

Preparation and Upconversion Photoluminescence of Er³⁺/Yb³⁺ Co-Doped CaWO₄ Particles *via* Microwave-Assisted Metathetic Route

CHANG SUNG LIM

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 356-706, South Korea

Corresponding author: Tel/Fax: +82 41 6601445; E-mail: cslim@hanseo.ac.kr

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Upconversion photoluminescence of Er³⁺ doped CaWO₄ (CaWO₄:Er³⁺) and Er³⁺/Yb³⁺ co-doped CaWO₄ (CaWO₄:Er³⁺/Yb³⁺) particles was successfully achieved by a cyclic microwave-assisted metathetic route. Well-crystallized CaWO₄:Er³⁺ and CaWO₄:Er³⁺/Yb³⁺ particles formed after heat-treatment at 600 °C for 3 h showed a fine and homogeneous morphology with particle sizes of 1-3 μm. At excitation at 980 nm, CaWO₄:Er³⁺ and CaWO₄:Er³⁺/Yb³⁺ particles exhibited a strong 525-nm emission band and a weak 550-nm emission band in the green region. The upconversion intensity of CaWO₄:Er³⁺/Yb³⁺ particles was much higher than that of the CaWO₄:Er³⁺ particles. The Raman spectra of the CaWO₄:Er³⁺/Yb³⁺ particles indicated the detection of additional peaks at higher frequencies (620, 573, 481, 371 and 355 cm⁻¹) and lower frequencies (315, 265, 217 and 203 cm⁻¹).

Key Words: Upconversion photoluminescence, CaWO₄:Er³⁺/Yb³⁺, Microwave-assisted metathetic synthesis, Optical properties.

INTRODUCTION

Recently, near-infrared light excited upconversion (UC) photoluminescence particles have shown potential applications in various fields including biomedical 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 Ln-doped upconversion CaWO₄, which is at type of metallic tungstate compound with a Scheelite-type structure of lattice parameters $a = b = 5.2425$ Å and $c = 11.3715$ Å, are relatively stable in air and have stable physical and chemical properties, low excitation threshold energy and low-cost productivity⁴⁻⁶. 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 Er³⁺ and Yb³⁺ 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 upconversion 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 Ln-doped CaWO₄ prepared using a range of processes, including solid-state reactions¹⁰⁻¹⁵, the sol-gel method¹⁶, the hydrothermal method¹⁷⁻¹⁹, the combustion method²⁰, the solvothermal route²¹ and the sonochemical method^{22,23}. 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, microwave synthesis has the advantages of 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 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^{4,24}.

In this study, Er³⁺ doped CaWO₄ (CaWO₄:Er³⁺) and Er³⁺/Yb³⁺ co-doped CaWO₄ (CaWO₄:Er³⁺/Yb³⁺) particles were synthesized by the cyclic microwave-assisted metathetic route, followed by heat-treatment. The synthesized Er³⁺ doped CaWO₄ (CaWO₄:Er³⁺) and Er³⁺/Yb³⁺ co-doped CaWO₄ (CaWO₄:

$\text{Er}^{3+}/\text{Yb}^{3+}$) 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 CaCl_2 , $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and ethylene glycol of analytic reagent grade were used to prepare the CaWO_4 , $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ compounds. For preparation of CaWO_4 , 1 mol % CaCl_2 and 1 mol % $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol. To prepare $\text{CaWO}_4:\text{Er}^{3+}$, 0.95 mol % CaCl_2 with 0.05 mol % $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ and 1 mol % $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol. But for preparation of $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, 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 % $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ 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 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. When ethylene glycol is used as the solvent, reactions proceed at the boiling point temperature. The microwave radiation is supplied to ethylene glycol and the components dissolving in the ethylene glycol couple with each other under the radiation. When a large amount of microwave radiation is supplied to the ethylene glycol, the charged particles vibrate interdependently within the electric field. 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 $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles were observed by using SEM/EDS (JSM-5600, JEOL, Japan). Their 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 the XRD patterns of (a) the data of JCPDS 72-1624 and the synthesized (b) $\text{CaWO}_4:\text{Er}^{3+}$ and (c) $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles. All of the XRD peaks could be assigned to the tetragonal-phase CaWO_4 with a scheelite-type structure, which was in good agreement with the crystallographic data of CaWO_4

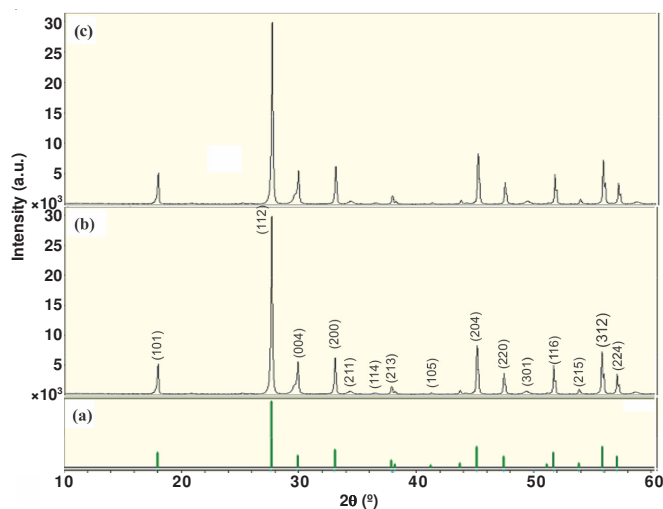


Fig. 1. X-Ray diffraction patterns of (a) the data of JCPDS 72-1624 and the synthesized (b) $\text{CaWO}_4:\text{Er}^{3+}$ and (c) $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles

(JCPDS 72-1624). This finding means that the tetragonal-phase $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ 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 $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ phases need to be heat treated at 600 °C for 3 h. The CaWO_4 had a Scheelite-type crystal structure with lattice parameters of $a = b = 5.2425 \text{ \AA}$ and $c = 11.3715 \text{ \AA}$. This finding suggests that the cyclic microwave-assisted metathetic route is suitable for growing $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ crystallites and for developing the strongest intensity peaks at the (112), (204) and (312) planes, which are the major peaks of CaWO_4 ⁴⁻⁶.

Fig. 2 shows SEM images of the synthesized (a) $\text{CaWO}_4:\text{Er}^{3+}$ and (b) $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles. The as-synthesized samples are well crystallized with a fine and homogeneous morphology with particle sizes of 1-3 μm . Fig. 3 shows the EDS pattern of the synthesized $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles. The EDS patterns show that the $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles are composed of Ca, W, O, Er and Yb. Microwave-assisted metathetic reactions, such as $\text{CaCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{CaWO}_4 + 2\text{NaCl}$, involve the exchange of atomic/ionic species, in which the driving force is the exothermic reaction accompanying the formation of NaCl ^{4,24}. 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 $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles. The cyclic microwave-assisted metathetic route²⁴ 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. $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, as well as CaWO_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. 4 shows the upconversion photoluminescence emission spectra of (a) $\text{CaWO}_4:\text{Er}^{3+}$ (CWO:Er) and (b) $\text{CaWO}_4:\text{Er}^{3+}/$

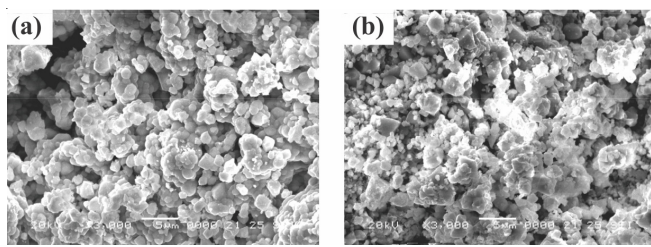


Fig. 2. Scanning electron microscopy images of the synthesized (a) CaWO₄:Er³⁺ and (b) CaWO₄:Er³⁺/Yb³⁺ particles

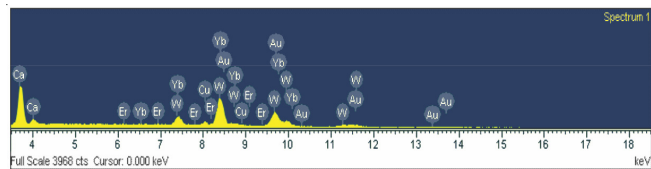


Fig. 3. Energy-dispersive X-ray spectroscopy patterns of the synthesized CaWO₄:Er³⁺/Yb³⁺ particles

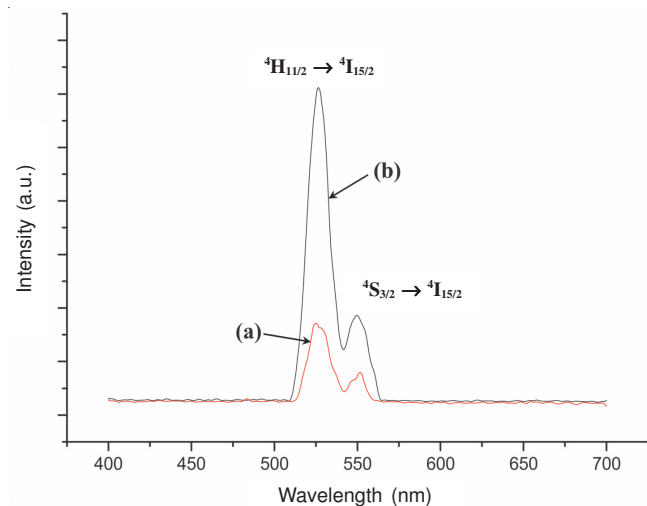


Fig. 4. Upconversion photoluminescence emission spectra of the synthesized (a) CaWO₄:Er³⁺ (CWO:Er) and (b) CaWO₄:Er³⁺/Yb³⁺ (CWO:Er/Yb) particles excited at 980 nm at room temperature

Yb³⁺ (CWO: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 Er³⁺ ions, respectively. The doping amounts of Er³⁺/Yb³⁺ had a great effect on both the morphological features and 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) CWO:Er/Yb is much higher than that of CWO: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 (ESA), energy transfer upconversion (ETU) and photon avalanche (PA)^{1,25,26}.

Fig. 5 shows the schematic energy level diagrams of Er³⁺ ions (activator) and Yb³⁺ ions (sensitizer) in the as-prepared CaWO₄:Er³⁺/Yb³⁺ samples and the upconversion mechanisms accounting for the green and red emissions at 980 nm laser excitation. In the complex Er³⁺/Yb³⁺ co-doped CaWO₄ system, an initial energy transfer from an Yb³⁺ ion in the ${}^2\text{F}_{5/2}$ state to an Er³⁺ ion populates the ${}^4\text{I}_{11/2}$ level. A second 980 nm photon or the energy transfer from an Yb³⁺ ion can then populate the ${}^4\text{F}_{7/2}$ level of the Er³⁺ ion. The Er³⁺ ion can then relax non-radiatively to the ${}^2\text{H}_{11/2}$ and ${}^4\text{S}_{3/2}$ levels and green ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ emissions occur⁷⁻⁹. The strong 525-nm emission band and the weak 550-nm emission band in the green region are 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 Er³⁺ ions, respectively.

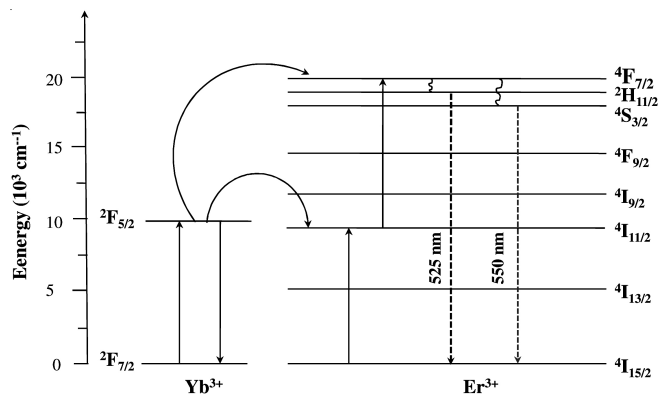


Fig. 5. Schematic energy level diagrams of Er³⁺ ions (activator) and Yb³⁺ ions (sensitizer) in the as-prepared CaWO₄:Er³⁺/Yb³⁺ samples and the upconversion mechanisms accounting for the green and red emissions at 980 nm laser excitation

Fig. 6 shows the Raman spectra of the (a) CaWO₄ (CWO) and CaWO₄:Er³⁺/Yb³⁺ (CWO: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) CaWO₄(CWO) 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 911, 840, 796, 403, 325 and 274 cm⁻¹, respectively. The external modes were localized at 211-115 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 [WO₄]²⁻. The Raman spectra of the (b) CaWO₄:Er³⁺/Yb³⁺ particles indicate additional peaks at both higher frequencies (620, 573, 481, 371 and 355 cm⁻¹) and lower frequencies (315, 265, 217 and 203 cm⁻¹). The Raman spectra of CaWO₄:Er³⁺/Yb³⁺ particles proved that the doping ion of Yb³⁺ can influence the structure of the host materials.

Conclusion

Upconversion photoluminescence of Er³⁺ doped CaWO₄ (CaWO₄:Er³⁺) and Er³⁺/Yb³⁺ co-doped CaWO₄ (CaWO₄:Er³⁺/Yb³⁺) particles was successfully achieved by a microwave-assisted metathetic route. Well-crystallized CaWO₄:Er³⁺ and CaWO₄:Er³⁺/Yb³⁺ particles formed after heat-treatment at

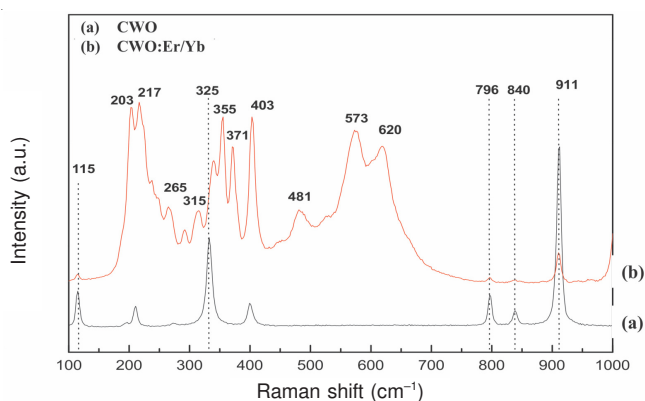


Fig. 6. Raman spectra of the synthesized (a) CaWO_4 (CWO) and (b) $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (CWO:Er/Yb) particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples

600 °C for 3 h showed a fine and homogeneous morphology with particle sizes of 1-3 μm . At excitation at 980 nm, $\text{CaWO}_4:\text{Er}^{3+}$ and $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ 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 $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles was much higher than that of the $\text{CaWO}_4:\text{Er}^{3+}$ particles. The Raman spectra of the (b) $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles indicated the detection of additional peaks at both higher frequencies (620, 573, 481, 371 and 355 cm^{-1}) and lower frequencies (315, 265, 217 and 203 cm^{-1}). The Raman spectra of $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles proved that the doping ion of Yb^{3+} can influence the structure of the host materials.

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