



Article Up-Conversion Luminescence and Optical Temperature Sensing Behaviour of Y₂O₃:Ho³⁺, Yb³⁺ Phosphors

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Abstract: The up-conversion (UC) and temperature sensing behaviours of Y_2O_3 :Ho³⁺, Yb³⁺ phosphors were investigated. A series of Y_2O_3 :Ho³⁺, Yb³⁺ phosphors were synthesized using a solution combustion method. The cubic structure of the Y_2O_3 with an Ia $\overline{3}$ space group was analysed by using X-ray powder diffraction. Scanning electron microscopy was conducted to study the surface morphologies of the UC phosphors. Under 980 nm excitation, the UC emissions of Ho³⁺ from the ${}^5S_2 \rightarrow {}^5I_8$, ${}^5F_5 \rightarrow {}^5I_8$ and ${}^5S_2 \rightarrow {}^5I_7$ transitions were observed, which occurred through UC energy transfer (ET) processes. The Yb³⁺ ion concentration severely affected the UC emission. The sensing behaviour of the phosphor was investigated through the green (5F_4 , ${}^5S_2 \rightarrow {}^5I_8$) to red (${}^5F_5 \rightarrow {}^5I_8$) fluorescence intensity ratio (FIR). The maximum absolute and relative sensitivity values of S_A = 0.08 K⁻¹ and S_R = 0.64% K⁻¹ were obtained. The results revealed that the prepared Y₂O₃:Ho³⁺, Yb³⁺ phosphor is suitable for optical sensing at high temperatures.

Keywords: Y₂O₃:Ho³⁺, Yb³⁺ upconversion; up-conversion energy transfer; fluorescence intensity ratio; optical temperature sensing

1. Introduction

Lately, up-conversion (UC) materials based on lanthanide ions have been investigated extensively because of their potential application in colour displays, solar cells, optical communication, optical temperature sensors, and the lamp industry [1–6]. For efficient UC emission, Yb³⁺ has been extensively utilized as a sensitizer for trivalent lanthanide ions (Ln^{3+}) doped into various hosts [7–10]. Yb³⁺ is an interesting ion that possesses only a ²F_{7/2} ground state and a ²F_{5/2} excited state that is set apart by approximately 10,000 cm⁻¹. Yb³⁺ is usually excited with near-infrared (NIR) and transfers energy to an activator resulting in visible emission through the energy transfer up-conversion (ETU) process. The energy level matching between Ho³⁺ and Yb³⁺ ions makes the couple to be a great choice for UC investigations [11]. Dwivedi et al. [7] investigated the UC luminescence of Gd₂O₃:Ho³⁺, Yb³⁺ phosphor and obtained a strong green UC emission. The visible UC luminescence of Y₂O₂S:Er³⁺, Yb³⁺ phosphor has been reported to be 2.2 times less bright than that of Y₂O₂S:Ho³⁺, Yb³⁺ phosphor [8]. The Ho³⁺, Yb³⁺ co-doping has also been proven to be a highly efficient UC system by other researchers [12].

The host material is of great importance in UC emission intensity. For efficient UC output, the host should have low energy phonons to minimize the probability of multiphonon relaxations of the lanthanide ions. The cubic phase of Y_2O_3 host possesses low phonon energy (~550 cm⁻¹), a wide bandgap, high melting point, and thermal stability that make it suitable for various phosphor applications [13,14]. Therefore, due to the matching ionic radii of Y³⁺ (0.900 Å), Ho³⁺ (0.901 Å), and Yb³⁺ (0.868 Å), Y₂O₃ may be considered as an



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). ideal host for Ho³⁺-Yb³⁺ couple [15]. Pandey et al. [16] reported that the Yb³⁺ co-doping in Y₂O₃:Ho³⁺ enhanced the green emission intensity by nearly ~290 times. Wei et al. [17] investigated the UC luminescence strong dependence on concentration doping in Ho³⁺, Yb³⁺ co-doped Y₂O₃ and obtained a strong green emission that is applicable in biomedical fluorescent labels.

Research interest in optical temperature sensing with UC phosphors based on lanthanide ions is increasing in recent years. The fluorescence intensity ratio (FIR) between two emission bands, which calls for either thermally coupled or non-thermally coupled energy levels of the luminescent ions, is used in this. [18,19]. In the literature, it is reported that the FIR of green to red emission of Ho^{3+} ion can be identified as an optical temperature sensing indicator [20]. The FIR technique offered a high detection resolution and good sensitivity as it is typically independent of excitation-power fluctuation and spectrum loss. The FIR of thermally coupled energy levels (TCLs) (Ho^{3+:5}F₃/ 3 K₈) can be explained by a Boltzmann distribution of electrons [21,22]. According to the Boltzmann distribution, the temperature sensing sensitivity proportional to ΔE , can barely be improved further to a higher level since the energy separation ΔE of such levels is typically limited to 200–2000 cm⁻¹ to avoid an intense overlap between the two emission bands [23]. For this reason, using non-thermally coupled energy levels (non-TCLs) (Ho³⁺: ${}^{5}F_{5}/{}^{5}F_{4}$, ${}^{5}S_{2}$) is regarded as a useful addition to improve FIR sensitivity [19,21,23]. However, studies on the temperature sensing performance with the non-TCLs for Ho³⁺/Yb³⁺:Y₂O₃ phosphor are currently few. Wang et al. [24] investigated the performance of the optical temperature sensing based on non-TCLs of Ho³⁺ ion ((${}^{5}F_{4}/{}^{5}S_{2} \rightarrow {}^{5}I_{8}$)/(${}^{5}F_{5} \rightarrow {}^{5}I_{8}$)) and found a maximum absolute sensitivity of 0.1603 K^{-1} . More deep investigations on the optical temperature sensing with non-TCLs of Ho³⁺ ion for Ho³⁺/Yb³⁺:Y₂O₃ phosphor are required.

In this work, Ho³⁺, Yb³⁺:Y₂O₃ up-conversion phosphors with various concentrations of Yb³⁺ were synthesized by the solution combustion method. The structural and optical properties were studied by X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), and UV-vis-NIR spectra measurements. The UC emission and temperature sensing behaviour of the Ho³⁺, Yb³⁺:Y₂O₃ were investigated. Power dependence measurements and an energy level diagram confirmed the phenomenon involved in the UC process. The green (${}^{5}F_{4}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$) to red (${}^{5}F_{5} \rightarrow {}^{5}I_{8}$) FIR was used to analyse the behaviour of temperature sensing of the developed phosphor.

2. Experimental

2.1. Synthesis

The phosphor powder samples of $Y_{2-x-y}O_3$: $Ho_{x=0.005}$, Yb_y (y = 0, 0.002, 0.006, 0.01, 0.05, 0.1, 0.2) were prepared by a solution combustion method. $Y(NO_3)_3 \cdot 4H_2O$ (Sigma Aldrich, Darmstadt, Germany, 99.99%), $Ho(NO_3)_3 \cdot 5H_2O$ (Sigma Aldrich, 99.99%), $Yb(NO_3)_3 \cdot 5H_2O$ (Sigma Aldrich, 99.99%), and CH_4N_2O (Sigma Aldrich, 99.5%) were starting materials. As an example, for y = 0.05, 1.6026 g of $Y(NO_3)_3 \cdot 4H_2O$, 0.0098 g of $Ho(NO_3)_3 \cdot 5H_2O$, 0.0994 g of $Yb(NO_3)_3 \cdot 5H_2O$, and 0.6690 g of CH_4N_2O were dissolved in 50 mL distilled water. The mixture was stirred using a magnetic stirrer in a 100 mL beaker for 30 min until a homogeneous solution was obtained. The solution was then heated at 500 ± 10 °C in a muffle furnace. The foam-like product was crushed using a pestle and mortar and was then annealed at 1100 °C in air for 2 h.

2.2. Characterization

The crystallinity and structure of the prepared samples were analysed by X-ray powder diffraction (XRPD) (Bruker AXS GmbH, Karlsruhe, Germany) using a Bruker D8 Advance diffractometer (40 mA, 40 kV) with Cu $K\alpha$ radiation (0.154 nm). The morphology of the samples was analysed by a scanning electron microscope (JEOL JSM-7800F) equipped with an energy dispersed X-ray spectroscopy (EDS) device (JEOL, Tokyo, Japan). The diffuse reflectance measurements were acquired using a Lambda 950 UV-vis-NIR spectrophotometer (PerkinElmer Ltd, Beaconsfield, United Kingdom) in the range of 200–1200 nm. The

UC emissions and decay curves were recorded using an FLS980 fluorescence spectrometer with 980 nm emitting diode lasers as the excitation source and power of 96 mW.

3. Results and Discussion

3.1. Structural and Surface Morphology Analysis

XRPD patterns of the $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_y phosphors are shown in Figure 1. The XRPD patterns agree with the standard reflection peaks reported in JCPDS# 71-0099 [25], and indicate the cubic structure with an Ia $\overline{3}$ space group of the Y₂O₃ crystal. The XRPD patterns of the Y_{2-x-y}O₃:Ho_{x=0.005}, Y_{by} phosphors are shown in Figure 1. The introduction of Ho³⁺ and Yb³⁺ ions as co-dopants into Y₂O₃ did not change the structure type, but a small shift towards high angles in the diffraction reflection peaks was observed with increasing Yb concentration (Figure 1b). The shift is attributed to the ionic radius difference between the Yb³⁺ (0.868 Å) and Y³⁺ (0.900 Å) ions. Also, the peak shift verifies that Yb³⁺ are effectively incorporated into the Y³⁺ site [15].



Figure 1. (a) XRPD patterns of the Y_2O_3 and $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yby (y = 0, 0.006, 0.2) phosphors (b) magnified view of the 222 diffraction peak.

The morphologies and elemental analyses of the prepared samples were studied using SEM and EDS, respectively. Figure 2 displays the SEM images of the prepared phosphors. All the images exhibited agglomerated spherical nanoparticles. The addition of Ho³⁺, Yb³⁺ did not change the morphology of the Y₂O₃ host. The EDS spectra of the Y_{2-x-y}O₃:Ho_{x=0.005}, Yb_{y=0.2} are displayed in Figure 3. All the Y, O, Yb, and Ho elements expected in the sample were observed, which confirms the successful incorporation of Ho³⁺ and Yb³⁺ into the Y₂O₃ host. In addition, carbon was also detected in the spectrum, which could be from the carbon tape used when mounting the samples. The extra peak detected



around 0.03 keV is due to electronic noise within the system. No impurities were detected in the spectra, which agrees with the XRD results.

Figure 2. SEM images of (a) the Y_2O_3 , (b) $Y_{2-x-y}O_3$:Ho_{x=0.005}, $Yb_{y=0}$, (c) $Y_{2-x-y}O_3$:Ho_{x=0.005}, $Yb_{y=0.006}$ and (d) $Y_{2-x-y}O_3$:Ho_{x=0.005}, $Yb_{y=0.2}$.



Figure 3. EDS spectra of the $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.2}.

3.2. Optical Properties

The reflectance spectra for the UC phosphors are presented in Figure 4. The absorption peak around 220 nm is associated with band-to-band transitions in the Y_2O_3 material [26]. The Ho³⁺ single doped Y_2O_3 exhibited sharp peaks centred at 361, 448, and 1008 nm due to ${}^{5}I_8 \rightarrow {}^{3}H_6$, ${}^{3}D_2$, ${}^{5}I_8 \rightarrow {}^{5}G_6$ and ${}^{3}S_2$, ${}^{5}F_4 \rightarrow {}^{5}I_6$ transitions of the Ho³⁺ ion, respectively [27,28]. The Ho³⁺ 4f-4f absorptions in the UV-vis region remained unchanged when Yb³⁺ was added, which confirms that the Ho³⁺ ion concentration remained uniform. An additional absorption peak observed at 976 nm was observed with Yb³⁺ ion, which is associated with the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of the Yb³⁺ ion [28].



Figure 4. Diffuse reflectance spectra of the $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_y UC phosphors.

The optical bandgap of the Y_2O_3 was estimated from the Tauc plot [29], which is given by:

$$(F(R)hv)^{\frac{1}{n}} = A(hv - E_g) \tag{1}$$

where *A* is a constant, *hv* is the photon energy, E_g is the energy bandgap and $n = \frac{1}{2}$ for the allowed direct bandgap of Y₂O₃. The diffuse reflectance, *R*, of the sample was used to calculate the Kubelka–Munk function *F*(*R*) [29]

$$F(R) = \frac{(1-R)^2}{2R}$$
(2)

Figure 5 shows the Tauc plot and estimated optical bandgap of pure Y_2O_3 . The linear fit extrapolation of the curve to zero absorption gives the optical bandgap [30–32]. The bandgap of the Y_2O_3 was estimated to be 5.74 eV, which agrees with the reported value of 5.8 eV reported by Jones et al. [33]. The optical bandgaps of the Y_2O_3 singly and co-doped with Ho³⁺ and Yb³⁺ ions were calculated using the same procedure and are tabulated in Table 1. An alteration in the optical bandgap of the Y_2O_3 material was observed. It is known that introducing dopants into the Y_2O_3 lattice creates energy levels in the energy gap between the valence and conduction bands, which would decrease the optical band gap [34]. It is also known that the defects of the material, which are introduced during synthesis, can influence the bandgap value [35].



Figure 5. Tauc plot of pure Y₂O₃.

Table 1. Optical bandgap of $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_y UC phosphors.

Sample	Bandgap (eV)		
Y ₂ O ₃	5.74		
Y _{2-x-y} O ₃ :Ho _{x=0.005}	5.72		
$Y_{2-x-y}O_3$:Ho _{x=0.005} , Yb _{y=0.006}	5.68		
Y _{2-x-y} O ₃ :Ho _{x=0.005} , Yb _{y=0.2}	5.61		

3.3. UC Luminescence Studies

Figure 6a presents UC emission spectra of the $Y_{2-x-y}O_3$: Ho_{x=0.005}, Yb_y nanophosphors excited using 980 nm excitation wavelength. The emission spectra are composed of four bands; the intense green, red, and near-infrared emission bands centred at 536, 550, 668, and 756 nm ascribed to the ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$, ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$, and ${}^{5}S_{2} \rightarrow {}^{5}I_{7}$ transitions of the Ho³⁺ ions, respectively [36–38]. The increase in the Yb³⁺ concentration strongly enhanced the green emission. The maximal enhancement of green (${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ and ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$) emission was reached at $y = 0.05 \text{ Yb}^{3+}$ concentration, while, for higher concentrations, the emission intensity was then quenched, whereas the maximal enhancement of the red (${}^{5}F_{5} \rightarrow {}^{5}I_{8}$) and NIR emission (${}^{5}S_{2} \rightarrow {}^{5}I_{7}$) occurred at y = 0.1 Yb³⁺ concentration, as shown in Figure 6b. The reduction in UC intensity is attributed to a self-quenching effect [39,40]. It is known that the Yb³⁺ ion serves as a sensitizer of the Ho³⁺ ion in the UC emission, and thus, the Yb³⁺ ion efficiently transfers its energy to the Ho³⁺ ion [33]. According to the up-conversion process, the optimal concentrations of green $({}^{5}S_{2} \rightarrow {}^{5}I_{8})$ and NIR $({}^{5}S_{2} \rightarrow {}^{5}I_{7})$ luminescence should be the same as these two transitions have the same initial level ${}^{5}S_{2}$. The reason behind the different optimal concentrations between these transitions is still unclear, therefore, further analysis is needed to obtain reliable conclusions. Pandey et al. [16] reported that Yb³⁺ co-doping enhances the intensity of UC emission. It was reported that green emission was enhanced by nearly ~290 times and red by approximately ~150 times. The Gd₂O₃:Ho³⁺, Yb³⁺ phosphor exhibited a strong green emission alongside additional UC emission bands [7].



Figure 6. (a) UC emission spectra of $Y_{2-x-y}O_3$: Ho_{x=0.005}, Yb_y powders and (b) green (${}^5S_2 \rightarrow {}^5I_8$), red (${}^5F_5 \rightarrow {}^5I_8$), and NIR (${}^5S_2 \rightarrow {}^5I_7$) emission intensity peak as a function of y.

The UC emission normally occurs through UC ET from the Yb³⁺ to the Ho³⁺ ones. The decay curves were acquired to further confirm the UC between the Yb³⁺–Ho³⁺ pair. Figure 7 displays the luminescence decay curves of the ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ transition (situated at 550 nm) recorded under the 980 nm excitation, where the intensity is plotted versus time. All the luminescence decay curves were fitted with a double exponential function [28]:

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$
(3)

where *I* is the intensity at time *t*, A_1 and A_2 are fitting constants, and τ_1 and τ_2 are the lifetimes. The average lifetimes (τ_{ave}) were determined using $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. The ⁵S₂ level's lifetime decreased as the Yb³⁺ concentration increased up to y = 0.05, but did not decrease further for higher doping concentrations, as presented in Figure 7b and Table 2. The decrease in the lifetime corresponds to the UC luminescence intensity improvement, which appears to indicate that it might be related to an efficient ET from Yb³⁺ to Ho³⁺. The trend in the lifetime for concentrations above y = 0.05 may be related to a self-quenching effect, as shown in Figure 6b.



Figure 7. (a) The fitted decay curves of Ho^{3+} , Yb^{3+} co-doped Y_2O_3 phosphors for different concentrations of the Yb^{3+} ions under the 980 nm excitation and (b) lifetime as a function of y.

Sample	Average Lifetime (µs)		
Y _{2-x} O ₃ :Ho _{x=0.005}	254		
$Y_{2-x-y}O_3$:Ho _{x=0.005} , Yb _{y=0.002}	241		
$Y_{2-x-y}O_3$:Ho _{x=0.005} , Yb _{y=0.006}	226		
$Y_{2-x-y}O_3$:Ho _{x=0.005} , Yb _{y=0.01}	223		
$Y_{2-x-y}O_3$:Ho _{x=0.005} , Yb _{y=0.05}	92		
$Y_{2-x-y}O_3$:Ho _{x=0.005} , Yb _{y=0.1}	99		
$Y_{2-x-y}O_3$:Ho _{x=0.005} , Yb _{y=0.2}	121		

Table 2. The lifetime of the ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ transition of the Ho³⁺ ion of the Y_{2-x-y}O₃:Ho_{x=0.005}, Yb_y at different Yb³⁺ concentration.

The relation of UC emission intensity to the laser power for the co-doped phosphor was investigated to determine the number of excitation photons needed for each emission photon. Figure 8a represents the emission spectra of $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.05} as a function of the laser power. The UC intensity continuously increased with laser power. The increase in laser power did not affect the peak position but enhanced the UC emission intensity for each of the observed bands (Figure 8b). The UC emission intensity relationship to laser power is modelled using the I αP^n [41] relation, where I, P, and n are the UC emission intensity, pump power, and the number of pump photons involved in the UC emission process, respectively. Figure 8c represents the ln(power) versus ln(intensity). These plots give straight lines with slopes (*n* values) of 1.69, 1.88, and 1.92 for green (536 and 550 nm) and red (668 nm) emissions, respectively. According to the energy level diagram (see Figure 9), 536 and 550 nm peaks (${}^{5}F_{4}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$) and 756 nm peak (${}^{5}S_{2} \rightarrow {}^{5}I_{7}$) result from the same populated levels (${}^{5}F_{4}$, ${}^{5}S_{2}$) of Ho³⁺, and therefore, they have nearly same slopes. Pandey et al., [16] found *n* values of 2.28 and 1.91 for the green (550 nm) and red (668 nm) emissions. All the slope values are close to two, indicating the involvement of two NIR photons in all of the emission bands.

The energy transfer (ET) mechanism of the UC in the Ho^{3+} , Yb^{3+} : Y_2O_3 powders is illustrated in Figure 9. The Yb³⁺ ion is excited from the ground state ${}^{2}F_{7/2}$ to the excited state ${}^{2}F_{5/2}$ through the 980 nm excitation. The absorbed energy is then transferred via a non-radiative resonance ET to the nearby Ho³⁺ ion, exciting an electron from the ⁵I₈ ground state to the ${}^{5}I_{6}$ excited level. The excited ions in the ${}^{5}I_{6}$ level are further excited to the ${}^{5}S_{2}$, ${}^{5}F_{4}$ level of the Ho³⁺ ion through energy transfer up-conversion (ETU). The populated ${}^{5}S_{2}$, ${}^{5}F_{4}$ levels relax to the ${}^{5}I_{8}$ and ${}^{5}I_{7}$ states radiatively and result in green emissions at 536 and 550 nm through the ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ transitions, and NIR emission at 756 nm through the ${}^{5}S_{2} \rightarrow {}^{5}I_{7}$ transitions. Moreover, the relaxation process from the ${}^{5}S_{2}$, ${}^{5}F_{4}$ level may populate the ${}^{5}F_{5}$ level via non-radiative multiphonon relaxation and result in a red emission at 668 nm through the radiative ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transition [42,43]. The UC emission can also take place through cooperative energy transfer (CET) between two Yb³⁺ ions and one Ho³⁺ ion. The ${}^{5}F_{4}$, ${}^{5}S_{2}$ excited states of Ho³⁺ ions are situated twice of that Yb³⁺: ${}^{2}F_{5/2}$ excited state. In this case, two Yb³⁺ ions can transfer their energy cooperatively to one Ho³⁺ ion in the ground state in which the Ho³⁺ ion is promoted to the ${}^{5}F_{4}$ and ${}^{5}S_{2}$ excited states. All these emissions are two-photon processes.



Figure 8. (a) Variation in the UC emission intensity of the $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.05} as a function of laser power, (b) power dependences of the UC intensities for various bands, and (c) dependences of peak intensity of the green and red UC emissions as a function of pump power.



Figure 9. UC energy level mechanism in the Ho^{3+} , Yb^{3+} : Y_2O_3 nanophosphor powders.

3.4. Optical Temperature Sensing

To study the properties of optical temperature sensing of the sample, the temperaturedependent UC was analysed using the FIR technique. Figure 10a shows the temperaturedependent UC spectra of the $Y_{2-x-y}O_3$: Ho_{x=0.005}, Yb_{y=0.05} phosphor, with the most intense green emission centred at 550 nm associated with the ${}^5S_2 \rightarrow {}^5I_8$ transition of the Ho³⁺ ion. For all the UC emission bands, no significant shift in wavelength position was observed from room temperature up to 623 K. It is also evident that as the temperature rises, thermal quenching causes all the bands to progressively lose their intensity (Figure 10b).

Figure 11 presents the temperature dependence of the I_{536}/I_{668} , I_{550}/I_{668} and $(I_{536}+I_{550})/I_{668}$ FIRs. Non-TCLs are often fitted by empirical functions due to the absence of quality physical models classifying temperature-dependences of the FIR parameters [44]. Therefore, FIR of the bands at 536, 550, and 668 nm can be fitted using the function:

$$FIR = \frac{I_2}{I_1} = B_0 + B_1 T + B_2 T^2 + B_3 T^3$$
(4)

where I_1 and I_2 are the integrated emission intensities, B_0 , B_1 , B_2 , B_3 are fitting constants, and T is the absolute temperature, respectively. The fitting data are included in Figure 11.

For temperature sensing, the relative sensitivity (S_R) and the absolute sensitivity (S_A) are two indispensable parameters which were calculated using the equations [45]

$$S_{A} = \frac{dFIR}{dT}$$
(5)

$$S_{\rm R} = \frac{1}{FIR} \left(\frac{dFIR}{dT} \right) \times 100\% \tag{6}$$



Figure 10. (a) UC emission of $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.05} at different temperatures, (b) UC intensity versus temperature.



Figure 11. FIR of I_{536}/I_{668} , I_{550}/I_{668} and $(I_{536}+I_{550})/I_{668}$ versus temperature.

Figure 12a,b shows the absolute and relative sensitivities versus temperature. As the temperature increased, both the absolute sensitivity and the relative sensitivity decreased. All the values reached maxima at 303 K. The maximum S_R values were determined to be 0.47 (I_{536}/I_{668}), 0.64 (I_{550}/I_{668}), and 0.59%K⁻¹ (($I_{536}+I_{550}$)/ I_{668}), respectively, while the S_A values were found to be 0.02 (I_{536}/I_{668}), 0.06 (($I_{536}+I_{550}$)/ I_{668}), and 0.08 K⁻¹ ((I_{550}/I_{668}), respectively. The ($I_{536}+I_{550}$)/ I_{668} FIR had the largest S_A , while I_{550}/I_{668} had the highest S_R values. The ${}^5F_5/{}^5F_4$, 5S_2 levels are non-thermally coupled energy levels, and thus, the temperature sensor sensitivity is substantially higher [21].

Table 3 compares the optical temperature sensing performance data of Ho, Yb codoped various UC hosts. From Table 3, in this work Ho, Yb:Y₂O₃ noticeably show better sensitivity results than other UC host materials. These results differ because other reported ones were acquired at different measuring temperature ranges and the hosts show a temperature-dependent nature. Different host materials could also make a difference in sensitivity due to the different properties of the hosts. Moreover, some studies report on temperature sensors that are based on ratiometric measurements of the sensing of the ${}^{3}K_{8} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$ transitions (blue band emissions), which are due to three photon UC processes, and they typically need much higher power of excitation [46,47]. Additionally, other studies focus on TCLs that use the ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ and ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ transitions in the two green bands, which may not be the best method for temperature monitoring since the bands are spectrally overlapped [48–50]. The difference in sensitivity results could also result due to the different experimental conditions of the Ho³⁺, Yb³⁺ co-doped UC host materials. Therefore, the Ho, Yb:Y₂O₃ phosphor used in this study represents a better optical temperature sensing option.



Figure 12. (a) Absolute sensitivity as a function of temperature and (b) relative sensitivity as a function of temperature.

Sample	Transitions	Temp Range (K)	Max S_A (K ⁻¹)	Max S _R (%K ⁻¹)	Ref.
Ho, Yb: Y ₂ O ₃	${}^{5}F_{4}, {}^{5}S_{2} \rightarrow {}^{5}I_{8}, {}^{5}F_{5} \rightarrow {}^{5}I_{8} \\ {}^{5}S_{2} \rightarrow {}^{5}I_{8}, {}^{5}F_{5} \rightarrow {}^{5}I_{8}$	303–623	0.08	- 0.64	This work
Ho, Yb: LuYO ₃	${}^5F_4, {}^5S_2 \to {}^5I_8, {}^5F_5 \to {}^5I_8$	298–578	0.1603	0.0102	[24]
Ho, Yb: NaLuF ₄	${}^{5}F_{2,3}, {}^{5}K_{8} \rightarrow {}^{5}I_{8}, {}^{5}G_{6}, {}^{5}F_{1} \rightarrow {}^{5}I_{8}$	390–780	0.0008	0.83	[46]
Ho, Yb: CaWO ₄	${}^{5}F_{2,3}, {}^{5}K_{8} \rightarrow {}^{5}I_{8}, {}^{5}G_{6}, {}^{5}F_{1} \rightarrow {}^{5}I_{8}$	303–923	0.0050	0.28	[47]
Ho, Yb: NaYF ₄	${}^{5}F_{4},{}^{5}S_{2}^{5}I_{8}$	313–393	0.0038	0.7230	[48]
Ho, Yb: Y_2O_3	${}^{5}F_{4},{}^{5}S_{2}^{5}I_{8}$	293–563	0.0071	-	[49]
Ho, Yb: Y_2O_3	${}^{5}F_{4}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$	348–598	0.013	0.622	[50]
Ho, Yb: Y ₂ O ₃	${}^{5}F_{4}, {}^{5}S_{2} \rightarrow {}^{5}I_{8}, {}^{5}S_{2}, {}^{5}F_{4} \rightarrow {}^{5}I_{7}$	0–300	0.0097	1.90	[51]

Table 3. Maximal S_A and S_R values of different Ho³⁺, Yb³⁺ co-doped UC hosts.

To further study the efficiency of the optical high temperature sensor, the temperature resolution or uncertainty (δT) associated with *FIRs* used was calculated as described in [52]:

$$\delta T = \frac{1}{S_R} \frac{\delta FIR}{FIR} \tag{7}$$

 δFIR represents the resolution/uncertainty of the FIR value. The temperature uncertainty (δT) depends on the signal-to-noise ratio of the emission spectra and relative sensitivity (S_R) [53]. The best temperature uncertainty determined at 303 K was for I_{536}/I_{668} *FIR*, i.e., $\delta T = 0.71$ K. For other *FIRs*, temperature uncertainty values were determined to be 0.51 K for I_{550}/I_{668} and 0.57 K for $(I_{536} + I_{550})/I_{668}$ at the same temperature, Figure 13. The temperature uncertainty at this temperature can be used for biological research [54]. As the temperature increased to 623 K, the temperature uncertainty reached maximum values at 7.61, 0.70, and 1.08 K for I_{536}/I_{668} , I_{550}/I_{668} and $(I_{536} + I_{550})/I_{668}$, respectively. The temperature uncertainty at 623 K results in sufficient optical temperature sensing. Moreover, such temperature uncertainty at high temperature could be potentially used in industrial applications, especially for processes which require high temperature conditions as well as other fields, i.e., submicron-scale resolution [44]. Moreover, stability and repeatability for optical temperature sensing are also important factors. Therefore, several heating-cooling cycling experiments were performed on the $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.05} phosphor to verify the repeatability of the synthesized material, Figure 14a–c. This was achieved by studying the FIR changes in the I_{536}/I_{668} , I_{550}/I_{668} , and $(I_{536} + I_{550})/I_{668}$ at 303 and 623 K, respectively. The deviation percentage of the FIR in the repeatability experiment was found to be 1.19%, 3.49%, and 3.25% for I_{536}/I_{668} , I_{550}/I_{668} , and $(I_{536} + I_{550})/I_{668}$, respectively. After 10 heating-cooling repeated cycles, the FIR values showed no obvious difference and could be reversed and repeated. These results indicate that the FIR based on non-TCLs own good stability, indicating that $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.05} phosphor has good signal reproducibility and is a capable candidate for optical temperature sensing.



Figure 13. Temperature uncertainty versus the temperature of the $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.05} phosphor.



Figure 14. Cont.



Figure 14. Repeatability test of (a) I_{536}/I_{668} , (b) I_{550}/I_{668} , and (c) $(I_{536} + I_{550})/I_{668}$ measured by alternating the temperature between 303 and 623 K.

4. Conclusions

The UC intensity and optical thermometry characteristics of Y_2O_3 :Ho³⁺, Yb³⁺ were investigated. The XRPD results confirmed the cubic structure of Y_2O_3 in space group Ia $\overline{3}$. The Yb³⁺ concentration did not change the agglomerated spherical nanoparticles morphology of the samples. From the diffuse reflectance spectra, the band gap decreased with increasing Yb³⁺ concentration. Under the 980 nm excitation wavelength, the UC luminescence showed four emission bands at 536, 550, 668, and 756 nm, assigned to the ${}^{5}F_4 \rightarrow {}^{5}I_8, {}^{5}S_2 \rightarrow {}^{5}I_8, {}^{5}F_5 \rightarrow {}^{5}I_8$, and ${}^{5}S_2 \rightarrow {}^{5}I_7$ transitions of the Ho³⁺ ions, respectively. The UC intensity had increased to a maximum value at y = 0.05 Yb³⁺ concentration. The UC process is ruled by a two-photon absorption process. The UC lifetime of the green emission

 $({}^5S_2 \rightarrow {}^5I_8)$ confirmed that the ET between the Yb^{3+} and Ho^{3+} plays a major role in the UC process. The optical temperature sensing behaviour was studied at a temperatures range of 303 K–623 K. The maximum absolute and relative sensitivity values were $S_A = 0.08 \ K^{-1}$ and $S_R = 0.64\% \ K^{-1}$, respectively. The results reveal that $Y_{2-x-y}O_3$:Ho_{x=0.005}, Yb_{y=0.05} is useful for optical high temperature sensors.

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References

- Mun, J.H.; Jouini, A.; Novoselov, A.; Yoshikawa, A.; Fukuda, T. Crystal growth and thermal conductivity of an Tm³⁺-doped Y₂O₃ for IR eye-safe laser. J. Ceram. Process Res. 2011, 12, 169–172.
- Mader, H.S.; Kele, P.; Saleh, S.M.; Wolfbeis, O.S. Upconverting luminescent nanoparticles for use in bioconjugation and bioimaging. *Curr. Opin. Chem. Biol.* 2010, 14, 582–596. [CrossRef]
- Le Toquin, R.; Cheetham, A. Red-emitting cerium-based phosphor materials for solid-state lighting applications. *Chem. Phys. Lett.* 2006, 423, 352–356. [CrossRef]
- 4. Wade, S.A.; Collins, S.F.; Baxter, G.W. Fluorescence intensity ratio technique for optical fiber point temperature sensing. *J. Appl. Phys.* **2003**, *94*, 4743–4756. [CrossRef]
- Fischer, S.; Goldschmidt, J.C.; Loper, P.; Bauer, G.H.; Bruggemann, R.; Kramer, K.; Biner, D.; Hermle, M.; Glunz, S.W. Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization. J. Appl. Phys. 2010, 108, 0044912. [CrossRef]
- 6. Ye, S.; Xiao, F.; Pan, Y.; Ma, Y.; Zhang, Q. Phosphors in phosphor-converted white light-emitting diodes: Recent advances in materials, techniques and properties. *Mater. Sci. Eng. R Rep.* **2010**, *71*, 1–34. [CrossRef]
- 7. Dwivedi, Y.; Bahadur, A.; Rai, S.B. Optical avalanche in Ho:Yb:Gd₂O₃ nanocrystals. J. Appl. Phys. 2011, 110, 043103. [CrossRef]
- 8. Luo, X.-X.; Cao, W.-H. Upconversion luminescence of holmium and ytterbium co-doped yttrium oxysulfide phosphor. *Mater. Lett.* **2007**, *61*, 3696–3700. [CrossRef]
- Lim, C.S.; Aleksandrovsky, A.; Molokeev, M.; Oreshonkov, A.; Atuchin, V. Microwavesol–gel synthesis and upconversion photoluminescence properties of CaGd₂(WO₄)₄:Er³⁺/Yb³⁺ phosphors with incommensurately modulated structure. *J. Solid State. Chem.* 2015, 228, 160–166. [CrossRef]
- Lim, C.S.; Aleksandrovsky, A.; Molokeev, M.; Oreshonkov, A.; Atuchin, V. Structural and Spectroscopic Effects of Li+ Substitution for Na+ in Li_xNa_{1-x}CaGd_{0.5}Ho_{0.05}Yb_{0.45}(MoO₄)₃ Scheelite-Type Upconversion Phosphors. *Molecules* 2021, 26, 7357. [CrossRef] [PubMed]
- 11. Sangeetha, N.M.; van Veggel, F.C.J.M. Lanthanum Silicate and Lanthanum Zirconate Nanoparticles Co-Doped with Ho³⁺ and Yb³⁺: Matrix-Dependent Red and Green Upconversion Emissions. *J. Phys. Chem. C* **2009**, *113*, 14702–14707. [CrossRef]
- 12. Jackson, S.; Li, Y. High-power broadly tunable Ho³⁺-doped silica fibre laser. *Electron. Lett.* 2004, 40, 1474–1475. [CrossRef]
- An, N.; Ye, L.; Bao, R.; Yue, L.; Wang, L. Up-conversion luminescence characteristics and temperature sensing of Y₂O₃: Ho³⁺/Yb³⁺ single crystal fiber. *J. Lumin.* 2019, 215, 116657. [CrossRef]

- 14. Singh, V.; Rai, V.K.; Ledoux-Rak, I.; Watanabe, S.; Rao, T.K.G.; Chubaci, J.F.D.; Badie, L.; Pelle, F.; Ivanova, S. NIR to visible up-conversion, infrared luminescence, thermoluminescence and defect centres in Y₂O₃: Er phosphor. *J. Phys D Appl. Phys.* **2009**, 42, 065104. [CrossRef]
- 15. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* **1976**, *32*, 751–766. [CrossRef]
- Pandey, A.; Rai, V.K.; Dey, R.; Kumar, K. Enriched green upconversion emission in combustion synthesized Y₂O₃:Ho³⁺–Yb³⁺ phosphor. *Mater. Chem. Phys.* 2013, 139, 483–488. [CrossRef]
- 17. Wei, X.; Li, Y.; Cheng, X.; Chen, Y.; Yin, M. Strong dependence of upconversion luminescence on doping concentration in holmium and ytterbium co-doped Y₂O₃ phosphor. *J. Rare Earths* **2011**, *29*, 536–539. [CrossRef]
- Wang, X.; Liu, Q.; Bu, Y.; Liu, C.-S.; Liu, T.; Yan, X. Optical temperature sensing of rare-earth ion doped phosphors. *RSC Adv.* 2015, 5, 86219–86236. [CrossRef]
- 19. Tian, Y.Y.; Tian, Y.; Huang, P. Eu³⁺:Gd₂O₃ nanocomposites for highly sensitive optical thermometry through the synergistic luminescence from lanthanide-transition metal ions. *Chem. Eng. J.* **2016**, *297*, 26–34. [CrossRef]
- Kumar, V.; Zoellner, B.; Maggard, P.A.; Wang, G. Effect of doping Ge into Y₂O₃:Ho,Yb on the green-to-red emission ratio and temperature sensing. *Dalton Trans.* 2018, 47, 11158–11165. [CrossRef]
- 21. Zhang, J.; Zhang, Y.Q.; Jiang, X.M. Investigations on upconversion luminescence of K₃Y(PO₄)₂:Yb³⁺-Er³⁺/Ho³⁺/Tm³⁺ phosphors for optical temperature sensing. *J. Alloys Compd.* **2018**, *748*, 438–445. [CrossRef]
- 22. Zhang, J.; Ji, B.; Chen, G.; Hua, Z. Upconversion Luminescence and Discussion of Sensitivity Improvement for Optical Temperature Sensing Application. *Inorg. Chem.* 2018, *57*, 5038–5047. [CrossRef]
- Ge, H.Q.; Zhang, J. Investigation on luminescence properties of BaY₂Si₃O₁₀:Er³⁺/Ho³⁺–Yb³⁺ for optical temperature sensing. J. Mater. Sci. Mater. Electron. 2018, 29, 20033–20039. [CrossRef]
- 24. Wang, S.; Zhu, K.; Wang, T.; Zhou, H.; Zhang, N.; Zhang, J.; Ye, L.; Jia, Z.; Tao, X. Sensitive Ho³⁺, Yb³⁺ co-doped mixed sesquioxide single crystal fibers thermometry based on upconversion luminescence. *J. Alloys Compd.* **2021**, *891*, 162062. [CrossRef]
- Khan, S.; Park, B.-I.; Han, J.S.; Lee, S.Y.; Cho, S.-H. Flame synthesized Y₂O₃:Tb³⁺–Yb³⁺ phosphors as spectral convertors for solar cells. *Res. Chem. Intermed.* 2018, 44, 4619–4632. [CrossRef]
- 26. Yang, M.; Sui, Y.; Wang, S.; Wang, X.; Wang, Y.; Lü, S.; Zhang, Z.; Liu, Z.; Lü, T.; Liu, W. Effects of Bi³⁺ doping on the optical properties of Er³⁺:Y₂O₃. *J. Alloys Compd.* **2011**, *509*, 827–830. [CrossRef]
- 27. Singh, V.; Rai, V.K.; Voss, B.; Haase, M.; Chakradhar, R.; Naidu, D.T.; Kim, S.H. Photoluminescence study of nanocrystalline Y₂O₃:Ho³⁺ phosphor. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2013**, *109*, 206–212. [CrossRef] [PubMed]
- 28. Guo, L.; Wang, Y.; Zhang, J.; Wang, Y.; Dong, P. Near-infrared quantum cutting in Ho³⁺, Yb³⁺-codoped BaGdF₅ nanoparticles via first-and second-order energy transfers. *Nanoscale Res. Lett.* **2012**, *7*, 636. [CrossRef] [PubMed]
- 29. Som, S.; Sharma, S.K.; Shripathi, T. Influences of Doping and Annealing on the Structural and Photoluminescence Properties of Y₂O₃ Nanophosphors. *J. Fluoresc.* **2013**, *23*, 439–450. [CrossRef]
- 30. Dejene, F.; Ali, A.; Swart, H.; Botha, R.; Roro, K.; Coetsee, L.; Biggs, M. Optical properties of ZnO nanoparticles synthesized by varying the sodium hydroxide to zinc acetate molar ratios using a Sol-Gel process. *Open Phys.* **2011**, *9*, 1321–1326. [CrossRef]
- 31. Atuchin, V.; Isaenko, L.; Kesler, V.; Lin, Z.; Molokeev, M.; Yelisseyev, A.; Zhurkov, S. Exploration on anion ordering, optical properties and electronic structure in K₃WO₃F₃ elpasolite. *J. Solid State Chem.* **2012**, *187*, 159–164. [CrossRef]
- Reshak, A.H.; Alahmed, Z.A.; Bila, J.; Atuchin, V.V.; Bazarov, B.G.; Chimitova, O.D.; Molokeev, M.S.; Prosvirin, I.P.; Yelisseyev, A.P. Exploration of the Electronic Structure of Monoclinic α-Eu₂(MoO₄)₃: DFT-Based Study and X-ray Photoelectron Spectroscopy. J. Phys. Chem. C 2016, 120, 10559–10568. [CrossRef]
- Jones, S.L.; Kumar, D.; Singh, R.K.; Holloway, P.H. Luminescence of pulsed laser deposited Eu doped yttrium oxide films. *Appl. Phys. Lett.* 1997, 71, 404–406. [CrossRef]
- Nunes, D.; Pimentel, A.; Matias, M.; Freire, T.; Araújo, A.; Silva, F.; Gaspar, P.; Garcia, S.; Carvalho, P.A.; Fortunato, E.; et al. Tailoring Upconversion and Morphology of Yb/Eu Doped Y₂O₃ Nanostructures by Acid Composition Mediation. *Nanomaterials* 2019, 9, 234. [CrossRef] [PubMed]
- Cabello-Guzmán, G.; González, D.; Caro-Díaz, C.; Lillo-Arroyo, L.; Valenzuela-Melgarejo, F.; Triviño, G.C.; Buo-no-Core, G.E.; Chornik, B.; Huentupil, Y. Preliminary evaluation of the up-conversion emission of Y₂O₃:Er-Yb thin films prepared by a solid state photochemical deposition method. *J. Lumin.* 2018, 204, 401–409. [CrossRef]
- 36. Ryba-Romanowski, W.; Golab, S.; Dominiak-Dzik, G.; Solarz, P.; Lukasiewicz, T. Conversion of infrared radiation into red emission in YVO₄:Yb,Ho. *Appl. Phys. Lett.* **2001**, *79*, 3026–3028. [CrossRef]
- Lim, C.S.; Aleksandrovsky, A.; Molokeev, M.; Oreshonkov, A.; Atuchin, V. The modulated structure and frequency upconversion properties of CaLa₂ (MoO₄)₄:Ho³⁺/Yb³⁺ phosphors prepared by microwave synthesis. *Phys. Chem. Chem. Phys.* 2015, 17, 19278–19287. [CrossRef]
- Lim, C.S.; Aleksandrovsky, A.; Molokeev, M.; Oreshonkov, A.; Atuchin, V. Microwave-Employed Sol–Gel Synthesis of Scheelite-Type Microcrystalline AgGd (MoO₄)₂:Yb³⁺/Ho³⁺ Upconversion Yellow Phosphors and Their Spectroscopic Properties. *Crystals* 2020, 10, 1000.
- Xiang, G.; Ma, Y.; Liu, W.; Jiang, S.; Luo, X.; Zhou, L.L.; Gu, Z.; Wang, J.; Luo, Y.; Zhang, Y.J. Improvement of Green Upconversion Monochromaticity by Doping Eu³⁺ in Lu₂O₃:Yb³⁺/Ho³⁺ Powders with Detailed Investigation of the Energy Transfer Mechanism. *Inorg. Chem.* 2017, *56*, 9194–9199. [CrossRef]

- Dan, H.K.; Zhou, D.C.; Wang, R.F.; Jiao, Q.; Yang, Z.W.; Song, Z.G.; Yu, X.; Qiu, J.B. Energy transfer and upconversion emission of Tm³⁺/Tb³⁺/Yb³⁺ co-doped transparent glass-ceramics containing Ba₂LaF₇ nanocrystals. *J. Non-Cryst. Solids* 2013, 378, 181–185. [CrossRef]
- 41. Li, J.-G.; Wang, X.; Liu, W.; Zhu, Q.; Li, X.; Sun, X. (La_{0.97}RE_{0.01}Yb_{0.02})₂O₂S Nanophosphors Converted from Layered Hydroxyl Sulfate and Investigation of Upconversion Photoluminescence (RE=Ho, Er). *Nanoscale Res. Lett.* **2017**, *12*, 508. [CrossRef]
- An, L.; Zhang, J.; Liu, M.; Wang, S. Up-conversion properties of Yb³⁺, Ho³⁺: Lu₂O₃ sintered ceramic. J. Lumin. 2007, 122–123, 125–127. [CrossRef]
- 43. Kir'yanov, A.; Aboites, V.; Belovolov, A.; Damzen, M.; Minassian, A.; Timoshechkin, M.; Belovolov, M. Visible-to-near-IR luminescence at stepwise up-conversion in Yb,Ho:GGG under IR diode pumping. J. Lumin. 2003, 102–103, 715–721. [CrossRef]
- Runowski, M.; Woz, P.; Stopikowska, N.; Martín, I.R.; Lavín, V.; Lis, S. Optical pressure sensing in vacuum and high-pressure ranges using lanthanide-based luminescent thermometer–manometer. ASC Appl. Mater. Interfaces 2020, 12, 43933–43941. [CrossRef]
- Piotrowski, W.; Trejgis, K.; Maciejewska, K.; Ledwa, K.; Fond, B.; Marciniak, L. Thermochromic Luminescent Nanomaterials Based on Mn⁴⁺/Tb³⁺ Codoping for Temperature Imaging with Digital Cameras. ACS Appl. Mater. Interfaces 2020, 12, 44039–44048. [CrossRef] [PubMed]
- Zhou, S.; Jiang, S.; Wei, X.; Chen, Y.; Duan, C.; Yin, M. Optical thermometry based on upconversion luminescence in Yb³⁺/Ho³⁺ co-doped NaLuF₄. J. Alloys Compd. 2014, 588, 654–657. [CrossRef]
- Xu, W.; Zhao, H.; Li, Y.; Zheng, L.; Zhang, Z.; Cao, W. Optical temperature sensing through the upconversion luminescence from Ho³⁺/Yb³⁺ codoped CaWO₄. Sens. Actuators B Chem. 2013, 188, 1096–1110. [CrossRef]
- Singh, P.; Yadav, R.S.; Singh, P.; Rai, S.B. Upconversion and downshifting emissions of Ho³⁺-Yb³⁺ co-doped ATiO₃ perovskite phosphors with temperature sensing properties in Ho³⁺-Yb³⁺ co-doped BaTiO₃ phosphor. *J. Alloys Compd.* 2021, *855*, 157452. [CrossRef]
- 49. Zhou, J.; Chen, Y.; Lei, R.; Wang, H.; Zhu, Q.; Wang, X.; Wu, Y.; Yang, Q.; Xu, S. Excellent photoluminescence and temperature sensing properties in Ho³⁺/Yb³⁺ codoped (Y_{0.88}La_{0.09}Zr_{0.03})₂O₃ transparent ceramics. *Ceram. Int.* **2019**, *45*, 7696–7702. [CrossRef]
- Hu, S.; Yuan, M.; Huang, H.; Song, C.; Han, K.; Cui, W.; Yang, Z.; Wang, H. Effect of Ce dopant on upconversion and temperature sensing performances in homogeneous ultrasmall Y₂O₃:Yb³⁺/Ho³⁺ nanoparticles through flame aerosol synthesis. *Ceram. Int.* 2013, 49, 10953–10960. [CrossRef]
- 51. Lojpur, V.; Nikolic, M.; Mancic, L.; Milosevic, O.; Dramicanin, M.D. Y₂O₃:Yb,Tm and Y₂O₃:Yb,Ho powders for low-temperature thermometry based on up-conversion fluorescence. *Ceram. Int.* **2013**, *39*, 1129–1134. [CrossRef]
- 52. Saidi, K.; Chaabani, W.; Dammak, M. Highly sensitive optical temperature sensing based on pump-power-dependent upconversion luminescence in LiZnPO₄:Yb³⁺–Er³⁺/Ho³⁺ phosphors. *RSC Adv.* **2021**, *11*, 30926–30936. [CrossRef] [PubMed]
- Saidi, K.; Dammak, M.; Carracedo, K.S.; Martínb, I.R. A novel optical thermometry strategy based on emission of Tm³⁺/Yb³⁺ codoped Na₃GdV₂O₈ phosphors. *Dalton Trans.* 2022, *51*, 5108–5117. [CrossRef]
- Stopikowska, N.; Runowski, M.; Wo'zny, P.; Goderski, S.; Lis, S. Improving temperature resolution of luminescent nanothermometers working in the near-infrared range using non-thermally coupled levels of Yb³⁺ & Tm³⁺. J. Lumin. 2020, 228, 117643.

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