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Synthesis of Tetragonal Microcrystalline NaCaY(WO4)3:Ho³⁺/Yb³⁺/Tm³⁺ Ternary Tungstates and Their Spectroscopic Properties

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Abstract: The microcrystalline Ho³⁺/Yb³⁺/Tm³⁺ tri-doped NaCaY_{1-x}(WO₄)₃ white phosphors were successfully synthesized with variations of Ho³⁺, Yb³⁺ and Tm³⁺ (x = Ho³⁺ + Yb³⁺ + Tm³⁺, Ho³⁺ = 0.04, 0.03, 0.02, 0.01, Yb³⁺ = 0.35, 0.40, 0.45, 0.50 and Tm³⁺ = 0.01, 0.02, 0.03, 0.04), and their upconversion (UC) photoluminescence (PL) properties were evaluated. The synthesized particles have been fairly crystallized and showed a superior microcrystalline morphology with particle sizes of 2-3 µm. The spectroscopic properties were examined comparatively using photoluminescence emission and Raman spectroscopy. Under excitation at 980 nm, the UC doped particles revealed white emissions corresponding to the ¹G₄ \rightarrow ³H₆ transitions of Tm³⁺ in the blue region, the ⁵S₂/⁵F₄ \rightarrow ⁵I₈ transitions of Ho³⁺ in the green region, the ⁵F₅ \rightarrow ⁵I₈ transitions of Tm³⁺ in the cred region. The pump power dependence was provided, and the individual chromacities corresponding to the equal points in the CIE diagram revealed white emissions. The Raman spectra of the doped particles indicated the domination of strong peaks induced by the disorder of the [WO₄]²⁻ groups.

Keywords: Tetragonal, Microcrystalline, Phosphors, Upconversion, Spectroscopic, Raman

1. Introduction

Lantanide activated upconversion (UC) materials have been widely applied in the fields, such as lighting sources, display terminals, and biological detectors [1]. In order to overcome the current limitations in traditional photoluminescence materials, the synthesis and characterization of UC particles have attracted considerable interest since they are considered as potentially active components in new optoelectronic devices and luminescent products [2,3]. Almost lanthanide doped $MR(WO_4)_2$ have a tetragonal scheelite structure with the space group $I4_{1/a'}$ and belong to the family of double tungstate compounds. For the trivalent lanthanide ions in the disordered tetragonal-phase it is possible to be partially substituted by Ho³⁺ and Yb³⁺ ions. Because of the similar radii of the trivalent lanthanide ions are effectively doped into the crystal lattices of

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the tetragonal phase in high red emitting efficiency under superior thermal and chemical stability. In the crystal structure, W^{6+} is coordinated by four O^{2-} at a tetrahedral site, which makes $[WO_4]^{2-}$ relatively stable [4-6]. The $[WO_4]^{2-}$ group has strong absorption in the near ultraviolet region, so that energy transfers process from $[WO_4]^{2-}$ group to rare earth ions can easily occur, which can greatly enhance the external quantum efficiency of rare earth ions doped materials.

The tri-doped Yb³⁺, Ho³⁺ and Tm³⁺ ions can remarkably enhance the UC efficiency for the shift from infrared to visible light due to the efficiency of the energy transfer from Yb³⁺ to Ho³⁺ and Yb³⁺ to Tm³⁺. Ho³⁺ exhibits ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transitions in the green region, ${}^{5}F_{5}$ '! ${}^{5}I_{8}$ transitions in the red region in UC process, while Tm³⁺ shows the ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ transitions in the blue region, and ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ and ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transitions in the red region [7-9]. These ions are effectively doped into the crystal lattices of the tetragonal phase due to the similar radii of the trivalent rare-earth ions, these results in high red emitting efficiency, and superior thermal and chemical stability in white emitting diode.

Several processes have been developed to prepare these rare earth doped double tungstates [10-16]. A microwave sol-gel based (MSB) process provides high homogeneity, and brings a unique alternative approach for the available synthesis of high-quality PL materials [5, 6, 16]. However, the synthesis of Ho³⁺/Yb³⁺/Tm³⁺tri-doped NaCaY_{1-x}(WO₄)₃ (KGW) phosphors via the MSB route has not been reported. In this study, the double tungstate KGW phosphors with the proper doping concentrations of Ho³⁺, Yb³⁺ and Tm³⁺ (x = Ho³⁺ + Yb³⁺ + Tm³⁺, Ho³⁺ = 0.04, 0.03, 0.02, 0.01, Yb³⁺ = 0.35, 0.40, 0.45, 0.50 and Tm³⁺ = 0.01, 0.02, 0.03, 0.04) were successfully prepared by the MSB derived method, followed by heat treatment. The synthesized particles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The pump power dependence of the UC emission intensity and Commission Internationale de L'Eclairage (CIE) chromatic coordinates were evaluated in detail. The spectroscopic properties were examined comparatively using photoluminescence (PL) emission and Raman spectroscopy.

Experimental

Precise stoichiometric amounts of Na₂WO₄•2H₂O (99%, Sigma-Aldrich, USA), (NH₄)₆W₁₂O₃₉•xH₂O (99%, Alfa Aesar, USA), Ca (NO₃)₂•4H₂O (99%, Sigma-Aldrich, USA), Y(NO₃)₃•6H₂O (99%, Sigma-Aldrich, USA), Ho(NO₃)₃•5H₂O (99.9%, Sigma-Aldrich, USA), Yb(NO₃)₃•5H₂O (99.9%, Sigma-Aldrich, USA), Tm(NO₃)₃•5H₂O (99.9%, Sigma-Aldrich, USA), citric acid (CA, 99.5%, Daejung Chemicals, Korea), NH₄OH (A.R.), ethylene glycol (EG, A.R.) and distilled water (DW) were used to prepare then compounds. The MSB process has been previously reported in the references of [5, 6, 16].

The phase composition of the synthesized particles was identified using XRD (D/ MAX 2200, Rigaku, Japan). The microstructure and surface morphology of the synthesized particles were observed using SEM (JSM-5600, JEOL, Japan). The PL 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 synthesized (a) NaCaY_{0.60}(WO₄)₂:Ho_{0.04}/Yb_{0.35}/Tm_{0.01}, (b) NaCaY_{0.55}(WO₄)₂:Ho_{0.03}/Yb_{0.40}/Tm_{0.02}, (c) NaCaY_{0.50}(WO₄)₂:Ho_{0.02}/Yb_{0.45}/Tm_{0.03}, and (d) NaCaY_{0.45}(WO₄)₂:Ho_{0.01}/Yb_{0.50}/Tm_{0.04}, particles. The diffraction patterns of the products can be mostly consistent with the standard data of CaWO₄ (JCPDS 41-1431). No impurity phases were detected. NaCaY(WO₄)₃ as a member of double tungstate family has a sheelite structure which is tetragonal with a space group $I4_{1/a}^{11}$. In NaCaY(WO₄)₃ matrix, Na⁺ and Y³⁺ are randomly arranged and form a disordered structure. Ho³⁺, Yb³⁺ and Tm³⁺ ions can be effectively doped in the NaCaY(WO₄)₃ lattice by partial substitution of Y³⁺ site due to the similar radii of Y³⁺, Ho³⁺ Yb³⁺ and Tm³⁺ form an identical S₄ local symmetry. Post heat-treatment plays an important role in a well-defined crystallized morphology. To achieve a well-defined crystalline morphology, the compounds need to be heat treated at 850°C for 16 h. It is assumed that the doping amount of Ho³⁺+Tm³⁺/Yb³⁺ has a great effect on the crystalline cell volume of the NCYW, because of the different ionic sizes of the substitution of Ho³⁺ (R=1.015 Å), Yb³⁺ (R=0.985 Å) and Tm³⁺ (R=0.994 Å) ions in the Y³⁺ (R=1.019 Å) sites [17].



Fig. 2 shows SEM images of the synthesized $NaCaY_{0.50}(WO_4)_2$:Ho_{0.02}/Yb_{0.45}/Tm_{0.03} particles. The as-synthesized samples are very similar morphologies and no discrepancy is observed, showing superior microcrystalline morphology with particle size of 2-3 im. The MSB derived process of triple tungstates provides unique characteristics and superior morphology for the available synthesis of UC particles.



Fig. 2: SEM images of the synthesized NaCaY_{0.50}(WO₄)₂:Ho_{0.02}/Yb_{0.45}/Tm_{0.03} particles.

Fig. 3 shows the UC PL emission spectra of the as-prepared (a) NaCaY_{0.60}(WO₄)₂: Ho_{0.04}/Yb_{0.35}/Tm_{0.01}, (b) NaCaY_{0.55}(WO₄)₂: Ho_{0.03}/Yb_{0.40}/Tm_{0.02}, (c) NaCaY_{0.50}(WO₄)₂: Ho_{0.02}/Yb_{0.45}/Tm_{0.03}, and (d) NaCaY_{0.45}(WO₄)₂: Ho_{0.01}/Yb_{0.50}/Tm_{0.04}, particles. Under excitation at 980 nm, the doped particles exhibited white emissions based on blue, green and red emission bands, which correspond to the ¹G₄ \rightarrow ³H₆ transitions of Tm³⁺ in the blue region, the ⁵S₂/⁵F₄ \rightarrow ⁵I₈ transitions of Ho³⁺ in the green region, the ⁵F₅ \rightarrow ⁵I₈ transitions of Ho³⁺ as well as the ¹G₄ \rightarrow ³F₄ and ³H₄ \rightarrow ³H₆ transitions of Tm³⁺ in the red region [21, 22]. The UC intensity of (c) NaCaY_{0.50}(WO₄)₂:Ho_{0.02}/Yb_{0.45}/Tm_{0.03} exhibits the optimal intensities of the 475-nm, 545-nm and 655-nm emission band in the blue, green and red regions, respectively. Consequently, the proper Yb³⁺: Ho³⁺+Tm³⁺ ratio is as high as 9: 1 for the white emitting diode based on the blue, green and red emissions.



Fig. 3: UC PL emission spectra of (a) $NaCaY_{0.60}(WO_4)_2$: $Ho_{0.04}/Yb_{0.35}/Tm_{0.01}$ (b) $NaCaY_{0.55}(WO_4)_2$: $Ho_{0.03}/Yb_{0.40}/Tm_{0.02}$ (c) $NaCaY_{0.50}(WO_4)_2$: $Ho_{0.02}/Yb_{0.45}/Tm_{0.03}$ and (d) $NaCaY_{0.45}(WO_4)_2$: $Ho_{0.01}/Yb_{0.50}/Tm_{0.04}$ particles excited under 980 nm at room temperature.

The logarithmic scale dependence of the UC emission intensities at 475, 545, 655 and 695 nm on the working pump power over the range of 20 to 110 mW in the NaCaY_{0.50}(WO₄)₂:Yb_{0.02}/Ho_{0.45}/Tm_{0.03} sample is shown in Fig. 4. In the UC process, the UC emission intensity is proportional to the slope value *n* of the irradiation pumping power, where *n* is the number of pumped photons required to produce UC emission [18]: $I \alpha P^n$ and $LnI \alpha nLnP$, where value *n* is the number of the pumped photons required to excite the upper emitting state, *I* is the UC luminescent intensity and *P* is the laser pumping power. As seen from Fig. 4, the calculated slope value *n* = 2.47 for blue emission at 475 nm, *n* = 1.75 for green emission at 545 nm, and *n* = 1.92 and 1.84 for red emissions at 655 and 695 nm, respectively. These results show that the UC mechanism of the blue, green and red emissions can be explained by the multi-step energy transfer process in Ho³⁺/Yb³⁺/Tm³⁺ tri-doped phosphors [7-9, 22-25].



Fig. 4 : Logarithmic scale dependence of the UC emission intensity on the pump power in the range from 20 to 110 mW at 475, 545, 655 and 695 nm in the $NaCaY_{0.50}(WO_4)_2$:Ho_{0.02}/Yb_{0.45}/Tm_{0.03} sample.

Fig. 5 shows (A) calculated chromaticity coordinates (x, y) values and (B) CIE (a) $NaCaY_{0.60}(WO_4)_2:Ho_{0.04}/Yb_{0.35}/Tm_{0.01}$ (b) chromaticity diagram for $NaCaY_{0.55}(WO_{4})_{2}:Ho_{0.03}/Yb_{0.40}/Tm_{0.02}$ (c) $NaCaY_{0.50}(WO_{4})_{2}:Ho_{0.02}/Yb_{0.45}/Tm_{0.03}$, and (d) NaCaY_{0.45}(WO₄)₂:Ho_{0.01}/Yb_{0.50}/Tm_{0.04} particles. The triangle depicted in Fig. 5(B) indicates standard coordinates for blue, green and red colors. The inset in Fig. 5(B) shows the chromaticity points for the samples (a), (b), (c) and (d). The chromaticity coordinates (x, y) are strongly dependent on the $Ho^{3+}/Yb^{3+}/Tm^{3+}$ concentration ratio. As indicated in Fig. 5(A), the calculated chromaticity coordinates x = 0.325 and y = 0.358 for (a) $NaCaY_{0.60}(WO_4)_2:Ho_{0.04}/Yb_{0.35}/Tm_{0.01}$ x = 0.281 and y = 0.292 for (b) $NaCaY_{0.55}(WO_4)_2:Ho_{0.03}/Yb_{0.40}/Tm_{0.02}$, x = 0.302 and y = 0.314 for (c) $NaCaY_{0.50}(WO_4)_2:Ho_{0.02}/Yb_{0.45}/Tm_{0.03}$, and x = 0.289 and y = 0.291 for (d) $NaCaY_{0.45}(WO_4)_2:Ho_{0.01}/Yb_{0.50}/Tm_{0.04}$ are corresponding to the standard equal energy point in CIE diagram in Fig. 6(B).



Fig. 5: (A) Calculated chromaticity coordinates (x, y) values and (B) CIE chromaticity diagram for NaGd_{1-x}(WO₄)₂:Ho³⁺/Yb³⁺/Tm³⁺ phosphors. The inset shows the emission points for the sample synthesized (a) NaCaY_{0.60}(WO₄)₂:Ho_{0.04}/Yb_{0.35}/Tm_{0.01} (b) NaCaY_{0.55}(WO₄)₂:Ho_{0.03}/Yb_{0.40}/Tm_{0.02} (c) NaCaY_{0.50}(WO₄)₂:Ho_{0.02}/Yb_{0.45}/Tm_{0.03}, and (d) NaCaY_{0.45}(WO₄)₂:Ho_{0.01}/Yb_{0.50}/Tm_{0.04} particles.

Fig. 6 shows the Raman spectra of the synthesized (a) pure NCYW (b) $NaCaY_{0.60}(WO_4)_2:Ho_{0.04}/Yb_{0.35}/Tm_{0.01}$ (c) $NaCaY_{0.55}(WO_4)_2:Ho_{0.03}/Yb_{0.40}/Tm_{0.02}$ (d) $NaCaY_{0.50}(WO_4)_2:Ho_{0.02}/Yb_{0.45}/Tm_{0.03}$, and (e) $NaCaY_{0.45}(WO_4)_2:Ho_{0.01}/Yb_{0.50}/Tm_{0.04}$. particles. excited by the 514.5-nm line of an Ar ion laser at 0.5 mW. Compared to the peaks for the (a) NCYW particles, the doped compounds (b)-(e) indicate well-resolved sharp peaks for a high crystallinity state of the synthesized particles. The internal vibration mode frequencies are dependent on the lattice parameters and the strength of the partially covalent bond between the cation and molecular ionic group WO₄. The Raman spectra of the doped particles indicate the very stable and dominant peaks at higher frequencies of 838, 916, 1110 and 1282 cm⁻¹ and at lower frequencies of 334 and 412 cm⁻¹. These peaks at higher and lower frequencies are attributed the strong mixing between the W-O bonds and the WO₄ stretching vibrations. The stretching vibrations of W-O bonds are observed at 838 ~ 1110 cm⁻¹. For these stretching vibrations, strong mixing occurs between the W-O bonds and the WO₄. The bands at 334 and 412 cm⁻¹ could be assumed to originate from vibrations of the longer W-O bonds, which are employed in the formation of the W-W bridge. The Raman spectra of the doped 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 the doped elements in Y³⁺ sites in the lattice result in a high probability of UC and phonon-splitting relaxation in NaCaY_{1-x}(WO₄)₃ crystals [23, 24].



Fig. 6: Raman spectra of the synthesized (a) pure NCYW (b) $NaCaY_{0.60}(WO_4)_2:Ho_{0.04}/Yb_{0.35}/Tm_{0.01}$ (c) $NaCaY_{0.55}(WO_4)_2:Ho_{0.03}/Yb_{0.40}/Tm_{0.02}$ (d) $NaCaY_{0.50}(WO_4)_2:Ho_{0.02}/Yb_{0.45}/Tm_{0.03}$, and (e) $NaCaY_{0.45}(WO_4)_2:Ho_{0.01}/Yb_{0.50}/Tm_{0.04}$ particles excited by the 514.5-nm line of an Ar ion laser at 0.5 mW.

Conclusions

The tetragonal microcrystalline NCYW:Ho³⁺/Yb³⁺/Tm³⁺ white phosphors were successfully synthesized by MSB derived method. The synthesized particles brought superior microcrystalline morphology with particle size of 2-3 μ m. Under excitation at 980 nm, the UC doped particles revealed white emissions based on blue, green and red emission bands, corresponding to the ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ transitions of Tm³⁺ in the blue region, the ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transitions of Ho³⁺ in the green region, the ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions of Ho³⁺ in the green region, the ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions of Ho³⁺ as well as the ${}^{1}G_{4} \rightarrow {}^{3}H_{4}$ or ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transitions of Tm³⁺ in the red region. The proper concentration ratio Yb³⁺:Ho³⁺+Tm³⁺ was revealed to be 9: 1 for white emitting diodes. The behavior of UC intensity is dependent on the Yb:Ho+Tm ratio and is explained in terms of the optimal number of Yb³⁺ ions at the characteristic energy transfer distance around the Ho³⁺ and Tm³⁺ ions. The calculated chromaticity coordinates were corresponding to the standard equal energy point in CIE diagram. The typical Raman bands were explained in the framework of the local distortions of WO₄ tetrahedral. The high emitting efficiency of NCYW:Ho³⁺/Yb³⁺/Tm³⁺ phosphors can be considered as potential applications of white emitting diodes in new optoelectronic devices.

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