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Preparation, Micromorphology and Optical Properties of SPION/$BaWO_4$:Er^{3+}, Yb^{3+} Composites *via* Cyclic Microwave-Assisted Metathetic Route

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Superparamagnetic iron oxide nanoparticles (SPIONs) incorporated Er^{3+}/Yb^{3+} co-doped $BaWO_4$ (SPION/$BaWO_4$:Er^{3+}/Yb^{3+}) composites were successfully prepared *via* cyclic microwave-assisted metathetic route. The micromorphology exhibited a well-defined and homogeneous morphology with sizes of 1-2 μm for the $BaWO_4$:Er^{3+}/Yb^{3+} particles and 0.1-0.5 μm for the Fe_3O_4 particles, respectively. The Fe_3O_4 particles were self-preferentially crystallized and immobilized on the surface of $BaWO_4$:Er^{3+}/Yb^{3+} particles. The synthesized SPION/$BaWO_4$:Er^{3+}/Yb^{3+} composites were characterized by X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy. Other optical properties were also examined by using photoluminescence emission data and Raman spectroscopy.

Keywords: Micromorphology, Optical properties, SPIONs, $BaMoO_4$:Er^{3+}/Yb^{3+}, Cyclic microwave-assisted metathetic route.

INTRODUCTION

Magnetic nanoparticles have been extensively studied in the fields of biomedical applications, including magnetic resonance imaging, gene/drug delivery and biosensors, as well as biochemical separation and concentration of trace amount of samples[1-3]. Recently, magnetic-fluorescent nanoparticles with both fluorescent and magnetic properties are attracting intense attentions of materials scientists, chemists and biologists because of their potential applications. 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[1-5].

The particles of rare-earth-doped upconversion $BaWO_4$ which shows a Schleelite-type structure with unit cell parameters a = b = 5.613 Å and c = 12.720 Å[6], are relatively stable in the air and have stable physical and chemical properties, low excitation threshold energy and low-cost productivity. Recently, several processes have been developed to increase the applications of rare-earth-doped metal tungstates prepared using a range of processes including solid-state reactions[7,8], the sol-gel method[9], the hydrothermal method[10,11], the combustion method[12], the solvothermal route[13] and the sonochemical method[14]. 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.

The cyclic microwave-assisted metathetic synthesis of materials is a simple and cost-effective method that provides a high yield with an easy scale-up and it is emerging as a viable alternative approach for the synthesis of high-quality novel inorganic materials in short time periods[15,16]. In this study, the Er^{3+}-doped $BaWO_4$ with SPIONs (SPION/$BaWO_4$:Er^{3+}) and Er^{3+}/Yb^{3+} co-doped $BaWO_4$ with SPIONs (SPION/$BaWO_4$:Er^{3+}/Yb^{3+}) composites were synthesized by the cyclic microwave-assisted metathetic method followed by heat-treatment. The synthesized SPION/$BaWO_4$:Er^{3+} and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Optical properties have been investigated by photoluminescence emission measurements and Raman spectroscopy.

EXPERIMENTAL

Appropriate stoichiometric amounts of $BaCl_2 \cdot 2H_2O$, $ErCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$, $Na_2WO_4 \cdot 2H_2O$, 5 nm sized Fe_3O_4 nanoparticles and ethylene glycol of analytic reagent grade were used to prepare the SPION/$BaWO_4$:Er^{3+}, $BaWO_4$:Er^{3+}, Yb^{3+} and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} compounds. To prepare SPION/$BaWO_4$:Er^{3+}, 0.95 mol % $BaCl_2 \cdot 2H_2O$ with 0.05 mol % $ErCl_3 \cdot 6H_2O$ and 1 mol % $Na_2WO_4 \cdot 2H_2O$ with 0.5 mol % Fe_3O_4 were dissolved in 30 mL ethylene glycol, respectively. To

prepare SPION/$BaWO_4$:Er^{3+}, Yb^{3+}, 0.9 mol % $BaCl_2 \cdot 2H_2O$ with 0.05 mol % $ErCl_3 \cdot 6H_2O$ and 0.05 mol % $YbCl_3 \cdot 6H_2O$ and 1 mol % $Na_2WO_4 \cdot 2H_2O$ with 0.5 mol % Fe_3O_4 were dissolved in 30 mL ethylene glycol, respectively. To prepare $BaWO_4$:Er^{3+}, Yb^{3+}, 0.9 mol % $BaCl_2 \cdot 2H_2O$ with 0.05 mol % $ErCl_3 \cdot 6H_2O$ and 0.05 mol % $YbCl_3 \cdot 6H_2O$ and 1 mol % $Na_2WO_4 \cdot 2H_2O$ were dissolved in 30 mL ethylene glycol, respectively.

The solutions were mixed and adjusted to pH 9.5 using NaOH. The solutions were stirred at room temperature. Then, the mixtures were transferred into 120 mL Teflon vessels. Each Teflon vessel was placed into a microwave oven operating at the frequency of 2.45 GHz with the maximum output power of 1250 W for 23 min. The working cycle of the microwave-assisted metathetic reaction was been controlled very precisely between 30 sec on and 30 sec off for 8 min, followed by a further treatment of 30 sec on and 60 sec off for 15 min. Ethylene glycol was evaporated slowly at its boiling point. Ethylene glycol is a polar solvent at its boiling point of 197 °C and it is a good candidate for the microwave process. The resulted powder 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. After this, the final products were heat-treated at 600 °C for 3 h.

The phase composition of final powder products formed after the cyclic microwave-assisted metathetic reaction and following heat-treatment was identified using XRD (D/MAX 2200, Rigaku, Japan). The microstructures and surface morphologies of the SPION/$BaWO_4$:Er^{3+} and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites were observed using SEM/EDS (JSM-5600, JEOL, Japan). Their photoluminescence spectra were recorded at room temperature using a spectrophotometer (Perkin Elmer LS55, UK). Raman spectroscopy measurements were performed using a LabRam HR (Jobin-Yvon, France) device. 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. 1 shows the XRD patterns of (a) pure $BaWO_4$ (JCPDS 43-0646) and (b) the synthesized SPION/$BaWO_4$:Er^{3+}/Yb^{3+} particles. All the diffraction peaks were assigned to the tetragonal-phase $BaWO_4$ with a Scheelite-type structure and Fe_3O_4, which were in good agreement with the crystallographic data of $BaWO_4$ (JCPDS 43-0646) and Fe_3O_4 (JCPDS 19-0629). The diffraction peaks marked with asterisk are related to Fe_3O_4. The result confirms that the SPION/BaWO4:Er^{3+}, Yb^{3+} composites can be prepared using the cyclic microwave-assisted metathetic route. The post-synthesis heat-treatment plays an important role in forming well-defined crystallized micromorphology. To achieve such morphology, the SPION/$BaWO_4$:Er^{3+} and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites need to be heated at 600 °C for 3 h. This suggests that the cyclic microwave-assisted metathetic route, in combination with subsequent heat-treatment, is a suitable way for the formation of SPION/$BaWO_4$:Er^{3+} and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} polycrystalline composites with well developed high-intensity peaks from the (112), (204) and (312) planes, which are the major peaks of $BaWO_4$[6].

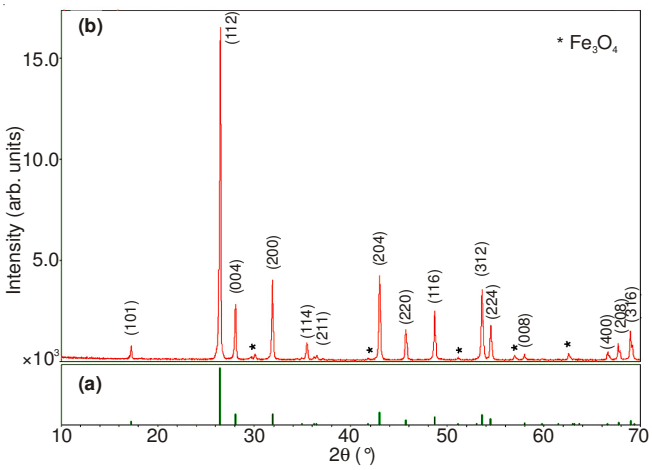


Fig. 1. XRD pattern of the synthesized SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites

The SEM image of the synthesized SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composite is shown in Fig. 2. The as-synthesized sample has a well-defined and homogeneous morphology with the $BaWO_4$:Er^{3+}, Yb^{3+} particle size of 1-2 μm and Fe_3O_4 particle size of 0.1-0.5 μm, respectively. The Fe_3O_4 particles were self-preferentially crystallized and immobilized on the surface of large $BaWO_4$:Er^{3+}, Yb^{3+} particles. The incorporation of Fe_3O_4 nanoparticles to the $BaWO_4$:Er^{3+}, Yb^{3+} compound particles can be successfully achieved using the cyclic microwave-assisted metathetic route. The microwave-assisted metathetic reactions, such as $BaCl_2 + Na_2WO_4 \rightarrow BaWO_4 + 2NaCl$, involve the exchange of atomic/ionic species, in which the driving force is the exothermic reaction accompanying the formation of NaCl[16]. The SPION/$BaWO_4$:Er^{3+} and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites were heated rapidly and uniformly by the cyclic microwave-assisted metathetic route. This classifies the method among simple and cost-effective ones and, evidently, the microwave-assisted metathetic technology is able to provide high yields with an easy scale-up as a viable alternative for the rapid synthesis of complex oxide composites[16].

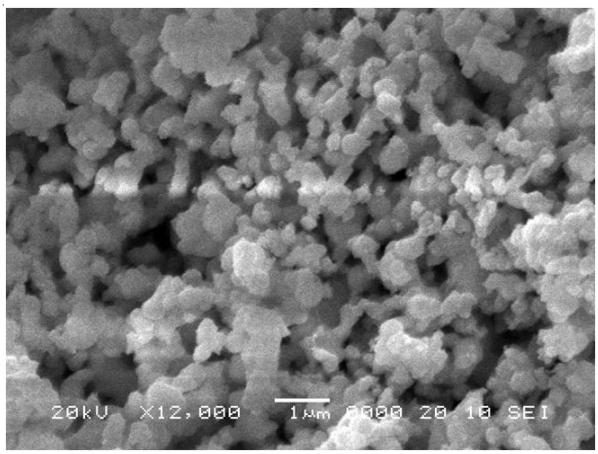


Fig. 2. A SEM image of the synthesized SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites

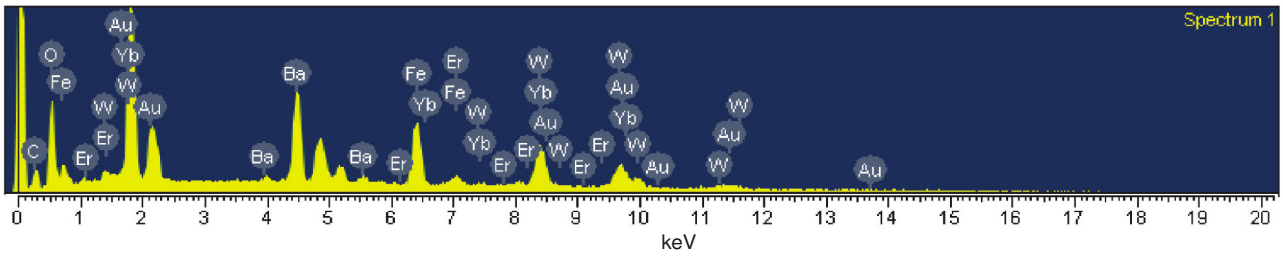
The EDS pattern, quantitative compositions, quantitative results and the SEM image of the synthesized SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composite are presented in Fig. 3. The EDS pattern

shown in Fig. 3a displays that the SPION/$BaWO_4$:Er^{3+}, Yb^{3+} sample is composed of Fe, Ba, W, O, Er and Yb with the dominance of Fe, Ba, W, O. The EDS pattern and quantitative compositions in Fig. 3a,b could be well assigned to the SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composite. Thus, the incorporation of Fe_3O_4 nanoparticles to the SPION/$BaWO_4$:Er^{3+}, Yb^{3+} compound particles can be successfully achieved using the cyclic microwave-assisted metathetic. The cyclic microwave-assisted metathetic reactions provide a convenient route for the synthesis of such complex products as SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites. 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 and without solvent waste generation.

The photoluminescence emission spectra recorded from the synthesized (a) SPION/$BaWO_4$:Er^{3+} and (b) SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites excited at 250 nm at room temperature are shown in Fig. 3. It is generally assumed that the measured emission spectrum of metal tungstates are mainly attributed to the charge-transfer transitions within the $[WO_4]^{2-}$ complex[17,18]. With the excitation at 250 nm, the SPION/$BaWO_4$:Er^{3+} and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites exhibit photoluminescence emission over the blue wavelength range of 390-420 nm. As it is evident from Fig. 3, the intensity of the photoluminescence emission from SPION/$BaWO_4$:Er^{3+}, Yb^{3+} is much stronger than that from SPION/$BaWO_4$:Er^{3+}. The four narrow shoulders in the emission spectra at approximately 490, 510, 520 and 600 nm are believed to be due to a defect structure[19]. Such peaks, producing a "spread-eagle" shape of the blue emission, can be explained by the influence of the Jahn-Teller effect[20] on the degenerated excited state of the $[WO_4]^{2-}$ tetrahedrons. The Jahn-Teller splitting effect essentially determines the shape of the emission band of MWO_4 (M = Ca, Ba) particles[21]. The additional emission bands can be explained by the existence of a Frenkel defect structure (oxygen ions shifted to the inter-position with the simultaneous creation of vacancies) in the surface layers of the $BaWO_4$ particles.

The Raman spectra of the $BaWO_4$:Er^{3+}, Yb^{3+} (BWO:ErYb) and SPION/$BaWO_4$:Er^{3+}, Yb^{3+} (F-BWO:ErYb) particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW are shown in Fig. 4. The internal modes were detected for the $BaWO_4$:Er^{3+}, Yb^{3+} (BWO:ErYb) particles in Fig. 5a at $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(E_g)$, $\nu_4(B_g)$ and $\nu_2(B_g)$ vibrations at 925, 831, 794, 352, 344 and 332 cm^{-1}, respectively. The well-resolved sharp peaks for the $BaWO_4$:Er^{3+}, Yb^{3+} (BWO:ErYb) particles provide that the synthesized particles are highly crystallized. From the comparison it can be depicted that the peak positions are

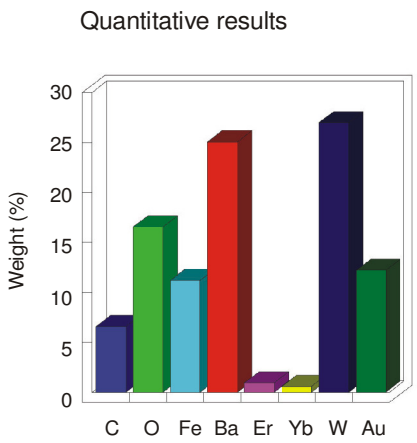
(a)



(b)

Spectrum	In stats.	C	O	Fe	Ba	Er	Yb	W	Au	Total
Spectrum 1	Yes	6.56	16.54	11.18	25.06	0.95	0.56	26.98	12.17	100.00
Mean		6.56	16.54	11.18	25.06	0.95	0.56	26.98	12.17	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.		6.56	16.54	11.18	25.06	0.95	0.56	26.98	12.17	
Min.		6.56	16.54	11.18	25.06	0.95	0.56	26.98	12.17	

(c)



(d)

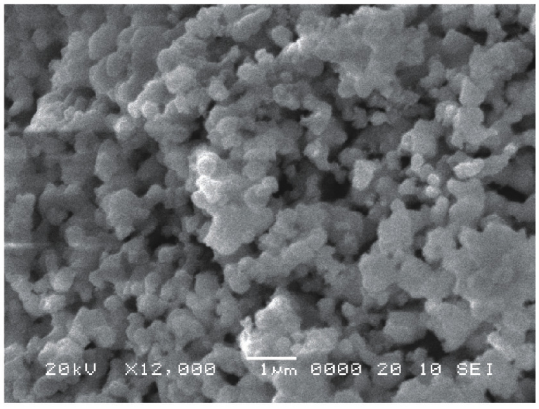


Fig. 3. EDS pattern, quantitative compositions, quantitative results and the SEM image of the synthesized SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites

practically the same, while the internal modes obtained from SPION/$BaWO_4$:Er^{3+}, Yb^{3+} (F-BWO:ErYb) in Fig. 5b are highly distorted than that of $BaWO_4$:Er^{3+}, Yb^{3+} (BWO:ErYb) in Fig. 5a. The vibration modes in the Raman spectrum of tungstates are classified into two groups, internal and external[22,23]. Internal vibrations are related to the $[WO_4]^{2-}$ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Ba^{2+} cation and rigid molecular units. The Raman spectrum of the synthesized SPION/$BaWO_4$:Er^{3+}, Yb^{3+} (F-BWO:ErYb) composites in Fig. 5b indicate additional peaks at both middle (504 and 375 cm^{-1}) and lower frequencies (313, 277, 242 and 205 cm^{-1}), which are attributed to the doping ions[24-27] of Er^{3+} and Yb^{3+}.

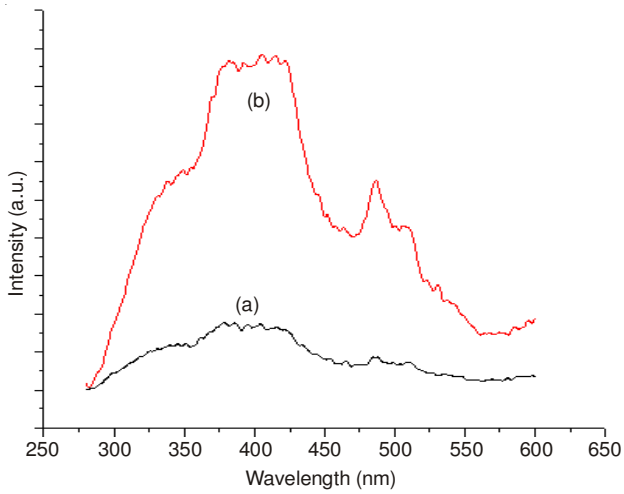


Fig. 4. Photoluminescence emission spectra of the synthesized (a) SPION/$BaWO_4$:Er^{3+} and (b) SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites

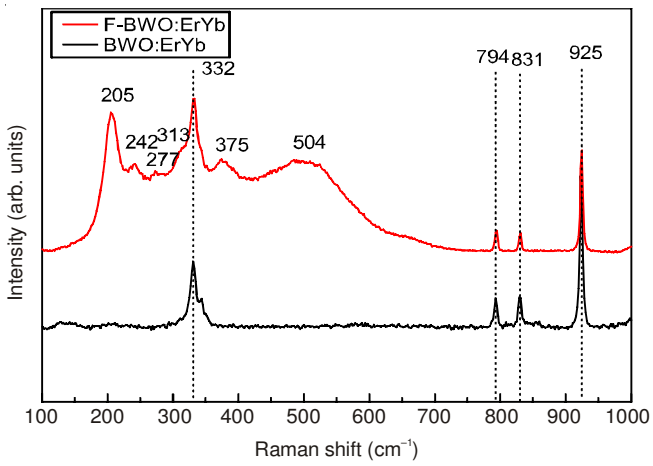


Fig. 5. Raman spectra of the synthesized (a) $BaWO_4$:Er^{3+}, Yb^{3+} (BWO:ErYb) particles and (b) SPION/$BaWO_4$:Er^{3+}, Yb^{3+} (F-BWO:ErYb) composites

Conclusion

The SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites were successfully prepared *via* cyclic microwave-assisted metathetic route. The microstructure exhibited a well-defined and homogeneous morphology with the $BaWO_4$:Er^{3+}, Yb^{3+} and Fe_3O_4 particle size of 1-2 and 0.1-0.5 µm, respectively. The Fe_3O_4 nanoparticles were self-preferentially crystallized and immobilized on the surface of $BaWO_4$:Er^{3+}, Yb^{3+} particles. With the excitation at 250 nm, the SPION/$BaWO_4$:Er^{3+}, Yb^{3+} composites exhibited photoluminescence emission in the blue wavelength range of 390-420 nm. The photoluminescence intensity of the SPION/$BaWO_4$:Er^{3+}, Yb^{3+} was much stronger than that of the SPION/$BaWO_4$:Er^{3+}. Raman spectra of the synthesized SPION/$BaWO_4$:Er^{3+}, Yb^{3+}(F-BWO:ErYb) composites indicated indicate additional peaks at both middle (504 and 375 cm^{-1}) and lower frequencies (313, 277, 242 and 205 cm^{-1}).

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