

Fabrication and Upconversion Photoluminescence of CaMoO_4 : Er^{3+} , Yb^{3+} Particles by A Cyclic Microwave-Assisted Metathetic Method[†]

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Well-crystallized $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped CaMoO_4 ($\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$) particles were successfully synthesized *via* a cyclic microwave-assisted metathetic method, followed by further heat-treatment at 600 °C for 3 h, showing a fine and homogeneous morphology with sizes of 0.2-1 μm . With excitation at 980 nm, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ 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 $\text{CaMoO}_4:\text{Er}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles indicated that the additional strong peaks at higher frequencies (618, 575, 492, 420 and 373 cm^{-1}) and at lower frequencies (290 and 234 cm^{-1}).

Key Words: Upconversion photoluminescence, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles, Cyclic microwave, Metathetic method, Raman spectroscopy.

INTRODUCTION

Upconversion photoluminescence particles have the ability to convert near infrared radiations with low energy into visible radiations with high energy. Recently, these upconversion photoluminescence particles have evolved in their applications, showing great potential for imaging and biodetection assays in both *in vitro* and *in vivo* with their high penetration depth into tissues, sharp emission bands and high resistance to photobleaching, which overcome the current limitations in traditional photoluminescence materials¹. Rare earth-doped upconversion CaMoO_4 particles are among the metallic molybdate compounds that have a scheelite-type structure, which have lattice parameters of $a = b = 5.212 \text{ \AA}$ and $c = 11.438^{2,3}$, are relatively stable in air and have stable physical and chemical properties, a low excitation threshold energy and a low-price productivity. Energy transfer plays a crucial role in luminescence materials because it varies the luminescence intensities according to the co-doped ion. Rare earth ions, such as Yb^{3+} and Er^{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 with Er^{3+} ion can remarkably enhance the upconversion

efficiency from infrared to visible lights due to the efficiency energy transfer from Yb^{3+} to Er^{3+} ^{4,5}.

Recently, several processes have been developed to enhance the applications of rare-earth-doped metal molybdates prepared using a range of processes, including solid-state reactions^{6,7}, co-precipitation⁸, the sol-gel method⁹, the hydrothermal method^{10,11}, the Pechini method¹², the solvothermal route¹³ and the microwave-assisted hydrothermal method¹⁴. To use the practical application of upconversion photoluminescence in products such as lasers, three-dimensional displays, light emitting devices and biological detection, well-defined features such as homogeneous upconversion particle size distribution and morphology are required. Compared with the usual methods, microwave synthesis has the advantages of very short reaction time, small-size particles and narrow particle size distribution and high purity for preparing polycrystalline samples¹⁵.

In this study, $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped CaMoO_4 ($\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$) particles were synthesized using a cyclic microwave-assisted metathetic route, followed by further heat-treatment. The synthesized $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ 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 CaCl_2 , $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and ethylene glycol of analytic reagent grade were used to prepare the CaMoO_4 , $\text{CaMoO}_4:\text{Er}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ and $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#\#$ compounds. To prepare (i) CaMoO_4 , 1 mol % CaCl_2 and 1 mol % $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 30 mL ethylene glycol. To prepare (ii) $\text{CaMoO}_4:\text{Er}^{3+}$, 0.95 mol % $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 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 (iii) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, 0.9 mol % CaCl_2 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. To prepare (iv) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$, 0.8 mol % CaCl_2 with 0.02 mol % $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.18 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. To prepare (v) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#\#$, 0.78 mol % CaCl_2 with 0.02 mol % $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.2 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. In the 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 out-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 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 °C, is a good candidate for the microwave process. 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 microstructure and surface morphology of the CaMoO_4 , $\text{CaMoO}_4:\text{Er}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ and $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#\#$ 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 samples was kept at 0.5 mW.

RESULTS AND DISCUSSION

Fig. 1 shows SEM images of the (a) CaMoO_4 , (b) $\text{CaMoO}_4:\text{Er}^{3+}$, (c) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and (d) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles after the cyclic microwave-assisted metathetic route followed by further heat-treatment at 600 °C for 3 h. The as-synthesized samples are well crystallized with a fine and homogeneous morphology with particles of different sizes of 1-4 μm for the (a) CaMoO_4 and 0.2-1 μm for the (b) $\text{CaMoO}_4:\text{Er}^{3+}$, (c) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and (d) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$. The samples of (a) CaMoO_4 , (b) $\text{CaMoO}_4:\text{Er}^{3+}$ and (c) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ show well crystallized morphology, while the sample of (d) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ shows a scattered morphology with obvious discrepancy in crystallization and

particle size. This discrepancy means that the doping amounts of the 0.05 mol % Er^{3+} for $\text{CaMoO}_4:\text{Er}^{3+}$ and 0.05 mol % Er^{3+} and 0.05 mol % Yb^{3+} for $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ have little effect on the morphological features. However, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ (d) compared to $\text{CaMoO}_4:\text{Er}^{3+}$ (b) and $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (c) has somewhat different shape. The doping amounts of 0.02 mol % Er^{3+} and 0.18 mol % Yb^{3+} for $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ have a great effect on the morphological features.

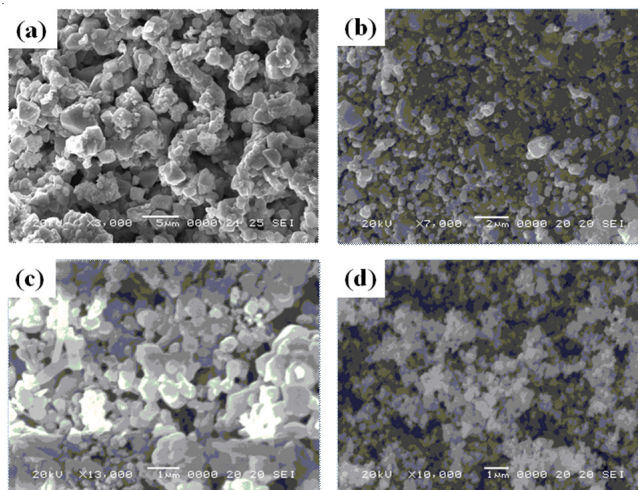


Fig. 1. Scanning electron microscopy images of the (a) CaMoO_4 , (b) $\text{CaMoO}_4:\text{Er}^{3+}$, (c) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and (d) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles after the cyclic microwave-assisted metathetic route followed by further heat-treatment at 600 °C for 3 h

Microwave-assisted metathetic reactions, such as $\text{CaCl}_2 + \text{Na}_2\text{MoO}_4 \rightarrow \text{CaMoO}_4 + 2\text{NaCl}$, involve the exchange of atomic/ionic species, in which the driving force is the exothermic reaction accompanying the formation of NaCl ¹⁶. 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 CaMoO_4 , $\text{CaMoO}_4:\text{Er}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ and $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#\#$ particles. The cyclic microwave-assisted metathetic route of metal molybdates¹⁷ provides the exothermic energy to synthesize the bulk of the material uniformly, so that fine particles with controlled morphology could be fabricated in an environmentally friendly manner without the generation of solvent waste. $\text{CaMoO}_4:\text{Er}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ and $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#\#$ particles, as well as CaMoO_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. 2 shows the upconversion photoluminescence emission spectra of (a) $\text{CaMoO}_4:\text{Er}^{3+}$ (CMO:Er), (b) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (CMO:Er/Yb) and (c) $\text{CaMoO}_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ (CMO: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, while the weak emission band in the red region of 655 nm corresponds to ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$. The doping amounts of Yb^{3+} had a great effect on both the morphological

features and their upconversion fluorescence intensity. The Yb³⁺ 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 Er³⁺ ion as an activator is the luminescence center in upconversion particles and the sensitizer enhances the upconversion luminescence efficiency. The upconversion intensity of (c) CaMoO₄:Er³⁺/Yb³⁺# (CMO:Er/Yb#) is much higher than those of (a) CaMoO₄:Er³⁺ (CMO:Er) and (b) CaMoO₄:Er³⁺/Yb³⁺ (CMO:Er/Yb).

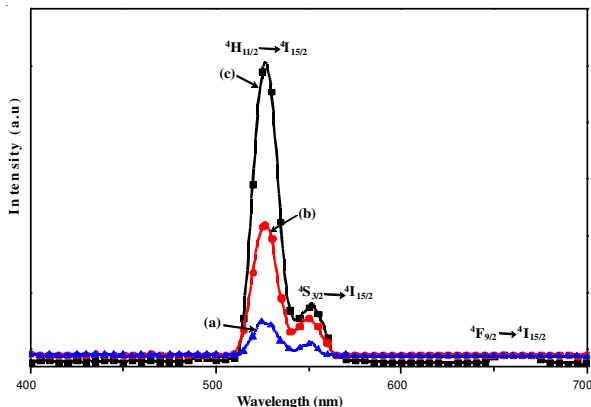


Fig. 2. Upconversion photoluminescence emission spectra of the (a) CaMoO₄:Er³⁺ (CMO:Er), (b) CaMoO₄:Er³⁺/Yb³⁺ (CMO:Er/Yb) and (c) CaMoO₄:Er³⁺/Yb³⁺# (CMO:Er/Yb#) particles excited at 980 nm at room temperature

Fig. 3 shows the Raman spectra of the (a) CaMoO₄ (CMO), (b) CaMoO₄:Er³⁺ (CMO:Er), (c) CaMoO₄:Er³⁺/Yb³⁺ (CMO:Er/Yb), (d) CaMoO₄:Er³⁺/Yb³⁺# (CMO:Er/Yb#) and (e) CaMoO₄:Er³⁺/Yb³⁺## (CMO: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) CaMoO₄(CMO) 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 878, 847, 793, 380, 357 and 321 cm⁻¹, respectively. A free rotation mode was detected at 180 cm⁻¹ and the external modes were localized at 140 and 109 cm⁻¹. The well-resolved sharp peaks of the CaMoO₄ 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 [MoO₄]²⁻. The Raman spectra of the (b) CaMoO₄:Er³⁺ (CMO:Er), (c) CaMoO₄:Er³⁺/Yb³⁺ (CMO:Er/Yb) and (d) CaMoO₄:Er³⁺/Yb³⁺# (CMO:Er/Yb#) particles indicate additional strong peaks at both higher frequencies (618, 575, 492, 420 and 373 cm⁻¹) and lower frequencies (290 and 234 cm⁻¹). They could be attributed to the bulk vibration modes of CaMoO₄ as a trace byproduct in the samples. Such detection shows that Raman spectroscopy is a more sensitive technique with higher resolution than XRD for phase identification. The combination of a heavy metal cation and the large interionic distance in the lattice result in a low probability of up-conversion and the phonon splitting relaxation in CaMoO₄ crystals.

Conclusion

Er³⁺/Yb³⁺ co-doped CaMoO₄ (CaMoO₄:Er³⁺/Yb³⁺) particles were successfully synthesized via a cyclic microwave-assisted metathetic route followed by further heat-treatment. With excitation at 980 nm, CaMoO₄:Er³⁺/Yb³⁺# particles exhibited

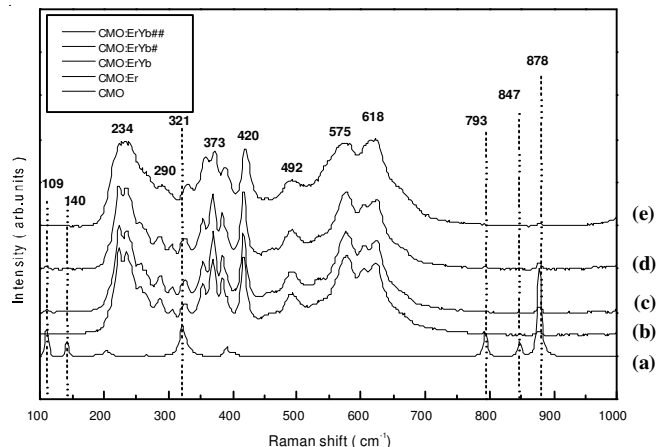


Fig. 3. Raman spectra of the (a) CaMoO₄ (CMO), (b) CaMoO₄:Er³⁺ (CMO:Er), (c) CaMoO₄:Er³⁺/Yb³⁺ (CMO:Er/Yb), (d) CaMoO₄:Er³⁺/Yb³⁺# (CMO:Er/Yb#) and (e) CaMoO₄:Er³⁺/Yb³⁺## (SMO:Er/Yb##) particles excited by the 514.5-nm line of an Ar-ion laser at 0.5 mW on the sample

a strong 525-nm emission band and a weak 550-nm emission band in the green region. The upconversion intensity of CaMoO₄:Er³⁺/Yb³⁺# particles was much higher than those of the CaMoO₄:Er³⁺ and CaMoO₄:Er³⁺/Yb³⁺ particles. The Raman spectra of CaMoO₄:Er³⁺, CaMoO₄:Er³⁺/Yb³⁺, CaMoO₄:Er³⁺/Yb³⁺# and CaMoO₄:Er³⁺/Yb³⁺## particles indicated that the additional strong peaks at higher frequencies (618, 575, 492, 420 and 373 cm⁻¹) and at lower frequencies (290 and 234 cm⁻¹).

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