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Insights into $Er^{3+} \leftrightarrow Yb^{3+}$ energy transfer dynamics upon infrared ~1550 nm excitation in a low phonon fluoro-tellurite glass system

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ABSTRACT

Highly upconverting, monolithic transparent inorganic glass co-doped with Er^{3+}/Yb^{3+} ions have been explored in view of their easy integration with Si-PV cell. A ~4 fold enhancement in the photo-current of mc-Si-PV cell has been observed using a Er^{3+}/Yb^{3+} co-doped sample compared to Er^{3+} ions singly doped glass. The role of Yb^{3+} ions on the enhancement of photo-current has been discussed in light of the $Er^{3+} \leftrightarrow Yb^{3+}$ energy transfer mechanism involved from IR to NIR and VIS upconversion process upon IR ~1550 nm excitation. The influence of excitation pump power and donor Er^{3+} ion concentration on the energy transfer upconversion (ETU) as well as excited state absorption (ESA) energy transfer mechanisms and its effect on the upconversion emission properties have been described in detail. The prominence of ETU or ESA process were elaborated considering the decay dynamics of NIR upconversion emission upon ~1550 nm excitation.

1. Introduction

Effective solar energy utilization is utmost important to meet the ever increasing energy demand [1]. Solar energy harvesting by means of first generation cost effective silicon photovoltaics (Si-PV) is technologically well established and still leading the global market with conversion efficiency ~18–20% using a limited portion of vast available solar energy. Theoretically, by utilizing the transmitted solar energy (~19% of the total energy hitting the earth surface i.e., ~164 W/m^2) below the bandgap ~1.1 eV of silicon, efficiency can be enhanced to ~47% which is beyond the Shockley-Queisser theoretical limit of ~33% [2,3]. Among various energy harvesting techniques to overcome the transmission losses, solar energy conversion by mean of up-conversion (UC) process has influenced the research community in a big way [2–6]. For that, trivalent rare earths (RE^{3+}), especially Er^{3+} doped/co-doped materials are widely explored due to its efficient UC emission properties in the high response region of Si-PV cell [3,7,8]. Proof of concept experiments have been demonstrated with well known commercial phosphor, β-$NaYF_4$-Er^{3+} where photo current enhancement of c-Si PV (crystalline-Si-PV) cell has been demonstrated [9,10] upon IR, 1550 nm excitation. It has been recently reported that, Gd_2O_2S:Er^{3+} phosphor showing enhanced UC efficiency than β-$NaYF_4$:Er^{3+} [2,10]. However, phosphors, usually a polycrystalline opaque material experiences scattering losses with deprived effective excitation of active ions and yet integration of these phosphors with Si-PV cell is still a challenging task [11–13]. Often, these phosphors have to be embedded in any organic polymers which are again light sensitive and easily degradable [14,15].

Efficient monolithic transparent inorganic materials doped with RE^{3+} ions are highly essential for easy integration with Si-PV cells and efficient extraction of solar energy compared to opaque phosphor materials. Oxide based inorganic glasses are potential alternative to address the above difficulties. However, UC emission in traditional glasses such as silicate, phosphates and borates are not very effective due to their high phonon energy which always favours fast multi phonon de-excitations from higher excited states of active RE^{3+} ions limiting the favourable mechanisms such as energy transfer upconversion (ETU) and excited state absorption (ESA) for UC process. In this contest, low phonon (~700 cm^{-1}) tellurium oxide based glasses could be very prospective compared to fluoride based glasses (~600 cm^{-1}) in terms of chemical stability. Plenty of the work has been reported on Er^{3+} doped and Er^{3+}/Yb^{3+} co-doped tellurium oxide based glasses [16–18]. However, most of the reported work has mainly focused either on Er^{3+}: ~1550 NIR (near infrared) emission

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properties or NIR to VIS (visible) up-conversion properties upon Er^{3+} or Yb^{3+} ions sensitization at 980 nm excitation. In view of c/mc-Si-PV cell structure, UC materials as a layer on the rear side of cell mainly aimed to utilize the transmitted IR photos which are below the bandgap of silicon (~1.1 eV). Since 980 nm sites within the high response region of c-Si-PV or mc-Si-PV cell, the use of UC materials upon 980 nm excitation is highly inefficient [14]. However, UC materials with excitation wavelength ~980 nm may be more appropriate for PV materials with bandgap > 1.5 eV such as amorphous silicon PV cell (which are less efficient and have low market value at present). Still the present studied UC materials can be readily applicable to use in all forms of Si-PV cells. The present work deals with a detailed case study on the energy transfer dynamics of $Er^{3+} \leftrightarrow Yb^{3+}$ ions upon ~1550 nm excitation of transparent UC materials and its influence on the enhancement of photo-current in mc-Si PV cell which have been less reported.

Although, there are few reports on the IR (~1.5 μm) to NIR and VIS UC in Er^{3+} ions doped low phonon tellurite [19] and fluoride [7,20] based glass systems, studies on Er^{3+}/Yb^{3+} co-doped oxide glasses are very limited [21]. Yb^{3+} ions having strong emission [22] (~1 μm) near the bandgap of silicon is highly beneficial if IR photons are upconverted to NIR region. UC from IR to NIR (~1 μm) would be more effective than UC of IR to VIS since high energy VIS photons will increase the usual thermalization losses encountered by Si-PV cells. To the best of our knowledge there are no such reports on the detailed IR to NIR UC properties in Er^{3+}/Yb^{3+} co-doped systems and its influence on the photo-current enhancement of Si-PV cell. The energy level structure of Er^{3+} ions will allow multi-photon absorption at different excited levels which in turn highly depends on the Er^{3+} ion concentration, source excitation pump power as well as more importantly on the excitation wavelength [23]. The energy transfer dynamics of Er^{3+} ions totally changes if we switch the excitation wavelength from ~980 to ~1550 nm and has peculiar behaviour in presence of Yb^{3+} ions. A careful analysis on the energy transfer dynamics would be highly beneficial for the optimization of active ion concentrations not only for Si-PV application but also for different other applications [24–26].

The present work describes in detail the effect of Er^{3+} ion concentration on the photo-current enhancement of Si-PV cell via IR to NIR and VIS UC emission process in Er^{3+}/Yb^{3+} co-doped low phonon fluoro-tellurite glass system exclusively upon IR, ~1.5 μm excitation (transparent to Si-PV cell). The enhancement of Si-PV cell photo-current on Yb^{3+} ion co-doping have been discussed in light of proper energy transfer mechanism by considering the experimental decay dynamics of Er^{3+}: $^4I_{11/2}$ and Yb^{3+}: $^2F_{5/2}$ excited sates upon ~1.5 μm excitation.

2. Experimental

A series of Er^{3+}/Yb^{3+} co-doped fluoro-tellurite glasses having chemical composition (mol%) $75TeO_2$ –$15BaF_2$ –$5AlF_3$ –(5-x)LaF_3 – xErF_3 –1YbF_3 (TBALF), (x=0.5, 1.0, 2.0 and 3.0), were prepared by melt quenching technique. For comparison studies and to know the influence of YbF_3, 1 mol% ErF_3 singly doped TBLAF glass was also prepared and studied alongside with the other co-doped samples. All the chemicals used were of AR grade with ≥99.99% purity supplied by Sigma-Aldrich, USA. Approximately, 15 g of each batch was thoroughly mixed to a fine power in an agate motor and transferred to a pure platinum crucible covered with a platinum lid for melting in an electrical furnace at 800–850 °C for about 1 h with intermittently stirred with thin platinum rod for attaining chemical homogeneity and bubble free melt, then it was poured onto a preheated graphite mould to form a clear glass followed by annealing at glass transition temperature for ~2 h to remove thermal stress if generated in the formed glasses during the quenching process.

The emission, excitation spectra and fluorescence decay kinetics of the samples were recorded at room temperature on spectrofluorimeter (Model: Quantum Master enhanced NIR from PTI, USA). The instrument was equipped with PMT (photo-multiplier tube) and liquid nitrogen (LN_2) cooled gated NIR-PMT (Model: NIR-PMT-R 1.7, Hamamatsu) as detectors for acquiring both study state spectra and phosphorescence decay in the VIS and near infrared (NIR) regions. Decay measurements were carried through Hamamatsu NIR-PMT in gated mode by employing a 60 W Xenon flash lamp as an excitation source. Suitable low pass and high pass filters supplied by Edmund Optics Inc, USA were used respectively at the source and detector side to avoid unwanted higher harmonic peaks related to the excitation and emission wavelength in the recorded emission spectrum. Up-conversion emission spectra were recorded by exciting the sample with a 1550 nm single mode fiber pigtailed CW laser diode (Model: LPSC-1550-FC) supplied by Thorlabs, USA. Photo-current measurements under 1550 LD excitation of locally purchased multi-crystalline silicon photovoltaic cell (5×5 cm^2; I_{sc}=200 mA, V_{oc}=2 V) were recorded using Keithley 2400 source meter.

3. Results and discussion

3.1. Upconversion emissions and Er^{3+} ion concentration effects

In Er^{3+}/Yb^{3+} co-doped samples, Yb^{3+} ion concentration has been fixed to 1 mol% to avoid the reabsorption losses which prevail at higher concentrations [22]. The UC emission spectrum of Er^{3+}/Yb^{3+} co-doped TBLAF glasses for different concentrations of Er^{3+} ions were recorded under 50 mW continuous 1550 nm laser diode (LD) excitation are shown in Fig. 1. The UC emission spectrum of singly Er^{3+} ions doped glass also shown in Fig. 1 for better comparison. Since the intensity of the NIR UC emission is enhanced to many folds in presence of Yb^{3+} ions, the VIS UC emission were hard to detect in the same intensity scale, and therefore a view of the VIS UC emission in the respective wavelength regions are represented as insets (a)–(c) in Fig. 1 itself. The corresponding transitions for UC emissions are also mentioned in the spectrum itself for clear understanding. As shown in Fig. 1, the intensity of NIR and VIS (green & red) UC emissions increased with the increase in Er^{3+} ion concentration up to 2 mol%. A further increase

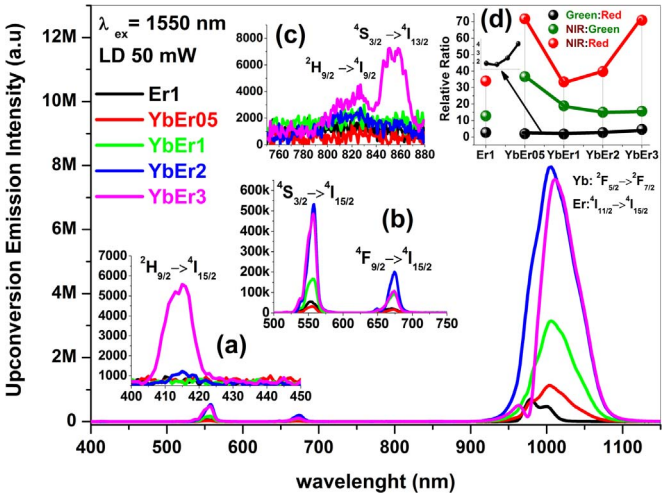

Fig. 1. Up-conversion (UC) emission spectra under 1550 nm LD excitation for different Er^{3+} ion concentrations. Inset (a-c) shows the magnified region of UC emissions in the respective wavelength region. Inset (d) shows the relative ratio of Green to Red, NIR to Green and NIR to Red UC emissions.