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Cyclic Microwave-Assisted Sol-Gel Process of $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$ Particles and their Upconversion Photoluminescence Properties

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Er^{3+} doped $\text{BaLa}_2(\text{MoO}_4)_4$ [$\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}$] and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaLa}_2(\text{MoO}_4)_4$ ($\text{BaLa}_2(\text{MoO}_4)_4\text{:Er/Yb}$) phosphors were successfully synthesized by a cyclic microwave-assisted sol-gel process followed by heat treatment. The microstructures exhibited well-defined and homogeneous morphology with particles sizes of 2-10 μm . With excitation at 980 nm, the doped particles exhibited a strong 525 and 550 nm emission bands in the green region and a weak 655 nm emission band in the red region. Raman spectra of the doped particles indicated the detection of additional strong peaks at higher frequencies (1000, 1040, 1092, 1138, 1175, 1238, 1362 and 1458 cm^{-1}) and weak peaks at lower frequencies (232, 380, 568 and 660 cm^{-1}).

Keywords: Cyclic microwave, Sol-gel process, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$, Upconversion photoluminescence.

INTRODUCTION

Rare earth-doped upconversion particles have attracted great interest in recent years due to the luminescent properties and potential applications in products such as lasers, three-dimensional displays, light-emitting devices, and biological detectors¹⁻³. Double molybdates are relatively stable in the air and has stable physical and chemical properties, a low excitation threshold energy, and low-cost productivity⁴⁻⁶. The upconversion process featuring multi-photon absorption and anti-stokes emission is fundamentally different from the conventional photoluminescence process, as the intermediate energy level is virtual and that for upconversion is real. Among the rare earth ions, the Er^{3+} ion is suitable for converting infrared to visible light through the upconversion process due to proper electronic energy level configuration. The co-doped Yb^{3+} ion and Er^{3+} ion can remarkably enhance the upconversion efficiency from infrared to visible light due to the efficiency energy transfer from Yb^{3+} to Er^{3+} . The Yb^{3+} ion as a sensitizer can be effectively excited by incident light source energy that is transferred to the activator, from which radiation can be emitted. The Er^{3+} ion activator is the luminescence center of the upconversion particles, while the sensitizer enhances the upconversion luminescence efficiency⁷⁻⁹.

Several processes have recently been developed to prepare the rare-earth doped double molybdates, including solid-state reactions¹⁰⁻¹⁴, co-precipitation^{15,16}, sol-gel method^{4-6,17-21}, hydrothermal method^{22,23}, Pechini method^{24,25}, organic gel-thermal

decomposition²⁶ and microwave-assisted hydrothermal method²⁷. 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. Usually, the double molybdates were prepared by solid-state method that requires high temperatures, lengthy heating process and subsequent grinding, which results in the loss of emission intensity and the increase of cost. Sol-gel process has some advantages over the conventional solid-state method, including good homogeneity, low calcination temperature and a small size and narrow particle size distribution for good luminescent characteristics. However, sol-gel process has a disadvantage to take a long time period of gelation. Compared with the usual methods, microwave synthesis has the advantages of very short reaction time, small-size particles, narrow particle size distribution and high purity for preparing polycrystalline samples. Microwave heating is delivered to the material surface by radiant and/or convection heating, which is transferred to the bulk of the material *via* conduction. Microwave energy is delivered directly to the material by molecular interactions under an electromagnetic field. This makes possible the rapid and uniform heating of thick materials²⁸⁻³². Cyclic microwave-assisted sol-gel process is a cost-effective method that provides high homogeneity with easy scale-up and is emerging as a viable alternative approach for the synthesis of high-quality luminescent materials in short time periods.

In this study, Er^{3+} doped $\text{BaLa}_2(\text{MoO}_4)_4$ and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaLa}_2(\text{MoO}_4)_4$ phosphors were synthesized by the cyclic microwave-assisted sol-gel process followed by heat treatment. The synthesized doped particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Optical properties were examined comparatively using photoluminescence (PL) emission and Raman spectroscopy.

EXPERIMENTAL

Appropriate stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$ (99 %, Sigma-Aldrich, USA), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99 %, Sigma-Aldrich, USA), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (99 %, Alfa Aesar USA), $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9 %, Sigma-Aldrich, USA), $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9 %, Sigma-Aldrich, USA), citric acid (99.5 %, Daejung Chemicals, Korea), NH_4OH (A.R.), ethylene glycol (A.R.) and distilled water were used to prepare $\text{BaLa}_2(\text{MoO}_4)_4$, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}\#$ compounds. To prepare $\text{BaLa}_2(\text{MoO}_4)_4$, 0.4 mol % $\text{Ba}(\text{NO}_3)_2$ and 0.4 mol % $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in 20 mL of ethylene glycol and 80 mL 4M NH_4OH under vigorous stirring and heating. Subsequently, 0.8 mol % $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and citric acid (with molar ratio citric acid: total metal ion = 2:1) were dissolved in 100 mL of distilled water under vigorous stirring and heating. Then the solutions were mixed together under vigorous stirring and heating. At the end, the highly transparent solutions were obtained and adjusted to pH 7-8 by addition of 8 M NH_4OH . In the second way, to prepare $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}$, 0.72 mol % $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 0.08 mol % $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used for the rare earth solution. In the third way, to prepare $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$, 0.68 mol % $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 0.04 mol % $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.08 mol % $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used for the rare earth solution. In the fourth way, to prepare $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}\#$, 0.6 mol % $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 0.02 mol % $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.18 mol % $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used for the rare earth solution.

The transparent solutions were placed into a microwave oven operating at a frequency of 2.45 GHz with a maximum out-power of 1250 W for 0.5 h. The working cycle of the microwave reaction was controlled very precisely between 30 s on and 30 s off for 15 min and 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 is 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, the reactions proceed at the boiling point temperature. When microwave radiation is supplied to the ethylene glycol based solution, the components dissolved in the ethylene glycol can couple. When a large amount of microwave radiation is supplied to the ethylene glycol, the charged particles vibrate in the electric field interdependently. The samples were treated with ultrasonic radiation for 10 min and to produce a light yellow transparent sol. The light yellow transparent sols were dried at 120 °C in a dry oven for 48 h to get black dried gels. The black dried gels were grinded and heat-treated at 900 °C for 12 h with 100 °C interval between 600-900 °C. Finally, the white particles were obtained for $\text{BaLa}_2(\text{MoO}_4)_4$

and pink particles for $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}\#$.

The phase composition of the synthesized particles was identified using XRD (D/MAX 2200, Rigaku, Japan). The microstructure and surface morphology of the $\text{BaLa}_2(\text{MoO}_4)_4$, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}\#$ particles were observed using SEM/EDS (JSM-5600, JEOL, Japan). The PL spectra were recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. Raman spectroscopy measurements were performed using a LabRam Aramis (Horiba 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. 1 shows the XRD patterns of the (a) JCPDS 36-0192 data of $\text{BaLa}_2(\text{MoO}_4)_4$, the synthesized (b) $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and (c) $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}\#$ particles. All of the XRD peaks could be assigned to the monoclinic-phase $\text{BaGd}_2(\text{MoO}_4)_4$ with a scheelite-type structure, which was in good agreement with the crystallographic data of $\text{BaLa}_2(\text{MoO}_4)_4$ (JCPDS 36-1092). This means that the obtained samples have a monoclinic phase with space group of C2/c after partially replacing La^{3+} by Er^{3+} and Yb^{3+} ions are effectively doped into crystal lattices of the monoclinic $\text{BaLa}_2(\text{MoO}_4)_4$ phase due to the similar radii⁴⁻⁶ of La^{3+} and by Er^{3+} and Yb^{3+} . Post heat-treatment plays an important role in a well-defined crystallized morphology. To achieve a well-defined crystalline morphology, the $\text{BaLa}_2(\text{MoO}_4)_4$, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}\#$ phases need to be heat treated at 900 °C for 12 h. It is assumed that the doping amount of $\text{Er}^{3+}/\text{Yb}^{3+}$ has a great effect on the crystalline cell volume of the $\text{BaLa}_2(\text{MoO}_4)_4$, because of the different ionic sizes and valence states.

Fig. 1. X-ray diffraction patterns of the (a) JCPDS 36-0192 data, the synthesized (b) $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and (c) $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}\#$ particles

Fig. 2 shows SEM images of the synthesized (a) $\text{BaLa}_2(\text{MoO}_4)_4$, (b) $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}$, (c) $\text{BaLa}_2(\text{MoO}_4)_4\text{:Er}^{3+}/\text{Yb}^{3+}$

Fig. 2. Scanning electron microscopy images of the synthesized (a) $\text{BaLa}_2(\text{MoO}_4)_4$, (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles

Yb^{3+} and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles. The as-synthesized samples are well crystallized with a fine and homogeneous morphology and particle size of 2–10 μm . The sample of (a) $\text{BaLa}_2(\text{MoO}_4)_4$ shows a very homogeneous morphology. The samples of (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ have

obvious discrepancies in particle size or morphology compared to the sample of (a) $\text{BaLa}_2(\text{MoO}_4)_4$. It is noted that the doping amounts of Er^{3+} and Yb^{3+} had effects on the morphological features. The combination of doping amounts of 0.02 mol % Er^{3+} and 0.18 mol % Yb^{3+} for (a) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ provides great effect on the morphological features. Fig. 3 shows the Energy-dispersive X-ray spectroscopy patterns of the synthesized (a) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles and quantitative results of the synthesized (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles. The EDS pattern shows that the (a) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles are composed of Ba, La, Mo, O and Er for $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and Ba, La, Mo, O, Er and Yb for $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles. The quantitative results of the synthesized (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles are well presented with the weight % of Ba, La, Mo, O and Er for $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and Ba, La, Mo, O, Er and Yb for $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles. The composition of Ba, La, Mo, O, Er and Yb exhibits that $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles can be successfully synthesized using the cyclic microwave-assisted sol-gel process. The cyclic microwave-assisted sol-gel process of double molybdates provides the energy to synthesize the bulk of the material uniformly, so that fine particles with controlled morphology can be fabricated in short time periods. The method is a cost-effective way to provide highly homogeneous products with easy scale-up and is a viable alternative for rapid synthesis of upconversion particles.

Fig. 3. Energy-dispersive X-ray spectroscopy patterns of the synthesized (a) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles, and quantitative results of the synthesized (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles

Fig. 4 shows the upconversion photoluminescence emission spectra of the as-prepared (a) $\text{BaLa}_2(\text{MoO}_4)_4$, (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles excited at 980 nm at room temperature. The strong 525-nm and 550-nm emission bands in the green region correspond 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, respectively, while the weak emission 655-nm band in the red region corresponds to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. The upconversion intensity of (a) $\text{BaLa}_2(\text{MoO}_4)_4$

Fig. 4. Upconversion photoluminescence emission spectra of (a) $\text{BaLa}_2(\text{MoO}_4)_4$, (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles excited at 980 nm at room temperature

has not been appeared. The upconversion intensity of (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ is much higher than those of (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ and (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles. Similar results are also observed from $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped in other host matrices, which are assigned in the upconversion emission spectra that the green emission intensity ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions)^{7,10,23,25,30-33} and the red emission intensity ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition)^{7,10,23,25,30-33}. The doping amounts of $\text{Er}^{3+}/\text{Yb}^{3+}$ had a great effect on both the morphological features and their upconversion fluorescence intensity. The Yb^{3+} 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 Er^{3+} ion as an activator is the luminescence center in upconversion particles, and the sensitizer enhances the upconversion luminescence efficiency.

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. Fig. 5 shows the schematic energy level diagrams of Er^{3+} ions (activator) and Yb^{3+} ions (sensitizer) in the as-prepared $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ samples and the upconversion mechanisms accounting for the green and red emissions at 980 nm laser excitation³⁰. In the complex $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaLa}_2(\text{MoO}_4)_4$ system, Er^{3+} and Yb^{3+} ions are initially excited from the ground states to the excited states by the ground state absorption (GSA) processes ($\text{Er}^{3+}: ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$, $\text{Yb}^{3+}: ^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) or ET process of $^2\text{F}_{5/2}(\text{Yb}^{3+}) + ^4\text{I}_{15/2}(\text{Er}^{3+}) \rightarrow ^4\text{F}_{7/2}(\text{Yb}^{3+}) + ^4\text{I}_{11/2}(\text{Er}^{3+})$ dependent on the population of the $^4\text{I}_{11/2}$ level in Er^{3+} . It is considered that these three processes are able to populate the $^4\text{F}_{7/2}$ level from the $^4\text{I}_{11/2}$ level in the Er^{3+} level and then the $^4\text{F}_{7/2}$ level relaxes rapidly and non-radiatively to the next lower $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ in Er^{3+} because of short lifetime

of the $^4\text{F}_{7/2}$ level. Then, the radiative transitions of $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ processes can produce green emissions at 525 and 550 nm³⁴. For the red emission, the $^4\text{F}_{9/2}$ level is populated by non-radiative relaxation from the $^4\text{S}_{3/2}$ to the $^4\text{F}_{9/2}$ level and cross relaxation (CR) *via* the $^4\text{F}_{7/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{9/2} + ^4\text{F}_{9/2}$ transition in Er^{3+} ³⁵. Finally, $^4\text{F}_{9/2}$ level relaxes radiatively to the ground state at $^4\text{I}_{15/2}$ level and releases red emission at 655 nm. The strong 525 and 550 nm emission bands in the green region as shown in Fig. 4 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 Er^{3+} ions, respectively, while the weak 655 nm emission band in the red region is assigned to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. The higher intensity of the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition in comparison with that $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transition may be induced with the concentration quenching effect by the energy transfer between nearest Er^{3+} and Yb^{3+} ions and the interactions between doping ions in $\text{BaLa}_2(\text{MoO}_4)_4$ host matrix^{7,34,35}.

Fig. 5. Schematic energy level diagrams of Er^{3+} ions (activator) and Yb^{3+} ions (sensitizer) in the as-prepared $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ system and the upconversion mechanisms accounting for the green and red emissions under 980 nm laser excitation³⁰

Fig. 6 shows the Raman spectra of the synthesized (a) $\text{BaLa}_2(\text{MoO}_4)_4$ (BLM), (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ (BLM:Er), (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (BLM:ErYb) and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ (BLM:ErYb#) particles excited by the 514.5 nm line of an Ar ion laser at 0.5 mW on the samples. The internal modes for the (a) $\text{BaLa}_2(\text{MoO}_4)_4$ (BLM) 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 316, 330, 370, 750, 828 and 906 cm^{-1} , respectively. The well-resolved sharp peaks for the $\text{BaLa}_2(\text{MoO}_4)_4$ 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 $[\text{MoO}_4]^{2-}$. The Raman spectra of the (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ (BLM:Er), (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (BLM:ErYb) and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ (BLM:ErYb#) particles indicate additional strong peaks at higher frequencies (1000, 1040, 1092, 1138, 1175, 1238, 1362 and 1458 cm^{-1}) and weak peaks at lower frequencies (232, 380, 6568 and 660 cm^{-1}). The Raman spectra of $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles proved that the doping ions can

influence the structure of the host materials. The combination of a heavy metal cation and the large inter-ionic distance for Er^{3+} and Yb^{3+} substitutions in La^{3+} sites in the lattice result in low probability of upconversion and the phonon-splitting relaxation in $\text{BaLa}_2(\text{MoO}_4)_4$ crystals. Raman spectra of Er^{3+} doped and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaLa}_2(\text{MoO}_4)_4$ recorded in the present study are assigned to the previously reported results for $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped MMoO_4 ($M = \text{Ba}, \text{Sr}, \text{Ca}$) systems³⁰⁻³². It could consider that the strong and strange effect in the Ln-doped crystalline samples may be generated by the disorder of the $[\text{MoO}_4]^{2-}$ groups with the incorporation of the Ln element into the crystal lattice or by a new phase formation.

Fig. 6. Raman spectra of the synthesized (a) $\text{BaLa}_2(\text{MoO}_4)_4$ (BLM), (b) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$ (BLM:Er), (c) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (BLM:ErYb) and (d) $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ (BLM:ErYb#) particles excited by the 514.5 nm line of an Ar ion laser at 0.5 mW on the samples

Conclusion

$\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaLa}_2(\text{MoO}_4)_4$ phosphors were successfully synthesized by a cyclic microwave-assisted sol-gel process followed by further heat treatment. Well-crystallized $\text{BaLa}_2(\text{MoO}_4)_4$, $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles were formed after heat treatment at 900 °C for 12 h, showing a fine and homogeneous morphology with particle sizes of 2-10 μm . With excitation at 980 nm, $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles exhibited a strong 525 and 550 nm emission bands in the green region that 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, respectively, while a weak 655 nm emission band in the red region corresponds to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. The upconversion intensity of the $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles was much higher than those of the $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ particles. The Raman spectra of the $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}$, $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{BaLa}_2(\text{MoO}_4)_4:\text{Er}^{3+}/\text{Yb}^{3+}\#$ particles indicated additional strong peaks at higher frequencies (1000, 1040, 1092, 1138, 1175, 1238, 1362 and 1458 cm^{-1}) and weak peaks at lower frequencies (232, 380, 6568 and 660 cm^{-1}).

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