Preparation of NaSrLa(WO₄)₃:Ho³⁺/Yb³⁺ ternary tungstates and their upconversion photoluminescence properties

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1. Introduction

Inorganic luminescent materials are of great importance for modern photonic technologies and different phosphors with specific spectroscopic parameters were found in the recent years [1–9]. Binary alkaline earth tungstates M₄Ln₃(WO₄)₆ (M: alkaline earth bivalent metal ion, Ln: trivalent rare-earth ions) belong to a group of scheelite-structured compounds. The scheelite-structured binary molybdates and tungstates have been reported in terms of excellent UC photoluminescence properties [9,10]. In particular, the rare-earth-doped binary NaLn(WO₄)₃ compounds possess the tetragonal phase with the space group I₄₁/a, and belong to the family of scheelite-type structure. It is well employed for the trivalent rare-earth ions in the disordered tetragonal-phase to be partially substituted by Ho³⁺ and Yb³⁺ ions in the lanthanide site of Ln³⁺ [11–13].

Among the rare-earth ions, the Ho³⁺ ion is a suitable activator due to its intense green emission of ⁵S₂→⁵I₇ transition and strong red emission of ⁵F₅→⁵I₉ transition upon 980 nm excitation, while the sensitizer Yb³⁺ enhances the UC luminescence efficiency owing to its strong absorption around 980 nm. The codoped Yb³⁺ ion and Ho³⁺ ion can remarkably enhance the UC efficiency due to the efficient energy transfer from Yb³⁺ to Ho³⁺ [11–13]. The ternary tungstates with general composition NaM₃Ln(x(WO₄)₃ (M=Ca²⁺, Sr²⁺ and Ba²⁺, and Ln=La³⁺, Gd³⁺ and Y³⁺) have not been reported up to now. As compared to the common technological methods, microwave synthesis has its advantages of a very short reaction time, small-size particles, narrow particle size distribution, and high purity of final polycrystalline samples purity [14,15]. In the present study, the ternary tungstate NaSrLa₁₋ₓ(WO₄)₃:Ho³⁺/Yb³⁺ phosphors with the proper doping concentrations of Ho³⁺ and Yb³⁺ (x=Ho³⁺+Yb³⁺, Ho³⁺=0, 0.05, 0.1, 0.2, and Yb³⁺=0, 0.2, 0.45) were successfully prepared by the microwave sol-gel method followed by heat treatment in the air. The particles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The optical properties were examined using photoluminescence (PL) emission and Raman spectroscopy. The synthesis and measurement conditions can be found in Supporting Information.
2. Results and discussion

The XRD patterns of the samples are shown in Fig. 1. In the synthesized samples, almost all XRD peaks were indexed by tetragonal phase with parameters close to SrWO₄ (JCPDS 08-0490). Therefore, the synthesized NaSrLa(WO₄)₃ particles belong to tungstate family with a scheelite-type structure. The crystal structure of SrWO₄ was taken as the starting model for Rietveld refinement using package TOPAS 4.2. As shown in Fig. 1S, the defined crystal structure contains WO₄ tetrahedrons coordinated by four (Sr/La/Ho/Yb)O₆ square antiprisms. The refinements were stable and give low R-factors (Tables 1S–3S, Figs. 2S–5S). The linear cell volume increasing per average ion radii IR(Na/Sr/La/Ho/Yb) proves the suggested chemical formulas (Fig. 6S) [16]. Consequently, the Ho³⁺ and Yb³⁺ ions can be efficiently incorporated into the NaSrLa(WO₄)₃ lattice by partial substitution for La³⁺. Thus, the post heat-treatment at 900 °C for 16 h plays an important role in reaching of the precursor crystallization.

The SEM images of the NaSrLa₀.₈(WO₄)₃:Ho₀.₂ and NaSrLa₀.₅₀(WO₄)₃:Ho₀.₀₅Yb₀.₄₅ particles are provided in Fig. 2. The as-synthesized samples possess the homogeneous morphology and particle size of 2–5 μm. The partly agglomerated particles are induced by the atom inter-diffusions between the grains. The morphology feature is insensitive to the Ho³⁺/Yb³⁺ doping concentrations. This suggests that the microwave sol-gel route is suitable for the creation of homogeneous NaSrLa₁−ₓ(WO₄)₃:xHo³⁺/Yb³⁺ crystallites.

Fig. 3 shows the UC photoluminescence emission spectra of the samples excited under 980 nm. The NaSrLa₀.₇(WO₄)₃:Ho₀.₁Yb₀.₂ and NaSrLa₀.₅₀(WO₄)₃:Ho₀.₀₅Yb₀.₄₅ particles exhibited yellow emissions based on the strong 545 and 655 nm emission bands. The UC intensities of NaSrLa(WO₄)₃ and NaSrLa₀.₅(WO₄)₃:Ho₀.₀₅ particles were not detected. The UC intensity of NaSrLa₀.₅(WO₄)₃:Ho₀.₀₅Yb₀.₄₅ sample is much higher than that of NaSrLa₀.₅(WO₄)₃:Ho₀.₀₅Yb₀.₂. The strong 545-nm emission band in the green region corresponds to the ⁵S₂/⁵P₄→⁷I₈ transition, while the very strong emission 655-nm band in the red region corresponds to the ⁵F₅→⁷I₄ transition [17,18]. The Ho³⁺ ion activator is the luminescence center for these UC samples, and the sensitizer Yb³⁺ enhances the UC luminescence intensity because of the efficient energy transfer from Yb³⁺ to Ho³⁺. The schematic energy level diagrams of Yb³⁺ and Ho³⁺ ions is shown in Fig. 7S. With increase of the Ho³⁺ and Yb³⁺ concentrations, the distance between Ho³⁺ and Yb³⁺ ions decreases, which can promote non-radiative energy transfer [19,20]. As shown in Fig. 3, the higher intensity of NaSrLa₀.₅(WO₄)₃:Ho₀.₀₅Yb₀.₄₅ is found at Yb³⁺:Ho³⁺ = 9:1, and, thus, the preferable Yb³⁺:Ho³⁺ ratio is as high as 9:1.

The insert in Fig. 3 shows a logarithmic scale dependence of the UC emission intensities at 545 and 655 nm on the working pump power over the range of 20–110 mW in the NaSrLa₀.₅(WO₄)₃:Ho₀.₀₅Yb₀.₄₅ sample. The UC emission intensity I is proportional to the slope value n of the irradiation pumping power P, where n is the number of pumped photons required to produce UC emission [20]:

\[
I \propto P^n \tag{1}
\]

\[
\ln I \propto n \ln P \tag{2}
\]

As evident from Fig. 4, the slope values are n=1.74 for green emission at 545 and n=1.84 for red emission at 655 nm, respectively. These results show that the UC mechanism can be explained by a two-photon UC process in Ho³⁺/Yb³⁺ co-doped phosphors.

The calculated chromaticity coordinates and CIE chromaticity diagram are shown in Fig. 8S. The inset shows the chromaticity points for the samples. The chromaticity coordinates (x, y) are strongly dependent on the Ho³⁺/Yb³⁺ concentration ratio. As shown in Fig. 4, the calculated chromaticity coordinates for NaSrLa₀.₇(WO₄)₃:Ho₀.₁Yb₀.₂ and NaSrLa₀.₅(WO₄)₃:Ho₀.₀₅Yb₀.₄₅ correspond to the yellow region in CIE diagram.

The Raman spectra of the synthesized samples are shown in Fig. 4. The sharp internal modes for the pure NaSrLa(WO₄)₃ were detected at 192, 328, 378, 830 and 920 cm⁻¹ that indicates high crystallinity of the particles. The Raman spectrum of the NaSrLa(WO₄)₃ shows the typical tungstate configuration with a wide empty gap over 400–800 cm⁻¹ [21,22]. The band at 920 cm⁻¹ corresponds to stretching vibrations of the