



Upconversion Properties of $\text{NaGd}(\text{WO}_4)_2:\text{Ho}^{3+}/\text{Yb}^{3+}$ Yellow Phosphors Synthesized by Cyclic Microwave-Modified Sol-Gel Method

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Upconversion properties of the $\text{NaGd}_{1-x}(\text{WO}_4)_2:\text{Ho}^{3+}/\text{Yb}^{3+}$ yellow phosphors with doping concentrations of Ho^{3+} and Yb^{3+} ($x = \text{Ho}^{3+} + \text{Yb}^{3+}$, $\text{Ho}^{3+} = 0.05, 0.1, 0.2$ and $\text{Yb}^{3+} = 0.2, 0.45$) were investigated. The synthesized particles were successfully synthesized by the microwave-modified sol-gel method. Well-crystallized particles showed a fine and homogeneous morphology with particle sizes of 2-5 μm . Under excitation at 980 nm, the upconversion intensity of $\text{NaGd}_{0.5}(\text{MoO}_4)_4:\text{Ho}_{0.05}\text{Yb}_{0.45}$ phosphors exhibited yellow emissions based on a strong 550 nm emission band in the green region and a very strong 655 nm emission band in the red region. The Raman spectra of the particles indicated the presence of strong peaks at higher frequencies.

Keywords: Upconversion properties, Yellow phosphors, Microwave, Sol-gel.

INTRODUCTION

Rare-earth doped upconversion (UC) materials have been widely applied in the fields, such as lighting sources, display terminals and biological detectors¹. Recently, the synthesis and the luminescence properties of upconversion particles have attracted considerable interest since they are considered as potentially active components in new optoelectronic devices and luminescent labels for imaging and biodetection assays, which overcome the current limitations in traditional photoluminescence materials^{2,3}. Most of the $\text{MR}(\text{WO}_4)_2$ ($\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+$; $\text{R} = \text{La}^{3+}, \text{Gd}^{3+}, \text{Y}^{3+}$) possess the tetragonal Scheelite structure with the space group $I4_{1/a}$ and belong to the family of double tungstates compounds. It is possible for the trivalent rare-earth ions in the disordered tetragonal-phase to be partially substituted by Ho^{3+} and Yb^{3+} ions, these ions are effectively doped into the crystal lattices of the tetragonal phase due to the similar radii of the trivalent rare earth ions (Re^{3+}). This results in high red emitting efficiency and superior thermal and chemical stability. In these compounds, W^{6+} is coordinated by four O^{2-} at a tetrahedral site, which makes $[\text{WO}_4]^{2-}$ relatively stable. Re^{3+} and M^+ are randomly distributed over the same cationic sublattice and they are coordinated by eight O^{2-} from near four $[\text{WO}_4]^{2-}$ with a symmetry S_4 without an inversion center⁴⁻⁶. The $[\text{WO}_4]^{2-}$ group has strong absorption in the near ultraviolet region, so that energy transfers process from $[\text{WO}_4]^{2-}$ group to rare earth ions can easily occur, which can greatly enhance the external quantum efficiency of rare-earth ions

doped materials. Among rare-earth ions, the Ho^{3+} ion is suitable for converting infrared to visible light through the upconversion process due to its appropriate electronic energy level configuration. The co-doped Yb^{3+} ion and Ho^{3+} ion can remarkably enhance the upconversion efficiency for the shift from infrared to visible light due to the efficiency of the energy transfer from Yb^{3+} to Ho^{3+} . The Yb^{3+} ion, as a sensitizer, can be effectively excited by an incident light source energy. This energy is transferred to the activator from which radiation can be emitted. The Ho^{3+} ion activator is the luminescence center of the upconversion particles, while the sensitizer Yb^{3+} enhances the upconversion luminescence efficiency⁷⁻⁹.

Several processes have been developed to prepare these rare-earth doped double tungstates. Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, small-size particles, narrow particle size distribution and high purity of final polycrystalline samples. Microwave heating is delivered to the material surface by radiant and/or convection heating, which is transferred to the bulk of the material *via* conduction¹⁰. A microwave-modified sol-gel method is a cost-effective method that provides high homogeneity and is easy to scale-up and it is emerging as a viable alternative approach for the quick synthesis of high-quality luminescent materials. However, the synthesis of $\text{NaGd}(\text{WO}_4)_2:\text{Ho}^{3+}/\text{Yb}^{3+}$ yellow phosphors by the microwave-modified sol-gel method has not been reported.

In this study, $\text{NaGd}_{1-x}(\text{WO}_4)_2:\text{Ho}^{3+}/\text{Yb}^{3+}$ phosphors with doping concentrations of Ho^{3+} and Yb^{3+} ($x = \text{Ho}^{3+} + \text{Yb}^{3+}$, Ho^{3+}

= 0.05, 0.1, 0.2 and Yb^{3+} = 0.2, 0.45) were prepared by the microwave-modified sol-gel method followed by heat treatment. The synthesized particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The optical properties were examined comparatively using photoluminescence (PL) emission and Raman spectroscopy.

EXPERIMENTAL

Appropriate stoichiometric amounts of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (99 %, Sigma-Aldrich, USA), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99 %, Sigma-Aldrich, USA), $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$ (99 %, Alfa Aesar, USA), $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9 %, Sigma-Aldrich, USA), $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9 %, Sigma-Aldrich, USA), citric acid (99.5 %, Daejung Chemicals, Korea), NH_4OH (A.R.), ethylene glycol (A.R.) and distilled water were used to prepare $\text{NaGd}(\text{WO}_4)_2$, $\text{NaGd}_{0.8}(\text{WO}_4)_2 \cdot \text{Ho}_{0.2}$, $\text{NaGd}_{0.7}(\text{WO}_4)_2 \cdot \text{Ho}_{0.1}\text{Yb}_{0.2}$ and $\text{NaGd}_{0.5}(\text{WO}_4)_2 \cdot \text{Ho}_{0.05}\text{Yb}_{0.45}$ compounds with doping concentrations of Ho^{3+} and Yb^{3+} (Ho^{3+} = 0.05, 0.1, 0.2 and Yb^{3+} = 0.2, 0.45). To prepare $\text{NaGd}(\text{WO}_4)_2$, 0.2 mol % $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 0.067 mol % $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$ were dissolved in 20 mL of ethylene glycol and 80 mL of 5M NH_4OH under vigorous stirring and heating. Subsequently, 0.4 mol % $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and citric acid (with a molar ratio of citric acid to total metal ions of 2:1) were dissolved in 100 mL of distilled water under vigorous stirring and heating. Then, the solutions were mixed together under vigorous stirring and heating at 80-100 °C. At the end, highly transparent solutions were obtained and adjusted to pH = 7-8 by the addition of NH_4OH or citric acid. In order to prepare $\text{NaGd}_{0.8}(\text{WO}_4)_2 \cdot \text{Ho}_{0.2}$, the mixture of 0.32 mol % $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 0.08 mol % $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used for the rare earth solution. In order to prepare $\text{NaGd}_{0.7}(\text{WO}_4)_2 \cdot \text{Ho}_{0.1}\text{Yb}_{0.2}$, the mixture of 0.28 mol % $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 0.04 mol % $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.08 mol % $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used for the rare earth solution. In order to prepare $\text{NaGd}_{0.5}(\text{WO}_4)_2 \cdot \text{Ho}_{0.05}\text{Yb}_{0.45}$, the rare earth containing solution was generated using 0.2 mol % $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 0.02 mol % $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.18 mol % $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

The transparent solutions were placed into a microwave oven operating at a frequency of 2.45 GHz with a maximum output-power of 1250 W for 0.5 h. The working cycle of the microwave reaction was controlled precisely using a regime of 40 s on and 20 s off for 15 min, followed by further treatment of 30 s on and 30 s off for 15 min. The ethylene glycol was evaporated slowly at its boiling point. Ethylene glycol is a polar solvent at its boiling point of 197 °C and this solvent is a good candidate for the microwave process. If ethylene glycol is used as the solvent, the reactions proceed at the boiling point temperature. When microwave radiation is supplied to the ethylene-glycol-based solution, the components dissolved in the ethylene glycol can couple. The charged particles vibrate in the electric field interdependently when a large amount of microwave radiation is supplied to the ethylene glycol. The samples were treated with ultrasonic radiation for 10 min to produce a light yellow transparent sol. After this, the light yellow transparent sols were dried at 120 °C in a dry oven to obtain black dried gels. The black dried gels were grinded and heat-treated at 900 °C for 16 h with 100 °C intervals

between 600-900 °C. Finally, white particles were obtained for $\text{NaGd}(\text{WO}_4)_2$ and pink particles for the doped compositions.

The phase composition of the synthesized particles was identified using XRD (D/MAX 2200, Rigaku, Japan). The microstructure and surface morphology of the $\text{NaGd}(\text{MoO}_4)_2$, $\text{NaGd}_{0.8}(\text{WO}_4)_2 \cdot \text{Ho}_{0.2}$, $\text{NaGd}_{0.7}(\text{WO}_4)_2 \cdot \text{Ho}_{0.1}\text{Yb}_{0.2}$ and $\text{NaGd}_{0.5}(\text{WO}_4)_2 \cdot \text{Ho}_{0.05}\text{Yb}_{0.45}$ particles were observed using SEM/EDS (JSM-5600, JEOL, Japan). The photoluminescence spectra were recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. Raman spectroscopy measurements were performed using a LabRam Aramis (Horiba Jobin-Yvon, France). The 514.5 nm line of an Ar ion laser was used as the excitation source and the power on the samples was kept at 0.5 mW.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of the (a) JCPDS 25-0829 data of $\text{NaGd}(\text{WO}_4)_2$, the synthesized (b) $\text{NaGd}(\text{WO}_4)_2$, (c) $\text{NaGd}_{0.8}(\text{WO}_4)_2 \cdot \text{Ho}_{0.2}$, (d) $\text{NaGd}_{0.7}(\text{WO}_4)_2 \cdot \text{Ho}_{0.1}\text{Yb}_{0.2}$ and (e) $\text{NaGd}_{0.5}(\text{WO}_4)_2 \cdot \text{Ho}_{0.05}\text{Yb}_{0.45}$ particles. The diffraction patterns of the products can be mostly consistent with the standard data of $\text{NaGd}(\text{WO}_4)_2$ (JCPDS 25-0829). No impurity phases were detected. $\text{NaGd}(\text{WO}_4)_2$ as a member of double tungstate family has a sheelite structure which is tetragonal with space group $I4_1/a^{11}$. In $\text{NaGd}(\text{WO}_4)_2$ matrix, Na^+ and Gd^{3+} are randomly arranged and form a disordered structure. Ho^{3+} and Yb^{3+} ions can be effectively doped in the $\text{NaGd}(\text{WO}_4)_2$ lattice by partial substitution of Gd^{3+} site due to the similar radii of Gd^{3+} , Ho^{3+} and Yb^{3+} , form an identical S_4 local symmetry. Post heat-treatment plays an important role in a well-defined crystallized morphology. To achieve a well-defined crystalline morphology, $\text{NaGd}(\text{WO}_4)_2$, $\text{NaGd}_{0.8}(\text{WO}_4)_2 \cdot \text{Ho}_{0.2}$, $\text{NaGd}_{0.7}(\text{WO}_4)_2 \cdot \text{Ho}_{0.1}\text{Yb}_{0.2}$ and $\text{NaGd}_{0.5}(\text{WO}_4)_2 \cdot \text{Ho}_{0.05}\text{Yb}_{0.45}$ phases need to be heat treated at 900 °C for 16 h. It is assumed that the doping amount of $\text{Ho}^{3+}/\text{Yb}^{3+}$ has a great effect on the crystalline cell volume of the $\text{NaGd}(\text{WO}_4)_2$, because of the different ionic sizes and energy band gaps.

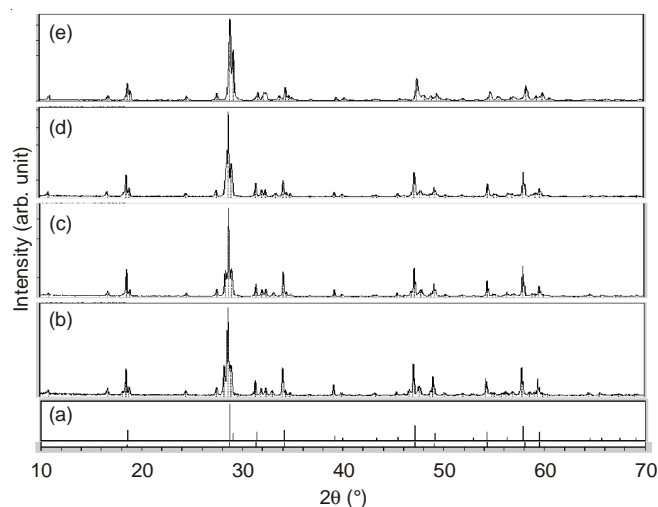


Fig. 1. X-ray diffraction patterns of the (a) JCPDS 25-0829 data of $\text{NaGd}(\text{WO}_4)_2$, the synthesized (b) $\text{NaGd}(\text{WO}_4)_2$, (c) $\text{NaGd}_{0.8}(\text{WO}_4)_2 \cdot \text{Ho}_{0.2}$, (d) $\text{NaGd}_{0.7}(\text{WO}_4)_2 \cdot \text{Ho}_{0.1}\text{Yb}_{0.2}$, and (e) $\text{NaGd}_{0.5}(\text{WO}_4)_2 \cdot \text{Ho}_{0.05}\text{Yb}_{0.45}$ particles

Fig. 2 shows a SEM image of the synthesized $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles. The as-synthesized sample is well crystallized with a fine and homogeneous morphology and particle size of 2-5 μm . It is noted that the structure has a tetragonal-phase after partial substitution of Gd^{3+} by Ho^{3+} and Yb^{3+} ions and the ions are effectively doped into crystal lattices of the $\text{NaGd}_2(\text{WO}_4)_2$ phase.

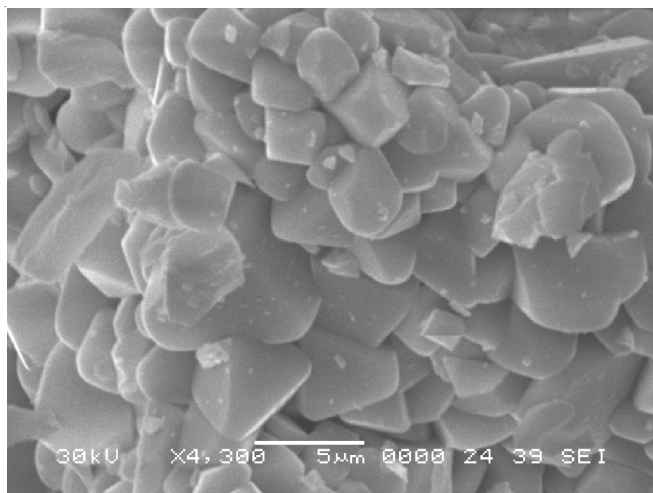


Fig. 2. Scanning electron microscopy image of the synthesized $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles

Fig. 3 shows the energy-dispersive X-ray spectroscopy patterns of the synthesized (a) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ and (b) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles and quantitative compositions of (c) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles. The EDS pattern shows that the (a) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ and (b) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles are composed of Na, Gd, W, O and Ho for $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ and Na, Gd, W, O, Ho and Yb for $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles. The quantitative compositions of (c) and (d) are in good relation with nominal compositions of the particles. The relation of Na, Gd, W, O, Ho and Yb components exhibit that $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ and $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles can be successfully synthesized using the microwave-modified sol-gel method. The microwave-modified sol-gel process of double tungstates provides the energy to synthesize the bulk of the material uniformly, so that fine particles with controlled morphology can be fabricated in a short time period. The method is a cost-effective way to provide highly homogeneous products and is easy to scale-up, it is a viable alternative for the rapid synthesis of upconversion particles.

Fig. 4 shows the upconversion photoluminescence emission spectra of the as-prepared (a) $\text{NaGd}(\text{WO}_4)_2$, (b) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$, (c) $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles excited under 980 nm at room temperature. The upconversion intensities of (c) $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles exhibited yellow emissions based on a strong 550 nm emission band in the green region and a strong 655 nm emission band in the red region. The upconversion intensities of (a) $\text{NaGd}(\text{WO}_4)_2$ and (b) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ particles were not detected. The upconversion intensity of (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ is much higher than that of (c)

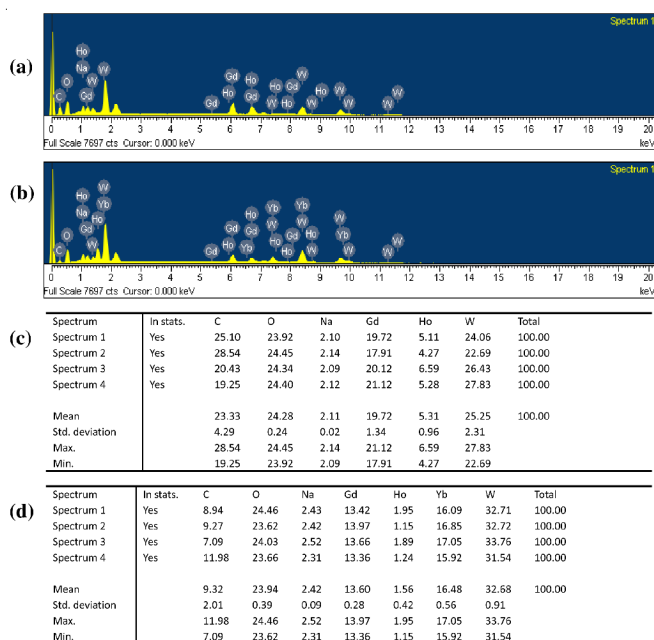


Fig. 3. Energy-dispersive X-ray spectroscopy patterns of the synthesized (a) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ and (b) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles, and quantitative compositions of (c) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles

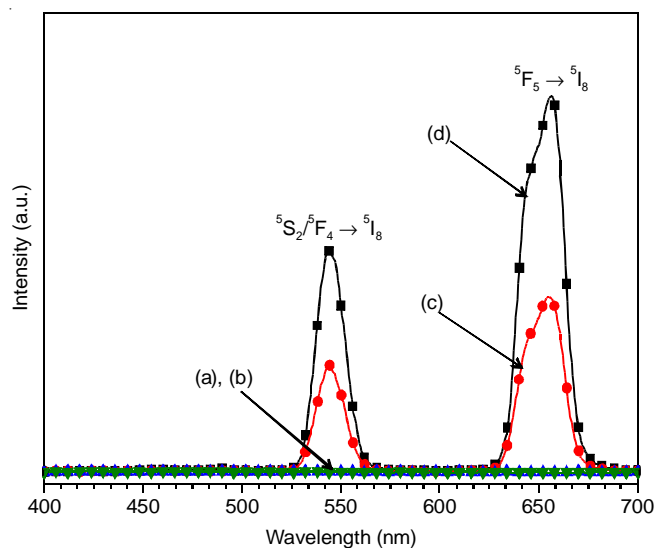


Fig. 4. Upconversion photoluminescence emission spectra of (a) $\text{NaGd}(\text{WO}_4)_2$, (b) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$, (c) $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles excited under 980 nm at room temperature

$\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}$ particles. The strong 550 nm emission band in the green region correspond to the ${}^5\text{S}_2/{}^5\text{F}_4 \rightarrow {}^5\text{I}_8$ transition, while the strong emission 655 nm band in the red region corresponds to the ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ transferred to the activator where radiation can be emitted. The Ho^{3+} ion activator is the luminescence center for these upconversion particles and the sensitizer Yb^{3+} enhances effectively the upconversion luminescence intensity because of the efficient energy transfer from Yb^{3+} to Ho^{3+} .

Fig. 5 shows the Raman spectra of the synthesized (a) $\text{NaGd}(\text{WO}_4)_2(\text{NGW})$, (b) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}(\text{NGW}:\text{Ho})$, (c) $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}(\text{NGW}:\text{HoYb})$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}(\text{NGW}:\text{HoYb}\#)$ particles excited by the 514.5 nm

line of an Ar ion laser at 0.5 mW. The internal modes for the (a) $\text{NaGd}(\text{WO}_4)_2(\text{NGW})$ particles were detected at 332, 406, 812, 880 and 918 cm^{-1} . The well-resolved sharp peaks for the $\text{NaGd}(\text{WO}_4)_2$ particles indicate a high crystallinity state of the synthesized particles. The internal vibration mode frequencies are dependent on the lattice parameters and the degree of the partially covalent bond between the cation and molecular ionic group $[\text{WO}_4]^{2-}$. The Raman spectra of the (b) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}(\text{NGW}:\text{Ho})$, (c) $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}(\text{NGW}:\text{HoYb})$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}(\text{NGW}:\text{HoYb}\#)$ particles indicate the domination of strong peaks at higher frequencies (840, 1108, 1180 and 1277 cm^{-1}). The Raman spectra of (b) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}(\text{NGW}:\text{Ho})$, (c) $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}(\text{NGW}:\text{HoYb})$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}(\text{NGW}:\text{HoYb}\#)$ particles prove that the doping ions can influence the structure of the host materials. The combination of a heavy metal cation and the large inter-ionic distance for Ho^{3+} and Yb^{3+} substitutions in Gd^{3+} sites in the lattice result in a high probability of up-conversion and phonon-splitting relaxation in $\text{NaGd}_{1-x}(\text{WO}_4)_2$ crystals. It may be that these very strong and strange effects are generated by the disorder of the $[\text{WO}_4]^{2-}$ groups with the incorporation of the Ho^{3+} and Yb^{3+} elements into the crystal lattice or by a new phase formation.

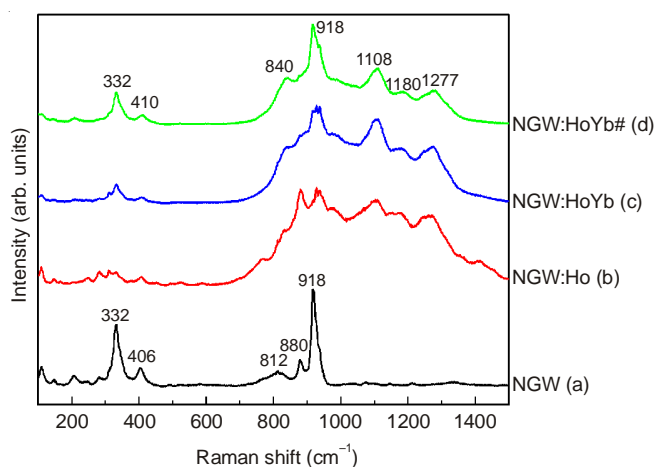


Fig. 5. Raman spectra of the synthesized (a) $\text{NaGd}(\text{WO}_4)_2(\text{NGW})$, (b) $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}(\text{NGW}:\text{Ho})$, (c) $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}(\text{NGW}:\text{HoYb})$ and (d) $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}(\text{NGW}:\text{HoYb}\#)$ particles excited by the 514.5 nm line of an Ar ion laser at 0.5 mW

Conclusion

The $\text{NaGd}_{1-x}(\text{WO}_4)_2:\text{Ho}^{3+}/\text{Yb}^{3+}$ yellow phosphors with doping concentrations of Ho^{3+} and Yb^{3+} ($x = \text{Ho}^{3+} + \text{Yb}^{3+}$, Ho^{3+}

$= 0.05, 0.1, 0.2$ and $\text{Yb}^{3+} = 0.2, 0.45$) were successfully synthesized by the microwave-modified sol-gel method. Well-crystallized particles formed after heat-treatment at 900 °C for 16 h showed a fine and homogeneous morphology with particle sizes of 2–5 μm . Under excitation at 980 nm, the upconversion intensities of $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}$ and $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles exhibited yellow emissions based on a strong 550 nm emission band in the green region and a very strong 655 nm emission band in the red region, which were assigned to the $^5\text{S}_2^5\text{F}_4 \rightarrow ^5\text{I}_8$ and $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transitions, respectively. The upconversion intensity of $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles was much higher than that of the $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}$ particles. The Raman spectra of the $\text{NaGd}_{0.8}(\text{WO}_4)_2:\text{Ho}_{0.2}$, $\text{NaGd}_{0.7}(\text{WO}_4)_2:\text{Ho}_{0.1}\text{Yb}_{0.2}$ and $\text{NaGd}_{0.5}(\text{WO}_4)_2:\text{Ho}_{0.05}\text{Yb}_{0.45}$ particles indicated the domination of strong peaks higher frequencies (840, 1108, 1180 and 1277 cm^{-1}) induced by the disorder of the $[\text{WO}_4]^{2-}$ groups with the incorporation of the Ho^{3+} and Yb^{3+} elements into the crystal lattice or by a new phase formation.

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