

Cooperative Energy Transfer and Frequency Upconversion in $\text{Yb}^{3+}\text{-Tb}^{3+}$ and $\text{Nd}^{3+}\text{-Yb}^{3+}\text{-Tb}^{3+}$ Codoped $\text{GdAl}_3(\text{BO}_3)_4$ Phosphors

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Abstract Polycrystalline $\text{GdAl}_3(\text{BO}_3)_4$ phosphors codoped with $\text{Yb}^{3+}/\text{Tb}^{3+}$ and/or $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tb}^{3+}$ have been synthesized by combustion method. Upon excitation with a 980 nm laser diode, an intense green upconversion luminescence has been observed in $\text{GdAl}_3(\text{BO}_3)_4:\text{Yb},\text{Tb}$ phosphor. The quadratic dependence of the luminescence on the pump-laser power indicating a cooperative energy transfer process. Meanwhile, it is noticed that upon excitation with 808 nm laser diode, intense luminescence has clearly been detected in $\text{GdAl}_3(\text{BO}_3)_4:\text{Nd},\text{Yb},\text{Tb}$ phosphor. The luminescence intensity exhibits also a quadratic dependence on incident pump-laser power. However, no green-emission has been observed in $\text{GdAl}_3(\text{BO}_3)_4$ phosphors codoped with $\text{Yb}^{3+}/\text{Tb}^{3+}$ or $\text{Nd}^{3+}/\text{Tb}^{3+}$ respectively upon excited at 808 nm laser diode. A proposed upconversion mechanism involving energy transfer from Nd^{3+} to Yb^{3+} , and then a cooperative energy transfer process from two excited Yb^{3+} to Tb^{3+} has been presented.

Keywords Luminescence · Phosphor · Cooperative energy transfer

Introduction

Over the past several years, extensive research has been focused on the rare-earth (RE) doped frequency upconversion materials for their potential applications in the fields of high-density data storage, cathode ray tubes, display devices and bio-probes [1–3]. Efficient blue, green and red upconversion emission and lasing have been demonstrated in various materials doped with RE such as Tm^{3+} , Er^{3+} , Ho^{3+} , Pr^{3+} , etc. [1, 4–6]. Recently, a new efficient approach has been proposed for generation of blue light via a cooperative upconversion from a pair of Yb^{3+} ions, and green light via a cooperative frequency upconversion from $\text{Yb}^{3+}/\text{Tb}^{3+}$ codoped fluoride or silica materials pumped by 980 nm laser diode (LD) [7–10]. However, despite fluoride materials possess low *phonon* energy, they exhibit relatively poor thermal stability and need to be prepared in an inert atmosphere. Oxyborate might be a scientific host community for upconversion phosphors, due to their advantages such as high transparency, exceptional optical damage threshold, and good thermal and chemical durability [11–13]. On the other hand, combustion method is considered to be a good way to synthesis inorganic oxides with improved properties for photonic applications. In the combustion method, dopant ions could be randomly distributed over the lattice sites resulting in much high upconversion efficiency [7, 14]. Moreover, combustion method ensures well atomic-level contact of the system, resulting in an instantaneous reaction. Therefore, in this method RE doped phosphors could be fabricated at a lower temperature in comparison with the traditional solid state synthesis process.

In the present paper, polycrystalline $\text{GdAl}_3(\text{BO}_3)_4$ phosphors codoped with $\text{Yb}^{3+}/\text{Tb}^{3+}$ and/or $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tb}^{3+}$ have been prepared by combustion method. The near-infrared to visible upconversion fluorescence properties in

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$\text{Yb}^{3+}/\text{Tb}^{3+}$ or $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tb}^{3+}$ codoped $\text{GdAl}_3(\text{BO}_3)_4$ phosphors have been investigated upon excitation with 980 nm and/or 800 nm LDs. The possible mechanism and related discussions for the upconversion phenomenon have been presented.

Experimental details

Powder samples of $\text{Gd}_{0.9-x}\text{Al}_3(\text{BO}_3)_4:\text{Yb}_{0.1},\text{Tb}_x$ ($0 \leq x \leq 0.3$) and $\text{Gd}_{0.69}\text{Al}_3(\text{BO}_3)_4:\text{Nd}_{0.01},\text{Yb}_{0.1},\text{Tb}_{0.2}$ have been synthesized by combustion method with urea as fuel. Gd_2O_3 (99.99%), Yb_2O_3 (99.99%), Tb_4O_7 (99.99%), Nd_2O_3 (99.99%), H_3BO_3 (AR), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR), nitric acid (AR), urea (AR) were used as raw materials. Details of the preparation procedures were reported previously [15]. In brief, $\text{Gd}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$ and $\text{Yb}(\text{NO}_3)_3$ solutions were made by dissolving their oxides in nitric acid, respectively. Stoichiometric amounts of these solutions with 5 mol% excess of H_3BO_3 were mixed according the chemical formulas stated above. Subsequently, urea was added into the solution with a molar ratio of *metal ions*:*urea*=1:3. After drying and burning, the products were sintered in hot active carbon atmosphere at 950°C for 10 h to complete the crystallization.

The crystal structures were analyzed by a Philips PW1830 X-ray powder diffractometer (XRD) with $\text{Cu } K\alpha$ radiation at 1.5406 Å. The luminescence measurements were performed on a computer-controlled Triax 320 fluorescence spectrofluorimeter (Jobin-Yvon Inc., Longjumeau, France) with 980 nm and 808 nm LDs (Coherent Co. USA) as the excitation sources. Emissions around 542 nm were detected using a *Scog HWB* 780 nm cutoff filter (Ygyes Co., China) in excitation with the 980 or 808 nm LDs. The ultraviolet-visible upconversion emission light was focused on to the monochromator and was monitored at the exit slit by a photon-counting R928 photomultiplier tube (Hamamatsu Co., Japan). The near infrared emission spectra in region of 840–1,200 nm were measured with a photon-counting R5108 photomultiplier

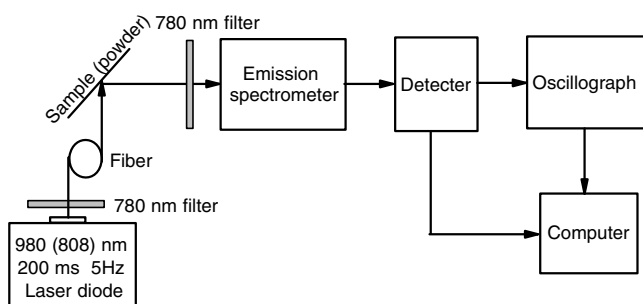


Fig. 1 Experiment setup for the measurements of the emission spectra and decay lifetimes

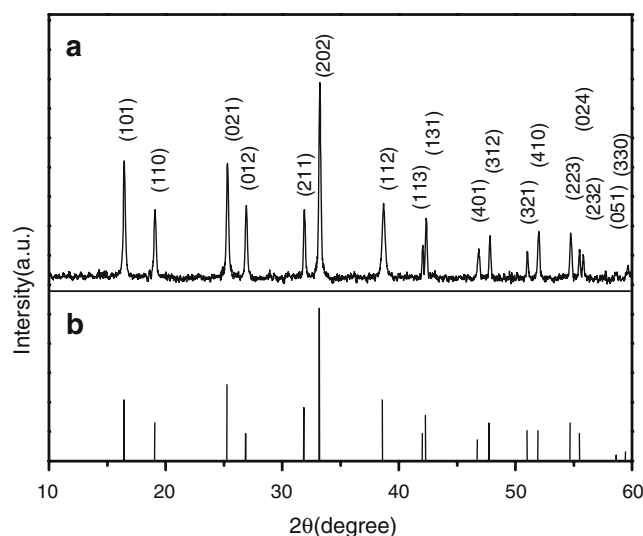


Fig. 2 X-ray diffraction pattern of the prepared rare-earth doped $\text{GdAl}_3(\text{BO}_3)_4$ phosphor (a), accompanied with reference $\text{GdAl}_3(\text{BO}_3)_4$ JCPDS card 38–1248 (b)

tube (Hamamatsu Co., Japan). Decay lifetimes were performed with a digital storage oscillograph (model TDS 3012B, Tektronix Co., Beaverton, OR), which was controlled by a personal computer as shown in Fig. 1.

Results and discussion

The powder appears to be a mixture of nanometer and sub-micrometer-sized white color particles as early reported in [15]. Figure 2 presents the XRD pattern of RE-doped polycrystalline $\text{GdAl}_3(\text{BO}_3)_4$ phosphors sintered at 950°C. All the diffraction peaks can be readily indexed to a pure hexagonal $\text{GdAl}_3(\text{BO}_3)_4$ with huntite structure (JCPDS card of 38–1248), indicating that codoping limited RE with

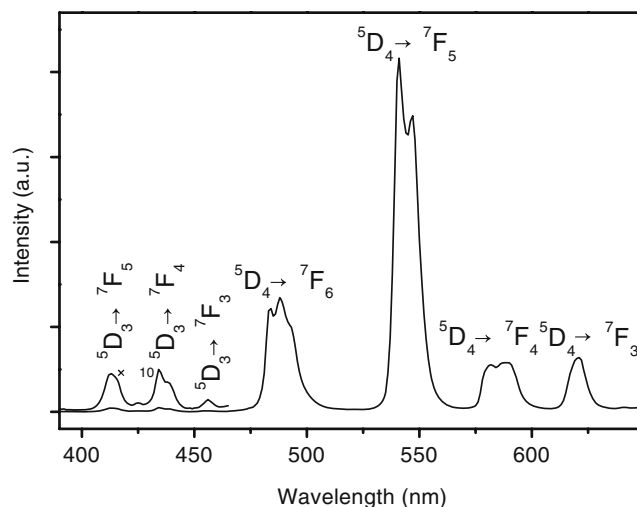


Fig. 3 Upconversion fluorescence spectrum of $\text{Gd}_{0.7}\text{Al}_3(\text{BO}_3)_4:\text{Yb}_{0.1},\text{Tb}_{0.2}$ phosphor under the excitation of 980 nm LD (295 mW)

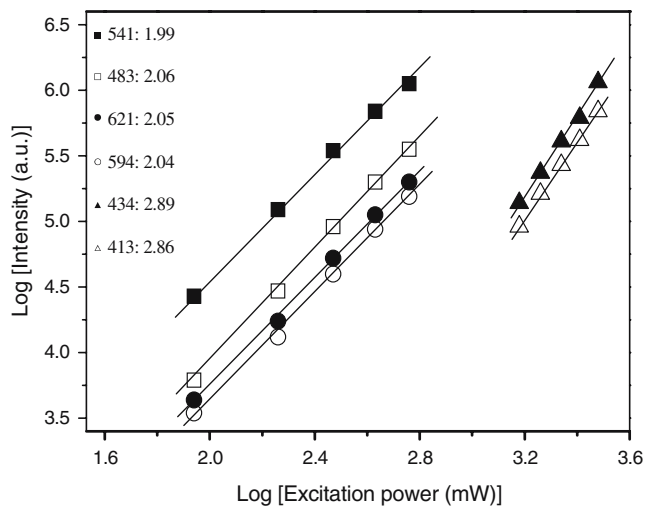


Fig. 4 Dependence of the upconversion fluorescence intensity of $\text{Gd}_{0.7}\text{Al}_3(\text{BO}_3)_4:\text{Yb}_{0.1},\text{Tb}_{0.2}$ on the pump-laser power

respect to Gd^{3+} ions does not cause any significant change in the host structure.

Figure 3 shows the recorded green upconversion of $\text{GdAl}_3(\text{BO}_3)_4:\text{Yb},\text{Tb}$ in the range of 390–650 nm under the excitation of 980 nm LD (58.7 W/cm^2). The main strong green emission at 541 nm is assigned to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ transition, and other three weaker emissions at 482, 588 and 622 nm are corresponded to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J=3, 5, 6$) transitions of Tb^{3+} ions, respectively. Meanwhile, this spectrum also includes several feeble bands in ultraviolet region at 412, 434 and 456 nm originating from the transitions ${}^5\text{D}_3 \rightarrow {}^7\text{F}_J$ ($J=3, 4, 5$) of Tb^{3+} , respectively. To identify the mechanisms of the upconversion emission, the dependence of the visible fluorescence intensity on the pump-laser power has been calculated as shown in Fig. 4.

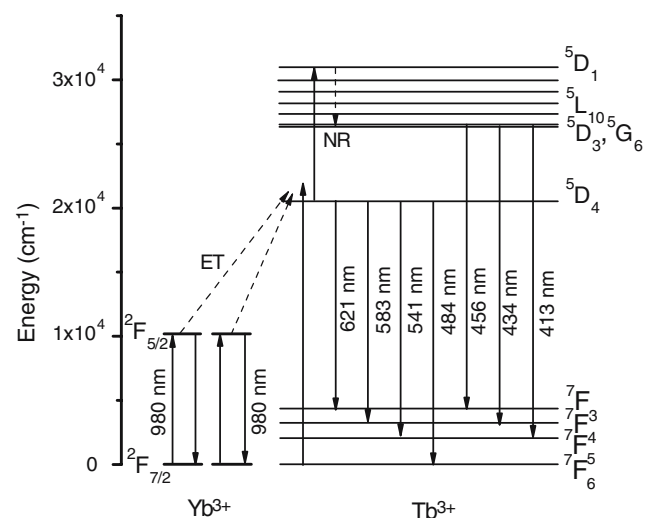


Fig. 5 Energy level diagram of the possible cooperative energy transfer mechanism in $\text{Yb}^{3+}/\text{Tb}^{3+}$ codoped $\text{GdAl}_3(\text{BO}_3)_4$ phosphors pumped by 980 nm LD

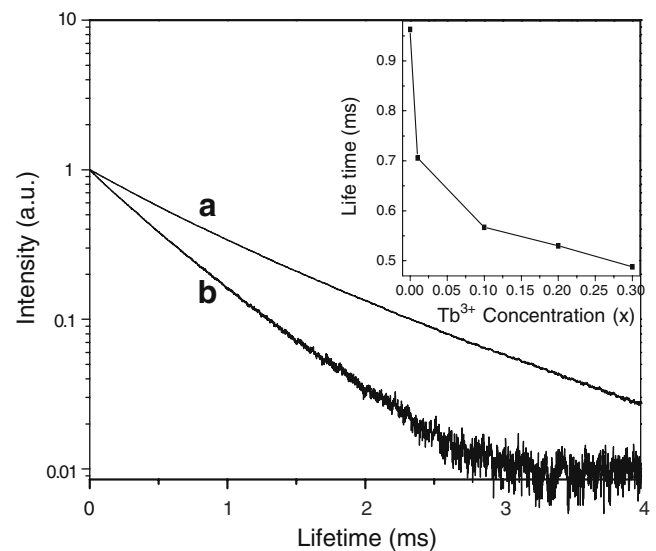


Fig. 6 Decay curves of $\text{Yb}^{3+} {}^2\text{F}_{5/2}$ upon excitation with a 980 nm LD in **a** $\text{Gd}_{0.99}\text{Al}_3(\text{BO}_3)_4:\text{Yb}_{0.01}$ and **b** $\text{Gd}_{0.7}\text{Al}_3(\text{BO}_3)_4:\text{Yb}_{0.1},\text{Tb}_{0.2}$. Inset shows the $\text{Yb}^{3+} {}^2\text{F}_{5/2}$ lifetimes versus Tb^{3+} concentration in the series of $\text{Gd}_{0.9-x}\text{Al}_3(\text{BO}_3)_4:\text{Yb}_{0.1},\text{Tb}_x$ ($0 \leq x \leq 0.3$)

The emission bands irradiated from $\text{Tb}^{3+} {}^5\text{D}_4$ plot on a double logarithmic scale. This power dependence reveals two photons are needed in the upconversion process [2]. Meanwhile, the shorter wavelength peaks at 412 and 434 nm originated from $\text{Tb}^{3+} {}^5\text{D}_3$ present cubelike dependence behaviour on the laser power, indicating that the emissions in the near ultraviolet region are three-photon processes. Figure 5 shows the energy level diagram with the principal radiative and nonradiative processes. Upon excitation with a 980 nm LD, cooperative energy transfer from two Yb^{3+} ions to one Tb^{3+} ion occurs, subsequently, visible green emissions from $\text{Tb}^{3+} {}^5\text{D}_4$ state resulted. Not

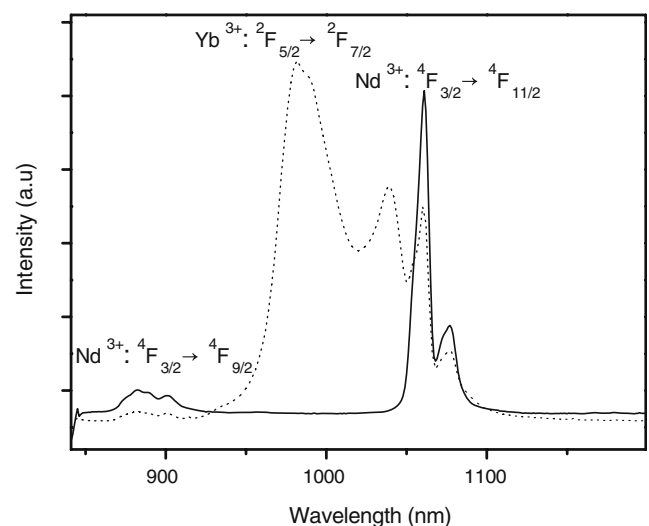


Fig. 7 Comparison of the luminescence spectra of single Nd^{3+} doped (solid line) and $\text{Nd}^{3+}/\text{Yb}^{3+}$ codoped (dot line) $\text{GdAl}_3(\text{BO}_3)_4$ samples under 808 nm LD excitation (295 mW)

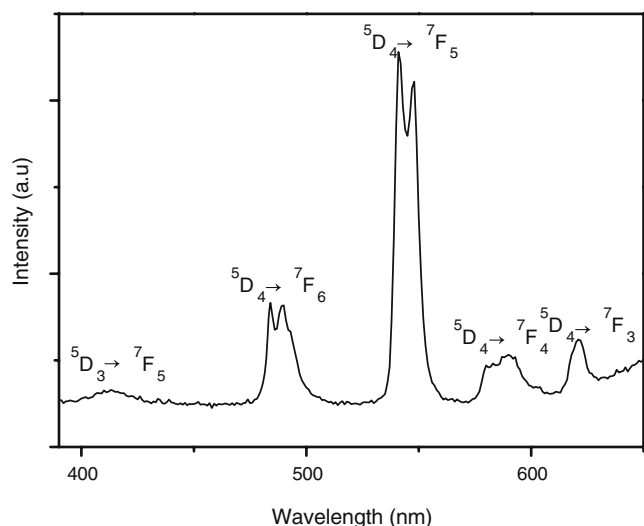


Fig. 8 Upconversion spectrum of $Gd_{0.69}Al_3(BO_3)_4:Nd_{0.01},Yb_{0.1},Tb_{0.2}$ phosphor under the excitation of 808 nm LD (295 mW)

all the excited state Tb^{3+} ions radiate to 7F_J state, but some of Tb^{3+} ions in the 5D_4 state are promoted to 5D_1 state by one Yb^{3+} in excitation state or by a phonon-assisted sequential multiphonon summation process. Then, they fast nonradiative relax down to 5D_3 , 5G_6 state, from where the shorter wavelength emissions yield.

The decay curve of the luminescence from the $Yb^{3+} {}^2F_{5/2}$ with series of concentration of Tb^{3+} (0, 1, 10, 20, 30 mol%) has been measured. The life time of $Yb^{3+} {}^2F_{5/2}$ level is about 0.96 ms in $Gd_{0.99}Al_3(BO_3)_4:Yb_{0.01}$, but it starts to decrease when Tb^{3+} ions are codoped into the samples as given in Fig. 6. On the other hand, in Yb^{3+} single doped sample the decay curve from $Yb^{3+} {}^2F_{5/2}$ level is exponential, however, in the Yb^{3+}/Tb^{3+} codoped samples the decay curves are nonexponential [7]. These phenomena are the

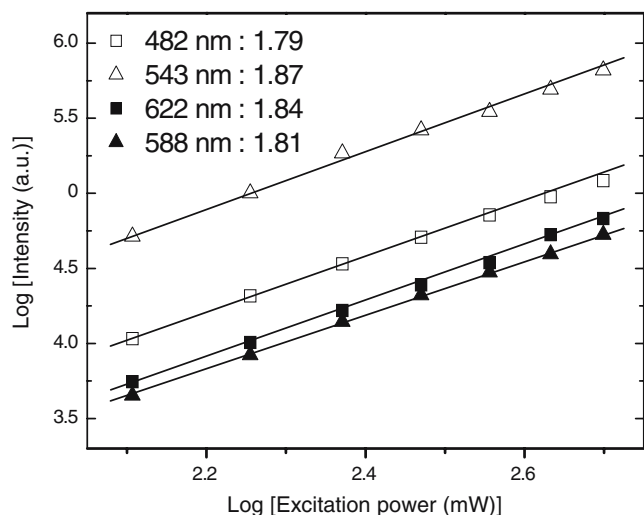


Fig. 9 The pump power dependence of the upconversion emission intensity in $Gd_{0.69}Al_3(BO_3)_4:Nd_{0.01},Yb_{0.1},Tb_{0.2}$ phosphor. $\lambda_{ex} = 808$ nm

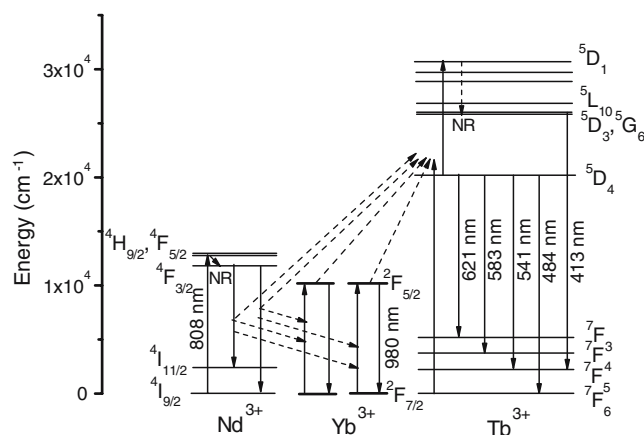


Fig. 10 Schematic diagram of the possible upconversion mechanisms in $Nd^{3+}/Yb^{3+}/Tb^{3+}$ codoped $GdAl_3(BO_3)_4$ phosphors excited by 808 nm LD

consequence of the energy transfer from Yb^{3+} to Tb^{3+} . The transfer efficiency could be calculated from the decay curves of Yb^{3+} and/or Tb^{3+} doped samples according to following equation [16]: $\eta_t = 1 - \frac{\tau_{Yb-Tb}}{\tau_{Yb}}$, where the energy transfer efficiency η_t is defined as the ratio of Yb^{3+} ions that depopulated by transferring their energy to Tb^{3+} ions over the total number of excited state Yb^{3+} ions, τ_{Yb-Tb} and τ_{Yb} are the life times monitored at 1,038 nm in presence and absence of the acceptor Tb^{3+} for the same concentration of Yb^{3+} , respectively. For the doped Tb^{3+} ions with high concentration are dispersedly distributed over the lattice sites, the different environment around the Yb^{3+} results in a varied energy transfer rate. The outstanding *feature* of our study is the high visible-light output with the excitation of NIR LD, for the non-radiative multiphoton relaxation is greatly reduced in the cooperative energy transfer process.

Neither Yb^{3+}/Tb^{3+} codoped $GdAl_3(BO_3)_4$ nor Nd^{3+}/Tb^{3+} codoped $GdAl_3(BO_3)_4$ phosphors shows upconversion emission with excitation of the commercial available 808 nm LD. However, it has been reported that Yb^{3+} could be excited by excited state Nd^{3+} in molybdate, vanadate crystals and fluoride glasses [17–19]. Thereby, the fluorescence properties of Nd^{3+} and Nd^{3+}/Yb^{3+} codoped $GdAl_3(BO_3)_4$ phosphors excited by 808 nm LD (58.1 W/cm²) have been investigated, and their emission spectra are presented in Fig. 7. Two emission bands at 883 and 1,060 nm have clearly been observed in the emission spectrum of the single Nd^{3+} doped sample, corresponding to the transitions ${}^4F_{3/2} \rightarrow {}^4I_J$ ($J=9/2, 7/2$) of Nd^{3+} , respectively. The emission line of Nd^{3+}/Yb^{3+} codoped sample contains both the emission bands of Nd^{3+} and the emission band of Yb^{3+} , but the emission of Nd^{3+} is greatly quenched in the codoped samples, which suggests that energy transfer from Nd^{3+} to Yb^{3+} is possible in this component. Therefore, an efficiency energy transfer from $Nd^{3+} \rightarrow Yb^{3+} \rightarrow Tb^{3+}$ is expected.

Figure 8 exhibits the upconversion spectrum of $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tb}^{3+}$ codoped $\text{GdAl}_3(\text{BO}_3)_4$ phosphor under the excitation of 808 nm LD (58.1 W/cm^2). Strong ultraviolet-visible emission bands at 413, 482, 541, 588 and 622 nm due to the transitions of Tb^{3+} ion have been observed, the corresponding spectrum with assignments of the bands are reproduced in the figure. To get more information about the upconversion mechanisms, we have measured the powder dependence of Tb^{3+} emissions in $\text{Gd}_{0.69}\text{Al}_3(\text{BO}_3)_4:\text{Nd}_{0.01},\text{Yb}_{0.1}\text{Tb}_{0.2}$ phosphor as shown in Fig. 9. The slopes 1.79, 1.87, 1.84 and 1.81 reveal two photons are included in populating the $\text{Tb}^{3+}:^5\text{D}_4$ state. The observed excitation power dependence and the measured upconversion emission wavelengths corroborate the frequency upconversion in $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tb}^{3+}$ codoped compound is under the processes of an energy transfer from Nd^{3+} to Yb^{3+} and a cooperative transfer process from two Yb^{3+} ions to one Tb^{3+} ion. It is noted that the upconversion luminescence intensity of $\text{Gd}_{0.69}\text{Al}_3(\text{BO}_3)_4:\text{Nd}_{0.01},\text{Yb}_{0.1},\text{Tb}_{0.2}$ phosphor under the excitation of 808 nm LD (292 mW) is one third of that of the $\text{Gd}_{0.7}\text{Al}_3(\text{BO}_3)_4:\text{Yb}_{0.1},\text{Tb}_{0.2}$ sample under the excitation of 980 nm LD (295 mW).

The schematic diagrams, showing the concept of energy transfer from Nd^{3+} to Yb^{3+} and cooperative transfer from Yb^{3+} to Tb^{3+} , are depicted in Fig. 10. The mechanism proposed to explain the energy transfer $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$, is a cross-relaxation process between the $\text{Nd}^{3+}:^4\text{F}_{3/2} \rightarrow ^4\text{I}_J$ ($J=11/2, 9/2$) levels and the $\text{Yb}^{3+}:^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ levels. Afterward, a pair of Yb^{3+} ions cooperatively transfers their energy to one Tb^{3+} ion, and the upconversion fluorescence is emitted. Due to the $^5\text{D}_3$ levels is $6,000 \text{ cm}^{-1}$ above the $^5\text{D}_4$ level, in $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tb}^{3+}$ codoped phosphors, the excitation of Tb^{3+} from $^5\text{D}_4$ level to $^5\text{D}_3$ level is presumed as cross-relaxation process. An energy transfer from Nd^{3+} or Yb^{3+} or a phonon-assisted process is assumed to be responsible for excitation process as shown in the schematic diagrams.

Conclusions

In summary, we report on the preparation and luminescence properties of polycrystalline $\text{GdAl}_3(\text{BO}_3)_4$ phosphors

codoped with $\text{Yb}^{3+}/\text{Tb}^{3+}$ and/or $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tb}^{3+}$ by combustion method with urea as fuel. An intense green upconversion has been observed in $\text{GdAl}_3(\text{BO}_3)_4:\text{Yb},\text{Tb}$ phosphors upon excitation with a 980 nm LD. The quadratic dependence of the green-upconversion on the pump-laser power indicating a cooperative energy transfer process. It is noted that upon excitation with 808 nm LD, intense green-upconversion has been detected in $\text{GdAl}_3(\text{BO}_3)_4:\text{Nd},\text{Yb},\text{Tb}$ phosphors. The green-upconversion intensity exhibits also a quadratic dependence on incident pump-laser power.

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