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#### Original research article

# Effect of annealing temperatures on luminescence properties in Ce<sup>3+</sup>-Yb<sup>3+</sup> codoped oxyfluoride glass-ceramics for solar cells



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#### ARTICLE INFO

Keywords: Ce<sup>3+</sup>/Yb<sup>3+</sup> Energy transfer Down-conversion Oxyfluoride glass ceramic Solar cell

#### ABSTRACT

An efficient near-infrared (NIR) down-conversion in  $Ce^{3^+}$ -Yb<sup>3+</sup> codoped oxyfluoride glass ceramics (GC) have been investigated with different annealing temperature. With an 430 nm ( $Ce^{3^+}$ :  $4f \rightarrow 5d$ ) excitation, the NIR emission at around 1000 nm ( $Yb^{3^+}$ :  $^2F_{5/2} \rightarrow ^2F_{7/2}$ ) was obtained which confirming efficient energy transfer between  $Ce^{3^+}$  ions and  $Yb^{3^+}$  ions. Subsequently, the possible mechanism of energy transfer was investigated and discussed. Finally, the energy conversion efficiency was measured which the Si solar cell covered by  $Ce^{3^+}$ -Yb<sup>3+</sup> codoped oxyfluoride GC. The maximum efficiency which increased by 0.3% indicated that the  $Ce^{3^+}$ /Yb<sup>3+</sup> sample had the potential applications for solar cells.

#### 1. Introduction

At present, solar cells are considered as the green and renewable energy, which can convert sun energy into useable forms directly. However, there is pretty huge factor limiting the efficiency of solar energy, which is so-called 'thermalization losses': the excess of energy of the absorbed UV and blue photons is dissipated as heat, largely because short wavelength region have a large energy mismatch with the response spectrum of silicon solar cells (Si-SC).

Down-conversion (DC) has provided a promising route for enhancing solar cell efficiency, which can convert the near-UV and blue photons (300–500 nm) to near-infrared (NIR) photons [1–3]. Two NIR photons can be obtained from conversion of one UV/blue photon. Moreover, energy losses by thermalization of electron hole pairs are minimized. A maximum conversion efficiency of 39.63% can be achieved in case of choosing the suitable DC material, well over the efficiency limit (29%) [4]. Rare earth (RE) doped materials are a promising way which can modify solar spectrum to enhance the energy conversion efficiency (ECE) of Si-SC, such as  $Tb^{3+}/Yb^{3+}$ ,  $Tm^{3+}/Yb^{3+}$  and  $Pr^{3+}/Yb^{3+}$  etc [5–10]. In these RE-doped materials,  $Yb^{3+}$  ions are generally selected as acceptors because they have a single excited state represented by symbol  ${}^2F_{5/2}$ , corresponding to emission spectrum at around 980 nm which matches to the band gap of Si–SC.

However, most RE ions generally show sharp line of spectra, such as  $Tb^{3+}$ ,  $Pr^{3+}$ ,  $Tm^{3+}$ ,  $Ho^{3+}$ ,  $Er^{3+}$ . These narrow spectra are associated with weak f-f electronic transitions, so that the transform of the sun spectrum is inefficient. Those for transition metal ions, which have shown broadband absorption and emission spectra, can also convert ultraviolet-visible sunlight to NIR spectra by means of  $Yb^{3+}$  ions. Unfortunately, transition metal ions may not be a good choice because they have low luminescence quantum yield due to the strong electron phonon coupling, though the luminescence spectrum shows a wide range [11,12].

Recently, NIR gain via DC has been widely witnessed in many RE ions doped oxyfluoride glass ceramics (GC). That is because oxyfluoride GC have low phonon energies compared with oxide glasses as well as excellent mechanical properties and chemical

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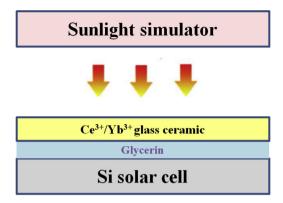


Fig. 1. Scheme of the DC solar cell device.

stability compared with fluoride glasses [13,14]. It is well known that the structure characteristic of oxyfluoride GC has a great effect on the DC efficiency. A much simpler strategy for enhancing DC is by controlled heat measurement.

Herein, we synthesized Ce<sup>3+</sup>/Yb<sup>3+</sup> codoped oxyfluoride GC containing CaF<sub>2</sub> nanocrystals as a function of annealing temperature. The dependence of the annealing temperature on the luminescence properties and ECE from the GC samples has been investigated.

#### 2. Experimental

A series of  $Ce^{3+}$ -Yb $^{3+}$  codoped oxyfluoride GC were prepared in our laboratory using the conventional melt quenching technique. The compositions of the glass samples were (in mol %):  $50SiO_2 - 15Al_2O_3 - 5BaCO_3 - 30CaF_2 - 0.5CeO_2 - 0.5Yb_2O_3$ . A 15 g reagent grade stoichiometric mixture of  $SiO_2$ ,  $Al_2O_3$ ,  $BaCO_3$ ,  $CaF_2$ ,  $CeO_2$ , and  $Yb_2O_3$  was mixed thoroughly and melted at 1450 C for 3 h in air atmosphere. The melt was poured onto a stainless-steel plate and then pressed by another plate to form precursor glasses. All the glasses were annealed at 400 °C for 2 h to remove thermal strains. Subsequently, four of these glasses were reheat-treated for 6 h at 610 °C, 620 °C, 630 °C and 640 °C, respectively, to form transparent GC. Finally, these samples were cut and polished in order to have the same dimension and used as DC solar cell devices for Si-SC.

DSC experiments were performed at an STA449C Jupiter (Netzsch, Germany) in an argon atmosphere at a heating rate of  $10\,\mathrm{K}$  min  $^{-1}$  in the range of 200–800 °C. The powder x-ray diffraction (XRD) profile was obtained on a Rigaku D/MAX-RA diffractometer with a Ni-filter and Cu K $\alpha$  ( =  $1.542\,\mathrm{\mathring{A}}$ ) radiation. The XRD patterns of the samples were collected in the range of 20 < 20 < 80. Optical absorption spectra ranging from 300 to 1100 nm were measured by a UV/VIS/NIR spectrophotometer (UV-3600, Shimadzu, Japan) at room temperature. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with a FS920 spectrophotometer (Edinburgh 6 Instruments) with a 450 W xenon lamp as the excitation source. To demonstrate the effect of DC glass plates on solar cell, the DC solar cell devices were fabricated, as depicted in Fig. 1. Glycerin was chosen as the filling layer to weaken the light scattering between the glass and solar cell. Current-voltage (I–V) measurements were performed under the Sunlight simulator (Keithley-2400).

#### 3. Results and discussion

Fig. 2 presents the DSC thermograms of the 0.5Ce<sup>3+</sup>-1Yb<sup>3+</sup> codoped 50SiO<sub>2</sub> - 15Al<sub>2</sub>O<sub>3</sub> - 5BaCO<sub>3</sub> -30CaF<sub>2</sub> glass sample. The glass

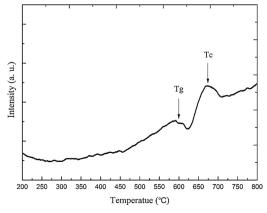


Fig. 2. DSC curve of the  $0.5Ce^{3+}$ – $1Yb^{3+}$  codoped glass sample.

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