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# Comparative Upconversion Emission Study of $XWO_4:Ho^{3+}$-$Yb^{3+}$ (X= Ba, Ca, Sr) Phosphors

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**Abstract**
The present research article explains the upconversion emission behaviour of $Ho^{3+}$-$Yb^{3+}$ codoped $XWO_4$ (X = Ba, Ca, Sr) phosphors synthesized using a solid-state reaction technique. The phase formation and structural study were confirmed through X-ray diffraction and Scanning electron microscopy analysis. The role of different host matrix on the upconversion emission spectra have been recorded by 980 nm excitation. The comparison of upconversion emission of $Ho^{3+}$-$Yb^{3+}$ codoped $XWO_4$ (X = Ba, Ca, Sr) phosphors was studied. A two-photon absorption process is proposed to achieve the observed upconversion emission via a suitable energy level structure.

**Keywords-** Tungstate host, Holmium-Ytterbium, Upconversion emission, Energy level diagram.

## 1. Introduction

Rare earths (REs) ion activated phosphor materials have been examined for decades due to their versatile applications. Oxide hosts are one of the key interests among researchers nowadays beside halides and sulphides, owing to their low toxic nature, high temperature and chemical stability, low phonon frequency, that lead to their good optical emission (Pandey et al., 2018). Lanthanides doped/codoped tungstate materials attracted attention due to the presence of the $WO_4^{2-}$ tetrahedron structure, and the efficient energy transfer to localized states of the incorporated lanthanides (Maheshwary et al., 2014). A

higher absorption coefficient and refractive index display better optical emission from the REs activated tungstate hosts, and strengthen the utility in several applications such as lasers, solar cells, catalysts, and optical fibers (Kim et al., 2014; Nithya and Roumana, 2020; Abubakar et al., 2022; Wu et al., 2022).

Maheshwary et al. (2014) reported on the structural and luminescence property of $Eu^{3+}$ doped $SrWO_4$ phosphor synthesized successfully at low temperature by polyol method under urea hydrolysis. They reported that photoluminescence properties of $Eu^{3+}$ doped $SrWO_4$ phosphor were due to the defects in $WO_4^{2-}$ tetrahedron groups. These nanophosphors can be used as a potential candidate in white LEDs due to the strong red emission in visible part. The influence of Li on the upconversion (UC) emissions of the Er-Yb codoped $ABO_4$ (A= Ca, Sr; B= W, Mo) phosphors was studied by Kim et al. (2014). Kang et al. (2013) investigated the optical properties of $Eu^{3+}$ activated $MWO_4$ (M= Ca, Ba, Sr) phosphors. In a previous study (Ding et al., 2015; Pandey et al., 2021) our group reported on the UC emission from Er-Yb codoped $SrWO_4$ phosphor and thin films. Recently, Liu et al. (2021) investigated UC emission from Ho/Er-Yb codoped $SrWO_4$ phosphors. The UC study of Ho/Tm-Yb codoped $CaWO_4$ phosphors was also reported by Hyan et al. (2014). Hydrothermal assisted Ho activated UC phosphor was prepared and studied by Dey et al. (2019). But no report on the comparison of the UC emissions from Ho-Yb codoped $XWO_4$ (X= Ba, Ca, Sr) phosphors were reported. So that, comparison of UC emission study of $Ho^{3+}$-$Yb^{3+}$ doped $XWO_4$ (X= Ba, Ca, Sr) phosphors are reported in this work. The structural and morphological analysis of Ho-Yb codoped $XWO_4$ (X= Ba, Ca, Sr) are also investigated.

## 2. Experimental Details

### 2.1 Material Preparation

The $XWO_4$ (X= Ba, Ca, Sr) codoped $Ho^{3+}$-$Yb^{3+}$ phosphors were prepared by a high temperature solid state reaction method (Pandey et al., 2015). A mixture containing analytical grade $WO_3$ and $BaO/CaO/SrCO_3$ with 0.2 mol% $Ho_2O_3$ and 3.0 mol% $Yb_2O_3$ oxide materials were mixed in a mortar and grinded about 2 h using acetone as a mixing medium. The prepared fine powders were kept into an alumina crucible and preheated at $800^0$C for 4 h in a furnace and then further heat treated at $1200^0$C for 4 h in an air medium. Finally, the formed phosphors were ground into a fine powder form and used for further optical and structural characterizations.

### 2.2 Characterization

The X-ray diffraction (XRD) patterns were measured using a Bruker-D8 Advance X-ray diffractometer with a Cu-$K_\alpha$ radiation ($\lambda$= 0.154 nm) in the 10 to 80 degree range to identify the phase formation and crystalline nature of the phosphors. Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS) images were recorded by using a JSM-7800F extreme-resolution analytical field emission scanning electron microscope (FESEM). The UC emission results for $Ho^{3+}$-$Yb^{3+}$ doped $XWO_4$ were recorded using a Horiba iHR-320 monochromator with a power tunable fiber coupled 980 nm diode laser with a 3 W power limit.

## 3. Results and Discussions

### 3.1 Structural Analysis

The XRD results measured from different samples of $Ho^{3+}$-$Yb^{3+}$ doped $XWO_4$ (X= Ba, Ca, Sr) phosphors heat treated at $1200^o$C is shown in Figure 1. The observed peaks matched with the standard JCPDS files. The $BaWO_4:Ho^{3+}$-$Yb^{3+}$ peaks indexed well with the tetragonal structured $BaWO_4$ through the JCPDS File No. 43-0646 (Liu et al., 2021). On the other hand, the JCPDS File No. 41-1431 of pure tetragonal $CaWO_4$ was matched for the $CaWO_4:Ho^{3+}$-$Yb^{3+}$ sample (Kim et al., 2014; Liu et al., 2021). $SrWO_4:Ho^{3+}$-$Yb^{3+}$ peaks were also identified as the tetragonal $SrWO_4$ pattern when compared with the JCPDS File No. 08-

0449 (Ding et al., 2015; Pandey et al., 2021). In all three cases, it is concluded that pure tetragonal phases were obtained with a suitable doping of $Ho^{3+}$-$Yb^{3+}$ ions.

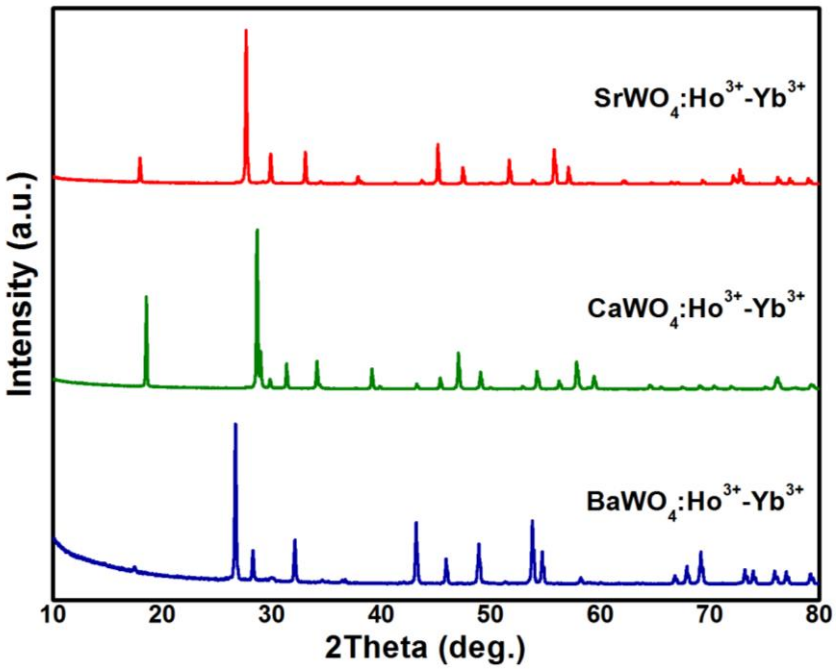


**Figure 1.** X-ray diffraction pattern of the $Ho^{3+}$-$Yb^{3+}$ codoped $XWO_4$ (X = Ba, Ca, Sr) phosphors.

### 3.2 SEM-EDS Analysis

Figure 2 shows the SEM and corresponding EDS images of the prepared phosphors in the 1 µm scale bars, respectively. The SEM images display agglomerated grains in case of the $SrWO_4:Ho^{3+}$-$Yb^{3+}$ (Figure 2 (a)) and the $BaWO_4:Ho^{3+}$-$Yb^{3+}$ (Figure 2 (c)) phosphors whereas well-arranged distribution of grains throughout the surface were found in case of the $CaWO_4:Ho^{3+}$-$Yb^{3+}$ phosphor (Figure 2 (b)). The EDS spectra corresponding to each micrograph confirmed the presence of all the elements used to form the phosphor materials.

### 3.3 Upconversion Analysis

Three main UC emission bands were detected around 544, 653, and 757 nm in Figure 3. These emission bands were well assigned by the $^5F_4/^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2 \rightarrow {}^5I_7$ transitions of the $Ho^{3+}$ ion (Pandey et al., 2016; Pandey et al., 2017; Pandey et al., 2018; Bednarska-Adam, 2022). The codoping of the $Yb^{3+}$ ion empowered the performance of the activator $Ho^{3+}$ ion. The green UC emission bands around 544 nm dominant over the other emission bands confirmed the reason for observing the emitted green light from the phosphors. Comparing the spectra, it is found that the intensity of the $CaWO_4:Ho^{3+}$-$Yb^{3+}$ phosphor was a maximum whereas that of $SrWO_4:Ho^{3+}$-$Yb^{3+}$ was a minimum. The UC emission intensity of the green band around 544 nm for the $CaWO_4:Ho^{3+}$-$Yb^{3+}$ phosphor was improved by ~3.7 and ~12.4 times in comparison to the $BaWO_4:Ho^{3+}$-$Yb^{3+}$ and the $SrWO_4:Ho^{3+}$-$Yb^{3+}$ phosphors, respectively. This improvement in the $CaWO_4:Ho^{3+}$-$Yb^{3+}$ phosphor was due to the better formation of smaller phosphors grains as confirmed from SEM image (Fig. 2) and might be the crystal field effect of the host matrix.

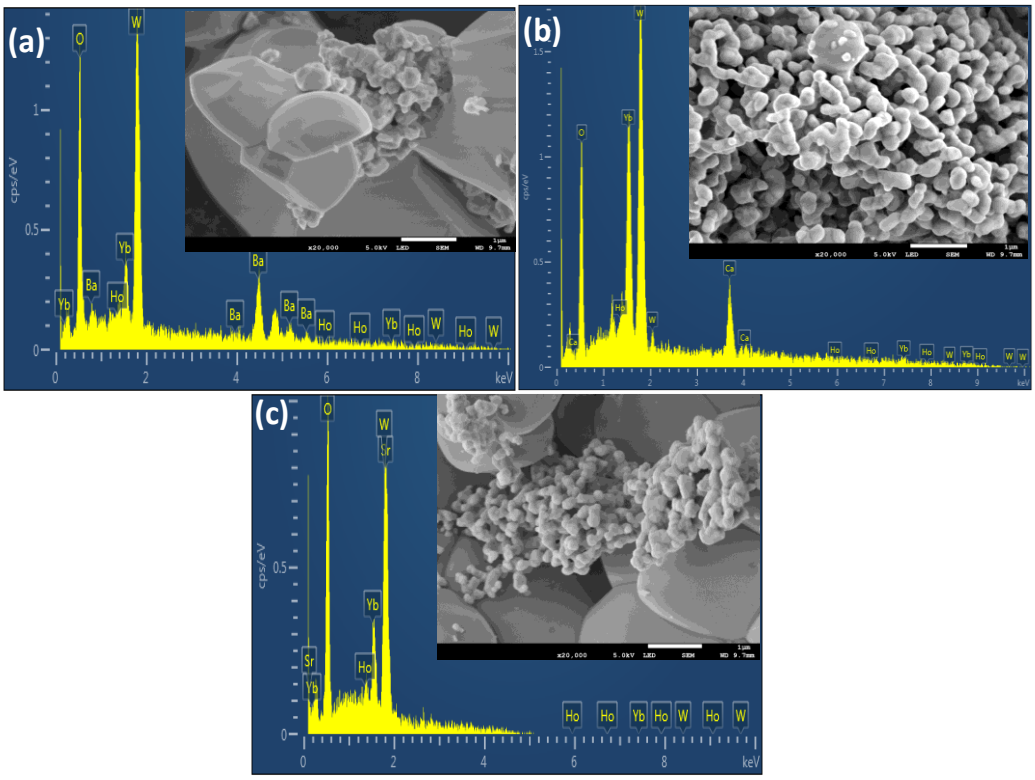


**Figure 2.** SEM and EDS images of the (a) $SrWO_4:Ho^{3+}$-$Yb^{3+}$ (b) $CaWO_4:Ho^{3+}$-$Yb^{3+}$ and (c) $BaWO_4:Ho^{3+}$-$Yb^{3+}$ phosphors.

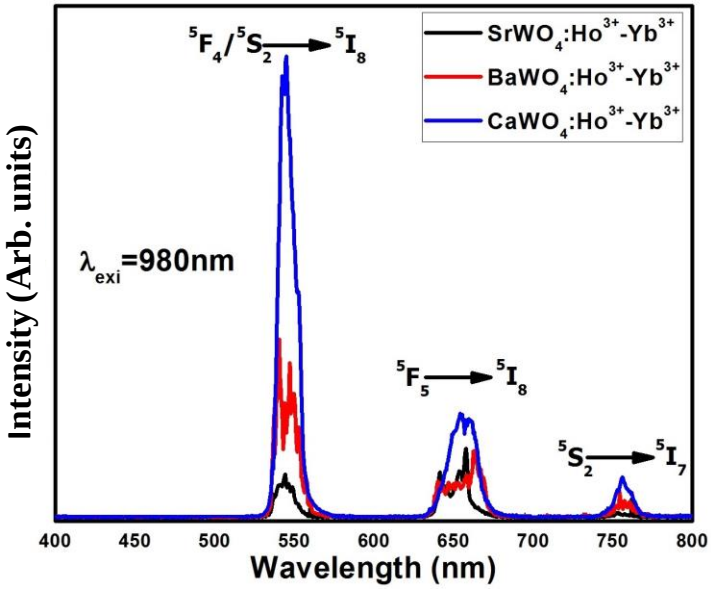


**Figure 3.** UC emission spectra of the $Ho^{3+}$-$Yb^{3+}$ codoped $XWO_4$ (X = Ba, Ca, Sr) phosphors.

A comparison of the UC emission spectra of the prepared phosphors under identical conditions excited by a 980 nm diode laser, recorded in the 400-800 nm range is shown in Figure 3. To understand the number of photons involved in the present UC emission process, a power dependence UC intensity study was performed and a two photons UC process was established. A two photon pumped energy transition scheme with possible ground state absorption (GSA), excited state absorption (ESA), and energy transfer (ET) processes of the $Ho^{3+}$ and $Yb^{3+}$ ions are presented in Figure 4. The energy level diagram of the $Ho^{3+}$ and $Yb^{3+}$ ions show the ground state ($^5I_8$) $Ho^{3+}$ ions pumped to the excited states $^5I_{5,6}$ and $^5F_{2,3,4}$ via a consecutive absorption of two photons through GSA and ESA processes as indicated (Pandey et al 2016; Pandey et al., 2017; Bednarska-Adam 2022). The populations in these states were amplified by the efficient ET from the $Yb^{3+}$ ions. Then after transitions from these excited states to the ground and first excited state gives radiative emission around 544 nm (green), 653 nm (red) and 757 nm (NIR), through the $^5F_4/^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2 \rightarrow {}^5I_7$ transitions, respectively. The nonradiative relaxation from the excited to meta energy states also take place (Chawarambwa et al., 2021; Perala et al., 2021).

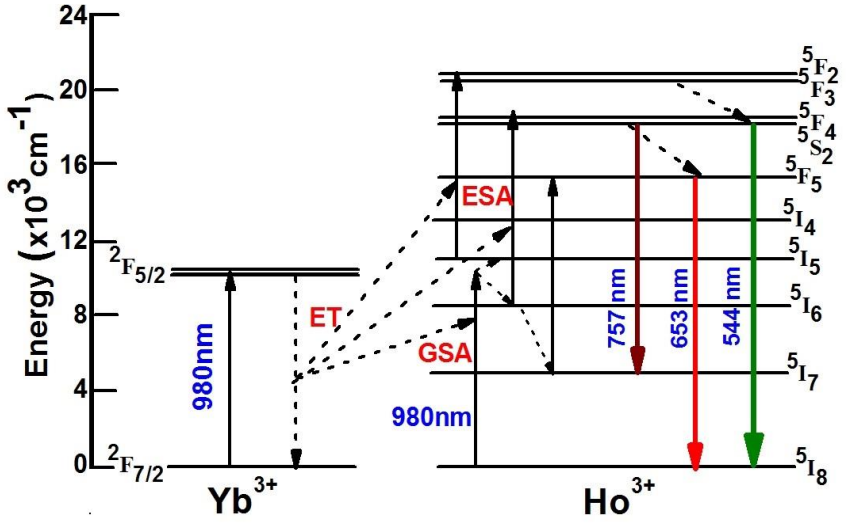


**Figure 4.** Energy level diagram for UC emissions of the $Ho^{3+}$-$Yb^{3+}$ codoped $XWO_4$ (X = Ba, Ca, Sr) phosphors.

## 4. Conclusions

Green light emitting $Ho^{3+}$-$Yb^{3+}$ codoped $XWO_4$ (X = Ba, Ca, Sr) phosphors were successfully synthesized by the solid state reaction method. The structural result shows the formation of single phase tetragonal $XWO_4$ (X = Ba, Ca, Sr) structures and microsized grains distributed throughout the surface. The upconversion emission resulted into three bands at 544, 653, and 757 nm assigned to the $^5F_4/^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2 \rightarrow {}^5I_7$ transitions of the $Ho^{3+}$ ion, respectively. On comparing the upconversion emissions, it is concluded that the $CaWO_4:Ho^{3+}$-$Yb^{3+}$ phosphor was the best amongst the three $XWO_4$ (X= Ba, Ca, Sr) codoped $Ho^{3+}$-$Yb^{3+}$ phosphors.

### Conflict of Interest

There is no conflict of interest.

### Acknowledgements

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