

Strong upconversion luminescence in $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped halide modified tellurite glass

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Upconversion luminescence of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped halide tellurite glass is investigated experimentally upon 976-nm excitation. Three intense emissions centered at 525, 545 and 655 nm owing to the transitions ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$, ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively, are observed when pumping power is as low as 20 mW. The upconversion mechanisms and power dependent intensities are discussed. The high-populated ${}^4I_{11/2}$ level is supposed to serve as the intermediate state responsible for the upconversion processes.

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Er^{3+} has been recognized as one of the most efficient rare earth (RE) ions for obtaining optical amplification^[1], as well as for realizing upconversion luminescence^[2,3]. Upconversion luminescence is considered as a promising solution to obtain efficient solid-state visible lasers pumped with commercially available infrared (IR) laser diodes (LDs)^[4]. Host material with low phonon energy is of great importance to obtain strong upconversion emission of Er^{3+} . The low phonon energy reduces the nonradiative energy losses owing to the multiphonon relaxation, which is critical in determining the upconversion efficiency^[5-8]. It would be preferable to find a novel glass host with low phonon energy without sacrificing the thermal stability at the same time, to realize strong upconversion emission. In this letter, we report on the investigations of upconversion luminescence from a new kind of Er^{3+} -doped halide tellurite glass upon 976-nm excitation. Experimental results indicate that it is a promising material for practical upconversion applications.

Glass sample with the composition $73\text{TeO}_2 + 5\text{BaF}_2 + 10\text{ZnBr}_2 + 10\text{PbCl}_2 + 2\text{Yb}_2\text{O}_3 + 0.5\text{Er}_2\text{O}_3$ (TFCBr) was prepared from reagent-grade barium fluoride (BaF_2), Zinc bromide (ZnBr_2), lead chloride (PbCl_2), and 5N purity tellurium oxide (TeO_2) by the conventional melting and quenching method described elsewhere. Appropriate amount of NH_4Cl was added into the composition in order to avoid the oxidative atmosphere. About 20-g batches of starting materials were fully mixed and then melted in a corundum crucible in an electric furnace at 750 – 800 °C. The obtained glass was cut and polished carefully in order to meet the requirements for optical measurements. Upconversion luminescence measurements were performed with a 976-nm LD (2 W) excitation and detected by a TRIAX550 spectrofluorimeter controlled by a computer. The measurements were taken at room temperature.

Figure 1 presents the upconversion fluorescence spectrum of Er^{3+} -doped TFCBr glass under 976-nm LD excitation. Three emission bands centered at 525, 545 and 655 nm are simultaneously observed and assigned to the transitions ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$, ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and

${}^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. Furthermore, the red emission intensity at 655 nm is relatively weaker than the green emission at 545 nm, but is much stronger than the emission at 525 nm by a factor of about 2. The upconversion fluorescence is bright that we can observe it easily by the naked eyes after pumping with the power of as low as 20 mW. We can not decrease the excitation power any more owing to the limits of the threshold of our LD. Besides, we have to point out that the mechanical strength of the glass sample is not strong enough since the bulk sample was broken up for pump powers as high as 500 mW.

The upconversion intensity I_{UP} is proportional to the m th power of IR excitation intensity^[9]. The logarithmic dependences of the integrated green (525 and 545 nm) and red (655 nm) emission intensities on the excitation power at 976 nm are presented in Fig. 2. The experimental data have been fit to straight lines with slope m . For the 525-, 545- and 655-nm emissions, m is 1.84, 1.74 and 1.78, respectively, which confirms that the processes for the three emissions are based in successive two photon absorptions, as shown in Fig. 3. The green emissions

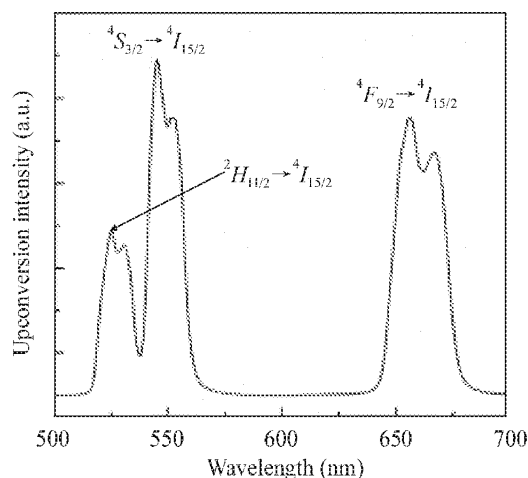


Fig. 1. Upconversion emission spectrum of Er^{3+} in TFCBr glass under 976-nm excitation.

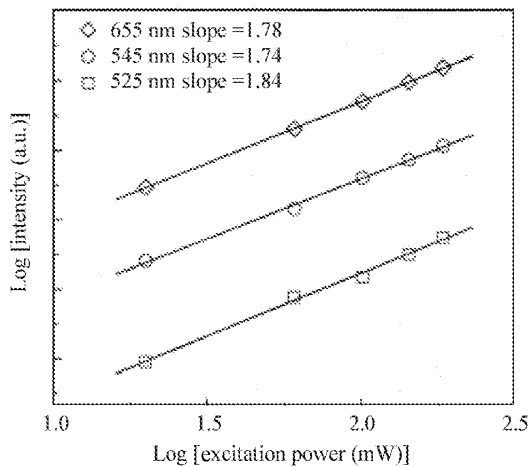


Fig. 2. Logarithmic plot of upconversion intensity as the function of excitation power at 976 nm.

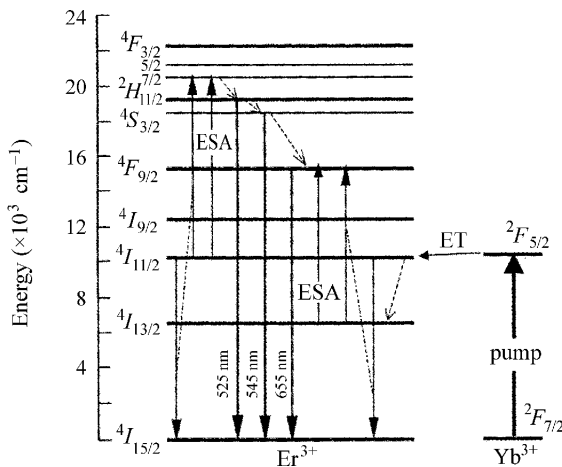


Fig. 3. Schematic diagram of possible upconversion processes and observed visible fluorescence of Er^{3+} in TFCBr glass.

centered at 525 and 545 nm occur from ${}^2H_{11/2}$ and ${}^4S_{3/2}$ levels, respectively. The ${}^2H_{11/2}$ level is populated from ${}^4S_{3/2}$ level via a fast thermal equilibrium between the levels^[10]. In a first step, Er^{3+} in the ground state was excited directly to the excited level ${}^4I_{11/2}$ and/or through phonon-assisted energy transfer from Yb^{3+} where Yb^{3+} absorbed the excitation photon directly which provokes the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Since Yb^{3+} has a much larger absorption cross section around 976 nm than Er^{3+} , the later process mainly contributes to the population accumulation on ${}^4I_{11/2}$ level. The lifetime of ${}^4I_{11/2}$ level of Er^{3+} in halide tellurite glass (about 400 μs) is longer than that in tellurite glass and much longer than those in other conventional glass hosts^[11], which stimulate other energy transfer processes based on ${}^4I_{11/2}$ level. In a second step, Er^{3+} populated ${}^4I_{11/2}$ level was excited to upper level ${}^4F_{7/2}$ by two main processes: excited state absorption (ESA) and interactions among Er^{3+} ions. In general, it has been shown that energy transfer between dopant ions can not be neglected in the samples with concentration larger than 0.5 mol%^[12], so both the two processes are

important to populate ${}^4F_{7/2}$ level. The populated ${}^4F_{7/2}$ level rapidly nonradiatively relaxes to the next lower ${}^2H_{11/2}$ and ${}^4S_{3/2}$ levels owing to the narrow energy gaps between them. Therefore, the above processes produce the two green ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ emissions. There are several possible ways for the population accumulation of ${}^4F_{9/2}$ level. Firstly, Er^{3+} ions on ${}^4S_{3/2}$ level populated as mentioned previously relax nonradiatively to ${}^4F_{9/2}$ level. Secondly, the long living ${}^4I_{13/2}$ level populated through a multiphonon relaxation from ${}^4I_{11/2}$ level was excited to ${}^4F_{9/2}$ level by ESA process. Thirdly, a cross relaxation process between ${}^4I_{13/2}$ and ${}^4I_{11/2}$ levels also contributes to the population of ${}^4F_{9/2}$ level, which can be described as ${}^4I_{11/2} + {}^4I_{13/2} \rightarrow {}^4F_{9/2} + {}^4I_{15/2}$. The latter two processes are dominant because of the long lifetime of ${}^4I_{13/2}$ level. Most Er^{3+} ions on ${}^4F_{9/2}$ level relax radiatively to the ground state ${}^4I_{15/2}$ level and thus produce the red emission.

We have demonstrated a high efficient IR to visible upconversion system of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped oxyhalide tellurite glass. Very intense green (525 and 545 nm) and red (655 nm) fluorescences are observed as excited by 976-nm LD. The green emissions are based in two successive photon absorptions by ESA and interactions among Er^{3+} ions, ${}^4I_{11/2} + {}^4I_{11/2} \rightarrow {}^4F_{7/2} + {}^4I_{15/2}$, while the red emission occurs mainly via ESA and cross relaxation processes ${}^4I_{11/2} + {}^4I_{13/2} \rightarrow {}^4F_{9/2} + {}^4I_{15/2}$. The long-lived ${}^4I_{11/2}$ level is supposed to serve as the intermediate state responsible for the upconversion processes.

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