Microwave-Assisted Metathetic Synthesis of $\text{Er}^{3+}/\text{Yb}^{3+}$ Co-Doped BaMoO_4 Particles and Their Upconversion Photoluminescence Properties†

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Er^{3+} doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}^{3+}$) and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$) particles were successfully synthesized by a cyclic microwave-assisted metathetic method showing a fine and homogeneous morphology with particle sizes of 0.5-1 μm . At excitation at 980 nm, $\text{BaMoO}_4:\text{Er}^{3+}$ and $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles exhibited a strong 525-nm emission band and a weak 550-nm emission band in the green region. The UC intensity of $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles was higher than that of the $\text{BaMoO}_4:\text{Er}^{3+}$ particles. The Raman spectrum of $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles indicated the detection of additional peaks at higher frequencies (390 and 505 cm^{-1}) and at lower frequencies (218 and 255 cm^{-1}).

Key Words: $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped BaMoO_4 , Microwave-assisted metathetic synthesis, Upconversion photoluminescence.

INTRODUCTION

The upconversion photoluminescence particles have shown potential applications in various fields including bio-medical imaging owing to their unique upconversion optical behaviours that offer improved light penetration depth, high chemical and photo stability, as well as the absence of auto-fluorescence during imaging, sharp emission bands and high resistance to photobleaching, which overcome the current limitations in traditional photoluminescence materials¹⁻³. Particles of rare earth-doped upconversion BaMoO_4 , which is at type of metallic molybdate compound with a schlegel-type structure of lattice parameters $a = b = 5.573 \text{ \AA}$ and $c = 12.786 \text{ \AA}$ ⁴⁻⁶, are relatively stable in air and have stable physical and chemical properties, low excitation threshold energy and low-cost productivity. Energy transfer plays a crucial role in luminescence materials because it varies the luminescence intensity depending on the co-doped ion. Rare earth ions, such as Er^{3+} and Yb^{3+} ions, act as efficient sensitizers or activators that transfer energy in several host lattices. The Yb^{3+} ion as a sensitizer can be excited effectively by the energy of the incident light source and this excitation transfers this energy to the activator, which emits radiation. The co-doped Yb^{3+} ion and Er^{3+} ion can remarkably enhance the upconversion efficiency from infrared to visible light due to the efficient energy transfer from Yb^{3+} to Er^{3+} ⁷⁻⁹.

Recently, several processes have been developed to increase the applications of rare-earth-doped metal molybdates

prepared using a range of processes, including solid-state reactions¹⁰⁻¹⁴, co-precipitation¹⁵, the sol-gel method¹⁶, the hydrothermal method¹⁷⁻¹⁹, the Pechini method²⁰, the solvothermal route²¹ and the microwave-assisted hydrothermal method²². For practical application of upconversion photoluminescence in such products as lasers, three-dimensional displays, light emitting devices and biological detectors, features such as homogeneous upconversion particle size distribution and morphology need to be well defined. Compared with the usual methods, cyclic microwave-assisted metathetic synthesis of materials is a simple and cost-effective method that provides high yield with easy scale up and is emerging as a viable alternative approach for the synthesis of high-quality novel inorganic materials in short time periods^{4,23}.

In this study, Er^{3+} doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}^{3+}$) and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$) particles were synthesized by the cyclic microwave-assisted metathetic route, followed by heat-treatment. The synthesized Er^{3+} doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}^{3+}$) and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$) particles were characterized by X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy. Optical properties were examined by using photoluminescence emission data and Raman spectroscopy.

EXPERIMENTAL

Appropriate stoichiometric amounts of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and ethylene glycol

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of analytic reagent grade were used to prepare the BaMoO_4 , $\text{BaMoO}_4\text{:Er}^{3+}$ and $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ compounds. To prepare BaMoO_4 , 1 mol % $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ and 1 mol % $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol. To prepare $\text{BaMoO}_4\text{:Er}^{3+}$, 0.95 mol % $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ with 0.05 mol % $\text{ErCl}_3\cdot 6\text{H}_2\text{O}$ and 1 mol % $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol. To prepare $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$, 0.9 mol % $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ with 0.05 mol % $\text{ErCl}_3\cdot 6\text{H}_2\text{O}$ and 0.05 mol % $\text{YbCl}_3\cdot 6\text{H}_2\text{O}$ and 1 mol % $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol.

The solutions were mixed and adjusted to pH 9.5 using NaOH. The aqueous solutions were stirred at room temperature. The mixtures were transferred into 120 mL Teflon vessels, respectively. Each Teflon vessel was placed into a microwave oven operating at a frequency of 2.45 GHz with a maximum output power 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, followed by a further treatment of 30 s on and 60 s off for 15 min. The ethylene glycol was evaporated slowly at its boiling point. Ethylene glycol, a polar solvent at its boiling point of 197 °C, is a good candidate for the microwave process. The resulting samples were treated with ultrasonic radiation and washed many times with hot distilled water. The white precipitates were collected and dried at 100 °C in a drying oven. The final products were heat-treated at 600 °C for 3 h. The phase of the particles after the cyclic microwave-assisted metathetic reaction and heat-treatment was identified using XRD (D/MAX 2200, Rigaku, Japan). The microstructures and surface morphologies of the $\text{BaMoO}_4\text{:Er}^{3+}$ and $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ particles were observed by using SEM/EDS (JSM-5600, JEOL, Japan). Their PL 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 samples was kept at 0.5 mW.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of (a) the data of JCPDS 29-01930 and the synthesized (b) $\text{BaMoO}_4\text{:Er}^{3+}$ and (c) $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ particles. All of the XRD peaks could be assigned to the tetragonal-phase BaMoO_4 with a scheelite-type structure, which was in good agreement with the crystallographic data of BaMoO_4 (JCPDS 29-01930). This finding means that the tetragonal-phase $\text{BaMoO}_4\text{:Er}^{3+}$ and $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ particles can be prepared using the cyclic microwave-assisted metathetic route. Post heat-treatment plays an important role in a well-defined crystallized morphology. To achieve a well-defined crystalline morphology, the $\text{BaMoO}_4\text{:Er}^{3+}$ and $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ phases need to be heat treated at 600 °C for 3 h. The BaMoO_4 formed by the Pechini method had a scheelite-type crystal structure with lattice parameters of $a = b = 5.573 \text{ \AA}$ and $c = 12.786 \text{ \AA}$. This finding suggests that the cyclic microwave-assisted metathetic route is suitable for growing $\text{BaMoO}_4\text{:Er}^{3+}$ and $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ crystallites and for developing the strongest intensity peaks at the (112), (204) and (132) planes, which are the major peaks of BaMoO_4 .

Fig. 1. X-ray diffraction patterns of (a) the data of JCPDS 29-01930 and the synthesized (b) $\text{BaMoO}_4\text{:Er}^{3+}$ and (c) $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ particles

Fig. 2 shows SEM images of the synthesized (a) $\text{BaMoO}_4\text{:Er}^{3+}$ and (b) $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ particles. The as-synthesized samples are well crystallized with a fine and homogeneous morphology with particle sizes of 0.5–1 μm . microwave-assisted metathetic reactions, such as $\text{BaCl}_2 + \text{Na}_2\text{MoO}_4 \rightarrow \text{BaMoO}_4 + 2\text{NaCl}$, involve the exchange of atomic/ionic species, in which the driving force is the exothermic reaction accompanying the formation of NaCl. microwave-assisted metathetic reactions occur so rapidly that the exothermic reaction is essentially used to heat up the solid products.

Fig. 2. Scanning electron microscopy images of the synthesized (a) $\text{BaMoO}_4\text{:Er}^{3+}$ and (b) $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ particles

The cyclic microwave-assisted metathetic reactions provide a convenient route for the synthesis of BaMoO_4 , $\text{BaMoO}_4\text{:Er}^{3+}$ and $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ particles. The cyclic microwave-assisted metathetic route provides the exothermic energy to synthesize the bulk of the material uniformly, so that fine particles with controlled morphology can be fabricated in an environmentally friendly manner without the generation of solvent waste. $\text{BaMoO}_4\text{:Er}^{3+}$ and $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$, as well as BaMoO_4 particles, were heated rapidly and uniformly by the cyclic microwave-assisted metathetic route. Therefore, this method is a simple and cost-effective method that can provide high yields with easy scale up, thus emerging as a viable alternative in the rapid synthesis of upconversion particles.

Fig. 3 shows the upconversion photoluminescence emission spectra of (a) $\text{BaMoO}_4\text{:Er}^{3+}$ (BMO:Er) and (b) $\text{BaMoO}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ (BMO:Er/Yb) particles excited at 980 nm.

The strong emission band of 525 nm and the weak emission band of 550 nm in the green region are assigned to the transitions $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ of Er^{3+} ions, respectively. The doping amounts of $\text{Er}^{3+}/\text{Yb}^{3+}$ had a great effect on both the morphological features and upconversion fluorescence intensity. The Yb^{3+} ion as a sensitizer can be effectively excited by the energy of the incident light source, which transfers this energy to the activator, where radiation can be emitted. The Er^{3+} ion as an activator is the luminescence center in upconversion particles and the sensitizer enhances the upconversion luminescence efficiency.

Fig. 3. Upconversion photoluminescence emission spectra of the synthesized (a) $\text{BaMoO}_4:\text{Er}^{3+}$ (BMO:Er) and (b) $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (BMO:Er/Yb) particles excited at 980 nm at room temperature

The upconversion intensity of (c) BMO:Er/Yb is much higher than that of BMO:Er. The upconversion process is a proven successful method for generating visible light from near infrared (NIR) radiation. Upconversion is a nonlinear optical process in which excitation of the lower electronic levels with low-energy radiation (NIR light) results in higher energy emission (visible or ultraviolet light) at higher electronic levels; thus it is ascribed as an anti-Stokes mechanism. This process requires the absorption of two or more photons to produce sufficient energy for upconversion emission. The different classes of upconversion processing mechanisms can lead to absorption of two or more photons: excited-state absorption, energy transfer upconversion and photon avalanche. The ETU process involves a sequential absorption of two photons, in which energy is transferred from an excited ion (sensitizer) to another neighboring ion (activator) and is independent of the excitation power so it can be quite efficient under optimized conditions with high dopant ion concentrations.

Fig. 4 shows the Raman spectra of the (a) BaMoO_4 (BMO), (b) $\text{BaMoO}_4:\text{Er}^{3+}$ (BMO:Er) and (c) $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (BMO: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) BaMoO_4 (BMO) and (b) $\text{BaMoO}_4:\text{Er}^{3+}$ (BMO:Er) particles were detected as $\nu_1(\text{A}_g)$, $\nu_3(\text{B}_g)$, $\nu_3(\text{E}_g)$, $\nu_4(\text{E}_g)$, $\nu_4(\text{B}_g)$ and $\nu_2(\text{B}_g)$ vibrations at 891, 838, 791, 359, 346 and 325 cm^{-1} , respectively. A free rotation mode was detected at 187 cm^{-1}

and the external modes were localized at 140 and 107 cm^{-1} . 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 $[\text{MoO}_4]^{2-}$. The Raman spectra of the (c) $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles indicate additional peaks at both higher frequencies (505 and 390 cm^{-1}) and lower frequencies (255 and 218 cm^{-1}). The Raman spectra of $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles proved that the doping ion of Yb^{3+} can influence the structure of the host materials.

Fig. 4. Raman spectra of the synthesized (a) BaMoO_4 (BMO), (b) $\text{BaMoO}_4:\text{Er}^{3+}$ (BMO:Er) and (c) $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (BMO:Er/Yb) particles excited by the 514.5-nm line of an Ar-ion laser at 0.5 mW on the samples

Conclusion

upconversion photoluminescence of Er^{3+} doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}_{3+}$) and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped BaMoO_4 ($\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$) particles was successfully achieved by a microwave-assisted metathetic route. Well-crystallized upconversion $\text{BaMoO}_4:\text{Er}^{3+}$ and $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles formed after heat-treatment at 600 $^{\circ}\text{C}$ for 3 h showed a fine and homogeneous morphology with particle sizes of 0.5-1 μm . At excitation at 980 nm, $\text{BaMoO}_4:\text{Er}^{3+}$ and $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles exhibited a strong 525-nm emission band and a weak 550-nm emission band in the green region, which were assigned to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions, respectively. The upconversion intensity of $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles was higher than that of the $\text{BaMoO}_4:\text{Er}^{3+}$ particles. The Raman spectrum of $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles indicated the detection of additional peaks at higher frequencies (390 and 505 cm^{-1}) and at lower frequencies (218 and 255 cm^{-1}). The Raman spectra of $\text{BaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles proved that the doping ion of Yb^{3+} can influence the structure of the host materials.

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