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Synthesis of NaLa(MoO_4)₂: Ho³⁺/Yb³⁺ Upconversion Phosphors via Microwave Sol-Gel Route and Their Spectroscopic Properties

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Abstract: NaLa_{1-x}(MoO₄)₂:Ho³⁺/Yb³⁺ phosphors with the correct doping concentrations of Ho³⁺ and Yb³⁺ were successfully synthesized by the microwave-modified sol-gel method. Well-crystallized particles formed after heat-treatment at 800°C for 16 h showed a fine and homogeneous morphology with particle sizes of 3-5 im. Under excitation at 980 nm, the UC intensities of the doped samples exhibited strong yellow emissions based on the combination of strong emission bands at 545-nm and 655-nm emission bands in green and red spectral regions, respectively. The strong 545-nm emission band in the green region corresponds to the ⁵S₂/⁵F₄ → ⁵I₈ transition in Ho³⁺ ions, while the strong emission 655-nm band in the red region appears due to the ⁵F₅ → ⁵I₈ transition in Ho³⁺ ions. The spectroscopic properties were examined comparatively using photoluminescence emission and Raman spectroscopy evaluated in detail.

Key words: Upconversion, Microwave sol-gel, Double molybdate, Raman spectroscopy

Introduction

Recently, design and synthesis for lanthanide activated photoluminescence particles have attracted considerable attention in their applications, such as fluorescent lamps, cathode ray tubes, solid-state laser, amplifiers for fiber optics communication and new optoelectronic devices, which show high luminescence quantum yields, since usually more than one metastable excited state exists and multiple emissions are observed [1-3]. Rareearth doped upconversion (UC) particles can convert near infrared radiation of low energy into visible radiation of high energy. The synthesis and the luminescence properties of UC particles have evolved in their applications, 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 [4-6].

Most of NaLn(MoO₄)₂ (Ln = La³⁺, Gd³⁺, Y³⁺) possess the tetragonal scheelite structure with the space group $I4_{1/a'}$ and belong to the family of double molybdates compounds. It

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is stable for the structure of NaLn(MoO₄)₂ to be transformed to the tetragonal scheelite structure from the monoclinic structure. It is possible for the trivalent rare earth ions in the tetragonal phase to be partially substituted by Ho³⁺ and Yb³⁺ ions. The Yb³⁺ ion, as a sensitizer, can be dramatically excited by an incident light source energy. This energy is transferred to the activator from which radiation can be emitted. The Ho³⁺ ion activator is the luminescence center of the UC particles, while the sensitizer enhances the UC luminescence efficiency [7-9].

For preparation of the double molybdate NaLn(MoO₄)₂, several processes have been developed via specific preparation processes [10-15]. Microwave heating is delivered to the material surface by radiant and/or convection heating, which heat energy is transferred to the bulk of the material via conduction [16]. It is a costeffective 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.

In this study, NaLa_{1-x}(MoO₄)₂:Ho³⁺/Yb³⁺ phosphors with the correct doping concentrations of Ho³⁺ and Yb³⁺ ($x = Ho^{3+} + Yb^{3+}$, Ho³⁺ = 0.05 and Yb³⁺ = 0.35, 0.40, 0.45 and 0.50) were successfully prepared by the microwave sol-gel method, followed by heat treatment. The synthesized particles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Pump power dependence and Commission Internationale de L'Eclairage (CIE) chromaticity of the UC emission intensity were evaluated in detail. The optical properties were examined comparatively using photoluminescence (PL) emission and Raman spectroscopy.

Experimental

In this study, precise amounts of Na₂MoO₄·2H₂O (99%, Sigma-Aldrich, USA), La(NO₃)₃ · $6H_2O(99\%, Sigma-Aldrich, USA), (NH_4)_6Mo_7O_{24} \cdot 4H_2O(99\%, Alfa Aesar, USA), Ho(NO_3)_3$ · 5H₂O (99.9%, Sigma-Aldrich, USA), Yb(NO₃)₃ · 5H₂O (99.9%, Sigma-Aldrich, USA), citric acid (99.5%, Daejung Chemicals, Korea), NH₄OH (A.R.), ethylene glycol (A.R.) and distilled water were used to prepare $NaLa(MoO_4)_2$, $NaLa_{0.6}(MoO_4)_2$:Ho_{0.05}Yb_{0.35}/ $NaLa_{0.55}(MoO_{4})_{2}:Ho_{0.05}Yb_{0.40'} NaLa_{0.50}(MoO_{4})_{2}:Ho_{0.05}Yb_{0.45} and NaLa_{0.45}(MoO_{4})_{2}:Ho_{0.05}Yb_{0.50}$ compounds with the correct doping concentrations of Ho³⁺ and Yb³⁺ (Ho³⁺ = 0.05 and $Yb^{3+}= 0.35, 0.40, 0.45 \text{ and } 0.50$). To prepare $NaLa(MoO_4)_2, 0.2 \text{ mol}\% Na_2MoO_4'''2H_2O$ and 0.114 mol% (NH₄)₆Mo₇O₂₄ · 4H₂O were dissolved in 20 mL of ethylene glycol and 80 mL of 5M NH₄OH under vigorous stirring and heating. Subsequently, 0.4 mol% La(NO₃)₃ \cdot 6H₂O and citric acid were dissolved in 100 mL of distilled water under vigorous stirring and heating. The molar ratio of citric acid to total metal ions was 2:1. Then, the solutions were mixed together vigorously and heated at 80-100°C. Finally, highly transparent solutions were obtained and adjusted to pH=7-8 by the addition of NH₄OH or citric acid. To prepare $NaLa_{0.6}(MoO_{4})_{2}:Ho_{0.05}/Yb_{0.35}$, the mixture of 0.24 mol% $La(NO_{3})_{3} \cdot 6H_{2}O$, 0.14 mol% $Yb(NO_{3})_{3}$ \cdot 5H₂O and 0.02 mol% Ho(NO₃)₃ \cdot 5H₂O was used for creation of the solution containing the rare-earth elements. To prepare NaLa_{0.55}(MoO₄)₂: Ho_{0.05}/Yb_{0.40}, the solution containing the rare-earth elements was employed using 0.22 mol% $La(NO_3)_3 \cdot 6H_2O_2$, and 0.02 mol%

Ho(NO₃)₃ · 5H₂O and 0.16 mol% Yb(NO₃)₃ · 5H₂O. To prepare NaLa_{0.50}(MoO₄)₂: Ho_{0.05}/Yb_{0.457} the mixture of 0.20 mol% La(NO₃)₃ · 6H₂O, 0.02 mol% Ho(NO₃)₃ · 5H₂O and 0.18 mol% Yb(NO₃)₃ · 5H₂O and was used for the creation of the solution containing the rare-earth elements. To prepare NaLa_{0.45}(MoO₄)₂:Ho_{0.05}/Yb_{0.50}, the solution containing the rare-earth elements was generated using 0.18 mol% La(NO₃)₃ · 6H₂O, and 0.02 mol% Ho(NO₃)₃ · 5H₂O and 0.2 mol% Yb(NO₃)₃ · 5H₂O. 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 30 min. The working cycle of the microwave reaction was controlled very 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 samples were treated with ultrasonic radiation for 10 min to produce a light yellowish transparent sol. After this, the light yellowish transparent sols were dried at 120°C in a dry oven to obtain black dried gels. The black dried gels were ground and heat-treated at 800°C for 16 h at 100°C intervals between 600-800°C. Finally, white particles were obtained for pure NaLa(MoO₄)₂ and pink particles were obtained 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 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. Pump power dependence of the UC emission intensity was measured at levels of working power from 20 to 110 mW. Raman spectra measurements were performed using a LabRam Aramis (Horiba Jobin-Yvon, France) with the spectral resolution of 2 cm⁻¹. The 514.5-nm line of an Ar ion laser was used as an excitation source; the power on the samples was kept at 0.5 mW level to avoid the sample's decomposition.

Results and Discussion

Fig. 1 shows XRD patterns of the (a) JCPDS 24-1103 pattern of NaLa(MoO_4), the synthesized (b) pure NaLa(MoO₄)₂ (c) NaLa_{0.60}(MoO₄)₂:Ho_{0.05}Yb_{0.35'} (d) NaLa_{0.55}(MoO₄)₂:Ho_{0.05}Yb_{0.40'} (e) $NaLa_{0.50}(MoO_4)_2:Ho_{0.05}Yb_{0.45}$ and (f) $NaLa_{0.45}(MoO_4)_2:Ho_{0.05}Yb_{0.50}$ particles. It was possible to assign almost all of the XRD peaks indexed to pure tetragonal phase, which can be mostly consistent with the standard data of NaLa(MoO₄), (JCPDS 24-1103). NaLa(MoO₄), as a member of double molybdate family has a sheelite structure with the lattice constants of a=5.344 A and c=11.730 A, which is tetragonal with space group $I_{4_{1/2}}$. It can be observed, that the diffraction peaks of the doped samples of Fig. 1(c)-(f) shift slightly to the high angle compared to that of pure sample of Fig. 1(b). In the crystal structure of $NaLa_{1,v}(MoO_{4})_{2,v}$ the La³⁺ ion site is supposed to be occupied by Ho³⁺ and Yb³⁺ ions with fixed occupations according to the nominal chemical formulas. The defined crystal structure contains MoO_A tetrahedrons coordinated by four $(La/Ho/Yb)O_{s}$ square antiprisms through the common O ions. In the doped crystals, the unit cell shrinkage results from the substitution of La³⁺ ions by Ho³⁺ and Yb³⁺ ions. It is assumed that the radiuses of Ho³⁺ (R=1.015 Å) and Yb³⁺ (R=0.985 Å) are smaller than that of La³⁺ (R=1.16 Å), when the coordination number is CN = 8 [17]. Consequently, it should be emphasized that the Ho^{3+} and Yb^{3+} ions can be effectively doped in the NaLa_{1-x}(MoO₄)₂ lattice by partial substitution of La³⁺ site, which leads to the unit cell shrinkage due to the similar radii of La³⁺ and by partial substitution of Ho³⁺ and Yb³⁺ while maintaining the tetragonal structure of the NaLa_{1-x}(MoO₄)₂.

Fig. 2 provides SEM images of the synthesized (a) NaLa_{0.60}(MoO₄)₂:Ho_{0.05}Yb_{0.35} and (b) NaLa_{0.45}(MoO₄)₂:Ho_{0.05}Yb_{0.50} particles. The as-synthesized samples are well crystallized with a fine and homogeneous morphology and particle size of 3-5 im. The samples have no discrepancy in aspect of morphological feature, and agglomerated particles induced by the inter-diffusions among the grains. It should be noted that the doping concentrations for Ho³⁺ and Yb³⁺ have no effects on the morphological feature. The microwave sol-gel method of the double moybdates 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 fabricate highly homogeneous products with easy scale-up and is a viable alternative for the rapid synthesis of UC particles. This suggests that the microwave sol-gel route is suitable for the creation of homogeneous NaLa_{1-x}(MoO₄)₂:Ho³⁺/Yb³⁺ crystallites.

Fig. 3 shows the UC photoluminescence emission spectra of (a) NaLa_{0.60}(MoO₄)₂:Ho_{0.05}Yb_{0.35'} (b) NaLa_{0.55}(MoO₄)₂:Ho_{0.05}Yb_{0.40'} (c) NaLa_{0.50}(MoO₄)₂:Ho_{0.05}Yb_{0.45} and (d) NaLa_{0.45}(MoO₄)₂:Ho_{0.05}Yb_{0.50} particles excited under 980 nm at room temperature. The doped samples exhibited strong yellow emissions based on the combination of strong emission bands at 545-nm and 655-nm emission bands in green and red spectral regions, respectively. The strong 545-nm emission band in the green region corresponds to the ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transition in Ho³⁺ ions, while the strong 655-nm emission band in the red region appears due to the ${}^{5}F_{5}$ '! ${}^{5}I_{8}$ transition in Ho³⁺ ions. The Ho³⁺ ion activator is the luminescence center for these UC particles, and the Yb³⁺ sensitizer dramatically enhances the UC luminescence efficiency. The UC intensity is dependent on the Yb³⁺:Ho³⁺ ratio in samples (a) 7:1, (b) 8:1, (c) 9:1and (d) 10:1. The higher intensity of (c) NaLa_{0.50}(MoO₄)₂:Ho_{0.05}Yb_{0.45} caused the ratio of Yb³⁺:Ho³⁺ to be 9:1, whereas the higher contents of the Yb³⁺ ion, used as a sensitizer owing to its strong absorption at around 980 nm, can remarkably enhance the UC luminescence through energy transfer.

The logarithmic scale dependence of the UC emission intensities at 545 and 655 nm on the working pump power over the range of 20 to 110 mW in the NaLa_{0.50}(MoO₄)₂:Ho_{0.05}Yb_{0.45} 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]:

$$I \propto P^n \tag{1}$$

$$LnI \propto nLnP$$
 (2)

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. The calculated slope values *n* in Fig. 4 indicate slope n = 1.87 for green emission at 545 nm; this value is 1.91 for red emission at 655 nm.



 $\begin{array}{l} \label{eq:Figure 1: X-ray diffraction patterns of the (a) JCPDS 24-1103 pattern of NaLa(MoO_4)_{2'} \ the synthesized (b) \\ pure \ NaLa(MoO_4)_{2,} \ (c) \ NaLa_{_{0,60}}(MoO_4)_2: Ho_{_{0,05}}Yb_{_{0,35'}} \ (d) \ NaLa_{_{0,55}}(MoO_4)_2: Ho_{_{0,05}}Yb_{_{0,40'}} \ (e) \\ NaLa_{_{0,50}}(MoO_4)_2: Ho_{_{0,05}}Yb_{_{0,45}} \ and \ (f) \ NaLa_{_{0,45}}(MoO_4)_2: Ho_{_{0,05}}Yb_{_{0,50}} \ particles \end{array}$



Figure 2: Scanning electron microscopy images of the synthesized (a) $NaLa_{0.60}(MoO_4)_2$:Ho_{0.05}Yb_{0.35} and (b) $NaLa_{0.45}(MoO_4)_2$:Ho_{0.05}Yb_{0.50} particles



Figure 3: Upconversion photoluminescence emission spectra of (a) $NaLa_{0.60}(MoO_4)_2$: $Ho_{0.05}Yb_{0.35'}$ (b) $NaLa_{0.55}(MoO_4)_2$: $Ho_{0.05}Yb_{0.40'}$ (c) $NaLa_{0.50}(MoO_4)_2$: $Ho_{0.05}Yb_{0.45}$ and (d) $NaLa_{0.45}(MoO_4)_2$: $Ho_{0.05}Yb_{0.50}$ particles excited under 980 nm at room temperature



Figure 4: Logarithmic scale dependence of the upconversion emission intensity on the pump power in the range from 20 to 110 mW at 545 and 655 nm in the NaLa_{0.50}(MoO₄)₂:Ho_{0.05}Yb_{0.45} sample



Figure 5: Raman spectra of the synthesized (a) pure $NaLa_2(MoO_4)_2$ (b) $NaLa_{0.60}(MoO_4)_2$: $Ho_{0.05}Yb_{0.35'}$ (c) $NaLa_{0.55}(MoO_4)_2$: $Ho_{0.05}Yb_{0.40'}$ (d) $NaLa_{0.50}(MoO_4)_2$: $Ho_{0.05}Yb_{0.45}$ and (e) $NaLa_{0.45}(MoO_4)_2$: $Ho_{0.05}Yb_{0.50}$ particles excited by the 514.5-nm line of an Ar ion laser at 0.5 mW

The Raman spectra recorded from the (a) pure NaLa(MoO₄)₂, (b) NaLa_{0.60}(MoO₄)₂:Ho_{0.05}Yb_{0.35}, (c) NaLa_{0.55}(MoO₄)₂:Ho_{0.05}Yb_{0.40}, (d) NaLa_{0.50}(MoO₄)₂:Ho_{0.05}Yb_{0.45} and (e) NaLa_{0.45}(MoO₄)₂:Ho_{0.05}Yb_{0.50} particles samples under the 514.5 nm excitation are shown in Fig. 5. The internal modes for the (a) pure NaLa(MoO₄)₂ particles were detected at lower frequencies of 200, 228, 318, 332 and 375 cm⁻¹ and at higher frequencies of 835, 906 and 938 cm⁻¹. The well-resolved sharp peaks for the NaLa(MoO₄)₂ indicate a high crystallinity state of the synthesized particles. The Raman spectra of (b) NaLa_{0.60}(MoO₄)₂:Ho_{0.05}Yb_{0.35}, (c) NaLa_{0.55}(MoO₄)₂:Ho_{0.05}Yb_{0.40}, (d) NaLa_{0.50}(MoO₄)₂:Ho_{0.05}Yb_{0.45} and (e) NaLa_{0.45}(MoO₄)₂:Ho_{0.05}Yb_{0.35}, and 565 cm⁻¹ and at higher frequencies of 890, 930, 1030, 1108 and 1283 cm⁻¹. Consequently, these strong yellow phosphors of NaLa_{1-x}(MoO₄)₂ doped with Ho³⁺/Yb³⁺ lead to high emitting efficiency and superior thermal and chemical stability, and these materials, can be considered potentially active components in new optoelectronic devices.

Conclusions

UC NaLa_{1-x}(MoO₄)₂:Ho³⁺/Yb³⁺ phosphors with the correct doping concentrations of Ho³⁺ and Yb³⁺ were successfully synthesized via the microwave sol-gel route. Well-crystallized particles formed after heat-treatment at 800°C for 16 h showed a fine and homogeneous morphology with particle sizes of 3-5 µm. Under excitation at 980 nm, the UC doped particles exhibited yellow emissions based on a strong 545-nm emission band in the green region and a very strong 655-nm emission band in the red region, which were assigned to the ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions, respectively. The higher intensity of NaLa_{0.50}(MoO₄)₂:Ho_{0.05}Yb_{0.45} provided that the ratio of Yb³⁺: Ho³⁺ would be 9:1, whereas the higher contents of Yb³⁺ ion as a sensitizer owing to its strong absorption around 980 nm can remarkably enhance the UC luminescence through energy transfer. The calculated slope values *n* indicate slope *n* = 1.87 for green emission at 545 nm; this value is 1.91 for red emissions for use potentially active components in new optoelectronic devices and luminescent devices.

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