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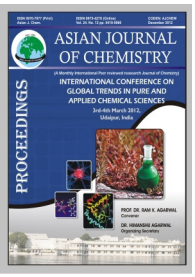

Synthesis and Characterization of Upconversion Photoluminescence Er^{3+}, Yb^{3+} Co-doped $SrMoO_4$ Particles *via* Microwave-Assisted Metathetic Route†

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Er^{3+}/Yb^{3+} co-doped $SrMoO_4$ ($SrMoO_4$:Er^{3+}/Yb^{3+}) particles were successfully synthesized *via* a cyclic microwave-assisted metathetic route followed by further heat treatment. Well-crystallized $SrMoO_4$:Er^{3+}/Yb^{3+} particles (100-500 nm) were formed after heat treatment at 600 ºC for 3 h and showed a fine and homogeneous morphology. With excitation at 980 nm, $SrMoO_4$:Er^{3+}/Yb^{3+}# exhibited a strong 525-nm emission band and a weak 550-nm emission band in the green region and a weak 655-nm emission band in the red region. The Raman spectra of $SrMoO_4$:Er^{3+}, $SrMoO_4$:Er^{3+}/Yb^{3+} and $SrMoO_4$:Er^{3+}/Yb^{3+}# particles indicated additional strong peaks at both higher frequencies (564, 524, 456 and 403 cm^{-1}) and lower frequencies (294, 251 and 220 cm^{-1}).

Key Words: Cyclic microwave, Metathetic synthesis, Upconversion photoluminescence, $SrMoO_4$:Er^{3+}/Yb^{3+} particles, Raman spectroscopy.

INTRODUCTION

Rare earth-doped upconversion particles have attracted great interest in recent years due to the luminescent properties induced by their potential applications in products such as lasers, three-dimensional displays, light-emitting devices and biological detectors[1-3]. Rare earth-doped upconversion $SrMoO_4$ particles are among the metallic molybdate compounds that have a scheelite-type structure, which have lattice parameters of a = b = 5.3796 Å and c = 11.9897[4-6], are relatively stable in air and have stable physical and chemical properties, a low excitation threshold energy and a low price productivity. The upconversion process featuring multi-photon absorption and anti-Stokes emission is fundamentally different from the conventional photoluminescence process, as the intermediate energy level is virtual and that for upconversion is real. Among the rare-earth ions, the Er^{3+} ion is suitable for converting infrared to visible light through the upconversion process due to its proper electronic energy level scheme. The co-doped Yb^{3+} ion with Er^{3+} ion can remarkably enhance the upconversion efficiency from infrared to visible light due to the efficiency energy transfer from Yb^{3+} to Er^{3+}. The Yb^{3+} ion as a sensitizer can be effectively excited by incident light source energy that is transferred to the activator, from which radiation can be emitted. The Er^{3+} ion activator is the luminescence center of the upconversion particles, while the sensitizer enhances the upconversion luminescence efficiency[7-9].

Several processes have recently been developed to enhance the applications of rare earth-doped metal molybdates prepared using a range of processes, including solid-state reactions[10-14], co-precipitation[15], the sol-gel method[16], the hydrothermal method[17-19], the Pechni method[20], the solvothermal route[21] and the microwave-assisted hydrothermal method[22]. For the practical application of upconversion photoluminescence in products such as lasers, three-dimensional displays, light-emitting devices and biological detectors, well-defined features of the upconversion particle such as homogeneous particle size distribution and morphology are required. Cyclic microwave-assisted metathetic material synthesis is a simple and cost-effective method that provides high yield with easy scale-up and is emerging as a viable alternative approach for rapid synthesis of high-quality novel inorganic materials[23].

In this study, Er^{3+}/Yb^{3+} co-doped $SrMoO_4$ ($SrMoO_4$:Er^{3+}/Yb^{3+}) particles were synthesized using the cyclic microwave-assisted metathetic route followed by further heat treatment. The synthesized $SrMoO_4$:Er^{3+}/Yb^{3+} particles were characterized by X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDS). Optical properties were examined using photoluminescence emission and Raman spectroscopy.

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EXPERIMENTAL

Appropriate stoichiometric amounts of $SrCl_2·6H_2O$, $ErCl_3·6H_2O$, $YbCl_3·6H_2O$, $Na_2MoO_4·2H_2O$ and ethylene glycol of analytic reagent grade were used to prepare the $SrMoO_4$, $SrMoO_4:Er^{3+}$, $SrMoO_4:Er^{3+}/Yb^{3+}$ and $SrMoO_4:Er^{3+}/Yb^{3+}$# compounds. Both 1 mol % $SrCl_2·6H_2O$ and 1 mol % $Na_2MoO_4·2H_2O$ for $SrMoO_4$ were dissolved in 30 mL of ethylene glycol. In the second way, both 0.95 mol % $SrCl_2·6H_2O$ with 0.05 mol % $ErCl_3·6H_2O$ and 1 mol % $Na_2MoO_4·2H_2O$ for $SrMoO_4:Er^{3+}$ was dissolved in 30 mL of ethylene glycol. In the third way, both 0.95 mol % $SrCl_2·6H_2O$ with 0.025 mol % $ErCl_3·6H_2O$ and 0.025 mol % $YbCl_3·6H_2O$ and 1 mol % $Na_2MoO_4·2H_2O$ for $SrMoO_4:Er^{3+}/Yb^{3+}$ were dissolved in 30 mL of ethylene glycol. In the fourth way, both 0.8 mol % $SrCl_2·6H_2O$ with 0.02 mol % $ErCl_3·6H_2O$ and 0.18 mol % $YbCl_3·6H_2O$ and 1 mol % $Na_2MoO_4·2H_2O$ for $SrMoO_4:Er^{3+}/Yb^{3+}$# were dissolved in 30 mL of ethylene glycol.

The solutions were mixed and adjusted to pH 9.5 using NaOH. The aqueous solutions were stirred at room temperature. In sequence, the mixtures were transferred into a Teflon vessel with a 120-mL capacity. The Teflon vessel was placed into a microwave oven operating at a frequency of 2.45 GHz with a maximum outpower of 1250 W for 23 min. The working cycle of the microwave-assisted metathetic reaction was controlled very precisely between 30 s on and 30 s off for 8 min and followed by further treatment of 30 s on and 60 s off for 15 min. The ethylene glycol was evaporated slowly above its boiling point. Ethylene glycol, a polar solvent with a boiling point of 197 ºC, is a good candidate for the microwave process. The final products were heat-treated at 600 ºC for 3 h.

The phase of the particles after the cyclic microwave-assisted metathetic reaction and subsequent heat treatment was identified using XRD (D/MAX 2200, Rigaku, Japan). The microstructure and surface morphology of the $SrMoO_4$, $SrMoO_4:Er^{3+}$, $SrMoO_4:Er^{3+}/Yb^{3+}$ and $SrMoO_4:Er^{3+}/Yb^{3+}$# 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 HR (Jobin-Yvon, France). The 514.5-nm line of an Ar ion laser was used as the excitation source and the power on the sample was kept at 0.5 mW.

RESULTS AND DISCUSSION

Fig. 1 shows SEM images of the (a) $SrMoO_4:Er^{3+}$, (b) $SrMoO_4:Er^{3+}/Yb^{3+}$ and (c) $SrMoO_4:Er^{3+}/Yb^{3+}$# particles after the cyclic microwave-assisted metathetic route followed by further heat treatment at 600 ºC for 3 h. The three as-synthesized samples (100-500 nm) are well crystallized with a spherical shape showing a fine and homogeneous morphology. The samples of (a) $SrMoO_4:Er^{3+}$ and (b) $SrMoO_4:Er^{3+}/Yb^{3+}$ have no obvious discrepancies in particle size or morphology, meaning that the doping amounts of the 0.05 mol % Er^{3+} for $SrMoO_4:Er^{3+}$ and 0.025 mol % Er^{3+} and 0.025 mol % Yb^{3+} for $SrMoO_4:Er^{3+}/Yb^{3+}$ had little effect on the morphological features. However, (c) $SrMoO_4$: Er^{3+}/Yb^{3+}# shows a scattered morphology with obvious discrepancy compared to (a) $SrMoO_4$: Er^{3+} and (b) $SrMoO_4:Er^{3+}/Yb^{3+}$. This discrepancy means that the doping amount of 0.02 mol % Er^{3+} and 0.18 mol % Yb^{3+} for $SrMoO_4:Er^{3+}/Yb^{3+}$# have a great effect on the morphological features.

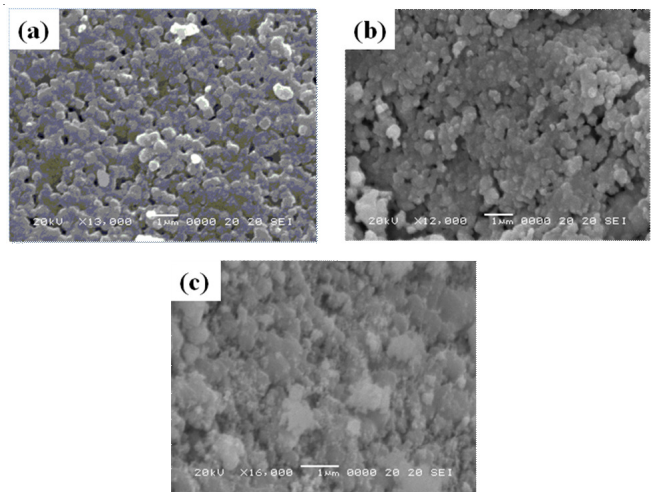

Fig. 1. Scanning electron microscopy images of the (a) $SrMoO_4:Er^{3+}$, (b) $SrMoO_4:Er^{3+}/Yb^{3+}$ and (c) $SrMoO_4:Er^{3+}/Yb^{3+}$# particles after the cyclic microwave-assisted metathetic route followed by further heat treatment at 600 ºC for 3 h

Microwave-assisted metathetic reactions such as $SrCl_2 + Na_2MoO_4 \rightarrow SrMoO_4 + 2NaCl$ involve the exchange of atomic/ionic species in which the driving force is the exothermic reaction accompanying the formation of NaCl[24,25]. Microwave-assisted metathetic reactions occur so rapidly that the exothermic reaction is essentially used to heat up the solid products. The cyclic microwave-assisted metathetic reactions provide a convenient route for the synthesis of $SrMoO_4$, $SrMoO_4:Er^{3+}$, $SrMoO_4:Er^{3+}/Yb^{3+}$ and $SrMoO_4:Er^{3+}/Yb^{3+}$# particles[26,27]. The exothermic energy helped uniformly heat the bulk of the material, resulting in fine particles with a controlled morphology that fabricate the product in a green manner without generating solvent waste. This method is a simple and cost-effective method that can provide a high yields with easy scale-up, thus emerging as a viable alternative in the rapid synthesis of upconversion particles.

Fig. 2 shows the upconversion photoluminescence emission spectra of the as-prepared (a) $SrMoO_4:Er^{3+}$ (SMO:Er), (b) $SrMoO_4$: Er^{3+}/Yb^{3+} (SMO:Er/Yb) and (c) $SrMoO_4:Er^{3+}/Yb^{3+}$# (SMO:Er/Yb#) particles excited at 980 nm at room temperature. The strong 525-nm emission band and the weak 550-nm emission band in the green region are assigned to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, respectively, while the weak emission 655-nm band in the red region corresponds to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The doping amounts of Yb^{3+} had a great effect on both the morphological features and their upconversion fluorescence intensity of the particles. The Yb^{3+} ion as a sensitizer can be effectively excited by the energy of the incident light source and this excitation can transfer this energy to the activator, which can emit radiation. The Er^{3+} ion as an activator is the luminescence center in upconversion particles and the sensitizer enhances the upconversion luminescence efficiency. The upconversion intensity of (c) $SrMoO_4:Er^{3+}/Yb^{3+}$#(SMO:Er/Yb#) is much higher than that of (a) $SrMoO_4:Er^{3+}$ (SMO:Er) and (b) $SrMoO_4:Er^{3+}/Yb^{3+}$ (SMO:Er/Yb).

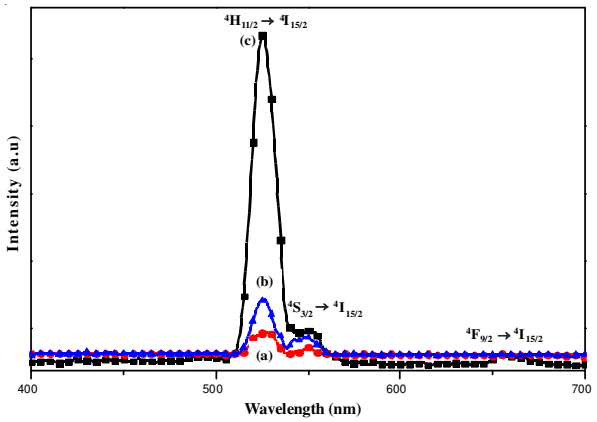

Fig. 2. Upconversion photoluminescence emission spectra of the (a) $SrMoO_4$:Er^{3+}(SMO:Er), (b) $SrMoO_4$:Er^{3+}/Yb^{3+}(SMO:Er/Yb) and (c) $SrMoO_4$:Er^{3+}/Yb^{3+}#(SMO:Er/Yb#) particles excited at 980 nm at room temperature

Fig. 3 shows the Raman spectra of (a) $SrMoO_4$(SMO), (b) $SrMoO_4$:Er^{3+}(SMO:Er), (c) $SrMoO_4$:Er^{3+}/Yb^{3+}(SMO:Er/Yb) and (d) $SrMoO_4$:Er^{3+}/Yb^{3+}#(SMO:Er/Yb#) particles on the samples excited by the 514.5-nm line of an Ar ion laser at 0.5 mW. The internal modes for the (a) $SrMoO_4$(SMO) particles were detected as $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(E_g)$, $\nu_4(B_g)$ and $\nu_2(B_g)$ vibrations at 887, 844, 795, 380, 357 and 327 cm^{-1}, respectively. A free rotation mode was detected at 180 cm^{-1} and the external modes were localized at 137 and 111 cm^{-1}. The well-resolved sharp peaks for the $SrMoO_4$ particles indicate the high crystallization of the synthesized particles. The internal vibration mode frequencies were dependent on the lattice parameters and the degree of the partially covalent bond between the cation and molecular ionic group $[MoO_4]^{2-}$. The Raman spectra of the (b) $SrMoO_4$:Er^{3+} (SMO:Er), (c) $SrMoO_4$:Er^{3+}/Yb^{3+} (SMO:Er/Yb) and (d) $SrMoO_4$:Er^{3+}/Yb^{3+}#(SMO:Er/Yb#) particles indicated that additional strong peaks at both higher frequencies (564, 524, 456 and 403 cm^{-1}) and lower frequencies (294, 251 and 220 cm^{-1}). They could be attributed to the bulk vibration modes of $SrMoO_4$ as a trace byproduct in the samples. The combination of a heavy metal cation and the large inter-ionic distance in the lattice result in low probability of upconversion and the phonon-splitting relaxation in $SrMoO_4$ crystals.

Conclusion

Er^{3+} and Yb^{3+} co-doped $SrMoO_4$ ($SrMoO_4$:Er^{3+}/Yb^{3+}) particles were successfully synthesized *via* a cyclic microwave-assisted metathetic route followed by further heat treatment. Well-crystallized $SrMoO_4$:Er^{3+}, $SrMoO_4$:Er^{3+}/Yb^{3+} and $SrMoO_4$:Er^{3+}/Yb^{3+}# particles were formed after heat treatment at 600 ºC for 3 h, showing a fine and homogeneous morphology and sizes of 100-500 nm. With excitation at 980 nm, $SrMoO_4$:Er^{3+}/Yb^{3+}# particles exhibited a strong 525-nm emission band and a weak 550-nm emission band in the green region. The upconversion intensity of the $SrMoO_4$:Er^{3+}/Yb^{3+}# particles was much higher than those of the $SrMoO_4$:Er^{3+} and $SrMoO_4$:Er^{3+}/Yb^{3+} particles. The Raman spectra of the $SrMoO_4$:Er^{3+}, $SrMoO_4$:Er^{3+}/Yb^{3+} and $SrMoO_4$:Er^{3+}/Yb^{3+}# particles indicated that the additional strong peaks at higher frequencies (564, 524, 456 and 403 cm^{-1}) and at lower frequencies (294, 251 and 220 cm^{-1}).

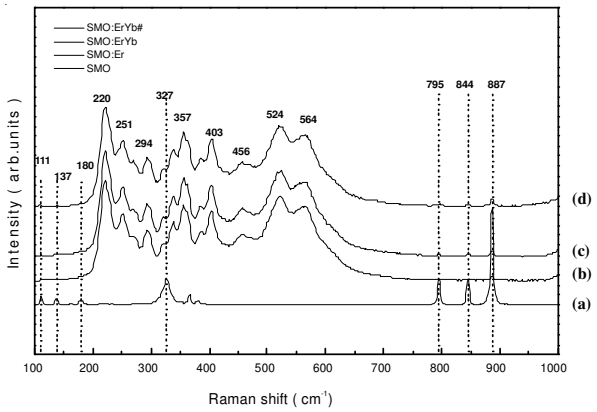

Fig. 3. Raman spectra of the (a) $SrMoO_4$(SMO), (b) $SrMoO_4$:Er^{3+}(SMO:Er), (c) $SrMoO_4$:Er^{3+}/Yb^{3+}(SMO:Er/Yb) and (d) $SrMoO_4$:Er^{3+}/Yb^{3+}#(SMO:Er/Yb#) particles excited by the 514.5-nm line of an Ar ion laser at 0.5 mW on the sample

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