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Effect of Yb^{3+} concentration on upconversion luminescence of AlON:Er^{3+} phosphors

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Abstract: AlON:1.6 mol.%Er^{3+}, x mol.%Yb^{3+} (x=0, 2.6, 3.1, 3.6, 4.1, 4.6) phosphors were synthesized successfully by aluminothermic reduction and nitridation (ATRN) method and characterized by X-ray diffraction (XRD), scanning electron microscopy (FESEM) and upconversion photoluminescence (UCPL) emission spectra. Under the excitation of diode laser 980 nm, the green (556 nm) and red (655 nm) upconverted emissions were observed, attributed to the $^4S_{3/2}\rightarrow^4I_{15/2}$ and $^4F_{9/2}\rightarrow^4I_{15/2}$ transition of Er^{3+} respectively. The emission intensity increased with increasing Yb^{3+} concentration due to the energy transfer (ET) between Yb^{3+} and Er^{3+}. The upconverted emission reached the highest as x=3.6, and was pump-power dependent involving a two-photon process.

Keywords: AlON; phosphor; upconversion luminescence; energy transfer; rare earths

As green energy materials, upconversion photoluminescence (UCPL) phosphors have attracted much attention due to their potential applications in solid state lasers, displays and biological fluorescence devices[1–5]. Rare earth (RE) ions, such as Er^{3+}, Tm^{3+}, Ho^{3+} and Pr^{3+}, have been commonly used as activator[6–9]. Meanwhile, Yb^{3+} ion has been used as an efficient sensitizer due to the large absorption cross section at 980 nm and further energy transfer to activator[10–13].

To weaken the possibility of nonradiative transitions, the host materials should have low phonon energy. With cubic spinel structure, aluminum oxynitride (AlON) exhibits interesting mechanical, optical and photoluminescent properties[14–16]. As UCPL phosphor, AlON doped with Er^{3+}, co-doped with Er^{3+} and Mg^{2+}, co-doped with Yb^{3+} and Tm^{3+} have been reported respectively[17–19]. The adopted approach was the two-step route: the AlON powder was synthesized by carbothermal reduction and nitridation (CTRN) firstly, and then mixed corresponding RE and sintered. The two-step approach has its drawbacks: complexity and potential inhomogeneity. Thus, the one-step route that simplifies the production technology as well as reduces the cost is critical importance. Besides the CTRN, AlON can also be prepared by the aluminothermic reduction and nitridation (ATRN) method. Furthermore, ATRN method can avoid the possible residual of carbon by CTRN[20,21]. If the ATRN method could be introduced into the one-step route, high quality AlON phosphors are expected to be obtained with simplicity and cost-effectiveness.

Herein, a series of Er^{3+}-Yb^{3+} codoped AlON phosphors were synthesized successfully by ATRN method for the first time. To demonstrate the sensibilization of Yb^{3+}, low concentration of Er^{3+} (1.6 mol.%) was introduced. The UCPL spectra with different Yb^{3+} concentrations were presented, along with the dependence of emission intensity upon pump power to investigate the UCPL mechanism.

1 Experimental

1.1 Preparation

The starting materials were commercially available and used without further purification, involving α-Al_2O_3 (99.9%, 30 nm) and Al (99.95%, 1–2 μm), Er_2O_3 (99.99%) and Yb_2O_3 (99.99%). The amount of α-Al_2O_3 and Al was weighed based on AlON with 27 mol.%. Er_2O_3 and Yb_2O_3 were worked out with 1.6 mol.% Er^{3+} and x mol.% Yb^{3+} (x=0, 2.6, 3.1, 3.6, 4.1, 4.6), respectively. All of the materials were mixed thoroughly in alcohol media and dried at 80 °C for 3 h in a vacuum drying oven. The homogeneous mixture was put into a BN crucible and calcined at 1550 °C for 1.5 h, then at 1750 °C for 2.5 h un-

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der flowing N_2 atmosphere, obtaining Er, Yb co-doped AlON product.

1.2 Characterization

Phase identification was carried out by an X-ray diffractometer (Japan Rigaku SCXmini) using Cu Kα radiation (λ=0.15406 nm) operated at 30 kV and 10 mA. The FESEM images were obtained with a JSM-6700F (JEOL) field-emission-type microscope with operation voltage in the range of 0.5–30 kV to observe the morphology. The UCPL emission spectra were measured with a Horiba JY Fluorolog-3 spectrometer at room temperature.

2 Results and discussion

Fig. 1 shows the XRD patterns of AlON powders doped with 1.6 mol.% Er^{3+} and different Yb^{3+} concentrations. For the specimens of Yb^{3+} concentration below 3.6 mol.%, the spectra can be attributed to spinel-type AlON (JCPDS No. 80-2172) without any impurity. In addition, the peaks are sharp and intense due to good crystalline. It is noteworthy that small amount $YbAlO_3$ (JCPDS No. 48-1633) appears for the specimens with higher Yb^{3+} concentrations (x>3.6). It is well-known that impure phase is negative to prepare high transparent ceramic. Thus, only the UCPL properties of the specimens with x≤3.6 are presented.

Fig. 2 shows the SEM images of pure AlON, solely doped AlON:1.6 mol.%Er^{3+}, and co-doped AlON:1.6 mol.%Er^{3+} and different Yb^{3+} concentrations. All of the specimens display irregular morphology. It is interesting that the average particle sizes of AlON and AlON:1.6 mol.%Er^{3+} are 2.1 and 2.4 μm respectively, while those of the codoped samples increase dramatically with the introduction of Yb^{3+} ions (above 10 μm). This phenomenon is attributed to the increase amount of transient liquid phases with Yb_2O_3 doped, resulting in accelerating the dissolution, diffusion, and precipitation processes[22].

Fig. 3 depicts the emission spectra of the phosphors under the excitation of λ_{ex}=980 nm of diode laser, showing Yb^{3+}-concentration dependence of the emission intensities. The green emission band is ranging from 519 to 566 nm, while the red one is stronger within the range of 640–695 nm. These emission bands are attributed to ($^2H_{11/2}$, $^4S_{3/2}$)→$^4I_{15/2}$ and $^4F_{9/2}$→$^4I_{15/2}$ transitions of Er^{3+} respectively. The UCPL processes of RE doping systems have been widely investigated. For the solely doped Er^{3+} system, the possible mechanism for the population of

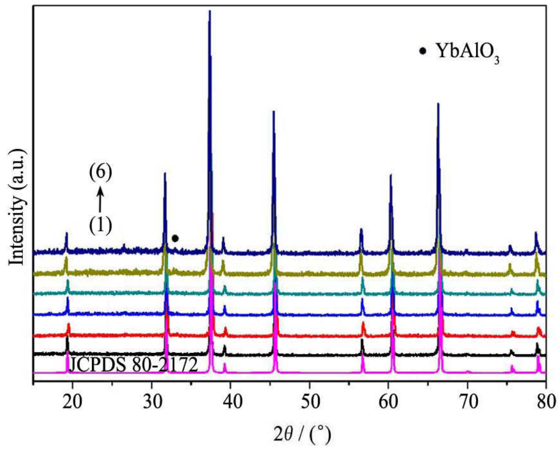

Fig. 1 Powder X-ray diffraction patterns of AlON:1.6Er^{3+},$x$$Yb^{3+}$ samples with x=0 mol.% (1), 2.6 mol.% (2), 3.1 mol.% (3), 3.6 mol.% (4), 4.1 mol.% (5) and 4.6 mol.% (6), respectively

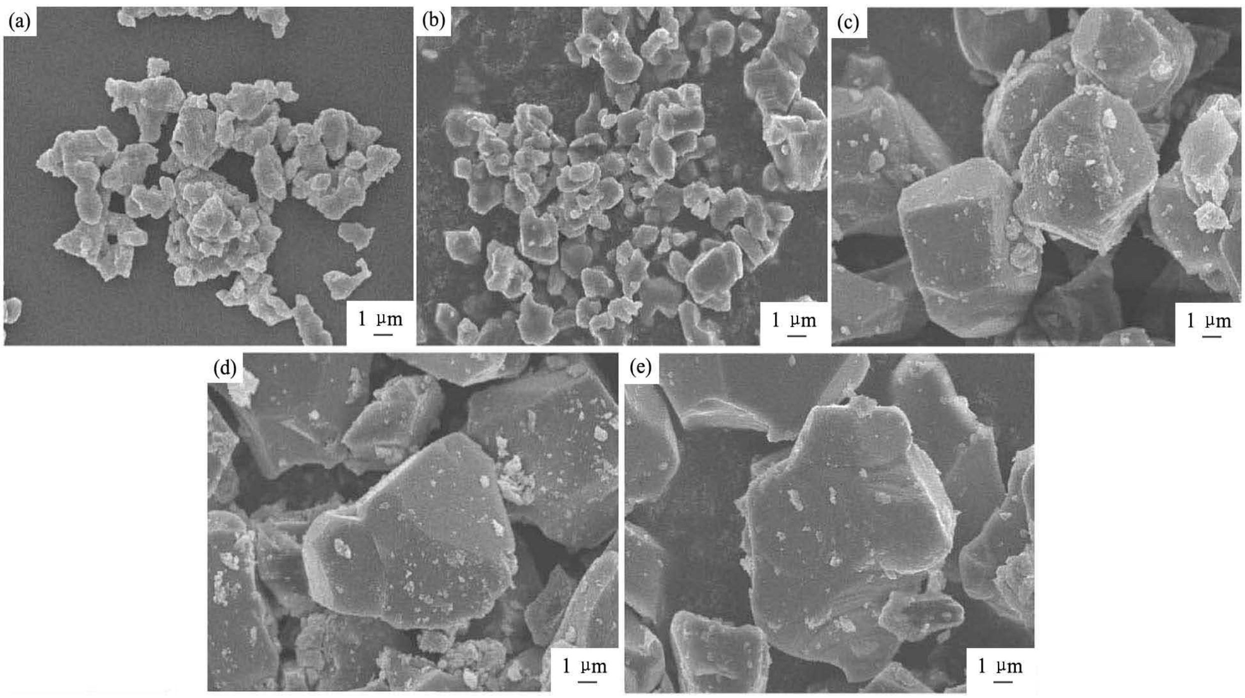

Fig. 2 SEM images of undoped AlON (a), AlON:1.6 mol.%Er^{3+} (b), AlON:1.6 mol.%Er^{3+}, 2.6 mol.%Yb^{3+} (c), AlON:1.6 mol.%Er^{3+}, 3.1 mol.%Yb^{3+} (d) and AlON:1.6 mol.%Er^{3+}, 3.6 mol.%Yb^{3+} (e)