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Original research article

Up-conversion luminescence in Yb^{3+}/Er^{3+} co-doped $ZnGa_2O_4$ and $ZnAl_2O_4$ powder phosphors

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A B S T R A C T

$ZnGa_2O_4$:Yb^{3+},Er^{3+} and $ZnAl_2O_4$:Yb^{3+},Er^{3+} up-conversion powder phosphors with different Yb/Er ratio are synthesized by solid-state method and subsequent thermal treatment at 1300 °C, which can generate strong up-conversion emissions in visible spectral range under 980 nm excitation. For the as-prepared $ZnGa_2O_4$:Yb^{3+},Er^{3+} phosphors, the green and red emissions around 524 nm (corresponding to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}), 549 nm (corresponding to $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}) and 659 nm (corresponding to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}) indicate the optimal Yb/Er ratio for the sample is 7/1, while the $ZnAl_2O_4$:Yb^{3+},Er^{3+} phosphors with the same green and red emissions is Yb/Er = 3/1. Besides the up-conversion luminescence, the morphology and crystal structure are also investigated. All $ZnGa_2O_4$:Yb^{3+},Er^{3+} powders contain regular long rods with diameter of about 600–900 nm, while agglomerates composed of non-regular particles with size about 200–400 nm are shown in all $ZnAl_2O_4$:Yb^{3+},Er^{3+} powders. Additionally, all samples are spinel structure with a high degree of crystallinity. Consequently, the particles of moderate size, stable crystal structure and enough high intensity of green and red emissions in all $ZnGa_2O_4$:Yb^{3+},Er^{3+} and $ZnAl_2O_4$:Yb^{3+},Er^{3+} powder phosphors endow them potential applications in infrared detection, display devices and so on.

1. Introduction

Due to the wide range of applications, there are considerable investigations in the up-conversion (UC) materials doped with trivalent rare-earth ions in recent years [1,2]. As we all known, the up-conversion materials can absorb two or more low-energy (long wavelength) photons and emit a high-energy (short wavelength) photon, which have potential applications in many fields, such as all-solid compact laser devices, full color displays, infrared quantum detectors, bio-labels and so on [3–7]. More than anything, the up-conversion luminescent intensity and efficiency are dependent primarily on the doping ions and host materials [1,2].

Erbium (Er) ion is an outstanding doping ion for up-conversion luminescence as an activator. It has metastable $^4I_{9/2}$ and $^4I_{11/2}$ level, which can be populated by near-infrared laser, special electronic structure and profuse energy levels from ultraviolet to near-infrared, which can generate colorful emissions [8,9]. Meanwhile, Ytterbium (Yb) ion is an excellent sensitizer for up-conversion luminescence, which can be efficiently excited by 980 nm laser and transfer the energy to activators (Er ion in particular) [10]. Up to now, Yb^{3+}-Er^{3+}, as an emblematical up-conversion ion-pair, has been investigated by a lot of scientists [11–17].

Zinc gallate ($ZnGa_2O_4$) and Zinc aluminate ($ZnAl_2O_4$) are called as spinel crystal material, whose Zn^{2+} ions occupy the

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tetrahedral sites and Ga^{3+} or Al^{3+} ions occupy the octahedral sites [18]. Besides, both two unit cells contain 8 tetrahedral cations, 16 octahedral cations and 32 oxygen anions [18]. Moreover, both the $ZnGa_2O_4$ and the $ZnAl_2O_4$ can emit blue photoluminescence without doping any ion [19]. Considering that the optical band gap of $ZnGa_2O_4$ and $ZnAl_2O_4$ crystal is 3.8 eV and 4.4 eV respectively, the energy transition and blue photoluminescence may be supplemented by intra bandgap defects, such as oxygen vacancies [20]. What's more, $ZnGa_2O_4$ and $ZnAl_2O_4$ can generate colorful emissions doped with some rare earth ions, such as green emission in $ZnGa_2O_4$:Er^{3+} [18], red emission in $ZnGa_2O_4$:Eu^{3+} [19], yellow emission in $ZnAl_2O_4$:Dy^{3+} [21] and so on.

Considering the previous researches above, the Yb^{3+}-Er^{3+} is an excellent up-conversion ion-pair candidate, while $ZnGa_2O_4$ and $ZnAl_2O_4$ are prominent host materials for photoluminescence. However, up to now, there are few papers reporting the up-conversion luminescence using $ZnGa_2O_4$ or $ZnAl_2O_4$ as the host materials. Stated thus, we synthesized $ZnGa_2O_4$:Yb^{3+},Er^{3+} and $ZnAl_2O_4$:Yb^{3+},Er^{3+} up-conversion phosphors by high temperature solid-state method in this paper. Furthermore, the morphology, crystal structure and up-conversion luminescent properties of as-prepared powder phosphors were also investigated.

2. Experimental procedure

Powder phosphors $ZnAl(Ga)_{2-x}O_4$:Yb_a,Er_b ($0.01 \le x \le 0.08$; $x = a + b$; a/b = 3/1, 5/1, 7/1, 10/1, respectively) were synthesized by a high temperature solid-state reaction. Stoichiometric amounts of ZnO (Sigma Aldrich 99.9% pure), Yb_2O_3 (Sigma Aldrich 99.99% pure), Er_2O_3 (Sigma Aldrich 99.99% pure), Al_2O_3 (Sigma Aldrich 99.9% pure) or Ga_2O_3 (Sigma Aldrich 99.99% pure) powders were mixed in an agate mortar with acetone and ground for 2 h to form homogeneous powders. Then the mixed powders were sintered at 1300 ℃ in air for 2 h to obtain the $ZnAl(Ga)_2O_4$:Yb,Er powder phosphors. All chemicals were used as-received without further purification.

The morphology was determined by scanning electron microscope (SEM SU-70). The element composition was investigated using a scanning electron microscopy with energy dispersive spectrometer (SEM SU-70/EDS). The crystal phase was analyzed by x-ray diffraction (XRD) conducted on a Rigaku Dmax-rc diffractometer with Ni-filtered Cu Kα radiation (V = 50 kV, I = 80 mA). The up-conversion emission spectra was measured by using a LSP920 spectrofluorometer excited by a 980 nm laser with different power as 112 mw, 483 mw, 818 mw, 1090 mw and 1360 mw (also known as 35.67 mw/cm^2, 153.82 mw/cm^2, 260.51 mw/cm^2, 347.13 mw/cm^2 and 433.12 mw/cm^2, respectively). All characterizations were carried out at room temperature.

3. Results and discussion

3.1. Morphological and structural characterization

The SEM image shown in Fig. 1 provides the morphological characterizations of $ZnGa_2O_4$:Yb^{3+},Er^{3+} powders with Yb/Er ratio of 3/1 (a), 5/1 (b), 7/1 (c) and 10/1 (d), while Fig. 2 provides the morphology of $ZnAl_2O_4$:Yb^{3+},Er^{3+} powders with Yb/Er ratio of 3/1 (a), 5/1 (b), 7/1 (c) and 10/1 (d), respectively.

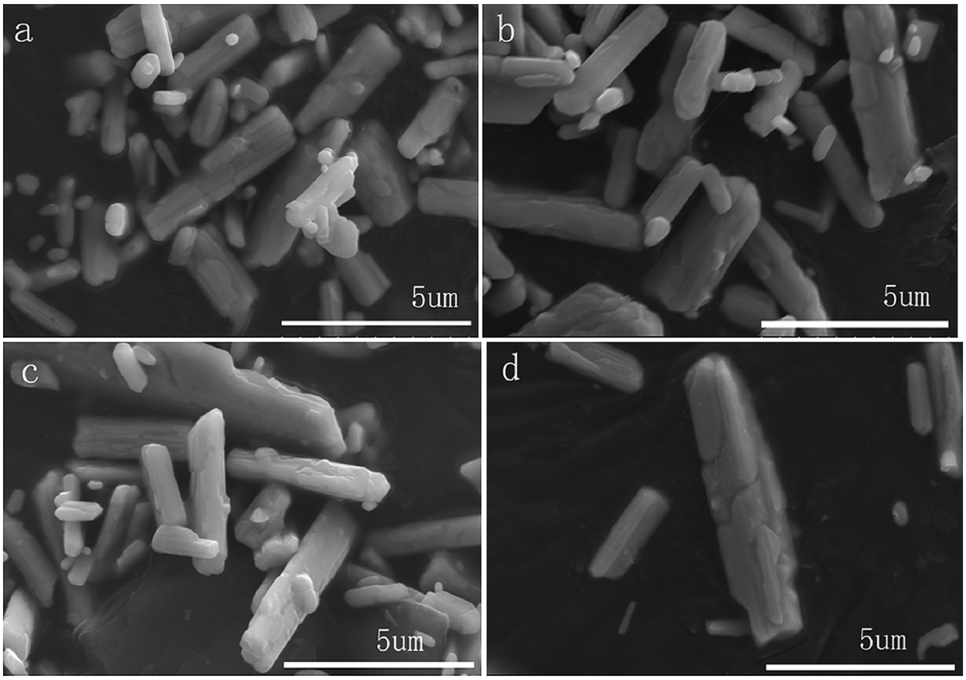

Fig. 1. SEM images of $ZnGa_2O_4$:Yb,Er samples (scale bar:5 µm): Yb/Er = 3/1 (a); Yb/Er = 5/1 (b); Yb/Er = 7/1 (c); Yb/Er = 10/1 (d).