



Investigation of energy transfer mechanisms between Bi²⁺ and Tm³⁺ by time-resolved spectrum



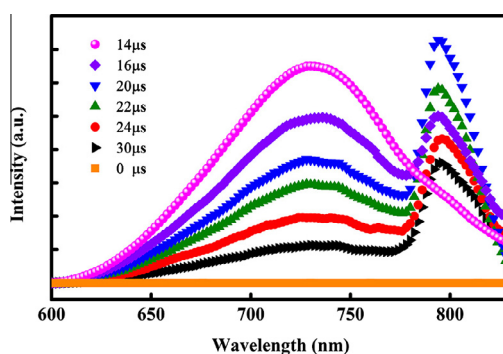
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HIGHLIGHTS

- Manifestation of Bi²⁺/Tm³⁺ codoped glasses as substrate for CdTe solar cell.
- Obtained an ultrabroadband response spectrum which covers the entire visible range.
- Energy transfer channel is exposed using various spectroscopic studies.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 February 2013
Received in revised form 14 April 2013
Accepted 19 May 2013
Available online 11 June 2013

Keywords:

Bi²⁺
Time-resolved
Luminescence down-shifting
CdTe solar cell
Energy transfer

ABSTRACT

Here, we report for the first time the optical properties of Bi²⁺ and Tm³⁺ co-doped germanate glasses and elucidate the potential of this material as substrates to improve the performance of CdTe solar cell. A strong emission peak at 800 nm is observed under the excitation of 450–700 nm in this material. The energy transfer processes from the transitions of Bi²⁺ [²P_{3/2}(1) → ²P_{1/2}]; Tm³⁺ [³H₆ → ³H₄] are investigated by time-resolved luminescence spectroscopy. A cover glass exhibiting an ultra-broadband response spectrum covering the entire solar visible wavelength region is suggested to enhance the conversion efficiency of CdTe solar cells significantly.

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Introduction

In recent years, thin-film cadmium telluride (CdTe) solar cell has been considered as one of the most promising candidates for large-scale applications in the field of photovoltaic energy conversion [1]. But the maximum achievable efficiency of single junction solar cell is limited by the inability for any proven semiconductor material to utilize the entire light spectrum available under solar irradiation for photo-conversion. The most efficient absorption band for CdTe solar cell locates in the region from 700 nm to 900 nm, however,

the peak of the solar radiation under AM 1.5 conditions locates at 520 nm [2]. CdTe solar cell does not respond to short wavelength light efficiently. While efforts are being undertaken to reduce this effect, a method to improve this poor short-wavelength response of CdTe solar cell is the application of a luminescent down-shifting (LDS) layer, which is first suggested by Hovel et al. [3]. LDS materials help to improve short-wavelength response by using luminescent materials which absorb light at short wavelengths and reemit longer wavelength light, and solve the mismatch of spectra response. It is a fact that not all photons impinged on this layer are directed to the solar cell, because there exist absorption losses in each layer, reflection at the PMMA–air interface, photon escape via the top plane and side plane of LDS layer etc. [1]. Therefore,

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many efforts are made to reduce such losses in solar cells [4]. In this work, we want to cut down the layers above the solar cell to reduce these losses. So the glass super-stratum of the solar cell with the characteristic of luminescent down-shifting is suggested to take the place of the ordinary glass substrate. And in that case, the single glass layer above the solar cell could play the roles of LDS layer and substrate. The LDS glass layer could improve short-wavelength response to enlarge the solar cell conversion efficiency by changing the visible light of wavelength region from 450 nm to 700 nm into near infrared (NIR) light of wavelength region from 700 nm to 900 nm, as well as be a covering of the solar cell.

The excellent choice of Tm^{3+} singly doped glasses will satisfy the demand of NIR emitting, in consideration of their fierce emission peak at 800 nm, due to the transition [$^3\text{F}_4 \rightarrow ^3\text{H}_6$] [5]. Excitation peaks arise from 468 nm and 688 nm when monitored at 800 nm [5]. Yet no transition is located at the wavelength region from 500 nm to 650 nm. So Tm^{3+} singly doped glass could not meet requirements of the entire visible light spectrum available under solar irradiation for photo-conversion.

Peng et al. declared that bismuth doped glasses have a potential application as solar spectral converters, owing to a broad absorption band in the visible wavelength region of bismuth [6], he also observed an emission peak at 750 nm and the three excitation peaks at 281, 335, 507 nm in Bi singly doped magnesium phosphate glasses. This emission peak should be assigned to the transition [$^2\text{P}_{3/2}(1) \rightarrow ^2\text{P}_{1/2}$] of Bi^{2+} [7]. After many investigations on the luminescence properties of the divalent bismuth in different glass matrix, Peng et al. point out that usually the absorption band of the divalent bismuth in different glass matrix locate in the region of ultraviolet light, blue light and a broadband from 400 nm to 650 nm, and the lifetime of divalent bismuth ions vary between 2 μs and 25 μs [8,9]. In many cases the broad absorption bands from 400 nm to 650 nm do overlap with the corresponding region of the solar spectrum. The spectral modulation of the entire visible wavelength region for solar spectrum could be achieved by co-doping Bi-Tm ions in the same glass. In the previous work, the energy transfer channel between Bi NIR centers and Tm^{3+} has been elaborated in details [10,11]. However, up to now, there has been no investigation on the energy transfer between Bi^{2+} and Tm^{3+} . In this paper, we choose $\text{GeO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system as the glass matrix materials, and co-dope the Bi^{2+} and Tm^{3+} to obtain the broad response spectrum.

Materials and methods

Glasses with molar compositions of $(75-x-y)\text{GeO}_2\text{-}14\text{MgO-}11\text{Al}_2\text{O}_3\text{-}x\text{Bi}_2\text{O}_3\text{-}y\text{Tm}_2\text{O}_3$ ($x = 0, 0.5; y = 0, 0.3, 0.5, 1, 1.2, 1.5$) were prepared by the conventional melting-quenching technique. In the following, sample nomenclature is GxByT. E.g., G0B1T for $x = 0$ and $y = 1$. The 4N pure GeO_2 , MgO , Al_2O_3 , Tm_2O_3 , Bi_2O_3 were selected as the raw materials. Batches of 20 g were mixed homogeneously in an agate mortar and melted in a pure-alumina crucible at 1500 °C for 10 min in the air, and then the melt was cast onto a stainless-steel plate, and cooled to room temperature. The obtained glasses were cut and polished to size of 10 mm \times 10 mm \times 1 mm for optical measurements. The UV and visible luminescence spectra, and time-resolved luminescence spectra were measured with Edinburgh Instruments FLS920. Simulated sunlight source (Nbet, Solar-500) was used as a continuous wavelength excitation source, and a home-made filter which cuts lights above 760 nm and below 400 nm to transmit the visible lights was used.

Discussion

Fig. 1a shows the emission spectrum of G0.5B1T glass excited at 688 nm, and the excitation spectrum of G0.5B1T glass monitored at

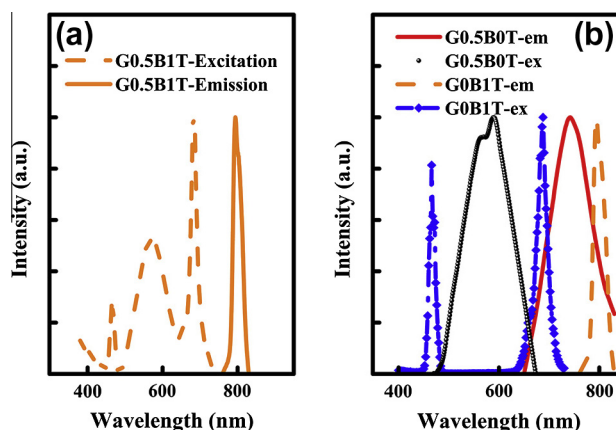


Fig. 1. (a) Emission spectrum of G0.5B1T glass excited at 688 nm, and excitation spectrum of G0.5B1T glass monitored at 800 nm. (b) Emission spectrum of G0.5B0T, G0B1T glasses excited at 570 nm, 688 nm, respectively, and the excitation spectrum in the visible wavelength region of G0.5B0T, G0B1T glasses monitored at 740 nm, 800 nm, respectively.

800 nm. Under excitation at 688 nm, the glass exhibits emission of Tm^{3+} [$^3\text{F}_4 \rightarrow ^3\text{H}_6$] peaking at 800 nm. The excitation spectrum monitored at 800 nm covers a very broad spectral region (from 450 nm to 700 nm) and consists of three main excitation bands, viz. 468 nm, 688 nm, and a broadband from 490 nm to 650 nm. The emission peak of the solar spectrum locates at 500 nm [2]. Yet the effective response wavelength region of the spectral response of CdTe solar cell is from 700 nm to 900 nm. The mismatch region between these two spectra is located from 400 nm to 700 nm. It is obvious that 800 nm emission is just located at the effective response wavelength region from 700 nm to 900 nm of CdTe solar cell. Meanwhile, excitation peaks at 468 nm, 688 nm, and the broadband from 490 nm to 650 nm could be well overlapped and constitute an ultra-broadband response spectrum covering the entire visible light spectrum for 800 nm emission. The material's excitation spectrum strongly overlaps with the visible portion of the solar radiation received at the Earth's surface. This overlap indicates that glasses may be efficiently activated by solar radiation.

Fig. 1b shows the emission spectrum of G0.5B0T, G0B1T glasses excited at 570 nm, 688 nm, respectively, and the excitation spectrum in the visible wavelength region of G0.5B0T, G0B1T glasses monitored at 740 nm, 800 nm respectively. Fig. 2a shows the excitation spectrum in the ultraviolet wavelength region of G0.5B0T glass monitored at 740 nm. Under excitation at 688 nm, the glass exhibits the emission peaking at 800 nm in G0B1T glass, and the excitation spectra monitored at 800 nm in G0B1T glass shows two excitation bands, viz. 468 nm (originating from the $^3\text{H}_6 \rightarrow ^1\text{G}_4$ transition), 688 nm (originating from the $^3\text{H}_6 \rightarrow ^3\text{F}_{2,3}$ transition).

An emission peak at 740 nm is observed in G0.5B0T glass, and the excitation spectra monitored at 740 nm in G0.5B0T glass show three excitation bands, viz., 280 nm, 380 nm, and a broadband from 490 nm to 650 nm peaking at 585 nm. From the previous work, the absorption band of the divalent bismuth in different glass matrix usually locate in the region of ultraviolet light, blue light and a broadband from 400 nm to 650 nm [12]. Three excitation bands corresponding to $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}(1)$, $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}(2)$ and $^2\text{P}_{1/2} \rightarrow ^2\text{S}_{1/2}$, can be usually detected in Bi^{2+} doped compounds. Accordingly, emission occurs via $^2\text{P}_{3/2}(1) \rightarrow ^2\text{P}_{1/2}$ transition. Usually the absorption band of $^2\text{P}_{1/2} \rightarrow ^2\text{S}_{1/2}$ lies between 231 and 286 nm, the absorption band of $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}(2)$ usually locates between 380 nm and 470 nm, and the absorption band of $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}(1)$ usually lies between 500 nm and 650 nm. The emission of

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