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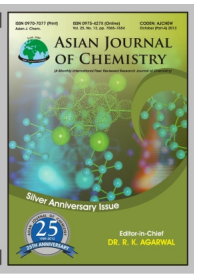

Fabrication and Characterization of SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} Composites by Cyclic Microwave-Assisted Metathetic Method

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Er^{3+}/Yb^{3+} co-doped $CaMoO_4$ ($CaMoO_4$:Er^{3+}/Yb^{3+}) composites with superparamagnetic iron oxide nanoparticles (SPIONs) incorporated were successfully synthesized by a cyclic microwave-assisted metathetic method, followed by heat-treatment. The microstructure exhibited well-defined and homogeneous morphology with $CaMoO_4$:Er^{3+}/Yb^{3+} particle sizes of 2-3 μm and Fe_3O_4 particle sizes of 0.1-0.5 μm. The Fe_3O_4 particles were self-preferentially crystallized and immobilized on the surface of $CaMoO_4$:Er^{3+}/Yb^{3+} particles. The synthesized SPION/$BaMoO_4$:Er^{3+}, Yb^{3+} composites were characterized by X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy. Optical properties were examined using photoluminescence emission data and Raman spectroscopy.

Key Words: Fe_3O_4, $CaMoO_4$:Er^{3+}/Yb^{3+}, Cyclic microwave-assisted metathetic synthesis, Photoluminesecnce, Raman spectroscopy.

INTRODUCTION

Recently, magnetic-fluorescent nanocomposites with both fluorescent and magnetic properties are attracting intense attentions because of their potential applications as dual-modality imaging probes in fluorescence detection, enhanced magnetic resonance imaging, selective magnetic separation, information storage in biotechnology, medicine and quality inspection. Superparamagnetic iron oxide nanoparticles (SPIONs) incorporated into photoluminescent composites containing two different functionalities could provide novel characteristics *via* the integration of fluorescent and magnetic properties, offering new potential in a wide range of applications in biomedical systems, such as targeted drugs, diagnostics, therapeutics and bio-imaging[1-3]. Particles of rare-earth-doped $CaMoO_4$, which is at type of metallic molybdate compound with a schleelite-type structure and 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 productivity.

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[7-11], co-precipitation[12], the sol-gel method[13], the hydrothermal method[14-16], the Pechini method[17], the solvothermal route[18] and the microwave-assisted hydrothermal method[19]. For practical application of photoluminescence in such products as lasers, three-dimensional displays, light emitting devices and biological detectors, features such as homogeneous particle size distribution and morphology need to be well defined. Compared with the usual methods, microwave synthesis has the advantages of short reaction time, small-size particles, 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. This makes it 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[4,5,20]. However, the cyclic microwave-assisted metathetic synthesis of the SPION/$CaMoO_4$:Er^{3+}/Yb^{3+} composites and their optical properties have not been reported. Understanding the precise nature of the SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites is required for a wide range of applications.

In this study, SPIONs incorporated Er^{3+}-doped $CaMoO_4$ ($CaMoO_4$:Er^{3+}) and Er^{3+}/Yb^{3+} co-doped $CaMoO_4$ ($CaMoO_4$:Er^{3+}/Yb^{3+}) composites were synthesized by the cyclic microwave-assisted metathetic method, followed by heat-treatment. The synthesized SPION/$CaMoO_4$:Er^{3+} and SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites 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 $CaCl_2$, $ErCl_3·6H_2O$, $YbCl_3·6H_2O$, $Na_2MoO_4·2H_2O$, 5-nm-sized Fe_3O_4 nanoparticles and ethylene glycol of analytic reagent grade were used to prepare the SPION/$CaMoO_4$:Er^{3+}, SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} and $CaMoO_4$:Er^{3+}, Yb^{3+} compounds. Fig. 1 shows flow chart for the synthesis of SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites by the cyclic microwave-assisted metathetic process. To prepare SPION/$CaMoO_4$:Er^3, 0.95 mol % $CaCl_2$ with 0.05 mol % $ErCl_3·6H_2O$ and 1 mol % $Na_2MoO_4·2H_2O$ with 0.5 mol % Fe_3O_4 were dissol-ved in 30 mL ethylene glycol, respectively. For synthesis of SPION/$CaMoO_4$:Er^{3+}, Yb^{3+}, 0.9 mol % $CaCl_2$ with 0.05 mol % $ErCl_3·6H_2O$ and 0.05 mol % $YbCl_3·6H_2O$ and 1 mol % $Na_2MoO_4·2H_2O$ with 0.5 mol % Fe_3O_4 were dissolved in 30 mL ethylene glycol, respectively. For preparation of $CaMoO_4$:Er^{3+}, Yb^{3+}, 0.9 mol % $CaCl_2$ with 0.05 mol % $ErCl_3·6H_2O$ and 0.05 mol % $YbCl_3·6H_2O$ and 1 mol % $Na_2MoO_4·2H_2O$ were dissolved in 30 mL ethylene glycol, respectively.

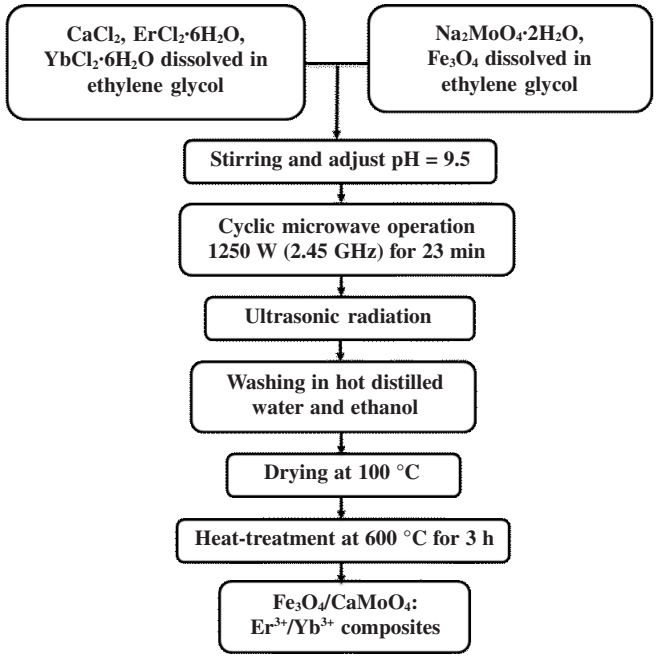

Fig. 1. Flow chart for the synthesis of SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites by the cyclic microwave-assisted metathetic process

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. 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 cyclic 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 at its boiling point. Ethylene glycol is a polar solvent at its boiling point of 197 ºC and 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 the 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 ºC in a drying oven. The final products were heat-treated at 600 ºC for 3 h.

The phase of the composites 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 Fe_3O_4/$CaMoO_4$:Er^{3+} and Fe_3O_4/$CaMoO_4$: Er^{3+}, Yb^{3+} composites were observed 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 an excitation source and the power on the samples was kept at 0.5 mW.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD pattern of the synthesized SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites. The diffraction peaks marked with*are indexed to Fe_3O_4. All of the XRD peaks could be assigned to the tetragonal-phase $CaMoO_4$ with a Scheelite-type structure and Fe_3O_4, which were in good agreement with the crystallographic data of $CaMoO_4$ (JCPDS 85-0585) and Fe_3O_4 (JCPDS 19-0629). This means that the SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites can be prepared using the cyclic microwave-assisted metathetic route. Post heat-treatment plays an important role in forming well-defined crystallized morphology. To achieve such morphology, the SPION/$CaMoO_4$:Er^{3+} and Fe_3O_4/$CaMoO_4$:Er^{3+}, Yb^{3+} composites need to be heat treated at 600 ºC for 3 h. This suggests that the cyclic microwave-assisted metathetic route is suitable for growing SPION/$CaMoO_4$:Er^{3+} and Fe_3O_4/$CaMoO_4$: Er^{3+}, Yb^3 composites and for developing the strongest intensity peaks at the (112), (204) and (312) planes, which are the major peaks of $CaMoO_4$[4-6].

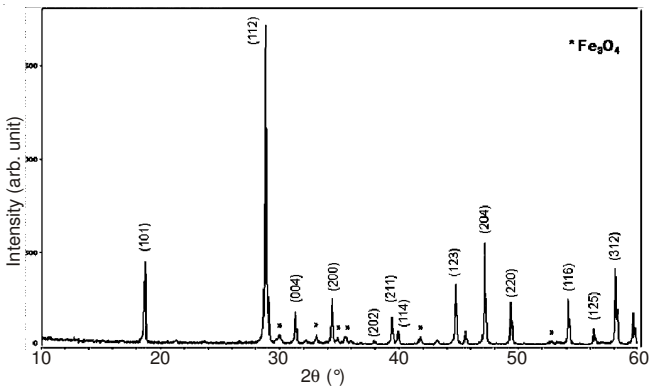

Fig. 2. XRD pattern of the synthesized SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites

Fig. 3 shows an SEM image of the synthesized SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites. The as-synthesized sample has well-defined and homogeneous morphology with $CaMoO_4$: Er^{3+}/Yb^{3+} particle sizes of 2-3 μm and Fe_3O_4 particle sizes of 0.1-0.5 μm, respectively. The Fe_3O_4 particles were self-preferentially

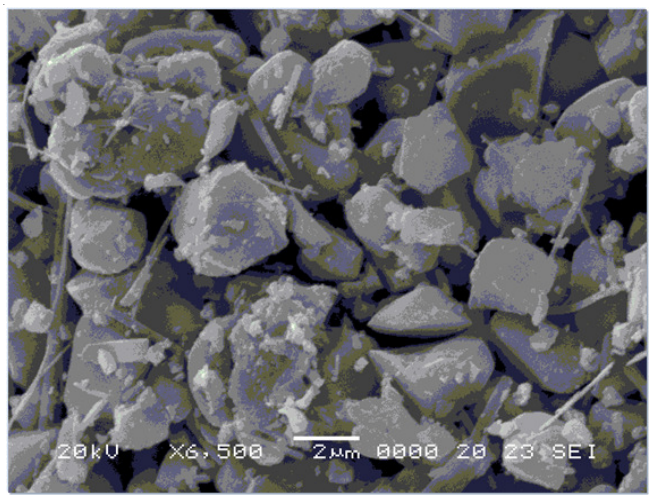

Fig. 3. SEM image of the synthesized SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites

crystallized and immobilized on the surface of $CaMoO_4$:Er^{3+}/Yb^{3+} particles. Fig. 4 shows (a) an EDS pattern, (b) quantitative compositions, (c) quantitative results and (d) SEM image of the synthesized SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites. The EDS pattern shows that the SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites are composed of Fe, Ca, Mo, O, Er and Yb in Fig. 4(a) and identified as the quantitative compositions in Fig. 4(b). The EDS pattern and quantitative compositions in Figs. 4 (a, b) could be assigned to the SPION/$CaMoO_4$:Er^{3+},Yb^{3+} composites. This means that the $CaMoO_4$:Er^{3+}, Yb^{3+} composites with Fe_3O_4 nanoparticles incorporated can be successfully synthesized using this cyclic microwave-assisted metathetic method. Cyclic microwave-assisted metathetic reactions, such as $CaCl_2 + Na_2MoO_4 \rightarrow CaMoO_4 + 2NaCl$, involve the exchange of atomic/ionic species, in which the driving force is the exothermic reaction accompanying the formation of NaCl[4,20]. Cyclic 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 SPION/$CaMoO_4$:Er^{3+} and SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites. The

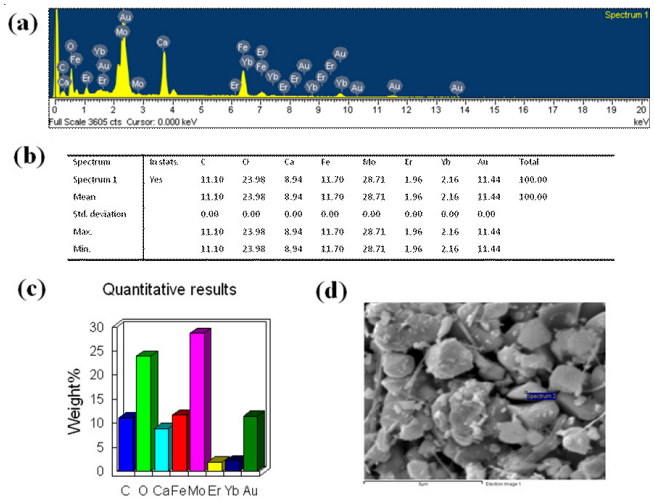

Fig. 4. A (a) EDS pattern, (b) quantitative compositions, (c) quantitative results and (d) a SEM image of the synthesized SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites

cyclic microwave-assisted metathetic route[20] 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. SPION/$CaMoO_4$:Er^{3+} and SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites were heated rapidly and uniformLy by the cyclic microwave-assisted metathetic route. This makes the method a simple and cost-effective and able to provide high yields with easy scale-up, as a viable alternative for the rapid synthesis of SPION/$CaMoO_4$:Er^{3+} and Fe_3O_4/$CaMoO_4$:Er^{3+}, Yb^{3+} composites.

Fig. 5 shows the photoluminescence emission spectra of synthesized (a) SPION/$CaMoO_4$:Er^{3+} and (b) SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} composites excited at 250 nm at room temperature. The emission spectrum of metal molybdates is due mainly to charge-transfer transitions within the $[MoO_4]^{2-}$ complex[21,22]. With excitation at 250 nm, the SPION/$CaMoO_4$:Er^{3+} and SPION/$CaMoO_4$: Er^{3+}, Yb^{3+} composites exhibit photoluminescence emission in the blue wavelength range of 420-430 nm. The photoluminescence intensity of the (b) SPION/$CaMoO_4$:Er^{3+}, Yb^3 is slightly stronger than that of the (a) SPION/$CaMoO_4$:Er^{3+}. The doping amounts of Er^{3+}/Yb^{3+} have an effect on the photoluminescence intensity. This suggests that the doping amounts play an important role in improving the luminescent efficiency. The photoluminescence intensity of energy-conversion materials depends strongly on not only the particle shape and distribution but also the doping amounts. Generally, for similar morphological samples, homogenized particles are favourable for the luminescent characteristics, because of the lesser contamination or fewer dead layers on the surface of the energy-conversion materials.

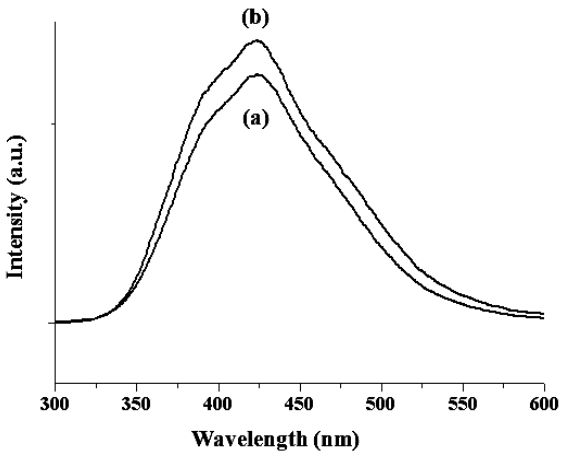

Fig. 5. Photoluminescence emission spectra of the synthesized (a) SPION/$CaMoO_4$: Er^{3+} and (b) SPION/$CaMoO_4$: Er^{3+}, Yb^{3+} composites excited at 250 nm at room temperature

Fig. 6 shows Raman spectra of the synthesized (a) $CaMoO_4$:Er^{3+}, Yb^{3+} (CMO:ErYb) particles and (b) SPION/$CaMoO_4$:Er^{3+}, Yb^{3+} (F-CMO:ErYb) composites excited by the 514.5-nm line of an Ar-ion laser at 0.5 mW. The Raman spectra show that the peak positions and intensities are the same. The internal modes for the synthesized (a) $CaMoO_4$: Er^{3+}, Yb^{3+} (CMO:ErYb) particles and (b) SPION/$CaMoO_4$: Er^{3+}, Yb^{3+} (F-CMO:ErYb) composites 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,

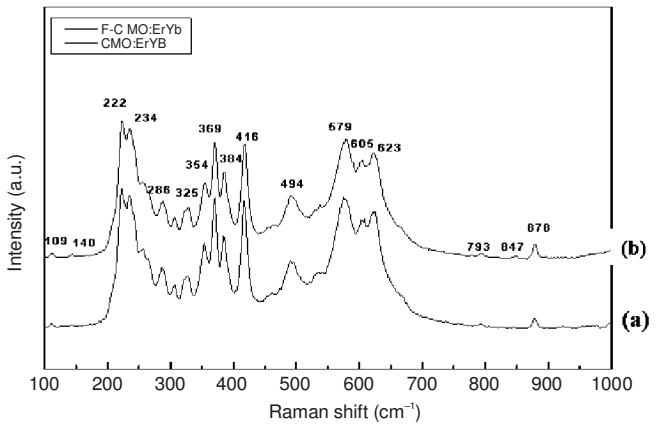

Fig. 6. Raman spectra of the synthesized (a) $CaMoO_4:Er^{3+}$ (CMO:ErYb) particles and (b) $Fe_3O_4/CaMoO_4:Er^{3+}$, Yb^{3+} (F-CMO:ErYb) composites excited by the 514.5-nm line of an Ar-ion laser at 0.5 mW on the samples

384, 369 and 354 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 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 synthesized (a) $CaMoO_4:Er^{3+}$, Yb^{3+} (CMO:ErYb) particles and (b) SPION/$CaMoO_4:Er^{3+}$, Yb^{3+} (F-CMO:ErYb) composites indicate the detection of additional strong peaks at both higher frequencies (623, 605, 579, 494 and 416 cm^{-1}) and lower frequencies (325, 286, 234 and 222 cm^{-1}). Atuchin *et al.*[23-25] could consider that the very strong and strange effect in the Ln-doped crystalline samples may be generated by the disorder of the MoO_4 groups with the incorporation of the Ln element into the crystal lattice or by a new phase formation. It is noted that the Fe_3O_4 particles have no influence on the Raman spectra, while the doping ion of Er^{3+}/Yb^{3+} can influence the Raman spectra. The Raman spectra proved that the doping ion of Er^{3+}/Yb^{3+} can influence the structure of the host materials.

Conclusion

SPION/$CaMoO_4:Er^{3+}, Yb^{3+}$ composites were successfully synthesized by a cyclic microwave-assisted metathetic method. The microstructure exhibited well-defined and homogeneous morphology with $CaMoO_4:Er^{3+}/Yb^{3+}$ particle sizes of 2-3 μm and Fe_3O_4 particle sizes of 0.1-0.5 μm. The Fe_3O_4 particles were self-preferentially crystallized and immobilized on the surface of $CaMoO_4:Er^{3+}/Yb^{3+}$ particles. With excitation at 250 nm, the SPION/$CaMoO_4:Er^{3+}$ and $Fe_3O_4/CaMoO_4:Er^{3+}$, Yb^{3+} composites exhibited PL emission in the blue wavelength range of 420-4300 nm. The Raman spectra of the synthesized $CaMoO_4:Er^{3+}$, Yb^{3+} (CMO:ErYb) particles and SPION/$CaMoO_4:Er^{3+}$, Yb^{3+} (F-CMO:ErYb) composites indicated the detection of additional strong peaks at both higher frequencies (623, 605, 579, 494 and 416 cm^{-1}) and lower frequencies (325, 286, 234 and 222 cm^{-1}). The Fe_3O_4 particles have no influence on the Raman spectra, while the doping ion of Er^{3+}/Yb^{3+} can influence the Raman spectra. The Raman spectra proved that the doping ion of Er^{3+}/Yb^{3+} can influence the structure of the host materials.

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