂ → ²F⁷/₂ energy level. Further, Yb³⁺ transfer its energy to the Ho³⁺ ion by three ETs. The first ET is ²F⁵/₂(Yb³⁺) → ⁵I₈(ET) that excited by 980 nm laser. First the Yb³⁺ is excited from ²F⁵/₂ → ²F⁷/₂ energy level. Further, Yb³⁺ transfer its energy to the Ho³⁺ ion by three ETs. The first ET is ²F⁵/₂(Yb³⁺) → ⁵I₈.
containing Ho³⁺ occurs at 5I6.

Another ET process 2F5 → 5I7 (Ho³⁺) transfers of each energy level.

The value in the sample containing 0.05 mol % Ho³⁺ and 9 mol % Yb³⁺ occurred at room temperature at 542 and 670 nm wavelengths were observed at room temperature.

The optimum UC emission centered at 670 and 542 nm wavelengths were observed at room temperature.

Taking into account the NR between energy levels and then is excited to the 5I5 level by 2F7 → 5I7 (Ho³⁺) + 2F7 → 5I7 (Yb³⁺) + 3I6 (Ho³⁺). Subsequently, the second ET is 2F7 → 3I6 (Ho³⁺) + 3I6 (Ho³⁺) → 5I7 (Yb³⁺) + 3I6 (Ho³⁺) → 2F7/2 (Yb³⁺) + 5I7 (Ho³⁺). The green emission is observed by radiative transition 3I6 (Ho³⁺) → 3I5 (Ho³⁺). The red emission centered maximum at 670 nm in accordance with 3F2 → 3I1 transition is possibly due to the two possible processes. One is the NR of Ho³⁺ ion that related to 3F4, 2S2 → 3I1 transition. The other is the NR of Ho³⁺ ion that occurs at 3I6 → 3I7 levels and then is excited to the 3I5 level by another ET process 2F3/2 (Yb³⁺) + 3I5 (Ho³⁺) → 3F2/2 (Yb³⁺) + 3I5 (Ho³⁺). Taking into account the n values and proposed energy level diagram, the results confirm that two photon UC processes is liable for the green and red UC in ZnO–TiO₂ composite containing Ho³⁺ and Yb³⁺, considering the NR between energy transfers of each energy level.

4. Conclusions

ZnO–TiO₂ composite phosphor with various concentrations of Ho³⁺ and Yb³⁺ were successfully synthesized by conventional solid-state reaction method. The maximum UC emission centered at 542 and 670 nm wavelengths were observed at room temperature. The green and red emission intensities reached a maximum value in the sample containing 0.05 mol % Ho³⁺ and 9 mol % Yb³⁺. The optimum ZnO/TiO₂ mixing ratio was ZnO:TiO₂ = 1:1 (in mole). Brightest UC luminescence of ZnO–TiO₂:Ho³⁺/Yb³⁺ occurred when the system consisted of mixed phases; Zn₂TiO₄, TiO₂, RE₂Ti₂O₇ and RE₂TiO₅. In addition, when using solid-state reaction method, it is possible that Ho³⁺ ion dissolved into Zn₂TiO₄ matrix more difficult than Er³⁺ ion due to the existence of RE₂TiO₅ phase that occurred only in Ho³⁺/Yb³⁺ system.

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