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Multi-photon up-conversion enhancement from $Gd_2(MoO_4)_3$:Er/Yb thin film via the use of sandwich structure

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ABSTRACT

Lanthanide-doped up-converting nano-particles reveal significant promise for data storage, biological imaging, and temperature sensing, but have not been extensively used due to their low emission intensity. Here, we investigate the up-conversion emissions of $Gd_2(MoO_4)_3$:Er/Yb thin films that are sandwiched by $Gd_2(MoO_4)_3$:Yb thin films. Our results show that the sandwiched thin films possess significant enhancement of emission intensities. The enhancement factors of the green and red emissions, radiated from $Gd_2(MoO_4)_3$:Er/Yb films, reach 9.5 and 5, respectively. Moreover, the ability of sandwich structured thin films in multi-photon up-conversion enhancement is more excellent than that of laser power, attributed to the suppression of undesired radiative/non-radiative recombination of the intermediate states. In addition, the intensity-based temperature absolutely sensitivity of sandwich structured $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} reaches $0.013\,K^{-1}$ at 498 K, which indicate this sandwich structured thin films have larger potential in thermal sensors. This sandwich structure might extend the applications of Ln^{3+}-doped materials in super-resolution imaging and temperature sensing.

1. Introduction

Lanthanide (Ln^{3+}) doped up-conversion nano-particles (NPs) are extensively used in many fields, such as data storage [1], colorful displays [2], vitro/vivo bioimaging [3,4] and solar cell [5] due to their unique ability to convert near-infrared light into visible and ultraviolet lights. Whereas, the excellent ability and abundant applications of Ln^{3+} doped up-conversion NPs are restricted by the low emission intensity [6,7]. In recent years, several explorations have been devoted to overcome this drawback, including core-shell structure constructing [8–10], host lattice manipulating [11–13], dye sensitization [14–16] and noble mental/semiconductor nano-particles modifying [17–25]. Su's investigation showed that the emission enhancements of Tb^{3+} and Eu^{3+} were realized through the $NaGdF_4$ @$NaGdF_4$ core-shell NPs, originated from the effectively prevention of surface quenching [8]. Wag's group found 34 times green and 101 times red emission enhancement were realized via introducing 0.5 mol% Li^+, which is due to disordering of the host lattice [12]. Chen's study utilized NIR dye to enhance the up-conversion efficiency of the emissions from $NaYbF_4$:Tm^{3+} (0.5%)@$NaYF_4$:Nd^{3+} core/shell NPs, stemed from the efficient multi-step energy-cascaded transfer [16]. In our previous work, we realized the emission enhancement through coating Au islands on the $Gd_2(MoO_4)_3$:Er/Yb thin film [20]. However, there is few established methods to suppress undesired radiative/non-radiative recombination of the intermediate energy levels, limiting the application in super-resolution imaging and so on [26].

Herein, we designed a sandwich structured thin films through spin-coating method to enhance the emission intensity of Er/Yb co-doped $Gd_2(MoO_4)_3$ (Er/Yb) thin films. The intensities of the up-conversion emissions from the sandwich structured thin films rise obviously, especially in short wavelength. It can be deduced that the sandwich structured thin films could suppress undesired radiative/non-radiative recombination of the intermediate energy levels.

2. Experimental details

2.1. Sample preparation

2.1.1. Materials

$Gd(NO_3)_3{\cdot}6H_2O$ (99.9%), $Yb(NO_3)_3{\cdot}6H_2O$ (99.9%) and $Er(NO_3)_3{\cdot}6H_2O$ (99.9%) were all purchased from Jining zhongkai New Type Material Science Co., Ltd. $(NH_4)_6Mo_7O_{24}$ (99%) and $C_6H_8O_7{\cdot}H_2O$ (95%) were purchased from Tianjin Fuguang Technology Co., Ltd. All the chemicals were used directly without further purification.

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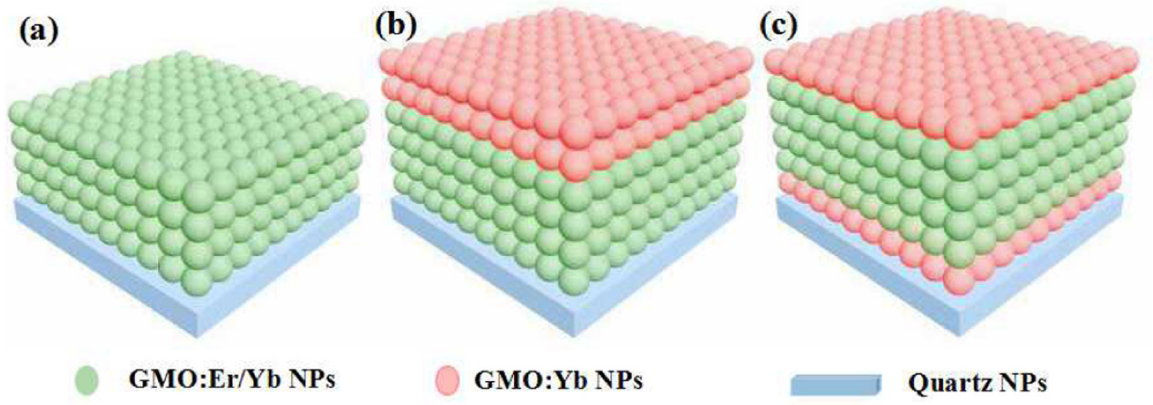

Fig. 1. Schematic representation of (a) Er/Yb (b) Er/Yb@Yb@Yb and (c) Yb@Er/Yb@Yb thin films.

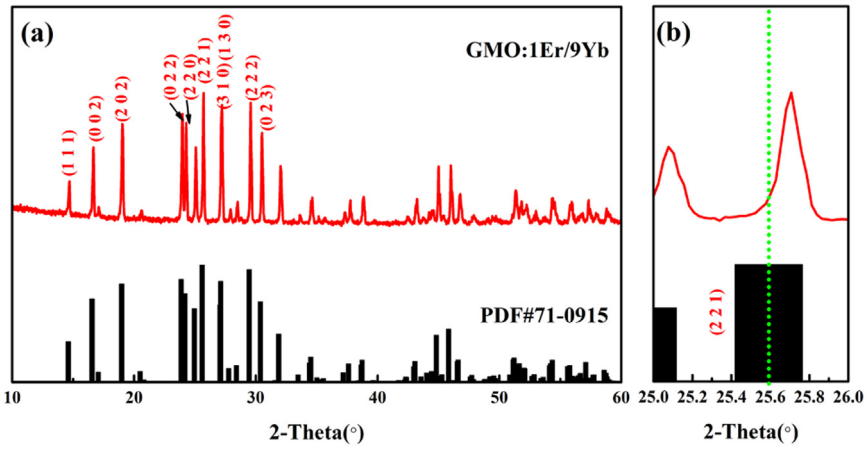

Fig. 2. (a) XRD patterns of Er/Yb co-doped $Gd_2(MoO_4)_3$ powder and the standard $Gd_2(MoO_4)_3$ pattern (PDF#71–0915); (b) enlarged (221) diffraction peak in the XRD patterns of Er/Yb co-doped $Gd_2(MoO_4)_3$ powder.

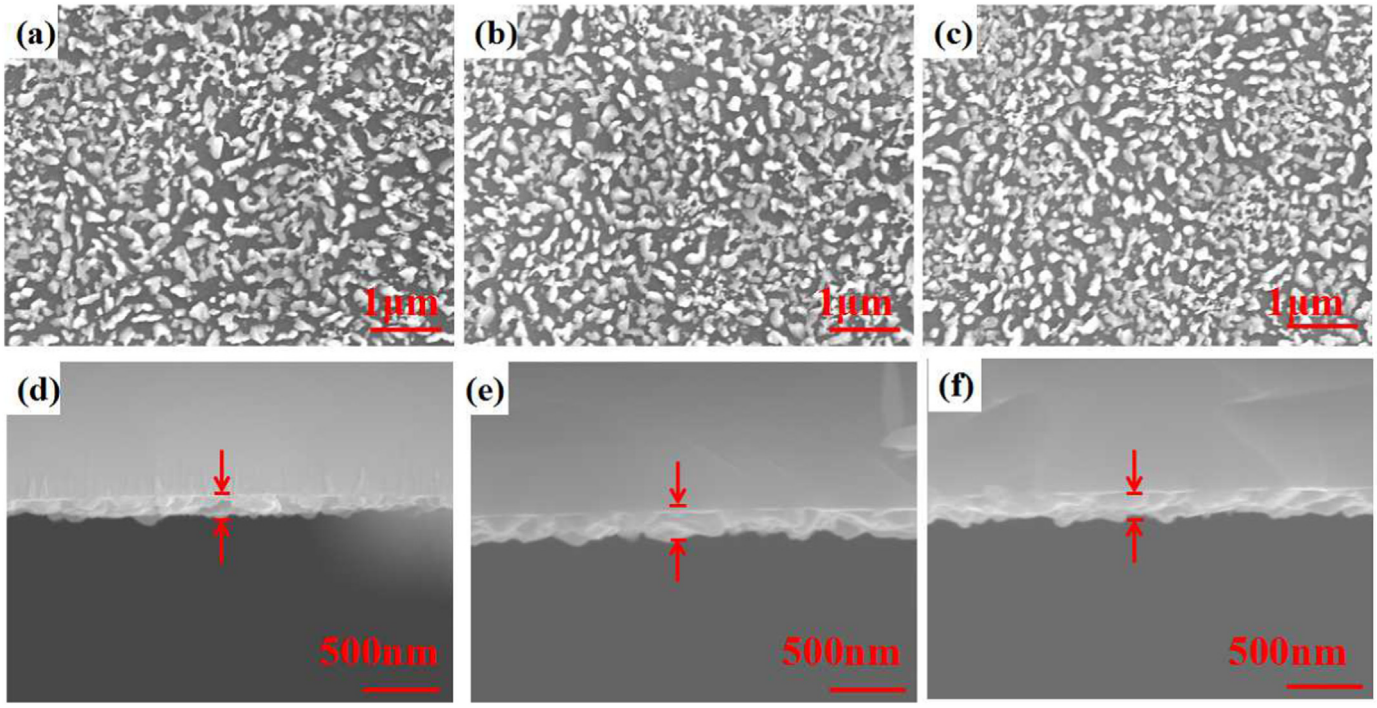

Fig. 3. Surface SEM photos of (a) Er/Yb, (b) Er/Yb@Yb@Yb and (c) Yb@Er/Yb@Yb; cross-section SEM photos of (d) Er/Yb, (e) Er/Yb@Yb@Yb and (f) Yb@Er/Yb@Yb.