Fabrication and characterization of upconversion photoluminescence CaMoO₄: Er³⁺/Yb³⁺ particles by a cyclic microwave-assisted metathetic method

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Er³⁺/Yb³⁺ co-doped CaMoO₄ (CaMoO₄:Er³⁺/Yb³⁺) particles were successfully synthesized by a cyclic microwave-assisted metathetic (MAM) method, followed by further heat-treatment. Well-crystallized CaMoO₄:Er³⁺/Yb³⁺ particles were formed after heat-treatment at 600 °C for 3 h, and showed a fine and homogeneous morphology with sizes of 0.2-1 µm. With excitation at 980 nm, CaMoO₄:Er³⁺/Yb³⁺ 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 upconversion (UC) 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:Er⁵⁺/Yb³⁺ and CaMoO₄:Er³⁺/Yb³⁺## particles indicated the detection of 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, CaMoO₄:Er³⁺/Yb³⁺ particles, Cyclic microwave, Metathetic method, Raman spectroscopy.

Introduction

Upconversion (UC) photoluminescence particles can convert near infrared radiation of low energy into visible radiation of high energy. Recently, these UC 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 materials [1-3]. Particles of rare earth-doped UC CaMoO₄, which is at type of metallic molybdate compound with a schleelite-type structure of lattice parameters a = b = 5.212 Å and c = 11.438 Å [4-6], are relatively stable in air and have stable physical and chemical properties, low excitation threshold energy, and low-cost production. Energy transfer plays a crucial role in luminescent materials because it varies the luminescent intensity depending on the co-doped ion. Rare earth ions, such as Yb³⁺ and Er³⁺ ions, act as efficient sensitizers or activators that transfer energy in several host lattices. The Yb³⁺ 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 Yb³⁺ ion and Er³⁺ ion can remarkably enhance the UC efficiency from infrared to visible light due to the efficient energy transfer from Yb³⁺ to Er³⁺ [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 reactions [10-14], co-precipitation [15], the sol-gel method [16], the hydrothermal method [17-19], the Pechini method [20], the solvothermal route [21] and the microwave-assisted hydrothermal method [22]. For practical application of UC photoluminescence in such products as lasers, three-dimensional displays, light emitting devices, and biological detectors, features such as homogeneous UC particle size distribution and morphology need to be well defined. Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, small-size particles and narrow particle size distribution, and high purity for preparing polycrystalline samples. Microwave energy is delivered directly to the material by molecular interactions under an electric field. Therefore, it is possible to rapidly and uniformly heat thick materials. Cyclic microwave-assisted metathetic (MAM) synthesis of materials is a simple and cost-effective method that provides a 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 [6, 23].

In this study, Er³⁺/Yb³⁺ co-doped CaMoO₄ (CaMoO₄: Er³⁺/Yb³⁺) particles were synthesized by the cyclic MAM route, followed by heat-treatment. The synthesized CaMoO₄:Er³⁺/Yb³⁺ particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Optical properties were examined by using photoluminescence (PL) emission data and Raman spectroscopy.
Experimental

Appropriate stoichiometric amounts of CaCl\(_2\), ErCl\(_3\), 6H\(_2\)O, YbCl\(_3\), 6H\(_2\)O, Na\(_2\)MoO\(_4\), 2H\(_2\)O and ethylene glycol of analytic reagent grade were used to prepare the doped CaMoO\(_4\). The white precipitates were formed by the Pechini method had a scheelite-type structure, which was in good agreement with the XRD patterns and the X-ray phase analysis. Post heat-treatment plays an important role in a well-defined crystallized morphology. To achieve a well-defined crystalline phase, the CaMoO\(_4\) phases need to be heat treated at 600 °C for 3 h. The CaMoO\(_4\) formed by the Pechini method had a scheelite-like crystal structure with lattice parameters of \(a = b = 5.212 \text{ Å}\) and \(c = 11.438 \text{ Å}\). This finding suggests that the cyclic MAM reaction is suitable for growing CaMoO\(_4\) crystallites and for developing the strongest intensity peaks of the (101), (112) and (312) planes, which are the major peaks of CaMoO\(_4\) [4-6]. The widths of the peaks increase slightly according to the amount of doping with Yb\(^{3+}\) in the cases of (b) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)# and (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)#. It is assumed that the doping amount of Er\(^{3+}\)/Yb\(^{3+}\)# has a great effect on the crystalline cell volume of the CaMoO\(_4\), because of the different ionic sizes and valence states.

Fig. 2 shows SEM images of the (a) CaMoO\(_4\), (b) CaMoO\(_4\):Er\(^{3+}\), (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\) and (d) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)# particles after the cyclic MAM 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) CaMoO\(_4\):Er\(^{3+}\), (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)## particles.

Results and Discussion

Fig. 1 shows the XRD patterns of the synthesized (a) CaMoO\(_4\):Er\(^{3+}\), (b) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\) and (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)# particles. All of the XRD peaks could be assigned to the tetragonal-phase CaMoO\(_4\) with a scheelite-type structure, which was in good agreement with the XRD data of CaMoO\(_4\) (JCPDS 85-0585). This finding means that the tetragonal-phase CaMoO\(_4\) can be prepared using the cyclic MAM route. Post heat-treatment plays an important role in a well-defined crystalline morphology. To achieve a well-defined crystalline phase, the CaMoO\(_4\) phases need to be heat treated at 600 °C for 3 h. The CaMoO\(_4\) formed by the Pechini method has a scheelite-type crystal structure with lattice parameters of \(a = b = 5.212 \text{ Å}\) and \(c = 11.438 \text{ Å}\). This finding suggests that the cyclic MAM route is suitable for growing CaMoO\(_4\) crystallites and for developing the strongest intensity peaks of the (101), (112) and (312) planes, which are the major peaks of CaMoO\(_4\) [4-6]. The widths of the peaks increase slightly according to the amount of doping with Yb\(^{3+}\) in the cases of (b) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)# and (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)#. It is assumed that the doping amount of Er\(^{3+}\)/Yb\(^{3+}\)# has a great effect on the crystalline cell volume of the CaMoO\(_4\), because of the different ionic sizes and valence states.

Fig. 2 shows SEM images of the (a) CaMoO\(_4\), (b) CaMoO\(_4\):Er\(^{3+}\), (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\) and (d) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)# particles after the cyclic MAM 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) CaMoO\(_4\):Er\(^{3+}\), (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)## particles.

Fig. 1. X-ray diffraction patterns of the synthesized (a) CaMoO\(_4\):Er\(^{3+}\), (b) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\) and (c) CaMoO\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)# particles.
the solid products. The cyclic MAM reactions provide an exothermic reaction is essentially used to heat up NaCl [24, 25]. MAM reactions occur so rapidly that the exothermic reaction accompanying the formation of atomic/ionic species, in which the driving force is uniformly, so that fine particles with a controlled size. This discrepancy means that the amounts of an obvious discrepancy in crystallization and particle size. 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 UC particles.

Fig. 4 shows the UC photoluminescence emission spectra of (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. The strong emission band of 525 nm and the weak emission band in the red region are assigned to the transitions 2H₁₁/₂ → 4I₁₅/₂ and 5S₅/₂ → 4I₁₅/₂ of Er³⁺ ions, respectively, while the weak emission band in the red region of 655 nm corresponds to the transition of 5F₉/₂ → 4I₁₅/₂. The UC intensity of CaMoO₄:Er³⁺/Yb³⁺# particles was much higher than those of the CaMoO₄: Er³⁺ and CaMoO₄:Er³⁺/Yb³⁺ particles. The amounts of doping by Er³⁺/Yb³⁺ had a great effect on both the morphological features and UC 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 UC particles, and the sensitizer enhances the UC luminescence efficiency. The UC intensity of (c) CMO:Er/Yb# is much higher than those of (a) CMO:Er, (b) CMO:Er/Yb. The UC process is a proven successful method for generating visible light from near infrared (NIR) radiation. UC is a nonlinear optical process in which excitation of the lower electronic levels with a 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-Stockes mechanism. This process requires the absorption of two or more photons to
produce sufficient energy for UC emission. The different classes of UC processing mechanisms can lead to absorption of two or more photons: excited-state absorption (ESA), energy transfer upconversion (ETU) and photon avalanche (PA) [1-3]. A typical ETU process involves the energy transfer between the two ions, the sensitizer and the activator. The ETU process involves a sequential absorption of two photons that transfers energy 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. 5 shows the schematic energy level diagrams of Er$^{3+}$ ions (activator) and Yb$^{3+}$ ions (sensitizer) in the as-prepared CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ samples and the UC mechanisms accounting for the green and red emissions at 980-nm laser excitation.

particles on the samples excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples. The well-resolved sharp peaks of the CaMoO$_4$ particles indicate the high crystallization of the synthesized particles. 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 [MoO$_4$]$^2-$. The Raman spectra of the (b) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ (CMO:Er), (c) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ (CMO:Er/Yb), (d) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$# (CMO:Er/Yb#) and (e) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$## (CMO:Er/Yb##) particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW. The internal modes for the (a) CaMoO$_4$ (CMO) particles were detected as $\nu(A_g)$, $\nu(B_g)$, $\nu(E_g)$, $\nu(D_g)$ and $\nu(B_u)$ 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 CaMoO$_4$ particles indicate the high crystallization of the synthesized particles. 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 [MoO$_4$]$^2-$. The Raman spectra of the (b) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ (CMO:Er), (c) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ (CMO:Er/Yb), (d) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$# (CMO:Er/Yb#) and (e) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$## (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$^{-1}$). The Raman spectra of CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$/Yb$^{3+}$ and CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$/Yb$^{3+}$# and CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$## and CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$#### particles proved that the doping ions can influence the structure of the host materials. This finding was attributed to the bulk vibration modes as a trace byproduct in the samples.

**Conclusions**

The UC photoluminescence of Er$^{3+}$/Yb$^{3+}$ co-doped CaMoO$_4$ (CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$) particles was successfully achieved by a cyclic MAM route. Well-crystallized CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$###### particles were formed after heat-treatment at 600 °C for 3 h, showing a fine and homogeneous morphology with particle sizes of 1-3 nm. With excitation at 980 nm, CaMoO$_4$:Er$^{3+}$/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 $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{5/2} \rightarrow ^4I_{15/2}$ transitions of Er$^{3+}$ ions, respectively, while a

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**Fig. 5.** Schematic energy level diagrams of Er$^{3+}$ ions (activator) and Yb$^{3+}$ ions (sensitizer) in the as-prepared CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ samples and the UC mechanisms accounting for the green and red emissions at 980-nm laser excitation.

**Fig. 6.** Raman spectra of the synthesized (a) CaMoO$_4$ (CMO), (b) CaMoO$_4$:Er$^{3+}$ (CMO:Er), (c) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ (CMO:Er/Yb), (d) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$# (CMO:Er/Yb#) and (e) CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$## (CMO:Er/Yb##) particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples.
Fabrication and characterization of upconversion photoluminescence CaMoO$_4$: Er$^{3+}$/Yb$^{3+}$ particles by a cyclic microwave-assisted method

A weak 655-nm emission band in the red region was assigned to the $^4$F$_{9/2} \rightarrow ^4$I$_{15/2}$ transition. The UC intensity of CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ particles was much higher than those of the CaMoO$_4$:Er$^{3+}$ and CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$ particles. The Raman spectra of CaMoO$_4$:Er$^{3+}$, CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$, CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$, CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$/Er$^{3+}$/Yb$^{3+}$ and CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$/Er$^{3+}$/Yb$^{3+}$ particles indicated the detection of additional strong peaks at higher frequencies (618, 575, 492, 420 and 373 cm$^{-1}$) and at lower frequencies (290 and 234 cm$^{-1}$). The Raman spectra of CaMoO$_4$:Er$^{3+}$, CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$, CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$/Er$^{3+}$/Yb$^{3+}$ and CaMoO$_4$:Er$^{3+}$/Yb$^{3+}$/Er$^{3+}$/Yb$^{3+}$ particles proved that the doping ions can influence the structure of the host materials. This finding was attributed to the bulk vibration modes as a trace byproduct in the samples.

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References