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Multicolor upconversion luminescence from RE^{3+}-Yb^{3+} (RE = Er, Tm, Tb) codoped $LaAlGe_2O_7$ glasses

Jie Ding[a,1], Qiang Zhang[b,c,*,1], Jimeng Cheng[b], Xiaofeng Liu[b,c], Geng Lin[b,c], Jianrong Qiu[d], Danping Chen[b,*]

[a] Sino-America Cancer Res Institute, Guangdong Medical College, Dongguan 523808, People's Republic of China
[b] Key Laboratory of Material Science and Technology for High Power Lasers, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China
[c] Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China
[d] State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

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ABSTRACT

RE^{3+}-Yb^{3+} (RE = Er, Tm, and Tb) codoped lanthanum aluminum germanate $LaAlGe_2O_7$ (LAG) glasses are prepared by melt-quenching method. The blank LAG glass has good transparency in UV/VIS/NIR/MIR range, which makes it suitable for RE ions doping. The doped glasses show strong upconversion (UC) emission under the excitation of a 980 nm laser diode assisted by two or three photons. The UC from Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+} codoped LAG glasses show high color purity. The mechanism is also discussed to explain the UC processes.

1. Introduction

In recent years, rare earth (RE) ions doped glass materials have attracted great attention due to their applications in solid-state lasers, display devices, optical fibers and amplifiers [1–3]. Especially the upconversion luminescence (UCL) of the RE ions in solid-state materials is of great importance for their potential use in visible lasers, 3D display and optical storage [4–11]. Glass material with low phonon energy, good thermal/chemical stability and high solubility of RE ions is preferred. Meanwhile, sensitizer is always used in the UCL materials to increase the absorption efficiency of excitation light. So modifications of the glass materials and choosing a suitable sensitizer have been attempted to enhance the UCL efficiency. Yb^{3+} ion is suitable for pumping with commercial InGaAs laser diodes and can transfer its energy to many other RE ions, so it has been used as sensitizer to realize efficient UCL in RE doped glass materials.

Optical properties of RE ion doped lanthanum aluminum germanate $LaAlGe_2O_7$ (LAG) phosphors have been researched by Li et al. [12–14]. The results show that LAG is a good host for RE doping. What is more, the doping concentration of RE ions in LAG could be very high. But it is difficult to grow bulk LAG crystal which restricts its applications. So we try to make LAG glass to balance this difficulty.

2. Experimental

LAG glasses with chemical composition of $(1-x-y)$ La_2O_3-Al_2O_3-$4GeO_2$-xRE_2O_3 (or Tb_4O_7)-yYb_2O_3 ($x = 0.01$, $y = 0.2$) in mol% have been prepared by melt-quenching method. We note LAGE, LAGTb and LAGTm as the Er, Tb and Tm doped LAG glasses, respectively. Reagent grade La_2O_3, Al_2O_3, GeO_2, Tm_2O_3, Er_2O_3 and Tb_4O_7 are used as raw materials. 16 g raw materials are fully mixed and melted at 1450 °C for 1 h in a corundum crucible in ambient atmosphere for each batch. The melts are poured on a stainless steel plate and then annealed to the room temperature. The glasses obtained are cut to 5 mm × 5 mm × 2 mm and polished for measurements.

Absorption spectra in the 190–2500 nm range are measured with a JASCO V-570 UV/VIS/NIR spectrophotometer. The measurement of infrared transmission spectrum of the blank LAG glass is carried out on a Thermo Nicolet (Nexus FT-IR

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[*] Corresponding authors at: Key Laboratory of Material Science and Technology for High Power Lasers, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China.
Fax: +86 21 59929373.
E-mail addresses: qiangzhang_china@126.com (Q. Zhang), d-chen@mail.siom.ac.cn (D. Chen).

[1] These two authors contribute equally to this paper.

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Table 1
Parameters of the blank LAG glass.

	Density ρ^* (g/cm^3)	Glass transition temperature T_g (°C)	Crystallization temperature T_x (°C)	Index of refraction n^*
LAG	4.94	752	970	1.750663@589.3nm

* These measurements are carried out at room temperature.

Spectrometer) spectrophotometer. The glass transition temperature (T_g) and onset crystallization temperature (T_x) of blank LAG glass are analyzed with differential thermal analyses (DTA) method at a heating rate of 10 °C/min. The density of the glass is measured by using Archimedes' method. The index of refraction is measured at 589.3 nm, with a precision V-prism refractometer (made in China) Na lamps as spectral source. An adjustable Apollo Instruments' laser diode with a central wavelength of 980 nm is used to excite the samples. The excitation, emission and upconversion luminescence (UCL) spectra are recorded with a FP-6500 spectrofluorometer. All the measurements are carried out at room temperature.

3. Result and discussion

The density, glass transition temperature (T_g), crystallization temperature (T_x) and index of refraction are listed in Table 1. The LAG glass has relatively high T_g and T_x which shows the good thermal stability of the host glass. The high density and index of refraction are also consistent with other heavy metal oxide glasses [15–18]. The absorption and Fourier transform infrared spectra of blank LAG glass are shown in Fig. 1(A) and (B), respectively. We can see that the sample has high transparency in UV/VIS/NIR/MIR range, which makes it suitable as matrix to dope RE ions with emission at UV/VIS/NIR/MIR. The inset of Fig. 1(A) shows the absorption spectra of LAGE, LAGTm and LAGTb in VIS/NIR range. The LAGE and LAGTm have obvious absorption because many of the transitions are electric dipole transition allowed [19]. But the transitions of LAGTb in visible range are electric dipole forbidden so the absorptions are very weak [19]. The absorption peaks are also labeled in the inset. The energy levels labeled in the inset correspond to the transitions from ground state to the excited state marked in the inset.

Fig. 2 shows the excitation (red line), emission (green line) and UCL (blue line) spectra of LAGE (A), LAGTm (B) and LAGTb (C). We

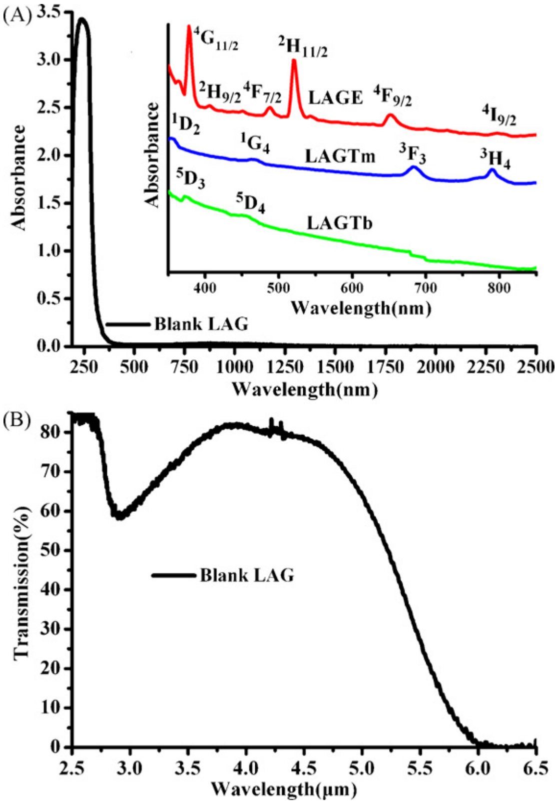

Fig. 1. Absorption and Fourier transform spectrum of LAG glass. The inset of (A) is the absorption spectra of LAGE, LAGTm and LAGTb in the 350–850 nm range.

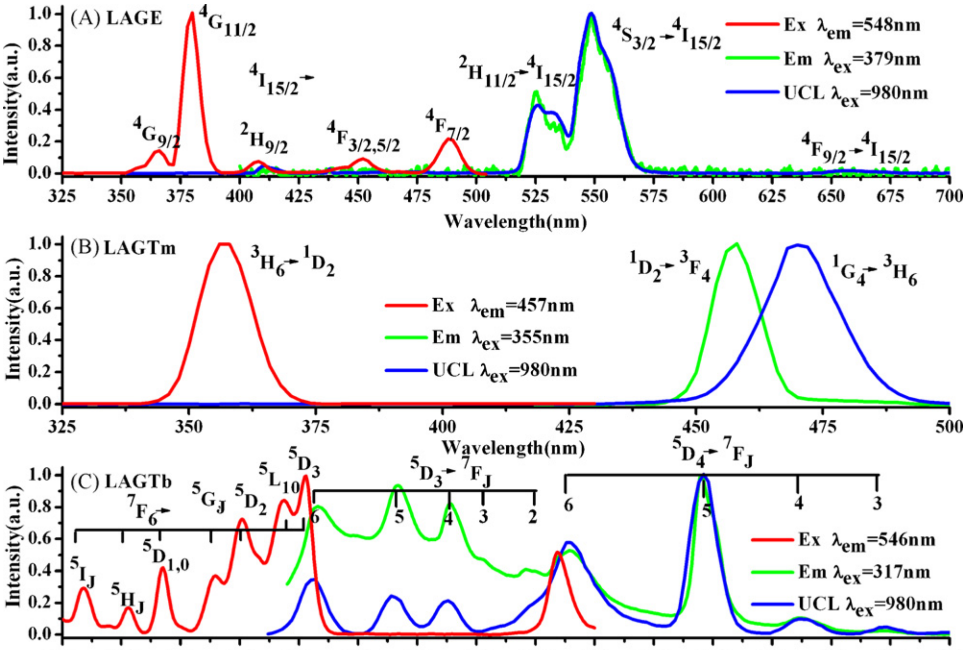

Fig. 2. Excitation, emission and UCL spectra of LAGE, LAGTm and LAGTb under the excitation of UV light and 980 nm LD.

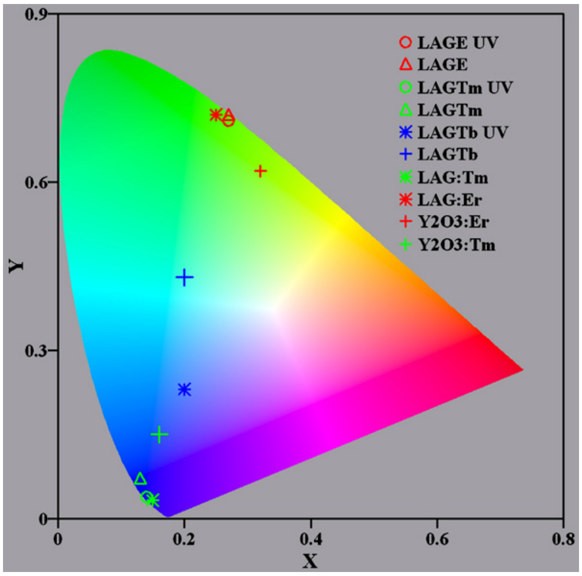

Fig. 3. CIE chromatically coordinates of doped LAG glasses, LAG and Y_2O_3 phosphors.

can see that the emission spectra of LAGE under the excitation of UV light or 980 nm laser diode are almost the same. The two strongest emission peaks at 525 nm and 547 nm are assigned to the transitions from $^2H_{11/2}$ and $^4S_{3/2}$ to $^4I_{15/2}$, respectively. There is also another much weaker band at 656 nm which comes from the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition [6,9,20–21]. In LAGTm case, the emission peak shifts from 457 nm to 470 nm when exciting LAGE with a 980 nm laser diode other than with a UV light. The 455 nm peak is ascribed to the $^1D_2 \rightarrow {}^3F_4$ transition of Tm^{3+}, while $^1G_4 \rightarrow {}^3H_6$ transition induces the 470 nm emission peak in the UCL process [8,22–23]. The difference is mainly caused by the inefficient excitation of $^1D_2$ energy level of Tm^{3+} by 980 nm laser diode. For LAGTb, the seven bands can be distinguished as the $^5D_3 \rightarrow {}^7F_J$ ($J = 2, 3, 4, 5, 6$) and $^5D_4 \rightarrow {}^7F_J$ ($J = 3, 4, 5, 6$) transitions of Tb^{3+} as shown in Fig. 2(C) [24–27]. The relative intensities of the $^5D_3 \rightarrow {}^7F_J$ transitions by infrared laser diode excitation are much weaker than by UV light; this is also caused by the inefficient excitation of $^5D_3$ state.

We can see that LAGE, LAGTm and LAGTb yield different fluorescent emission under the 980 nm excitation: blue for LAGTm; green for LAGE and LAGTb. The CIE chromaticity coordinates of LAGE, LAGTm and LAGTb under the 980 nm excitation are (0.27, 0.72), (0.125, 0.072) and (0.204, 0.434), respectively. Meanwhile, the corresponding CIE chromaticity coordinates of the samples under the UV excitation are (0.27, 0.71), (0.13, 0.05) and (0.20, 0.23); these values have also been plotted in Fig. 3. As shown in Fig. 3, both the LAGE and LAGTm under the UV and 980 nm laser diode excitation show high color purity. Compared to CIE standard source *C* [illuminant $C = (0.3101, 0.3162)$], the color purities of LAGE are 94% and 94.5% under the UV and 980 nm laser diode excitation, respectively. For LAGTm, the color purities are 94% and 92%. The CIE coordinates of LAG:Er, LAG:Tm [14], Y_2O_3:Er and Y_2O_3:Tm[28] phosphors are also added for comparison purpose. The color purities of LAGE and LAGTm are comparable with those of doped LAG phosphors while better than Y_2O_3: Er and Y_2O_3: Tm's. The high color purities from UCL of LAGE and LAGTm show potential application as green and blue components in solid-state 3D display and visible lasers. However, the color purity of LAGTb is not so good for its neighboring multi-peaks in the green range.

For any process of UC luminescence, the visible output intensity I_{UC} is approximately proportional to the *n*th power of infrared excitation intensity P_{IR} [9,25]:

$I_{UC} \propto (P_{IR})^n$, where *n* represents the number of photons required to populate the emitting states. The ln–ln plots of UC intensity I_{UC} versus infrared excitation intensity P_{IR} of LAGE, LAGTm and LAGTb are shown in Fig. 4. The laser power is varied from 400 mW to 1.5 W with a focal diameter of about 1 mm. According to the value of the *n* obtained from the power law, the UC process of $^1G_4 \rightarrow {}^3H_6$ transition of LAGTm and $^5D_3(^5G_6) \rightarrow {}^7F_J$ ($J = 4, 5$) transitions of LAGTb are three photons processes and other transitions of LAGE, LAGTm and LAGTb labeled in Fig. 2 are two photons processes.

The UC excitation mechanisms involved in the population of the relevant excited-state emitting levels of the LAGE, LAGTm and LAGTb are indicated in the simplified energy level diagram as depicted in Fig. 5. For LAGE, the green fluorescence signals originate from a nearly resonant two photons process which involves ground state absorption ($^4I_{15/2} \rightarrow {}^4I_{11/2}$) and an excited-state absorption ($^4I_{11/2} \rightarrow {}^4I_{7/2}$) [9]. The excited state $^4I_{7/2}$ is depopulated by multi-phonon relaxation to $^2H_{11/2}$ and $^4S_{3/2}$ from which radiative decays

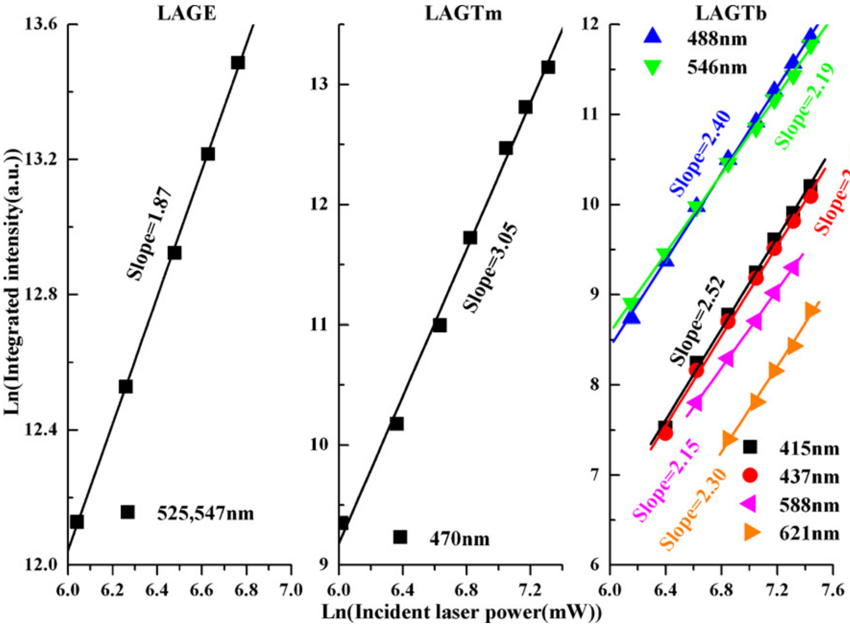

Fig. 4. Ln–ln plots of UCL intensity of LAGE, LAGTm and LAGTb versus incident laser power.

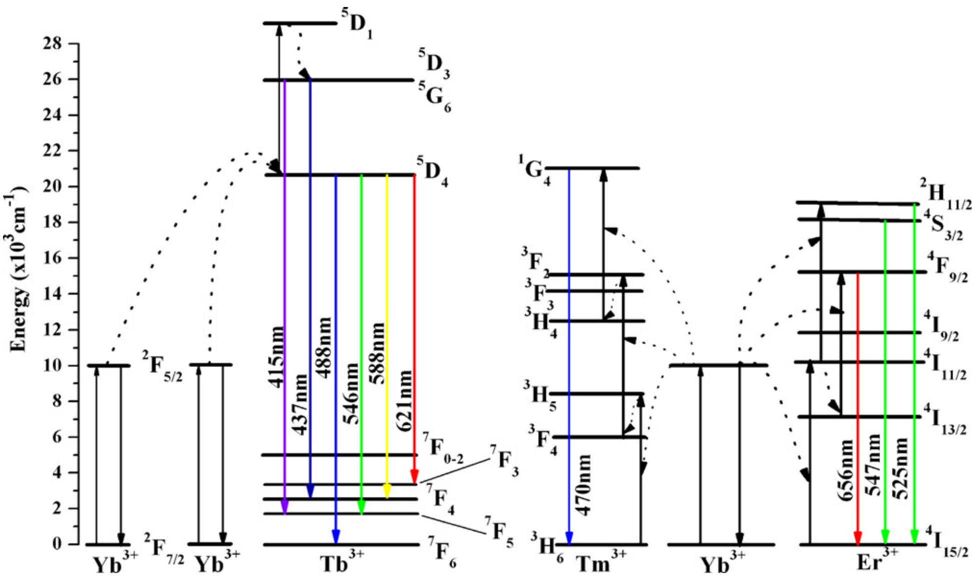

Fig. 5. UCL mechanics of LAGE, LAGTm and LAGTb under excitation of 980 nm LD.

to the ground state generate the 525 nm and 547 nm. The red UC at 656 nm originates from the transition from $^4F_{9/2}$ to $^4I_{15/2}$ with the intermediate $^4I_{13/2}$ energy level which is strongly populated from the well populated $^4I_{11/2}$ level [9]. For LAGTm the excited Yb^{3+} ions transfer its energy to $^3H_5$ level of Tm^{3+} ions. Then the population at $^3H_5$ decays rapidly to the $^3F_4$ level of Tm^{3+}. Another excited Yb^{3+} ions then populate Tm^{3+} ions from $^3F_4$ to $^3F_{2,3}$. After $^3F_{2,3}$ is depopulated to $^3H_4$ and sequentially populated to $^1G_{4,}$ blue emission at 470 nm is observed which corresponds to the $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions [8,23]. For Tb^{3+} and Yb^{3+} in LAG glass, the $^5D_4$ of Tb^{3+} ions is excited by cooperative energy transfer from two excited Yb^{3+} ions at $^2F_{5/2}$, which induces the emission from $^5D_4$ to ^7F_J. For the 415 nm and 437 nm, the excited Tb^{3+} ions at $^5D_4$ absorb the energy from another excited Yb^{3+} ion and are promoted to the $^5D_1$ energy. Tb^{3+} ions in $^5D_1$ level relax to $^5D_3$ ($^5G_6$) and radiative decays to ^7F_J ($J = 5, 4$) [26,29].

4. Conclusion

$LaAlGe_2O_7$ (LAG) glass is obtained by simply melt-quenching method. Blank LAG glass shows good transparency in UV/VIS/IR range which makes it suitable for doping active ions with emission at UV/VIS/IR range. The LAG glass also has low phonon energy which enhances the UC emission of RE^{3+}-Yb^{3+} (RE = Er, Tm and Tb) ions. Compared with the RE^{3+} doped LAG phosphors, the RE^{3+}-Yb^{3+} codoped LAG glasses also show comparable color purities. The high transparency and efficient UC in doped LAG glasses also show great potential applications in visible lasers and 3D displays [30].

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