SENSITIZED THULIUM BLUE AND RED UPCONVERSION EMISSION AND ENERGY-TRANSFER PROCESSES IN $Nd^{3+}/Yb^{3+}/Tm^{3+}$-CODOPED $PbGeO_3$-BASED GLASS EXCITED AROUND 800 nm

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Abstract

In this work, we report on the generation of bright blue and red upconversion luminescence through the sensitization of thulium ions in $Nd^{3+}/Yb^{3+}/Tm^{3+}$ triply-doped 70%$PbGeO_3$:15%PbF_2:15%CdF_2 glass excited by a diode laser source around 800 nm.

Introduction

Infrared-to-visible frequency upconversion in lanthanide doped materials has been extensively investigated owing to the potential applications in visible upconversion lasers, fiber amplifiers, high density memories or solid-state color-displays. Thus, there exists a need for novel solid-state materials capable of producing efficient frequency upconversion processes. It is also important to study new routes for the upconversion excitation in alternative host materials and identify the major relaxation and interaction mechanisms between rare-earth ions implanted into the glass. The ion-pair interaction referred to as energy-transfer, where the species excited by a pump photon called donnor transfer its excitation to the other species called acceptor present in the system, has received much attention in Er^{3+}-, Pr^{3+}-, and Tm^{3+}-doped samples sensitized with Yb^{3+}. In some peculiar situations, however, the ytterbium ions can play a role of an energy-transfer bridging ion between a donnor and an acceptor ion.

Experimental Setup

The fluorogermanate glass samples used in our measurements had a composition of 70%$PbGeO_3$:15%PbF_2:15%CdF_2 and triply-doped with $Nd^{3+}/Yb^{3+}/Tm^{3+}$. Glasses were prepared with high purity (99.9999%) rare-earth oxides and all special care was taken in the lab during the glass preparation in order to avoid contamination due to other rare-earth ions. The host material presents very good optical quality, is stable against atmospheric moisture. The material also exhibits high solubility allowing the incorporation of high lanthanide concentrations apart from being nonhygroscopic and possess high thermal stability against crystallization. The samples thickness were ~ 1.0 mm and the excitation source was a cw diode laser operated at 840 nm. The pump beam was focused down into the samples by a 5 cm focal length lens. The fluorescence signal was collected by a fiber-bundle, and was dispersed by a 0.34 m scanning spectrograph with operating resolution of 0.5 nm and detected by a S-20 uncooled photomultiplier tube. A lock-in amplifier in conjunction with a storage-scope coupled to a microcomputer was used for data acquisition and storage.

Results and Discussions

Figure 1, shows upconversion fluorescence spectra of Tm^{3+} ions under 800 nm excitation, for a sample codoped with Yb(dotted line) and a $Nd^{3+}/Yb^{3+}/Tm^{3+}$ triply-doped sample(solid line). It is observed that the presence of Nd^{3+} in the system, produces a tenfold enhancement in the blue emission associated to the $^1G_4 - {}^3H_6$ transition of Tm^{3+} ions, as compared to samples doped with Tm^{3+}/Yb^{3+}. The dependence of the upconversion emission intensity as a function of the excitation power was examined and a quadratic power law behavior was obtained indicating the participation of two pump photons in the upconversion excitation mechanism. The upconversion excitation process of the Tm^{3+} ion $^1G_4$ emitting level was achieved by a initial energy-transfer process from the 800 nm excited Nd^{3+} to Yb^{3+}. The excited Yb^{3+} then, transfer its energy to a Tm^{3+} ion at the $^3H_4$ level excited by a pump photon at 800 nm. The upconversion excitation process is illustrated in the simplified energy-level diagram of figure 2.

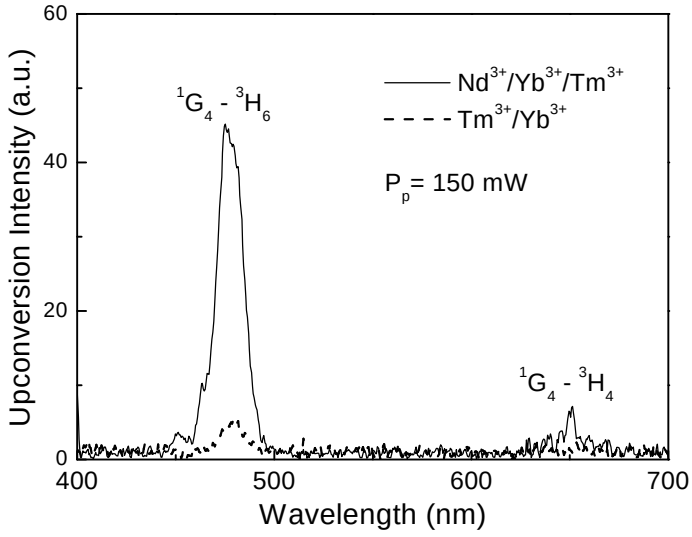

Figure 1

Figure 1 - Room-temperature upconversion emission spectrum for the $Nd^{3+}/Tm^{3+}/Yb^{3+}$ triply-doped sample under 50 mW excitation power at 840 nm.

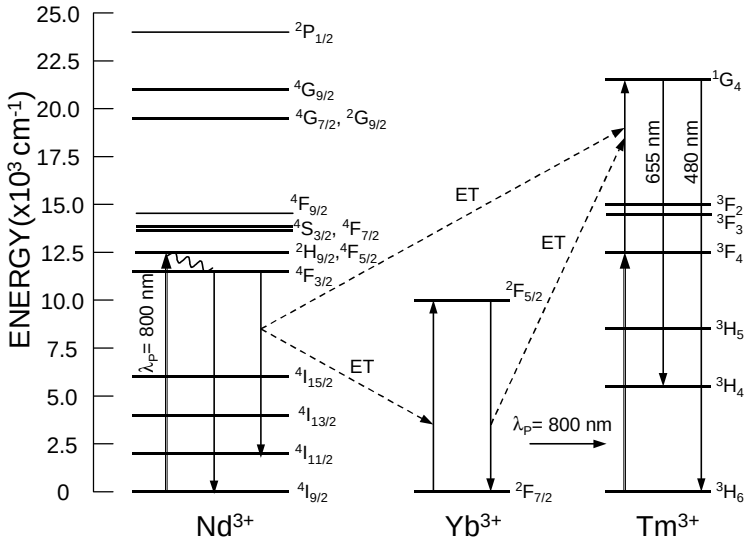

Figure 2

Figure 2 – Simplified energy-level diagram for the $Nd^{3+}/Tm^{3+}/Yb^{3+}$ ion system. Downwards arrows stand for upconversion emission

Conclusions

In this work, we have presented the generation of bright blue and red upconversion luminescence through the sensitization of thulium ions in $Nd^{3+}/Yb^{3+}/Tm^{3+}$ triply-doped $70\%PbGeO_3{:}15\%PbF_2{:}15\%CdF_2$ glass samples excited by a diode laser source around 800 nm. The results indicated that the presence of Nd ions in the system strongly affects the blue emission by thulium ions.

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