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Multimodal emissions from Tb^{3+}/Yb^{3+} co-doped lithium borate glass: Upconversion, downshifting and quantum cutting

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ABSTRACT

This paper reports the optical properties of Tb^{3+}/Yb^{3+} co-doped lithium borate (LB) glass prepared by melt quench method. The absorption spectrum of the Yb^{3+} doped LB glass contains intense NIR band centered at 976 nm due to $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition. The emission spectra of the prepared glasses have been monitored on excitation with 266, 355 and 976 nm. The Yb^{3+} doped glass emits a broad NIR band centered at 976 nm whereas the Tb^{3+} doped glass gives off visible bands on excitations with 266 and 355 nm. When the Tb^{3+} and Yb^{3+} ions are co-doped together, the emission intensity in the visible region decreases whereas it increases in the NIR region significantly. The increase in the emission intensity in the NIR region is due to efficient cooperative energy transfer (CET) from Tb^{3+} to Yb^{3+} ions. The quantum cutting efficiency for Tb^{3+}/Yb^{3+} co-doped glass has been calculated and compared for 266 and 355 nm excitations. The quantum cutting efficiency is larger for 355 nm excitation (137%). The Tb^{3+}/Yb^{3+} co-doped LB glass also emits upconverted visible bands on excitation with 976 nm. The mechanisms involved in the energy transfer have been discussed using schematic energy level diagram. The Tb^{3+}/Yb^{3+} co-doped LB glass may be used in the optical devices and in solar cell for solar spectral conversion and behaves as a multi-modal photo-luminescent material.

1. Introduction

The solar spectral conversion has been fascinating an important source of energy because the fossils fuels are continuously decreasing. The researchers have paid their attention to investigate an alternate source of energy. The sunlight is freely available and can be used to harvest for technological applications. Solar cell is an alternate source of energy storage, which converts solar energy into electrical energy. The silicon solar cell having band gap 1.12 eV can easily absorb near infrared (NIR) photons (~1.10 eV) of the solar spectrum but the ultraviolet (UV) part of the solar spectrum remains unutilized. It is noticed that the incident photons with energy lower than silicon band gap will transmit without absorption while the photons with higher energy lose their excess energy due to thermalization by the charge carriers. Among the rare earth ions, the Yb^{3+} ion emits the NIR photons (~1.10 eV), which are absorbed by a silicon solar cell and plays an important role to enhance its efficiency [1,2].

It is well known that the $Yb^{3+}O^{2-}$ charge transfer state (CTS) plays very important role to enhance the NIR emission intensity of Yb^{3+} ion. The excited state ($^2F_{5/2}$) of Yb^{3+} ion lies at ~1,0246 cm^{-1} (976 nm). It has been observed in the case of YPO_4 that the CTS of Yb^{3+}-O^{2-} is located at ~49,000 cm^{-1} (204 nm) and there is a large energy difference ~38754 cm^{-1} (258 nm) between the CTS (Yb^{3+}-O^{2-}) and $^2F_{5/2}$ state [3–5]. Thus, the electron may decay radiatively from CTS (Yb^{3+}-O^{2-}) to the 4 f state of Yb^{3+} ion and give charge transfer band in UV–Vis region. In a glass material, the CTS of the Yb^{3+}-O^{2-} is broad and there is a large possibility of overlapping between CTS and 4 f level of Yb^{3+} ion. This suggests that the probability of non-radiative transition is large. As a result, the CTS emission band is not observed in glass [6]. The Yb^{3+}-O^{2-} CTS absorbs UV part of solar energy and transfers it to $^2F_{5/2}$ level of Yb^{3+} non-radiatively. Finally, a broad band centered at 976 nm due to $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition is observed, which is useful in silicon solar cell [1,7,8].

The efficiency of solar cell can be enhanced significantly through the quantum cutting (QC) process. Quantum cutting is a process in which a high energy photon is converted into two or more low energy photons. The different mechanisms involved in the quantum cutting process have been discussed by J. Zhou et al. [9]. They have summarized quantum cutting in different combinations of Ln^{3+}(trivalent lanthanide ions)/Yb^{3+} co-doped host materials. The excitation energy of a donor (Ln^{3+}) ion is transferred simultaneously to the two acceptor (Yb^{3+}) ions. This is possible if the energy of the Ln^{3+} excited state is almost doubled to that of $^2F_{5/2}$ state of Yb^{3+} ion. The quantum cutting phenomena has wide applications in different fields such as noble gas

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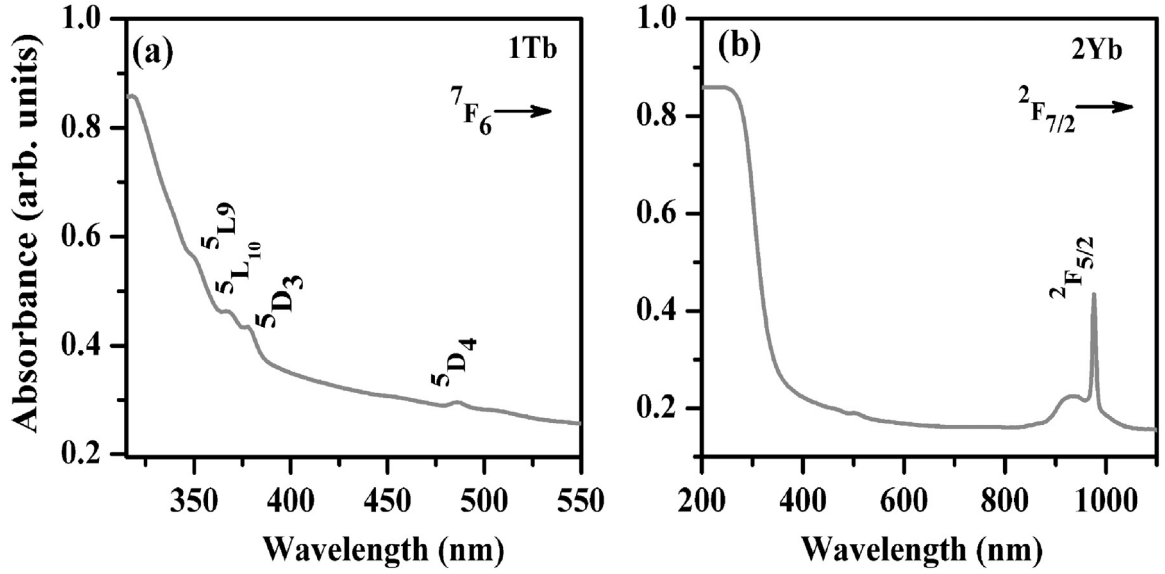

Fig. 1. Absorption spectra of (a) 1 mol% Tb^{3+} and (b) 2 mol% Yb^{3+} doped LB glasses.

discharge tube lamp, solar cells, etc [9–12]. The quantum cutting efficiency of rare earth ions doped in different host materials has been discussed by X. Huang et al. [13]. They have found that the quantum efficiency is host dependent. The quantum cutters such as Nd^{3+}-Yb^{3+}, Pr^{3+}-Yb^{3+} and Er^{3+}-Yb^{3+} ions have been found to enhance the efficiency of solar cell in which Nd^{3+}, Pr^{3+} and Er^{3+} ions can efficiently absorb UV light and transfer their excitation energy to the Yb^{3+} ions; thereby emitting in the NIR region [13]. These ions also emit visible bands due to downshifting (DS) process in which a high energy photon is converted into a photon with low energy [13]. The QC emission from Tb^{3+}, Yb^{3+} ions was studied in different types of host by different researchers [1,2,13–15]. However, QC emission from Tb^{3+}-Yb^{3+} co-doped LB glass has not been reported to our knowledge. The quantum efficiency reported in Tb^{3+}–Yb^{3+} co-doped oxyfluoride glass is 120% [15]. This value is smaller compared to what reported by us (137%) in LB glass. The LB glass is a good host material because it possesses comparatively low phonon frequency and gives intense emission of the acceptor ions due to reduction in non-radiative relaxation. The LB glass is an important host because the energy transfer from Tb^{3+} to Yb^{3+} and relaxation of electron from CTS band to $^2F_{5/2}$ state of Yb^{3+} ion collectively enhances the NIR emission intensity drastically. This glass has optical transparency, which is beneficial for solar cell [9]. It has also stability even at higher temperature.

On the other hand, some rare earth ions also possess upconversion properties. Upconversion is a process in which a low energy photon is converted into a photon with high energy. [16]. The presence of Yb^{3+} ion enhances the upconversion emission intensity of the rare earth ions many times because it has large absorption cross section for 976 nm radiation. The upconversion emission from Tb^{3+}, Yb^{3+} ions in different hosts have studied by different researchers [16–19]. They have explained that the Yb^{3+} ion absorbs 976 nm radiation efficiently and transfer its energy to Tb^{3+} ion via CET. As a result, the Tb^{3+}, Yb^{3+} co-doped glass emits intense green emission on excitation with 976 nm. In this paper, the QC emission has been observed from Tb^{3+}, Yb^{3+} co-doped LB glass on excitations with 266 and 355 nm. The non-radiative energy transfer from Yb^{3+}-O^{2-} charge transfer (CT) state to $^2F_{5/2}$ level of Yb^{3+} ion gives NIR emission. When the Tb^{3+} and Yb^{3+} ions are co-doped together, the intensity of NIR emission is enhanced significantly due to involvement of downconversion CET. The QC efficiency of Tb^{3+}/Yb^{3+} co-doped LB glass has also been calculated. Furthermore, the Tb^{3+}, Yb^{3+} co-doped LB glass also gives upconverted visible emissions through upconversion CET on excitation with 976 nm. Thus, the Tb^{3+}/Yb^{3+} co-doped LB glass behaves as a multi-modal photo-luminescent material.

2. Experimental

The Tb^{3+}, Yb^{3+} doped and co-doped LB glasses were prepared by melt quench method [14]. The H_3BO_3, Li_2CO_3, Yb_2O_3 and Tb_4O_7 have been used as starting materials. The compositions used are given as:

$$(80-x)\ H_3BO_3+20\ Li_2CO_3+xYb_2O_3+1\ Tb_4O_7$$

where x varies as 0, 1, 2, 3 and 5 mol%.

The absorption spectra of the samples were recorded using UV–vis–NIR spectrometer (Perkin Elmer, lambda-750) in the range of 200–1100 nm. The photoluminescence spectra of the samples were recorded on excitation with 266 and 355 nm radiation using Nd: YAG pulse laser (repetition rate ~10 Hz, pulse width ~7 ns). A computer controlled Ocean optics spectrometer (model no. QE65000) has been also used to monitor the photoluminescence spectra. The life time measurements have been carried out using Fluorolog-3 spectrofluorometer (Model: FL3-11, Horiba Jobin Yvon) equipped with 25 W Xenon pulsed flash lamp. The upconversion emission spectra of the samples were monitored on excitation with 976 nm diode laser.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of 1 mol% Tb^{3+} and 2 mol% Yb^{3+} doped LB glasses are shown in Fig. 1. The absorption spectra of Tb^{3+} doped LB glass contains several weak peaks due to 4f-4f transitions of Tb^{3+} ion near band edge absorption of LB glass (see Fig. 1(a)). The peaks are observed at 350, 369, 377 and 489 nm, which are assigned to arise due to $^7F_6 \rightarrow {}^5L_9$, $^5L_{10}$, $^5D_3$ and $^5D_4$ transitions, respectively [20]. The peak observed at 489 nm is mainly responsible for downconversion CET. The absorption spectra of Yb^{3+} doped LB glass shows a broad absorption band in the range of 200–300 nm due to absorption of LB glass [21]. It also contains a broad peak centered at 976 nm assigned to arise due to $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ion (Fig. 1(b)).

We have also recorded the excitation spectrum of 1 mol% Tb^{3+} doped LB glass in the range of 255–535 nm at λ_{emi}=542 nm (see Fig. 2). The excitation peaks observed at 317, 339, 350, 368, 377 and 485 nm are assigned to arise due to $^7F_6$ to $^3H_7$, $^5L_7$, $^5L_9$, $^5L_{10}$, $^5D_3$ and $^5D_4$ transitions, respectively [22]. The peaks observed in the 255–310 nm region are due to 4f–5d transition of Tb^{3+} ion. It is clear from