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Visible and near infrared up-conversion luminescence in Yb^{3+}/Tm^{3+} co-doped yttria-alumino-silicate glass based optical fibers

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ABSTRACT

We report blue light up-conversion (UC) emission in Yb–Tm co-doped nano-phase separated yttria-alumino-silicate (YAS) glass based D-shaped with low-index cladding optical fibers. Y_2O_3 creates an environment of nano structured YAS glass phases with Yb and Tm rich zone into the core glass which confirmed from TEM analyses. This kind of glass host assists in distributing of Yb and Tm rich zone uniformly throughout the core region. Yb and Tm doped regions exist mainly into nano YAS phases, defined as RE rich nano YAS-RE phases. All samples exhibit UC luminescence peaks at 483 nm, 650 nm and 817 nm for Tm^{3+} and 1044 nm for Yb^{3+} under excitation by 975 nm laser light. In such type of nano-engineered glass–ceramic based host, almost all the Yb ions transferred its energy to the nearer Tm ions. In particular 483 nm emission is attributed to ${}^1G_4 \rightarrow {}^3H_6$ transition through a three step resonance energy transfer (ET) from excited Yb^{3+}. The highest emission intensity is obtained with a concentration of 0.5 wt% Tm^{3+} and 2.0 wt% Yb^{3+}. The ET between Yb^{3+} and Tm^{3+} is increased with increase of Yb^{3+} concentration with respect to Tm^{3+}. The experimental fluorescence life-times of Tm^{3+} upconversion emission at visible wavelengths into such kind of fiber is reported under 975 nm pump excitation. The present study is important for development of an efficient tunable 483 nm fluorescence light source.

1. Introduction

Recently, there has been a great deal of interest in the development of thulium doped optical fibers (TDFs). This is due to promising applications of TDFs in many areas such as fiber laser around 2 μm [1–4], S-band (1460–1530 nm) fiber amplifiers [5,22] and high intensity UC luminescence at 470 nm and 810 nm regions [6,7]. A very promising UC luminescence and amplification are reported for Tm doped soft glasses, e.g. fluoride, chalcogenide glasses and the fibers [7–11]. Several attempts were made for Tm doped fluoride glass as well as chalcogenide glass based fiber [7–13]. It is found that the intensity of UC luminescence of Tm doped silica glass based fiber is not so good as reported for Tm doped soft glass based fibers or glasses [7–11,14]. Therefore there is a scope of developing a modified Tm doped silica glass which can generate promising high intensity UC luminescence as happened in Tm doped soft glass. Recently, Yb–Tm co-doped fiber has been introduced. It is found that Yb ions act as a good sensitizer for Tm ions. Yb^{3+} ions possess higher absorption cross-section at 975 nm than that for Tm^{3+} ions at 800 nm which is the excitation wavelength for Tm ions [9,11]. The excited Yb^{3+} ions sensitize nearby acceptors Tm^{3+} ions through ET process [6,8–11]. In order to generate an efficient tunable visible UC luminescence using Tm–Yb co-doped silica glass, it is crucial to select an appropriate modified silicate glass host for doping with both Tm and Yb ions.

Due to high phonon energy of silica host, the efficiency of radiative processes such as UC luminescence is decreased [14]. It is reported that for ET from ${}^2F_{5/2}$ level of Yb to neighboring Tm^{3+} ions, about 1515 cm^{-1} energy is released to the lattice phonons [11]. Accompanied with this, the non-radiative transitions of ${}^3H_5 \rightarrow {}^3F_4$ and ${}^3F_{2,3} \rightarrow {}^3H_4$ for excited Tm^{3+} ions, about 1162 cm^{-1} energy is released towards lattice phonon for each transition. The silica glass has phonon energy about 1100 cm^{-1}, which is quite nearer to those non-radiative transitions [11]. Therefore during those non-radiative transitions, there is always a possibility of interaction with the lattice phonons. Due to the lattice phonon interaction, the transition rate of Yb–Tm, ${}^3H_5 \rightarrow {}^3F_4$ and ${}^3F_{2,3} \rightarrow {}^3H_4$ are slowed down. As a consequence, UC luminescence intensity is decreased in silica glass. In this report, fabrication and

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spectroscopic characteristics of double-clad large-core Yb–Tm co-doped fiber are demonstrated using a newly developed homogeneously distributed nano-structured YAS glass phase embedded into glass matrix. Presence of Al_2O_3 into host glass increases refractive index (RI) of silica by 2.3×10^{-3} per mole and is used as intermediate core glass network modifier [14,18,19]. It also helps to distribute Tm and Yb ions homogeneously into YAS glass phases and decrease phonon energy of silica glass [14]. Other dopant i.e.Y_2O_3 helps to create nano-structured YAS glass phase within silicate host and act as glass network generator [15,16,19]. This modified silica glass host is chosen due to its optical transparency from 200 nm to beyond 3000 nm wavelength region [17]. Not only so, nano YAS phases incorporated most of the Yb and Tm ions within themselves and created some YAS-RE (YAS-rare earth) rich zones within the optical fiber core. Furthermore, due to low phonon energy of YAS, magnitude of radiative emission probability of metastable states of Tm^{3+} is increased and therefore non-radiative loss due to multi-phonon emission which is caused by non-radiative transitions reduces significantly. As a result intense up-conversion luminescence bands at 483 nm and 817 nm from Tm^{3+} by indirect cladding pumping excitation using 975 nm multimode DL are observed. These phase separated YAS-RE also increases the ET process from Yb to Tm. In this system 975 nm excitation wavelength can only be absorbed by Yb^{3+}. Thus, the pump source excites the Yb^{3+} first and then the energy is transferred to nearby Tm^{3+} to excite them indirectly in an efficient manner. Finally the spectroscopic process is analyzed by photo-physical kinetic mechanism. According to the analysis 483 nm emissions is attributed to a three step ET from excited Yb^{3+}. Whereas, 817 nm emission occurred for a two step ET from excited Yb^{3+}. Experimental life times of Tm^{3+} luminescence are reported. The value of third ET coefficient which indirectly represented the Yb to Tm ET efficiency for developed fibers is evaluated through photo-physical kinetic mechanishm.

2. Fiber sample fabrication and its material analysis

Yb–Tm co-doped YAS core glass based multimode optical fibers were fabricated by modified chemical vapor deposition (MCVD) process in conjunction with solution doping (SD) technique. Since 1987, SD technique has been used to incorporate rare earths into the silica glass matrix at the core of optical fibers [20]. The first reported Tm doped fiber laser at 2 μm by Hana et al. had been fabricated using solution doping techniques [1]. A detailed analysis on fabrication conditions required to develop high-power fiber laser using MCVD process associated with SD had been reported by Kirchhof et al. in 2006 [21]. The effect of high Tm concentration, achieved by concentration doping technique, on S-band amplification has reported by Aozasa et al. in 2006 [22]. Those earlier literatures help us to develop a suitable fabrication process using MCVD process associated with SD technique would be discussed in the following subsequent stages.

A high purity silica glass tube of outer/inner diameter 20/17 mm was used for deposition of 3–8 multiple porous un-sintered SiO_2 soot layers to make different preform samples, maintaining a suitable deposition temperature at around 1400–1450 °C with the help of single-wavelength online IR Pyrometer (Williamson Corp, USA) with an accuracy of ±5 °C. Fig. 1 shows the scanning electron microscopic (SEM) image of multiple porous soot layers before solution soaking.

An alcoholic solution containing Tm, Yb, Y and Al in their respective chlorides of Alfa standard was used to soak the porous layer for about 30–60 min to achieve efficient doping. To ensure enough soaking time, conductivity test of precursor solution during SD, is done to study soaking kinetic path. Fig. 2 shows the plot of change in conductivity of the solution versus time which was obtained by measuring the conductance of the solution at a constant time interval (Radiometer analytical model: CDM 210) during solution soaking process. The conductance is changed due to gradual increase of dopant ions into the porous layers. The plot is generated according to the following equation.

$$\frac{d(C_t - C_\alpha)}{dt} = k(C_0 - C_t)^n \qquad (1)$$

where, 'C_t' is the conductance of the solution at time't' during soaking, 'C_α' is the conductance of the solution after infinitely long soaking time (here it is taken after 3 h from the starting point), 'C_0' is the conductance of the solution at the starting time of soaking (taken within 1 min after pouring the solution into the tube), 'k' is the rate constant and 'n' is the order of soaking kinetic path. This plot suggests that after 45 min. of soaking there is no increase in conductance. That means after 45 min. almost all the pores of the un-sintered shoot are filled up by the dopant ions present in the solution. Therefore it is expected that, an equilibrium condition is established between the un-sintered shoot layers and solution for different samples.

Such conductance study proved that within the optimum time period (i.e. 45 min) an appreciable amount of solution is soaked into the porous structure which makes more efficient doping of Tm and Yb ions into porous medium.

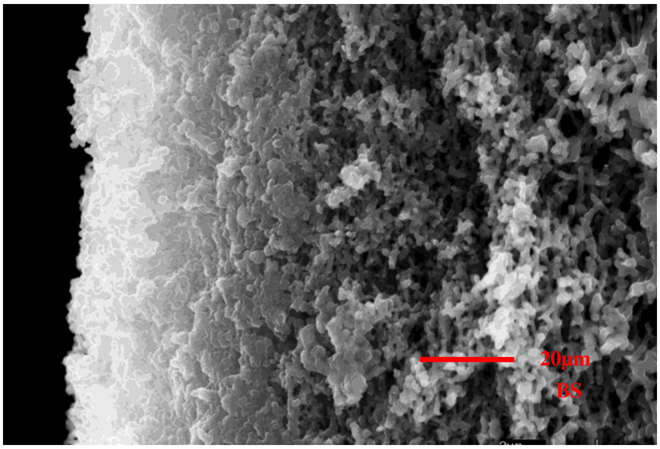

Fig. 1. SEM image of multiple un-sintered soot layers before solution soaking.

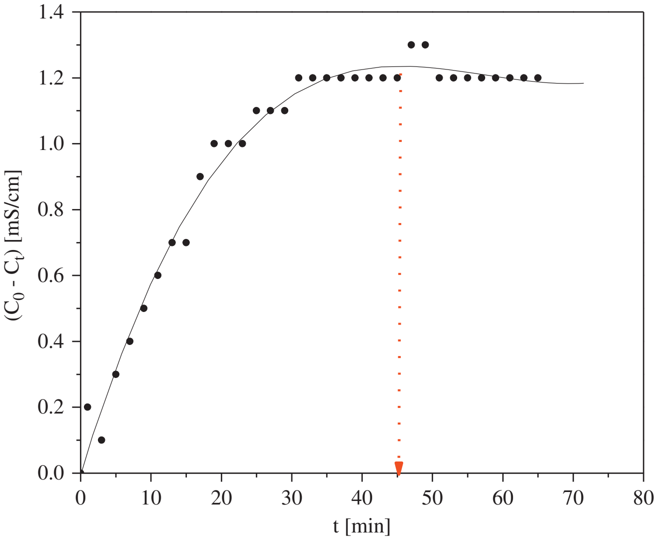

Fig. 2. The changes in conductivity of doping solution (C_t–C_o) versus soaking time (t) during the solution soaking process.