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Studies on Pr^{3+}–Yb^{3+} codoped ZBLA as rare earth down convertor glasses for solar cells encapsulation

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ABSTRACT

The non-absorption of photons with energies below the bandgap (E_g) and the thermalization of photons with energies higher than E_g are the dominant loss processes of single-junction solar cells. Rare earth doped glasses give the opportunity to convert the incident photons wavelength and hence to increase or decrease their energies. The conversion of photons energies by "up or down conversion" leads to the possibility to increase the efficiencies of all classes of single-junction solar cells. Depending on the nature of doping materials, two low energy photons can be converted into one high-energy photon (up-conversion), or one high energy photon, can be converted into two low energy photons (down-conversion). In this paper, Pr^{3+}–Yb^{3+} down-conversion co-doped ZBLA glasses were tested as encapsulation materials for silicon solar cells. The *J–V* characterizations were done under solar simulator irradiation. The influence of Yb^{3+} concentration on the solar cells performances was investigated, showing that an optimum value between 0.5 and 2 mol% conducts to an increase of the device efficiency comparing to mono-doped ZBLA material.

1. Introduction

Since the 50's, when the concept of the first semiconducting photovoltaic cell was experimentally proved, different materials and technologies have been tested in order to increase the conversion efficiencies and to reduce the production costs. For the industrial development of photovoltaic solar panels, many aspects should be taken into account such as: the materials and technology costs [1–9], the lifetime of materials and devices [10,11], the solar cells efficiency and the quality of encapsulation materials.

The efficiency of single-junction solar cells is limited by a series of optical and electrical losses. The dominant loss processes (more than 60%) is due to the mismatch between the broad solar spectrum and the mono-energetic absorption characteristics of the single gap semiconducting material. Due to the discrete band structure of semiconductors, only photons with energies close to bandgap energy (E_g) are efficiently absorbed and contribute to the electrical output of the solar cell. In order to reduce these spectral losses and increase the energy conversion efficacy, many strategies can be considered: multi-junction cells (multiple semiconductors stacked cells) [12–14], intermediate band semiconductors solar cells [15–17] or up and down converters [18–20].

The mechanisms of up-conversion, down-conversion or down shifting can be exploited in order to convert the infrared or ultraviolet light into visible light, which can thus be efficiently absorbed by the most of semiconducting materials used for solar cells. The increase of the number of absorbed photons leads to an increase of the generated electron–hole pairs number and thus to an increase of the generated photocurrent. Two configurations are possible: (1) front converter (the converter is placed on the top of the solar cell) and (2) rear converter (the converter is placed behind the solar cell). The configuration (1) is used in the case of down-conversion and down-shifting whereas the configuration (2) is used in both cases: up-conversion and down conversion. Up and down converters are based on rare earth doped materials which may modify the photons energies in order to adjust them to the corresponding value of the band gap of the active material [21]. By tuning the properties of the optical convertors in function of the optical band gap of the solar cell semiconductor, this concept can be used to improve the efficiency of all types of solar cells (Si, GaAS, CIS, CIGS, DSSC or OSC). The first theoretical studies on the

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improvement of solar cells efficiency by the use of energy convertors, were done by Trupke et al. [17,22]. The theoretical calculations show that the device efficiency can be increased in the following configurations: front down-converter, rear up-converter and rear down-convertor. The front up-converter configuration does not increase the device efficiency [23].

The phenomenon of "up and down conversion" has been demonstrated experimentally for rare earth (RE) doped materials (glass or crystal) under monochromatic laser radiation excitation, but only few experimental studies have been performed under solar simulator conditions [24–26]. A down-conversion process was revealed for the rare earth ions-pairs RE^{3+}–Yb^{3+} (RE = Pr, Tb, Tm). Owing to the broad absorption band of Pr^{3+} in the blue and the possible resonant energy transfer to Yb^{3+}, the Pr^{3+}–Yb^{3+} couple is of special interest. Indeed, the emission of Yb^{3+} (around 1000 nm) is close to the silicon bandgap (1.12 eV) and can thus be absorbed by silicon solar cell without any losses.

Besides, if a lot of work has been done concerning the improvement of the efficiency by the optimization of the of active materials properties, only a slight number of papers mention the importance of encapsulation glasses [27–31]. However, the losses in efficacy due to the encapsulation can reach 15–20%. The usual materials used for encapsulation are silica glasses and at our best knowledge there are not any studies on other glasses as encapsulation materials for photovoltaic solar cells.

In this paper we report for the first time the solar cells photoelectrical response under solar simulator irradiation using rare earth Pr^{3+}–Yb^{3+} co-doped ZBLA glasses as spectral front down-converter encapsulation material.

The dependency of the devices efficiency was studied in function of Yb^{3+} concentration.

2. Experimental

Fluorozirconate RE doped ZBLA glasses with molar composition $57ZrF_4$–$34BaF_2$–$5LaF_3$–$4AlF_3$–$0.5PrF_3$–$xYbF_3$ (from $x = 0$ to 10) were synthesized by a melting and quenching method starting from high purity fluorides (purity > 99.9%). The fluoride components were mixed and melted at 875 °C for 10 min in a dry glove box (H_2O = 1 ppm) under inert atmosphere (argon). After cooling, the samples were cut and polished in order to have the same dimensions and used as encapsulating glasses for silicon solar cells.

Current density–voltage (*J–V*) characteristics in the dark and under illumination were measured using a Keithley 236 source measurement unit. For cell characterization during illumination, a 100 mW/cm^2 white light from a AM 1.5 solar simulator (Steuernagel Solar constant 575) was used. Commercial Si solar cells (10 mm × 10 mm × 200 µm) were illuminated through different encapsulation glasses in the configuration described in Fig. 1. The front collecting electrode grid of the reference cell consists of silver paste electrodes having a 140 µm width. The distance between electrodes is 1.9 mm. The efficiency of the reference cell without encapsulation is about 8% for a delimited mask of 4 mm × 4 mm adapted to the samples dimensions. The *J–V* characteristics and efficiencies were calculated by considering the irradiation area delimited without subtracting the silver paste electrodes area. All measurements were done under argon atmosphere with less than 0.1 ppm oxygen and moisture. The optical properties of Pr^{3+}–Yb^{3+} co-doped ZBLA glasses were analyzed in the 300–2100 nm range using a Lambda 950 Perkin Elmer spectrophotometer with a resolution of 1.0 nm.

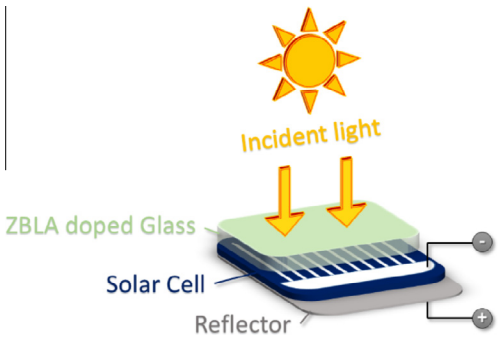

Fig. 1. *J–V* characteristics measurements configuration.

3. Results and discussion

The schematic energy levels diagrams of Pr^{3+} and Yb^{3+} ions and the possible energy transfer (ET) processes involved in the down-conversion mechanism are described in Fig. 2.

Taking into account that the Silicon band gap is 1.12 eV (1107 nm), photons having energies greater than or equal to 1.12 eV are absorbed but their energy is not exploited enough efficiently to create electron–hole pairs. In the case of Pr^{3+}–Yb^{3+} co-doped ZBLA glasses, photons having energies higher than 2.57 eV (482 nm) can be absorbed by Pr^{3+} ions and excite the levels $^3P_0$, $^3P_1$, and $^3P_2$. By successive des-excitation of these levels, two photons can be emitted. In the presence of Yb^{3+}, after the excitation of the levels $^3P_0$, $^3P_1$, or $^3P_2$ of Pr^{3+}, a depopulation of the excited state can occur through two sequential resonant ET steps between Pr^{3+} and Yb^{3+} with $^1G_4$ acting as the intermediate level by two routes [32,33]:

Route (1): first the obtained energy difference due to the transition Pr^{3+} ($^3P_0 \rightarrow {}^1G_4$) (as photon emission) is transferred to the $^2F_{5/2}$ level of Yb^{3+} then the transition Yb^{3+} ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) conducts to the emission of the first low energy photon (1.08–1.37 eV); secondly the Pr^{3+} ($^1G_4 \rightarrow {}^3H_4$) transition may conduct to the emission of the second low energy photon, either by Pr^{3+} or by Yb^{3+} whether a second ET occurs from Pr^{3+} to Yb^{3+}. If ET does not occur, the $^1G_4$ level Pr^{3+} can emit one low energy photon (1.19 eV) (Fig. 2).

Route (2): a cooperative down conversion occurs where the Pr^{3+} splits its excited state energy ($^3P_0$) in two, by simultaneous

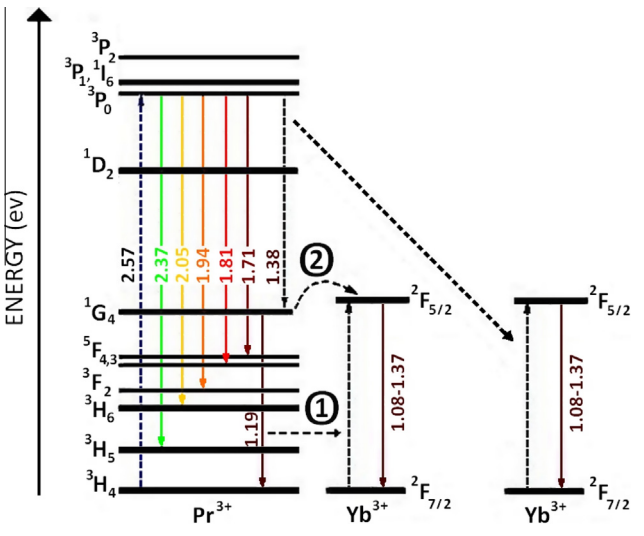

Fig. 2. Schematic energy level diagram of Pr^{3+} and Yb^{3+} ions explaining the energy transfer process between the dopants (a) route 1 and (b) route 2.