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Laser-diode-excited Blue Upconversion in Tm^{3+}/Yb^{3+}-codoped TeO_2-Ga_2O_3-R_2O (R=Li, Na, K) Glasses

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Abstract This paper reports on intense blue upconversion in Tm^{3+}/Yb^{3+} codoped TeO_2-Ga_2O_3-R_2O(R=Li, Na, K) glasses upon excitation with commercial available laser diode (LD). Effects of alkali ions on the Raman spectra, thermal stability and spectroscopic properties of the tellurite-gallium glasses have also been investigated. Energy transfer and the involved upconversion mechanisms have been discussed. Intense blue upconversion emission centered at 476 nm along with a weak red emission at 650 nm has been observed upon excitation of 977 nm LD, assigned to the transitions of $^1G_4 \rightarrow {}^3H_6$, and $^1G_4 \rightarrow {}^3H_4$ and/or $^3F_{2,3} \rightarrow {}^3H_6$ of Tm^{3+}, respectively. The blue upconversion intensity has a cubelike dependence on incident pump laser power, indicating a three-photon process. However, a quadratic dependence of the 476 nm upconversion intensity on the incident pump laser power has been observed when samples under excitation of 808 nm LD due to a two-photon absorption process. Enhanced upconversion luminescence have been observed with replacing K^+ for Na^+ and Li^+.

Keywords Tm^{3+}/Yb^{3+} · Upconversion · Tellurite gallium glasses

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Introduction

The development of laser diode (LD) pumped up-conversion (UC) lasers is a promising idea for solid-state visible wavelength lasers in recent years. Particularly, the solid-state compact blue-emitting lasers are desirable for their splendid application prospects in high-density data storage, high-resolution printing, communications and medical laser [1, 2]. Frequency UC rare-earth(RE)-doped fiber or glass chip lasers have demonstrated important advantages over others due to their simple system, the possibility of pumping by commercially available semiconductor diode-lasers and emitting high quality light [3–6].

Optical properties of trivalent RE ions such as Ho^{3+}, Pr^{3+} and Tm^{3+} in glasses have been extensively studied for developing UC blue lasers operated at room temperature [1–6]. Tm^{3+} ion has stable excited levels for emitting blue UC fluorescence. The host material for Tm^{3+} ion is an important factor in obtaining high efficient UC, because host glass with low phonon energy can reduce the multiphonon relaxation (MPR) and produce strong UC luminescence.

A recent demonstration of blue-UC lasing in Tm^{3+}/Yb^{3+} codoped glass laser has shown 375 mW output power [3]. However, low thermal stability and difficulty of fabrication have so far hindered fluoride glasses for commercial applications. Tellurite glasses have attractive properties, such as low phonon energy (700 ~ 800 cm^{-1}), large amount of RE dopants, ease of fabrication [7, 8]. Furthermore, the combinations of tellurite and gallium systems have further extended the families of optical glasses which might provide much lower phonon energy (Gallium glasses, phonon energy ~600 cm^{-1})0, higher thermal stability.

In this paper, we report on the thermal stability and spectroscopic properties of Tm^{3+}/Yb^{3+} codoped TeO_2-

Table 1 Properties of glasses samples and the thermal properties of the host glasses

Sample glasses	$N_{Tm}^{3+}\times10^{20}$ (ions·cm^{-3})	ρ (g.cm^{-3})	n_d	T_g (°C)	T_x (°C)	ΔT (°C)
TGL	2.41	5.01	2.050	317.6	–	–
TGN	2.39	5.16	2.052	326.7	488.6	161.9
TGK	2.38	5.31	2.061	328.4	456.8	128.4

Ga_2O_3-R_2O(R=Li, Na, K) glasses for blue UC laser under the excitation of 977 and 808 nm laser diode (LD).

Experiment

Samples preparation

The glass samples were prepared from TeO_2 (99.99%), Ga_2O_3 (99.9%), Li_2CO_3 (99.9%), Na_2CO_3 (99.9%), K_2CO_3 (99.9%), Tm_2O_3 (99.99%) and Yb_2O_3 (99.99%) according to the compositions in mol%: $80TeO_2$-$10Ga_2O_3$-$10R_2O$ (R=Li, Na, K)-$0.3Tm_2O_3$-$0.3Yb_2O_3$ and the samples are named as TGL, TGN and TGK in turn. About 15 g batches of starting materials were fully mixed and then melted at 850°C in covered platinum crucibles in a furnace. When the melting was completed, the glass liquids were cast into stainless steel plates. After annealing, all glasses were cut and polished carefully in order to meet the requirements for optical measurements. The concentration of Tm^{3+}, densities and the refractive indexes of all glasses are list in Table 1.

Properties measurements

Glass transition (T_g) and crystallization on set temperature (T_x) were measured on the powered samples using a Netzsch STA 449C Jupiter differential scanning calorimeter (DSC) at a heating rate 10 K/min. Raman scattering spectra were obtained by using a microscope spectrophotometer (model RM 2000, Renishaw) with a 514.5 nm laser as an excitation source with 20 mW in power. The absorption spectra were recorded by a Perkin-Elmer Lambda-900 UV/VIS/NIR spectrophotometer ranging 350–2,100 nm with the resolution of 1 nm. Upconversion luminescence spectra were measured on a TRIAX320 spectrometer (Jobin-Yvon Co.) with 977 and 808 nm LD as excitation sources. All the measurements were performed at room temperature.

Results and discussion

Figure 1 shows the T_g, T_x, and $\Delta T=T_x-T_g$ of all samples and the values are also summarized in Table 1. It is found that T_g increases slightly with increasing the radius of alkali ion in the tellurite gallium glasses. The difference between the T_g and T_x has frequently been quoted as a rough indicator of glass stability against devitrification. To avoid any crystallization during fiber drawing, it is desirable for a glass to have as large a ΔT as possible [9]. It is worth noting that no obvious crystallization peak is detected in TGL, while TGN and TGK exhibit superior ΔT=161°C and 128°C, respectively, which suggests their suitability as potential candidates for fiber drawing.

The Raman scattering spectra of TGL, TGN and TGK glasses are shown in Fig. 2. The broad bands centered at

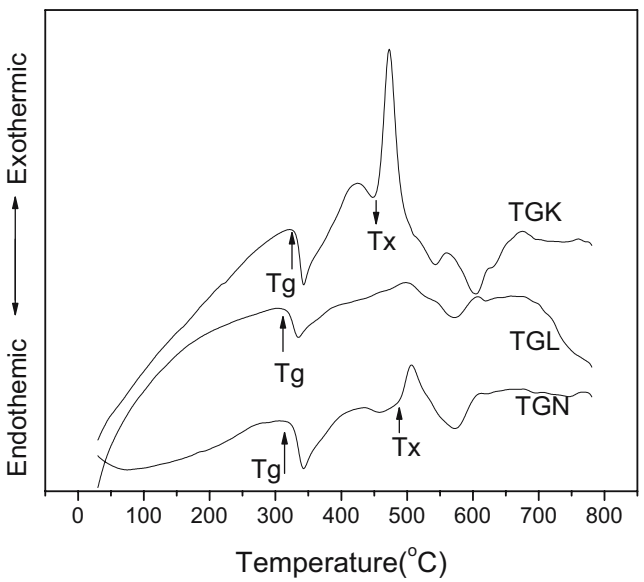

Fig. 1 DSC curves of TGL, TGN and TGK

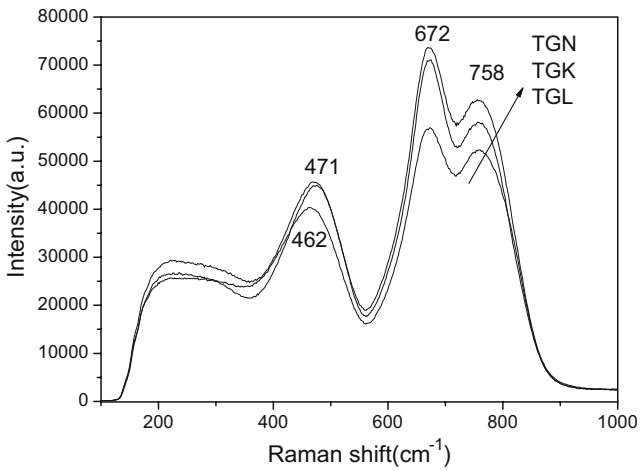

Fig. 2 Raman spectra of TGL, TGN and TGK

462 cm^{-1} originated from the stretching vibrations of Ga-O-Ga, Ga-O-Te and Te-O-Te. The bands at around 672 cm^{-1} due to the stretching vibrations of TeO_4 and GaO_4 [10]. The stretching vibrations of TeO_{3+1} and TeO_3 are assigned to the bands at around 758 cm^{-1}. The maximum phonon energy of the samples are located at around 758 cm^{-1} [11–13].

Tm^{3+}/Yb^{3+} codoped tellurite gallium glasses exhibit yellowish green color in transmitted light. Figure 3 presents the room temperature optical absorption spectra for Tm^{3+}/Yb^{3+} codoped tellurite gallium glasses in the 340–2,100 nm spectral range. The assignments of the absorption bands indicate the excited levels of Tm^{3+} and Yb^{3+}. The relative intensities of the various peaks remain almost unchanged when the radius of alkali ion changes.

According to the absorption spectra, the spontaneous emission probability (A), fluorescence branching ratio (β), and the radiative lifetime (τ_{rad}) of Tm^{3+} ions in various hosts are calculated by the Judd-Ofelt theory [14–16] and are summarized in Table 2. It is noted that A of the $^1G_4 \rightarrow {}^3H_6$ transition decrease from 2,134 to 1,016 s^{-1}, and τ_{rad} of the $^1G_4$ level increase from 219 to 466 μs with the increase of the radius of alkali ion. The long radiative lifetime of Tm^{3+}: $^1G_4$ of TeO_2-Ga_2O_3-K_2O might be benefit for the population of Tm^{3+}: $^1G_4$. β of the $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} are 46.7, 49.7 and 47.4% for TGL, TGN and TGK, respectively, which indicates that the blue emission could be easily realized.

Figure 4a shows the UC emissions of Tm^{3+}/Yb^{3+} codoped TeO_2-Ga_2O_3-R_2O(R=Li, Na, K) glasses in the visible wavelength range 450–750 nm excited at 977 nm. Two emissions centered at 476 and 650 nm are clear observed, which belong to the transitions of $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$ and $^3F_{2,3} \rightarrow {}^3H_6$, respectively. The blue emission at 476 nm is the strongest one observed in the UC spectrum. The blue and red emission intensities increase as K^+ ion replacing Na^+ and Li^+. The blue

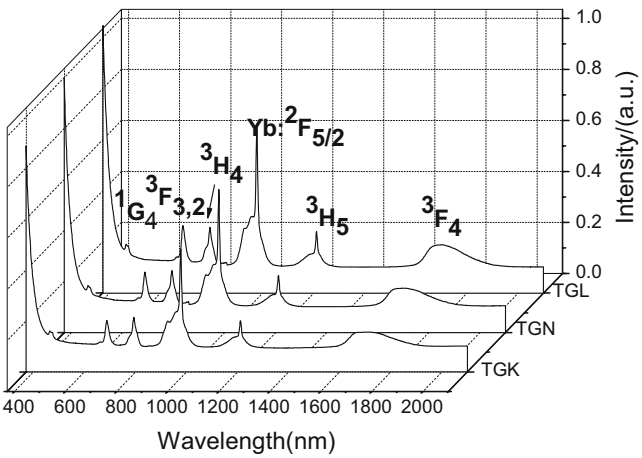

Fig. 3 Absorption spectra of TGL, TGN and TGK doped with 0.3 mol%Tm_2O_3 and 0.3 mol%Yb_2O_3 in the visible and near infrared wavelength region at room temperature

Table 2 Predicted spontaneous emission probability A, the fluorescence branching ratio β, and the radiative lifetime τ_{rad} of Tm^{3+} ions in TGL, TGN and TGK

Sample	Initial state	Final state	ν (cm^{-1})	A (S^{-1})	β	τ_{rad} (us)
TGL	$^1G_4$	$^3H_6$	21,422	2,134.0	0.467	219
		$^3F_4$	15,541	348.6	0.076	
		$^3H_5$	13,175	1,461.2	0.320	
		$^3H_4$	8,815	469.2	0.103	
		$^3F_3$	6,870	124.0	0.027	
		$^3F_2$	6,315	35.4	0.008	
TGN	$^1G_4$	$^3H_6$	21,422	1,148.5	0.497	433
		$^3F_4$	15,541	147.4	0.064	
		$^3H_5$	13,175	691.7	0.299	
		$^3H_4$	8,815	257.5	0.111	
		$^3F_3$	6,870	50.9	0.022	
		$^3F_2$	6,315	14.4	0.006	
TGK	$^1G_4$	$^3H_6$	21,422	1,016.1	0.474	466
		$^3F_4$	15,541	135.4	0.063	
		$^3H_5$	13,175	682.0	0.318	
		$^3H_4$	8,815	253	0.118	
		$^3F_3$	6,870	47	0.022	
		$^3F_2$	6,315	12	0.005	

emission intensity of TGK is 3.6 times higher than that of TGL. Plotting the UC emission intensity versus pump power in log–log representation yields a straight line with a slope n, which is shown in the inset of Fig. 4a. The values of n obtained are 3.22 and 2.84 for the 476 and 650 nm emissions, respectively, suggesting that three-photon absorption processes contribute to the 476 nm emissions while two and three photons mixed absorption processes attribute to the 650 nm emissions.

The blue UC emissions of these glasses excited at 808 nm are illustrated in Fig. 4b. Weak 476 nm blue fluorescence assigned to the $^1G_4 \rightarrow {}^3H_6$ are depicted. Enhanced blue-upconversion luminescence have clearly been observed with replacing K^+ for Na^+ and Li^+ in the glass studied. The slope for the UC emission intensity versus pump power in log–log representation shown in the inset of Fig. 4b is 2.39, which confirms that two-photon absorption processes significantly contribute to the 476 nm emissions.

The relevant possible blue–red UC excitation schemes [17] are shown in Fig. 5. For the emissions under excitation of 977 nm LD, The UC excitation mechanism can be explained in four steps as follows. In the first step, a 977 nm photon is absorbed by a Yb^{3+} which provokes the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. The second step involves the excitation of a Tm^{3+} in the $^3H_5$, by means of the energy transfer mechanism of excited Yb^{3+} to Tm^{3+}. Tm^{3+} in the $^3H_5$ excited state relaxes nonradiatively to the metastate level $^3F_4$. As the third step, either the same Yb^{3+} which absorbs a second 977 nm photon or another nearby Yb^{3+}

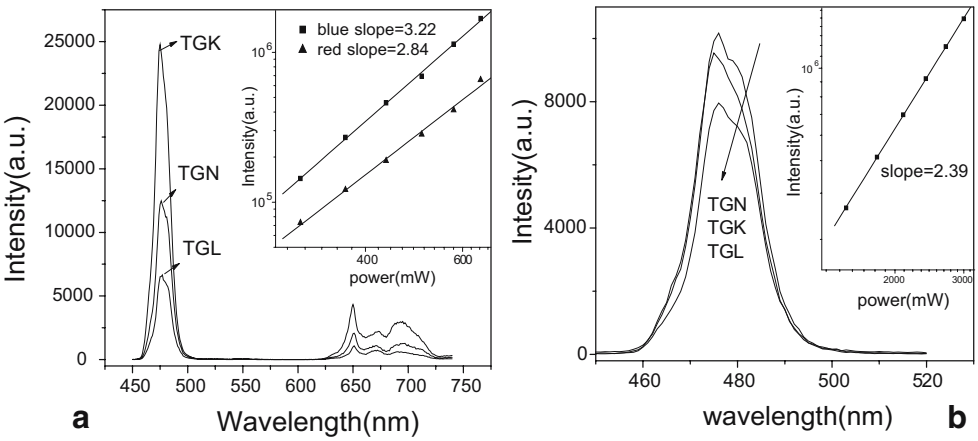

Fig. 4 Upconversion spectra of TGL, TGN and TGK excited by **a** 977 nm LD **b** 808 nm LD. *Inset* shows the dependence of upconversion emission intensity on 977 nm (**a**) and 808 nm (**b**) excitation power in sample TGK

being still in the $^2F_{5/2}$ state, transfers its energy to the same Tm^{3+}. The Tm^{3+} reaches the $^3F_{2,3}$ level and the $^3F_{2,3}$ state also relaxes by a multiphonon assisted process to the $^3H_4$ level. Finally, the population of $^1G_4$ is based on the processes: $^2F_{5/2}(Yb^{3+})$ + $^3H_4(Tm^{3+})\rightarrow{}^2F_{7/2}(Yb^{3+})$ + $^1G_4(Tm^{3+})$. In addition, there still exist excited state absorption (ESA) of Tm^{3+} in UC processes: (1) $^3H_6$ + hν(977 nm)$\rightarrow{}^3H_5$, (2) $^3F_4$ + hν(977 nm)$\rightarrow{}^3F_{2,3}$, (3) $^3H_4$+ hν(977 nm) $\rightarrow{}^1G_4$. During the UC processes, there might be cross-relaxation (CR) processes between Tm^{3+} ions: (1) $^3H_4$ + $^3H_6\rightarrow{}^3F_4$ + $^3F_4$; (2) $^1G_4$+ $^3H_6\rightarrow{}^3H_5$+ $^3H_4$; (3) $^1G_4$ + $^3F_4\rightarrow{}^3H_4$+$^3F_{2,3}$; (4) $^1G_4$+ $^3H_5\rightarrow{}^3F_{2,3}$ + $^3F_{2,3}$ and energy back transfer: $^3H_4$ (Tm^{3+})+$^2F_{7/2}$ (Yb^{3+}) $\rightarrow{}^3H_6$ (Tm^{3+})+$^2F_{5/2}$ (Yb^{3+}), etc. Among the processes, ET is the major [16]. From the $^1G_4$ level, the Tm^{3+} ions decay radiatively to the $^3H_6$ ground state, generating intense blue emission around 476 nm or decay to the $^3F_4$ level generating weak red (650 nm) emission. Tm^{3+} ions at $^3F_{2,3}$ level decay to the $^3H_6$ ground state also generating red (650 nm) emission. Therefore, the 650 nm emission peaks are attribute to the transitions $^1G_4\rightarrow{}^3H_4$ and $^3F_{2,3}\rightarrow{}^3H_6$ of Tm^{3+}.

For the excitation processes of the $^1G_4\rightarrow{}^3H_6$ (blue emissions) transitions excited at 808 nm can be explained as following two kinds of processes. The first one is that Tm^{3+} at ground state is excited to $^3H_4$ level by GSA: $^3H_6$ + hν(808 nm) $\rightarrow{}^3H_4$, then Tm^{3+} at $^3H_4$ level is excited to $^1G_4$ level by ESA: $^3H_4$ + hν(808 nm) $\rightarrow{}^1G_4$. Tm^{3+} ions at $^1G_4$ level decay radiatively to the ground state generating 476 nm blue emissions. The second process can be explained as follows: a Tm^{3+} ion at the ground state is excited to $^3H_4$ level by means of GSA. Then, Tm^{3+} ion at the $^3H_4$ level transfers its energy to Yb^{3+} ion at the ground states: Yb^{3+}:$^2F_{7/2}$+ Tm^{3+}:$^3H_4\rightarrow Yb^{3+}$:$^2F_{5/2}$+ Tm^{3+}:$^3H_6$. Therefore, Yb^{3+} ion is excited to the $^2F_{5/2}$ level indirectly. Yb^{3+} in the $^2F_{5/2}$ state transfers its energy to the Tm^{3+} at the $^3H_4$ level. Finally, Tm^{3+} is excited to the $^1G_4$ level by ET from Yb^{3+}: $^2F_{5/2}$ with multiphonon assisted: Yb^{3+}:$^2F_{5/2}$+Tm^{3+}:$^3H_4\rightarrow Yb^{3+}$:$^2F_{7/2}$+ Tm^{3+}:$^1G_4$. Tm^{3+} ions at the $^1G_4$ level decay radiatively to the ground state generating 476 nm blue emissions. It can be concluded that a two-phonon upconversion process is responsible for blue (476 nm) emission under 808 nm excitation.

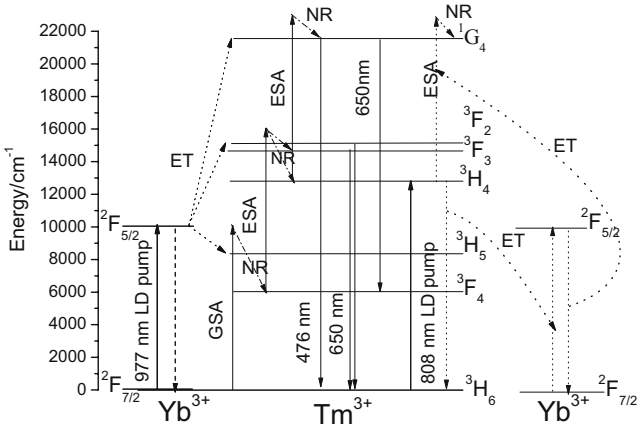

Fig. 5 Schematic energy level diagram of tellurite-gallium glasses, the possible upconversion mechanisms with 977 nm and 808 nm excitation at the room temperature

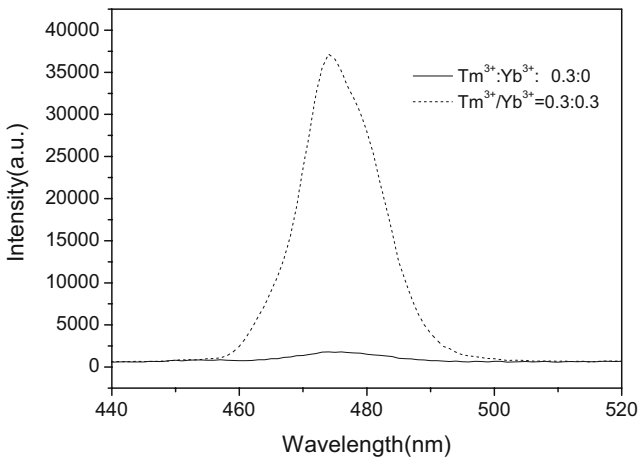

Fig. 6 Upconversion of Tm^{3+}-doped and Tm^{3+}/Yb^{3+}-codped tellurite glasses pumped by 808 nm LD

Figure 6 shows upconversion spectra of a Tm^{3+} single doped and a Tm^{3+}/Yb^{3+} codoped tellurite gallium glasses excited at 808 nm. It is note that the upconversion intensity of Tm^{3+}/Yb^{3+} codoped tellurite gallium glass is 36 times higher than that of Tm^{3+} single doped glass, might be caused by the lager ET process between Tm^{3+} and Yb^{3+} with incorporation of Yb^{3+} in the glass [18].

Base on their thermal stability, optical properties and upconversion emission performance discussed, we conclude that Tm^{3+}/Yb^{3+}-codoped TeO_2-Ga_2O_3-(Li_2O-Na_2O-K_2O) glasses could be suggested as promising materials in the upconversion laser technology and for achieving high optical performance.

Conclusions

In summary, the thermal stability and spectroscopic properties of Tm^{3+}/Yb^{3+}-codoped TeO_2-Ga_2O_3-R_2O(R=Li, Na, K) glasses have been investigated under excitation of 977 and 808 nm LD. The tellurite-gallium glasses exhibit excellent thermal properties against devitrification with ΔT greater than 120°C. Intense upconversion emissions centered at around 476 and 650 nm have been clearly observed upon excitation with 808 nm and 977 nm LD and the involved mechanisms have been also investigated. Enhanced upconversion luminescence have been observed with replacing K^+ for Na^+ and Li^+ in the glass studied.

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