Eu-doped LGF Luminescent Down Converter Possible for TiO_2 Dye Sensitized Solar Cells

Hyun-Ju Kim[a], Jae-Sung Song, Dong-Yun Lee, and Won-Jae Lee
Electric & Magnetic Devices Research Group, Korea Electrotechnology Research Institute, 28-1 Sungju-dong, Changwon, Gyeongnam 641-120, Korea

[a]E-mail : hjk9123@keri.re.kr

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For improving solar efficiencies, down conversion of high-energy photons to visible lights is discussed. The losses due to thermalization of charge carriers generated by the absorption of high–energy photons, can largely be reduced in a solar cell if more than one electron-hole pair can be generated per incident photon. The solar cell was constructed of dye-sensitized anatase-based TiO_2, approximately 30 nm particle size, 6 μm thickness, and 6 x 6 mm^2 active area, Pt counter electrode and I_3^-/I^- electrolyte. After correction for losses due to light reflection and absorption by the conducting glass, the conversion of photons to electric current is practically quantitative in the plateau region of the curves. The incident photon to current conversion efficiency(IPCE) of N3 used as a dye in this work is about 80 % at around 590 nm and 610 nm which is the emission spectrum of Eu doped LGF. The Eu doped LGF powder was prepared by conventional ceramic process, and used as a down converter for DSC after spin coated on the slide glass and fired.

Keywords : Down converter, Solar cell, Charge carrier, Photon, TiO_2

1. INTRODUCTION

The dye sensitized solar cell(DSC) consisting of nanocrystalline TiO_2 electrode, an electrolyte containing I^-/I_3^- redox couple, and Pt coated counter electrode is a promising alternative to the inorganic solar cell. The cell is based on the mechanism of a photoelectric generation and chemical reaction between electrodes and dye. The heating of charge carriers, which are generated by the absorption of high-energy photons, is one of the major loss mechanisms by which energy is wasted in conventional p-n junction type solar cells[1]. Instead of that, major loss of the dye sensitized solar cell is caused by the degredation of dye and electrolyte due to high-energy photons [2,3].

TiO_2 electrode has an anatase and rutile phases are well known to be formed as a meta-stable phase at temperatures lower than ~ 400 ℃ and as a thermodynamically stable phase at higher temperatures, respectively. Also, TiO_2 crystallines transforms anatase to rutile phase easily by high temperature treatment with inevitable growth of the particles size[4,5].

A luminescence converter that, in an ideal case, converts high-energy photons into two or more lower energy photons is located on the front surface of a dye-sensitized solar cell. The luminescence converter is insulated from the solar cell. The absorption of low energy photons emitted by the converter leads to the excitation of electrons in dye, so significant improvements of efficiency are predicted by locating of down converter in front of DSC[6].

In this study, the role of down converter in DSC. We used the $LiGdF_4$: Eu (LGF) prepared by a conventional ceramic process, as a down converting material, because that material has a sharp high-energy absorption spectra.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of phosphor

$LiGdF_4$: Eu (LGF) was prepared by a conventional ceramic processes. Firstly GdF_3(99.99 %, Aldrich), LiF (99.99 %, Aldrich), EuF_3(99.99 %, Aldrich) are thoroughly mixed in a mortar. A small excess of LiF referred to GdF_3 was added in order to compensate for the volatilization of that in synthesis process. The mixture was filled in an alumina crucible and located in a tube furnace. The tube of the furnace was evacuated and purged with dried argon especially at three times. Thereafter, the temperature of the furnace was raised to

650 ℃ and kept for 8h. Finally the synthesized sample was ground in a mortar and sieved through 325 mesh sieve. The formation of the phase was proven by XRD analysis. And the particle size and shapes of the sample were determined by SEM.

2.2 Constitution of dye sensitized solar cell

The screenprintable TiO_2 (Degusa P25) slurry was prepared by mixing 4-hydroxy benzoic acid (Merck,p.a.) with absolute ethanol(Merck,p.a.);TiO_2 powder was slowly added during mixing. This mixture was stirred until a homogeneous paste was formed. After milling, the ethanol was removed completely by vacuum decicator delivering a dry compact powder. This powder was dispersed with a kneader slowly in a mixture of 5 % ethylcellulose and anhydrous terpinol. After the mixture became homogeneous, terpinol was added to the dispersion and the needing was continued again until a homogeneous mixture was formed. The slurry was coated on ITO glass (8.3 ohm/sq, 88.2 % transmittance in the visible) using screen printer. The TiO_2 coated in ITO glass was annealed at 500 ℃ for 30min in air. After annealing, the thickness of TiO_2 film was about 6 μm.

In order to sensitize, TiO_2 electrodes were immersed in a solution of 0.02 mg/cc red dye (RuL2(NCS)2[L= 2,2'-bipyridine-4,4'-dicarboxylic acid] (N3) in absolute ethanol for 24h at room temperature, and rinsed by absolute ethanol. The transparent Pt counter electrodes were deposited on the ITO glass by DC-magnetron sputter under Pt target, 100 Watts sputter power, 5 mTorr working pressure and Ar gas atmosphere for 5 s. The Pt electrode and the dye-adsorbed TiO_2 electrode were bonded together, using adhesive, Solaronix SA (Amosil 4). The redox electrolyte containing I^-/I_3^- redox couple was introduced into the solar cell by capillary effect, having approximately 40μm thickness between two electrodes. The gap was sealed with small amounts of sealant, Amosil 4.

A schematic representation of a solar cell system in combination with a down-converter proposed by T. Trupke *et al.*[1] is shown in Fig. 1. A luminescence converter that, in an ideal case, converts high-energy photons into two or more lower energy photons is located on the front surface of a conventional single junction solar cell. Spin coated LGF on the slide glass was used as a luminescence converter after annealed at 450 ℃ in Ar atmosphere for 30 min.

2.3 Measurements

X-ray diffraction(XRD) and scanning electron microscopy(SEM) were employed for the characterization of crystal structure and microstructure of the powders and films. A short-circuit photo-current (J_{sc}) and an open-circuit voltage(V_{oc}) were measured using KERI-made program-attached monochromator and Keithley 2400 source meter. Also, current-voltage(I-V) curve and leakage current–bias field of DSC and front down conversion DSC as a function of incident wavelength were measured.

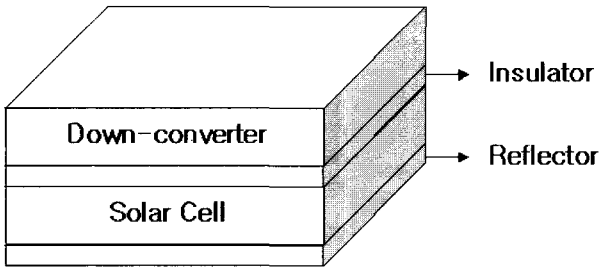

Fig. 1. Schematic diagram of front down conversion dye sensitized solar cell [1].

3. RESULTS AND DISCUSSION

As a halide complexes, the most common species is the MRX4 complexes (where M denotes an alkali atom, R a rare-earth atom, and X a halogen atom). We had attention on $LiGdF_4$ crystal singly doped with Eu^{3+}, because the crystal had a sharp excitation spectrum at long wavelength in contrast to another MRX4 complexes such as K_3GdF_6 and $K_5Li_2GdF_{10}$ crystals. Ultra violet (UV) excitation and emission spectra of 1.5 % Eu doped LGF crystal are shown in Fig. 2

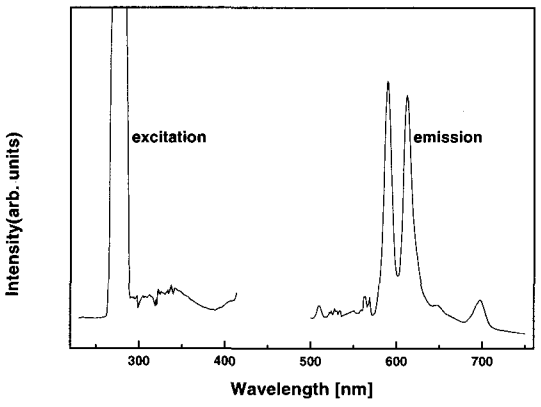

Fig. 2. Excitation and emission spectra of Eu-doped $LiGdF_4$ powder.

The excitation spectrum of LGF appeared at around 275 nm assigned to transition from the ground 8S7/2 state to the 6IJ multiplets of Gd^{3+}. Excitation into the 6IJ multiplets brought about strong luminescence as can be seen in emission spectrum appeared at around 590 nm and 610 nm in Fig. 2. The emission lines are associated

of Eu^{3+}. The process of excitation energy transfer from Gd^{3+} to Eu^{3+} is progressed in a two-step. As a consequence, the excitation of one gadolinium ion is transferred to two europium ions, which relaxed by radiative transitions in the visible region. The XRD pattern of Eu-doped LGF powder prepared by a conventional mix and firing procedure, was analyzed and indexed. And the results are shown in Fig. 3. As can be seen in Fig. 3, the main phase is pure $LiGdF_4$ (tetragonal) and phase of $LiEuF_4$ (tetragonal) exists as a minor phase. Fig. 4 shows the SEM image of the morphologies of the LGF:Eu powder. The apparent morphologies of the powders show that the primary particle size is around 0.5 μm and the agglomeration and an irregular shape appear in the secondary particle. And the particle size of the secondary particle is larger than that of primary particle as about 6 μm.

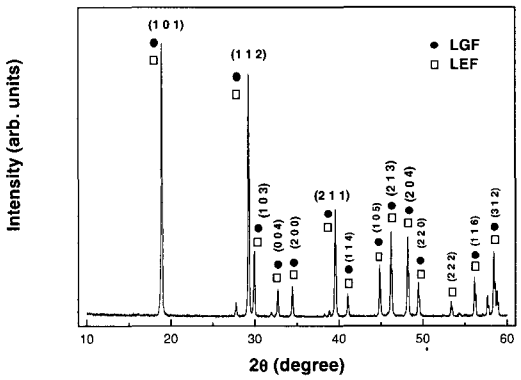

Fig. 3. XRD pattern of Eu-doped $LiGdF_4$ powder.

Fig. 4. SEM image of Eu doped $LiGaF_4$ powder.

The measuring system consists of 1mW-generated halogen lamp as a light source, grating monochromator, a lock in amplifier, voltage source, and current meter. Photocurrent at various wavelength as a function of potential of the cell was measured and shown in Fig. 5.

Monochromatic efficiencies of solar cells were calculated, using the following equations.

$$E_{eff} = V_{oc} \times J_{sc} \times FF/P_i, \quad (1)$$

Where, V_{oc} = open circuit potential, J_{sc} = short circuit photocurrent density, and P_i = incident light intensity,

$$FF = (V \times J)_{max}/(V_{oc} \times J_{sc}) \quad (2)$$

where, FF = fill factor.

At the wavelength of 550 nm, open circuit potential was approximately 0.75 Volt, the short circuit photocurrent density was 1.57 mA/ cm^2, and fill factor was around 50.3 %. And 5.6 mW/cm^2 incident light intensity beam was used as a light source. From this results, the calculated monochromatic efficiency at the wavelength of 550 nm of this cell was about 9.62 %.

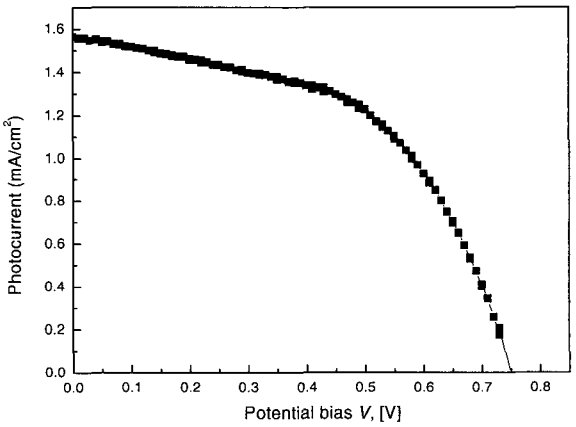

Fig. 5. Photocurrent at 550 nm as a function of potential of the ITO glass/ Ru-red dye-absorbed TiO_2/ Iodine electrolyte/ sputtered Pt / ITO glass structured solar cell.

The incident photon to current conversion efficiency (IPCE) of DSC by N3 and black dye as a function of excitation wavelength plotted by A. Hagfeldt and M. Gratzel[7] is shown in Fig. 6. Two species of dye , N3 and black dye are compared. Both chromophores show very high IPCE values in the visible range. After correction for losses due to light reflection and absorption by the conducting glass, the conversion of photons to electric current is practically quantitative in the plateau region of the curves. The IPCE of N3 which was used as a dye in this work is about 80 % at around 590 nm and 610 nm which is the emission spectrum of Eu doped LGF. From this results, we can expect efficiency increases of DSC by using of Eu doped LGF as a down-converter in the front side of the cell.

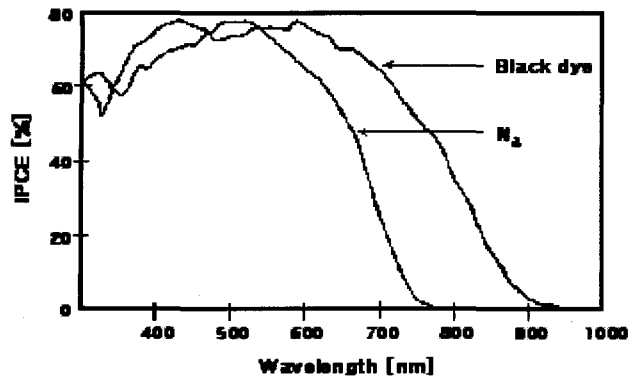

Fig. 6. Incident photon to current conversion efficiency (IPCE) of DSC by N3 and black dye as a function of excitation wavelength[7].

4. CONCLUSION

The dye sensitized solar cell (DSC) consisting of nanocrystalline TiO_2 electrode, an electrolyte containing I^-/I_3^- redox couple, and a Pt-coated counter electrode is a promising alternative to the inorganic solar cell. And down conversion of high energy to the lower energy to increase the cell efficiency was studied. ITO glass/Ru-red dye-absorbed TiO_2/Iodine electrolyte/sputtered Pt/ITO glass structured cell had an open circuit potential of approximately 0.75 Volt, the short circuit photocurrent density of 1.57 mA/cm^2, and fill factor of around 50.3 % at the excitation wavelength of 550nm. And 5.6 mW/cm^2 incident light intensity beam was used as a light source. From this result, the calculated monochromatic efficiency at the wavelength of 550 nm of this cell was about 9.62 %. After correction for losses due to light reflection and absorption by the conducting glass, the conversion of photons to electric current is practically quantitative in the plateau region of the curves. The IPCE of N3 used as a dye in this work is about 80 % at around 590 nm and 610 nm which is the emission spectrum of Eu doped LGF. From this results, we can expect efficiency increases of DSC by using of Eu - doped LGF as a down-converter in the front side of the cell.

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