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Luminescent borate glass for efficiency enhancement of CdTe solar cells

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ABSTRACT

Rare-earth (RE) doped borate glasses are investigated for their potential as photon down-shifting cover glass for CdTe solar cells. The barium borate base glass is doped with trivalent rare-earth ions such as Sm^{3+}, Eu^{3+}, and Tb^{3+} showing an intense luminescence in the red (Sm^{3+}, Eu^{3+}) and green (Tb^{3+}) spectral range upon excitation in the ultraviolet and blue. Additionally, the glasses are double-doped with two RE ions for a broad-band absorption. The gain in short-circuit current density of CdTe solar cells with different thicknesses of the CdS buffer layer is calculated. Though the single-doped glasses already reveal a slight increase in short-circuit current density, the double-doped glasses allow for higher efficiency gains since a significant broader spectral range is covered for absorption. For a Tb^{3+}/Eu^{3+} double-doped glass with a RE doping level of 1 at% each, an efficiency increase of 1.32% can be achieved.

1. Introduction

Photovoltaic devices have a poor spectral response in the short-wavelength spectral range due to absorption or thermalization losses in the front layers. In particular for CdTe modules, the CdS layer with a band gap energy of 2.4 eV strongly absorbs ultraviolet (UV) and blue light. One possibility to overcome this low external quantum efficiency (EQE) at short wavelengths is to modify the solar spectrum by applying a luminescent layer on top of the solar cell to absorb high energy photons and to emit low energy photons in the visible spectral range. This application was first described by Hovel et al. [1].

Over the decades many models have been developed to calculate the theoretical efficiency limits of a solar cell with a frequency down-shifter on top. The best-known model has been proposed by Trupke et al. [2], assuming an ideal down-converter, equal refractive index of converter and solar cell of $n=3.6$, and neglecting reflection losses. The maximum efficiency increases for black-body radiation from 30.9% for a conventional solar cell to 38.6% with down-shifter in front of an absorber with a band gap of 1.1 eV. For a CdTe solar cell with a band gap energy of 1.45 eV the efficiency increases from 30.5% to 36% [2]. Improving this model by considering reflection losses at the interfaces [3] results in an efficiency increase from 21% for the conventional cell with a band gap energy of 1.1 eV to 26% for a cell with an ideal down-converter on top. For solar cells with a band gap energy of 1.45 eV the efficiency can be increased to 23.5%. Applying anti-reflective coating to the model has only little impact on the maximal efficiency [4]. Calculations with a more realistic down-shifter were performed by Richards et al. [5]. Absorption and emission spectra of luminescent dyes are included in the calculation. The efficiency of the CdTe module with a doped PMMA (polymethyl methacrylat) sheet in front could be increased to 11.2% compared to a module covered with an undoped PMMA sheet with an efficiency of 9.6%. These calculations make the application of a down-shifter attractive for photovoltaic devices.

In this work, luminescent barium borate glass is investigated for its potential as photon down-shifting superstrate for CdTe thin film solar cells. The glass is activated by additional doping with rare-earth (RE) ions such as Sm^{3+}, Eu^{3+}, and Tb^{3+}. Calculations are performed to reveal the maximal efficiency gain for CdTe solar cells with a CdS buffer layer thickness of 45 and 300 nm.

2. Experimental details

Borate glasses using barium oxide as a network modifier were prepared. A ratio of two moles of boron oxide (B_2O_3) and one mole of barium oxide (BaO) was used. In this ratio the glass network consists of the highest possible amount of four-coordinated boron [6]. The

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glasses were additionally doped with samarium oxide (Sm_2O_3), europium oxide (Eu_2O_3), and terbium oxide (Tb_2O_3). Single-doped (i.e. only one RE ion) and double-doped glasses (i.e. two different RE ions) were prepared. The exact composition of the different samples is listed in Table 1. The chemicals were weighed in a platinum gold crucible (Pt/Au 95/5) and melted at 1100 °C for approximately 3 h. The melt was then poured onto a brass block at 500 °C which is below the glass transition temperature of barium borate glasses of T_g=605 °C [7]. The glass was kept at this temperature for 3 h to eliminate residual mechanical and thermal stresses before being slowly cooled to room temperature. The glass was then cut into squares of 20 mm × 20 mm with a thickness of 3.2 mm and polished to optical quality (Fig. 1).

Transmission spectra were recorded with a UV/Vis/NIR spectrophotometer (Perkin Elmer Lambda 1050) coupled to a 150 mm integrating sphere with tungsten halogen and deuterium lamps as light sources and photomultiplier (Hamamatsu R6872) and peltier-cooled InGaAs diode as detectors. Absolute photoluminescence quantum efficiency measurements were performed with a C9920-02G system (Hamamatsu) coupled to a 3.3 in integrating sphere with a xenon lamp (150 W) as excitation source and a photonic multichannel analyzer (PMA 12) as a detector. The setup has a measurement accuracy of approx. ±5%. The quantum efficiency is determined from emission spectra in the spectral range from 500 to 900 nm for Sm^{3+} and Eu^{3+}, and from 470 to 900 nm for Tb^{3+}.

Table 1
Nominal composition of the investigated samples and quantum efficiency, QE, at 402 nm (Sm^{3+}), 464 nm (Eu^{3+} and double-doped), and 484 nm (Tb^{3+}).

Dopant	Composition/mol%			RE-content/at%	QE/%
	B_2O_3	BaO	RE_2O_3		
Sm^{3+}	66.47	33.23	0.3	0.15	31
	66.33	33.17	0.5	0.25	19
	66.00	33.00	1.0	0.50	10
	65.33	32.67	2.0	1.00	2
Eu^{3+}	66.00	33.00	1.0	0.50	82
	65.33	32.67	2.0	1.00	87
	64.66	32.33	3.0	1.50	82
	63.33	31.66	5.0	2.50	87
Tb^{3+}	66.00	33.00	1.0	0.50	64
	65.33	32.67	2.0	1.00	75
	64.66	32.33	3.0	1.50	75
	63.33	31.66	5.0	2.50	70
Sm^{3+}/Eu^{3+}	65.33	32.67	1/1	0.5/0.5	26
Tb^{3+}/Eu^{3+}	65.33	32.67	1/1	0.5/0.5	86
	64.00	32.00	2/2	1/1	81

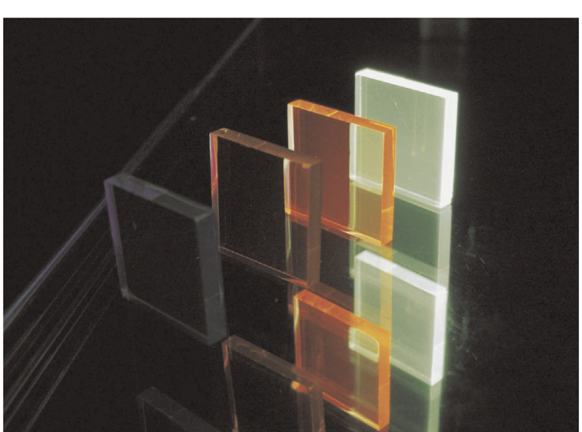

Fig. 1. RE-free reference sample and RE-doped barium borate glasses (from left): reference sample, Sm^{3+}, Eu^{3+} and Tb^{3+} with a concentration of 0.5 at% each under excitation with UV light.

3. Results and discussion

3.1. Rare-earth ion absorption and luminescence quantum efficiency

The transmission spectra of barium borate glass doped with 0.5 at% Sm^{3+}, Eu^{3+}, and Tb^{3+} and a sample thickness of 3.2 mm are shown in Fig. 2. The typical Sm^{3+} related absorption bands (Fig. 2a) result from transitions from the ground state level $^6H_{5/2}$ to the excited states $^4K_{15/2}$, $^4D_{1/2}$, $^4D_{3/2}$, $^6P_{5/2}$, and $^4G_{7/2}$ (344–475 nm). Eu^{3+} related absorption bands (Fig. 2b) can be attributed to transitions from the ground state level $^7F_0$ to the excited states $^5H_4$, $^5D_4$, $^5G_2$, $^5L_6$, $^5D_2$, and $^5D_1$ (319–532 nm). Tb^{3+} related absorption bands (Fig. 2c) result from transitions from the ground state level $^7F_6$ to the excited states $^5H_7$, $^5D_2$, $^5G_5$, $^5G_6$, and $^5D_4$ (317–484 nm). The transmission spectrum of the rare-earth free reference sample is shown for comparison. See Dieke et al. [8] for detailed information on the various energy levels.

The absorption coefficient for the most intense absorption transitions is shown in Fig. 2d; for doping levels up to 1 at% for Sm^{3+} and 2.5 at% for Eu^{3+} and Tb^{3+}, a clear linear dependence is found. The absorption coefficient of Sm^{3+} is more than three times higher than that of Eu^{3+}; Tb^{3+} has the lowest absorption coefficient.

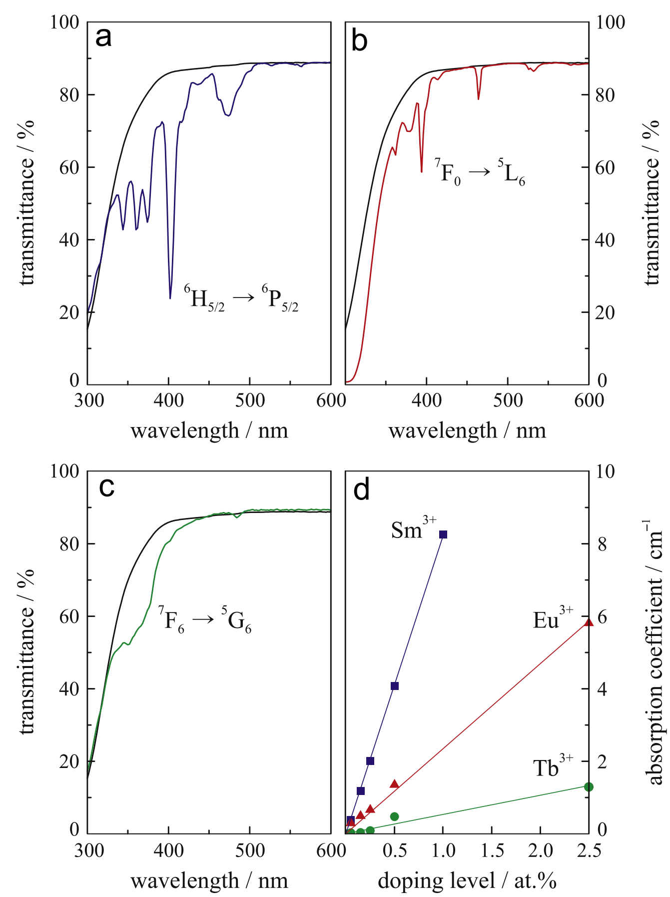

Fig. 2. Transmittance of (a) Sm^{3+}, (b) Eu^{3+}, and (c) Tb^{3+} doped barium borate glasses. The RE doping level is 0.5 at%, the sample thickness 3.2 mm. The transmittance of rare-earth free reference glass is shown for comparison (black curve). (d) Absorption coefficient for Sm^{3+} (squares), Eu^{3+} (triangles), and Tb^{3+} doping (circles) for a wavelength of 402, 393, and 378 nm, respectively. The solid lines represent the result of a linear fit.