Up- and Downconversion Luminescence in $\text{Ho}^{3+}, \text{Yb}^{3+}$ -Co-Doped Y_2O_3 Transparent Ceramics Prepared by Spark Plasma Sintering

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Abstract: We employed spark plasma sintering (SPS) in the presence of sintering aids to fabricate high-quality $\text{Ho}^{3+}, \text{Yb}^{3+}$ -co-doped Y_2O_3 transparent ceramics suitable for use as a laser gain medium, and analyzed their microstructure and optical properties. $\text{Ho}^{3+}, \text{Yb}^{3+}$ -co-doped Y_2O_3 transparent ceramics with different contents of Yb^{3+} were fabricated by SPS and exhibited high transparency in both near-infrared and visible regions. All specimens showed high transparency in both the near-infrared and visible-light regions, and sample microstructure was almost unaffected by the amount of doped Yb^{3+} . The transmission spectra of 1 mol% Yb^{3+} doped specimens exhibited transmissivities of 73.4 and 81.0% at wavelengths of 700 and 1500 nm, respectively. Relatively high transmissivity was quickly achieved through the addition of a sintering aid (1 mol% La_2O_3) which accelerated mass transport during sintering. The effect of Yb^{3+} doping on the upconversion photoluminescence of $\text{Y}_2\text{O}_3:\text{Ho}^{3+}, \text{Yb}^{3+}$ was examined. Irradiation at 980 nm resulted in strong green photoluminescence (552 nm) and weak red photoluminescence (669 nm). Excitation at 447 and 980 nm resulted in strong green emission ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$) from Ho^{3+} . The effects of Yb^{3+} content and laser input power on emission intensity and luminescence decay were investigated in detail. Under excitation at 980 nm, the presence of Yb^{3+} increased emission intensity over the entire range, while the opposite behavior was observed under excitation at 447 nm.

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1. INTRODUCTION

Transparent polycrystalline ceramics have recently emerged as advanced structural and functional materials of high importance [1], because such ceramics can often be excited by laser diode pumping systems, making them suitable for numerous applications in diverse areas of industry [2]. Non-linear optics-based high-power lasers emitting in the infrared range of 2–5 μm usually contain Ho^{3+} -doped transparent ceramics as a gain medium. A great deal of research is currently focused on fabricating lasers based on Ho^{3+} -doped ceramics for applications such as atmospheric pollutant monitoring, remote sensing, lidar, and

medical surgery [3-5].

The luminescence efficiency of solid-state lasers is closely related to the fluorescence characteristics of their gain media. Based on changes in the incident and released photon wavelengths, that fluorescence is classified as either downconversion or upconversion. In the former case, two or more low-energy photons are produced from one high-energy photon [6], while in the latter case, low-energy photons are converted into a high-energy photon in an anti-Stokes process [7,8]. Among the various ions, Ho^{3+} show the highest upconversion photoluminescence efficiency due to their long fluorescence lifetime and the large region of stimulated luminescence [9]. Yb^{3+} ions are very easily excited by 980 nm radiation, and the energy of this radiation can be easily transferred to other ions [10]. This implies that the upconversion efficiency of Ho^{3+} can be significantly increased in the presence of co-doped Yb^{3+} [11].

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The luminescence efficiency of fluorescent substances is greatly affected by the phonon energy of the host matrix, since the extent of non-radiative energy loss, and hence, that of quenching, decreases with decreasing phonon energy. Consequently, Y_2O_3 is viewed as a promising material for upconversion lasers in view of its high thermal conductivity, ideal physical/chemical stability, suitability for doping with trivalent rare-earth-element ions, high transparency in a broad spectral range (infrared to visible-light regions), and relatively low phonon energy ($430\text{--}550\text{ cm}^{-1}$) [12].

In general, most gain media used in solid-state lasers are of the single-crystal type [13]. However, the high melting point ($\sim 2430\text{ }^\circ\text{C}$, close to the melting point of Ir crucibles ($2450\text{ }^\circ\text{C}$)) of Y_2O_3 and the occurrence of a cubic-to-hexagonal Y_2O_3 phase transition at $2350\text{ }^\circ\text{C}$ complicate the fabrication of single crystals with high optical quality by conventional techniques such as the Czochralski method [14]. On the other hand, research has recently been directed at using Y_2O_3 transparent ceramics as laser media, as these materials exhibit the advantages of simple fabrication, low cost, uniform dopant concentration, and excellent mechanical properties [15].

Y_2O_3 transparent ceramics are fabricated using sintering methods such as hot pressing [16], hot isostatic pressing [17,18], and pressureless sintering [19–21]. In particular, spark plasma sintering (SPS) has the benefits of rapid temperature increase up to $2000\text{ }^\circ\text{C}$, accelerating the formation of necks between powder grains, and crystal grain surface purification, thermal diffusion, and electrotransport effects. This allows the process to achieve complete sintering in a very short time and at a low temperature [22–27].

Transparent ceramics are commonly manufactured using sintering aids, which govern the microstructure of these ceramics and can be used to increase their optical quality and promote densification. For example, the use of La_2O_3 in the sintering of Y_2O_3 ceramics results in improved transmissivity, as the former oxide induces grain growth and promotes densification by increasing grain boundary mobility [28] and thereby facilitates the annihilation of oxygen vacancies between grain boundaries [29].

In this study, we employed SPS in the presence of sintering aids to fabricate high-quality Ho^{3+} , Yb^{3+} -co-doped Y_2O_3 transparent ceramics suitable for use as a laser gain medium

and analyzed their microstructure and optical properties. In particular, we confirmed the effect of Yb^{3+} content on photoluminescence intensity, excitation spectrum intensity, and fluorescence lifetime under 447 nm excitation. We further studied the photoluminescence intensity and the related emission mechanism at 545 and 655 nm under 980 nm excitation, and evaluated the effects of incident light intensity on output fluorescence intensity.

2. EXPERIMENTAL PROCEDURE

2.1. Sample preparation

High-purity Y_2O_3 (99.99%; Cenotec, Korea), La_2O_3 (99.9%; Kojundo, Japan), Ho_2O_3 (99.9%; Rare Metallic Co., Ltd., Japan), and Yb_2O_3 (99.9%; Shin-Etsu Chemical, Japan) powders were used. A mixture of La_2O_3 (1 mol%), Ho_2O_3 (1 mol%), Yb_2O_3 (0–3 mol%), and Y_2O_3 (balance) powders was ball-milled for 24 h with 1.5-mm-diameter zirconia balls at a 1:10 weight ratio and subsequently dried at $60\text{ }^\circ\text{C}$ in an electric oven for 24 h. The dried powder was placed into a graphite foil-wrapped graphite die (internal diameter = 15 mm) and sintered at a temperature of $1625\text{ }^\circ\text{C}$, a vacuum of 10 Pa, and a uniaxial pressure of 30 MPa (Fig. 1) using an S-515S SPS system (Sumitomo Coal Mining, Japan).

Three sintering processes were employed. Under process (I), the sample was heated from room temperature to the final sintering temperature ($1625\text{ }^\circ\text{C}$) at a heating rate of $100\text{ }^\circ\text{C min}^{-1}$ and then held at this temperature for 15 min; under

Fig. 1. Time dependence of the temperature and applied pressure during SPS process for $\text{Y}_2\text{O}_3\text{:Ho}^{3+}$, Yb^{3+} with La 1 mol% powders.

process (II), pressure was maintained at 30 MPa from the beginning. Under process (III), after sintering was complete, pressure was released at 1100 °C, and the electric current was blocked.

The sintered specimens (diameter = 15 mm, thickness = 1 mm) were annealed for 4 h under an oxygen atmosphere in a box furnace at 1000 °C using a heating rate of 10 °C min⁻¹. For microstructure and optical characteristics evaluation, both specimen sides were subjected to surface-grinding and then polished with 1 μm diamond paste.

2.2. Characterization

Crystal phase composition was determined using X-ray diffraction (XRD; Rigaku-denki, D/MAX-2500, Japan; Cu K_{α} , 40 kV, 30 mA) analysis in a 2θ range of 20–80°. The average grain size was determined by field-emission scanning electron microscopy (FE-SEM; NOVA Nano SEM 450, FEI, Czech Republic) at acceleration voltages of 5–15 kV. In-line transmittance and absorption were measured in a wavelength range of 300–2000 nm using a UV-Vis-NIR spectrophotometer (Lambda 950, Perkin-Elmer, USA). Irradiation at 980 nm was performed at room temperature employing an MDE981H8 laser (Latech Co., Korea), and the resulting upconversion emission was recorded in a wavelength range of 300–800 nm using a fluorescence spectrometer (LS55, Perkin-Elmer, USA). For fluorescence lifetime measurement, samples were irradiated at 445 nm and room temperature using a time-correlated single-photon counting spectrofluorometer (iHR320, Horiba, Japan) and a Xe lamp, and the resulting downconversion emission was measured.

3. RESULTS AND DISCUSSION

The XRD patterns of vacuum-sintered (1625 °C, 30 MPa, 15 min) $\text{Y}_2\text{O}_3\text{:Ho}^{3+}, \text{Yb}^{3+}$ specimens with different Yb^{3+} contents (Fig. 2(a)) showed the presence of standard cubic Y_2O_3 (JCPDS Card No 41-1105) in all cases, with no other impurities were detected. La_2O_3 was found to be completely dissolved in Y_2O_3 , and Ho^{3+} (1 mol%) and Yb^{3+} (0–3 mol%) matched perfectly with the space group $Ia\bar{3}$. Examination of the (222) peak region (Fig. 2(b)) confirmed that this peak shifted to higher angles with increasing content of Yb^{3+} ,

Fig. 2. X-ray diffraction patterns of $\text{Y}_2\text{O}_3\text{:Ho}^{3+}, \text{Yb}^{3+}$ transparent ceramics doped with various Yb^{3+} concentration of 0 mol%, 1 mol%, 2 mol%, and 3 mol in (a) 20–60° and (b) 29.0–29.5° range.

which was ascribed to the concomitant shrinkage of the Y_2O_3 unit cell. In turn, this shrinkage was attributed to the fact that the radius of Yb^{3+} (0.868 Å [30]) is smaller than those of Ho^{3+} (0.901 Å [30]) and Y^{3+} (0.900 Å [30]).

FE-SEM imaging of the etched surface of the $\text{Y}_2\text{O}_3\text{:Ho}^{3+}, \text{Yb}^{3+}$ ceramics (Fig. 3) confirmed that all specimens exhibited a relatively fine and uniform microstructure without abnormal growth. The average grain size (~13 μm) was found to be independent of Yb^{3+} content. This finding confirmed that the content of Yb^{3+} does not have a large effect on the sinterability of Y_2O_3 , since Yb_2O_3 and Y_2O_3 have similar crystal structures, and the corresponding self-diffusion coefficients are of the same order [31].

Fig. 3. SEM micrographs of the $\text{Y}_2\text{O}_3\text{:Ho}^{3+}$, Yb^{3+} transparent ceramics doped with various Yb^{3+} concentration of (a) 0 mol%, (b) 1 mol%, (c) 2 mol%, and (d) 3 mol%

Fig. 4. Photographs of transparent $\text{Y}_2\text{O}_3\text{:Ho}^{3+}$, Yb^{3+} ceramics specimen doped with various Yb^{3+} concentration of (a) 0 mol%, (b) 1 mol%, (c) 2 mol%, and (d) 3 mol% (1 mm thick).

Figure 4 shows a photograph of the 1-mm-thick $\text{Y}_2\text{O}_3\text{:Ho}^{3+}$, Yb^{3+} specimens, both sides of which were mirror-finished after vacuum sintering (1625 °C, 30 MPa, 15 min) and annealing (1000 °C, 4 h, air). All of the specimens were transparent enough to allow one to read text placed behind them.

Figure 5(a) shows the transmission spectra of all samples, while Fig. 5(b) shows the absorption spectrum of the 1 mol% Yb^{3+} specimen, revealing that this specimen exhibited transmissivities of 73.4 and 81.0% at wavelengths of 700 and 1500 nm, respectively. Thus, relatively high transmissivity was quickly achieved through the addition of a sintering aid (1 mol% La_2O_3) which accelerated mass transport during

Fig. 5. (a) Transmission spectra of $\text{Y}_2\text{O}_3\text{:Ho}^{3+}$, Yb^{3+} transparent ceramics doped with various Yb^{3+} concentration and (b) absorption spectrum of $\text{Y}_2\text{O}_3\text{:Ho}^{3+}$, Yb^{3+} transparent ceramics with 1 mol% Yb^{3+} doping concentration.

sintering. The absorption spectrum of the 1 mol% Yb^{3+} specimen featured peaks at 450, 540, 650, and 980 nm, which were ascribed to the $^5\text{I}_8 \rightarrow ^5\text{G}_6$, $^5\text{S}_2$, F_5 transitions of Ho^{3+} and the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition of Yb^{3+} , respectively [32]. Importantly, transmissivity at 980 nm decreased with increasing Yb^{3+} content of, which indicates that this ion absorbed radiation at 980 nm and transferred its energy to a different ion.

Figure 6(a) shows the effect of Yb^{3+} content on downconversion photoluminescence intensity. Irradiation at 447 nm resulted in strong green photoluminescence (540 and 555 nm) and weak red photoluminescence (615 nm),

Fig. 6. (a) Downconversion photoluminescence spectra of $\text{Y}_2\text{O}_3:\text{Ho}^{3+}, \text{Yb}^{3+}$ transparent ceramics excited under 447 nm at room temperature, doped with various Yb^{3+} concentration of 0 mol%, 1 mol%, 2 mol%, and 3 mol%. (b) Photoluminescence excitation spectra of $\text{Y}_2\text{O}_3:\text{Ho}^{3+}, \text{Yb}^{3+}$ transparent ceramics about 550 nm emission at room temperature.

with the former corresponding to the $^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$ transitions of Ho^{3+} , respectively [33]. With the introduction of Yb^{3+} , photoluminescence intensity decreased in all regions. This behavior was attributed to the fact that the $^2\text{F}_{5/2}$ level of Yb^{3+} is positioned between the $^5\text{I}_5$ and $^5\text{I}_6$ levels of Ho^{3+} , which precludes the immediate relaxation of the latter ions to the ground state and results in cross-relaxation at the level of Yb^{3+} , and, hence, in a decrease of Ho^{3+} emission energy [34].

Figure 6(b) shows the effect of Yb^{3+} concentration on the

Fig. 7. Emission decay curves of the Ho^{3+} 550 nm emission under 447 nm excitation.

excitation spectrum for the 550 nm emission and reveals the presence of numerous transitions between 330 and 500 nm, e.g., $^5\text{I}_8 \rightarrow ^3\text{H}_5, ^5\text{G}_2; ^5\text{I}_8 \rightarrow ^5\text{G}_4, ^3\text{K}_7; ^5\text{I}_8 \rightarrow ^5\text{G}_5; ^5\text{I}_8 \rightarrow ^5\text{G}_6; ^5\text{I}_8 \rightarrow ^5\text{F}_2, ^3\text{K}_8; ^5\text{I}_8 \rightarrow ^5\text{F}_3$. Notably, the intensity of all signals decreased with increasing Yb^{3+} content, which was attributed to a concomitant increase in cross-relaxation occurrence frequency. In turn, this frequency increase resulted in the depopulation of $^5\text{F}_4/^5\text{S}_2$ and $^5\text{F}_5$ levels and hence hindered downconversion photoluminescence at 550 nm [35].

Figure 7 shows the effect of Yb^{3+} content on fluorescence decay curves. These curves were fitted using a linear exponential function, and decay times of $\sim 140, 125, 110$, and $100 \mu\text{s}$ were obtained for Yb^{3+} contents of 0, 1, 2, and 3 mol%, respectively. As a result, the decay time decreased with increasing Yb^{3+} content, an effect ascribed to the provision of a new decay pathway by the Yb^{3+} ions, i.e., these ions facilitated the relaxation of Ho^{3+} [36].

Figure 8 shows the effect of Yb^{3+} content on the upconversion photoluminescence of $\text{Y}_2\text{O}_3:\text{Ho}^{3+}, \text{Yb}^{3+}$. Irradiation of the above samples at 980 nm resulted in strong green photoluminescence (552 nm) and weak red photoluminescence (669 nm). The former photoluminescence corresponds to the $^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$ transitions of Ho^{3+} , while the latter is ascribed to the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transition of Ho^{3+} [37]. This behavior reflected the occurrence of an upconversion process, in which Ho^{3+} absorbs low-energy photons at 980 nm and emits higher-energy photons at 552 and 669 nm [32].

Fig. 8. Upconversion photoluminescence spectra of $\text{Y}_2\text{O}_3:\text{Ho}^{3+}$, Yb^{3+} transparent ceramics excited under 980 nm at room temperature, doped with various Yb^{3+} concentration of 0 mol%, 1 mol%, 2 mol%, and 3 mol% in (a) 500 - 600 nm and (b) 600 - 700 nm range.

Doping with Yb^{3+} significantly increased photoluminescence intensity in all regions, with the largest increase observed for 2 mol% Yb^{3+} . Notably, photoluminescence intensity decreased when going from 2 mol% to 3 mol% Yb^{3+} . This is attributed to the enhancement of non-radiative transitions caused by interactions between Yb^{3+} ions at high Yb content [38].

Figure 9 shows that, like the upconversion photoluminescence intensity, green and red emission intensities increased with increasing near-infrared excitation power. Previously, upconversion photoluminescence intensity was found to be

Fig. 9. Plots of logarithm of $I_{\text{Intensity}}$ versus I_{pump} in (a) 550 nm and (b) 650 nm of $\text{Y}_2\text{O}_3:\text{Ho}^{3+}$, Yb^{3+} transparent ceramics.

proportional to the n -th power of pump power. Here, the dependence of photoluminescence intensity ($I_{\text{Intensity}}$) on excitation intensity (I_{pump}) was modeled as $I_{\text{Intensity}} \propto I_{\text{pump}}^n$, where n is a constant [39]. The slopes (i.e., values of n) of each trend line in Fig. 9 are summarized in Table 1.

Figure 10 shows the mechanism of fluorescence upon the excitation of Ho^{3+} and Yb^{3+} ions at 447 or 980 nm. In the case of downconversion (excitation at 447 nm), ground-state ($^1\text{I}_8$) electrons are excited to the $^5\text{G}_6$ level via the ground state absorption (GSA) process [11], which is followed by slow transitions to lower-lying levels (e.g., $^5\text{F}_2/{}^3\text{K}_8$, $^5\text{F}_3$, $^5\text{S}_2$, and $^5\text{F}_5$) through several stages of non-radiative transfer.

Table 1. Slope of lines fitted to plots of 1 mol% Ho^{3+}/x mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ($x = 0, 1, 2, 3$) transparent ceramics.

Yb^{3+} concentration	0 mol%	1 mol%	2 mol%	3 mol%
550 nm	1.631	1.634	1.563	1.724
650 nm	0.714	1.803	1.961	1.866

Fig. 10. Schematic energy level diagrams of Yb^{3+} , Ho^{3+} in Y_2O_3 host matrix and the fluorescence emission mechanism of $\text{Y}_2\text{O}_3:\text{Ho}^{3+}$, Yb^{3+} transparent ceramics under 447 and 980 nm excitation.

Eventually, the ground state is re-populated, and the initially absorbed energy is released [33]. The presence of Yb^{3+} ions facilitates cross-relaxation which is characterized by the $^5\text{F}_3 \rightarrow ^5\text{I}_5$ and $^5\text{F}_5 \rightarrow ^5\text{I}_7$ transitions of Ho^{3+} [34].

With increasing Yb^{3+} content, the fluorescence induced by 447-nm excitation disperses to various wavelengths, which results in a decrease in fluorescence intensity in the visible-light region as shown in Fig. 6. Under 447 nm excitation, the interception of energy from the Yb^{3+} ions by the Ho^{3+} ions is more dominant than transition from the Ho^{3+} ions. This makes the Ho^{3+} ions energy levels less populated, resulting in decreased emission intensity [33,34].

In the case of upconversion (excitation at 980 nm), Ho^{3+} ions cannot directly absorb the incident radiation [39]. However, since these ions are embedded into the Y_2O_3 host matrix with a phonon frequency of 500 cm^{-1} , the energy difference between incident radiation and the $^5\text{I}_6$ level of Ho^{3+} can be bridged by one or two phonons, which allows the ground-state electrons of Ho^{3+} to be excited to the $^5\text{I}_6$ level and then to higher-lying $^5\text{S}_2$ and $^5\text{F}_4$ levels (via energy

reabsorption through the excited state absorption (ESA) process) [37].

On the other hand, Yb^{3+} ions can directly absorb 980-nm radiation by undergoing a $^2\text{F}_{7/2}$ (ground state) $\rightarrow ^2\text{F}_{5/2}$ transition. Subsequent relaxation to the ground state results in a release in energy and induces transitions to the $^5\text{I}_5$ and $^5\text{I}_6$ levels (via ESA) as well as to the $^5\text{S}_2$ and $^5\text{F}_4$ levels (via GSA) of Ho^{3+} [36]. As shown in Fig. 2(b), an XRD peak shift can be observed with increased Yb^{3+} doping concentration. The lattice distortion caused by the difference in the ionic radii of Y^{3+} and Yb^{3+} decreases lattice constants and cell volumes, leading to slight structure distortion and decreasing distances between the Yb^{3+} and Ho^{3+} ions. As a consequence, this makes it easier to transfer energy among ions, increasing the intensity of emission under 980 nm excitation. Yb^{3+} ions can also receive energy via inverse energy transfer, which can be explained with the same theory [37-39]. Consequently, the intensity of green photoluminescence increases with increasing Yb^{3+} content as shown in Fig. 8.

4. CONCLUSION

Highly transparent $\text{Y}_2\text{O}_3:\text{Ho}^{3+}, \text{Yb}^{3+}$ ceramics were prepared by SPS (30 MPa, 15 min) using La_2O_3 as a sintering aid. All specimens showed high transparency in both the near-infrared and visible-light regions, and sample microstructure was almost unaffected by the amount of doped Yb^{3+} . In the downconversion, strong green photoluminescence (540 and 555 nm) and weak red photoluminescence (615 nm) were observed, and photoluminescence intensity decreased in all regions with increasing Yb^{3+} content. In the case of upconversion, strong green photoluminescence (545 nm) and weak red photoluminescence (655 nm) were observed. Upon the introduction of Yb^{3+} , photoluminescence intensity greatly increased in every region, with the highest increase observed for 2 mol% Yb^{3+} .

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