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Optimizing Er/Yb ratio and content in Er–Yb co-doped glass-ceramics for enhancement of the up- and down-conversion luminescence

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ABSTRACT

Er^{3+}–Yb^{3+} co-doped transparent glass-ceramics with varying Er/Yb content and ratio have been prepared. High quantum yields for up- and down-conversion luminescence by energy transfer from Yb^{3+} to Er^{3+} and from Er^{3+} to Yb^{3+}, respectively, have been detected and optimized with respect to the Er/Yb content and ratio, and proposed in particular for up- and down-conversion of solar spectrum for enhancement of the efficiency of solar cells. The rise and decay kinetics for the population of the excited levels of Er^{3+} and Yb^{3+} have been studied and fit. Based on these experimental data, the mechanisms for the energy transfers have been suggested with emphasis on the optimized Er/Yb content and ratio for enhancement of the efficiency of the $Er^{3+} \leftrightarrow Yb^{3+}$ energy transfers.

1. Introduction

The Shockley–Queisser criterion states that the maximum efficiency of silicon solar cells cannot exceed 30% [1,2]. The up-conversion [3–6 and Refs. therein] and down-conversion [7–12 and Refs. therein] layers applied to the back and front surfaces of the solar cells, respectively, have been proposed for overcoming the above criterion, potentially resulting in the enhanced efficiency of the solar cells.

The $Er^{3+}-Yb^{3+}$ co-doped hosts have been proposed for obtaining up-conversion and down-conversion luminescence by energy transfer from Yb^{3+} to Er^{3+} [4,13–15 and Refs. therein] and from Er^{3+} to Yb^{3+} [9], respectively. The quantum yield for the up- and down-conversion luminescence has been found to be strongest for the fluoride/halide hosts for the following reasons [4–6,9,13–15]: (i) ionic bonding of fluorides/halides allows high doping level with rare earths resulting in short inter-dopant distances and therefore in high energy transfer rate between $Er \leftrightarrow Yb$ and (ii) low phonon energy of fluorides, such as 250 cm^{-1} in PbF_2 or 340 cm^{-1} in $NaYF_4$, which prevents a non-radiative losses of energy in the excited states of rare-earth dopants. As far as the iodine and bromide hosts are not durable, the fluorides hosts, such as PbF_2:$Er^{3+}-Yb^{3+}$ nanocrystals embedded in oxyfluoride glass matrix, e.g. in [9,13,15 and Refs. therein] or micro-crystalline $NaYF_4$:$Er^{3+}-Yb^{3+}$, e.g. in [4,14 and Refs. therein], have been considered as most promising hosts for the $Er^{3+}-Yb^{3+}$ co-doping aiming at the highest quantum yields for up- and down-conversion luminescence. In particular, the theoretical maxima of the quantum yield for the up- and down-conversion luminescence, of 50% [13] and 200% [9], respectively, may be nearly approached in the case of PbF_2:$Er^{3+}-Yb^{3+}$ nanocrystals embedded in transparent glass-ceramics host. More examples of efficient up-conversion luminescence materials/nanoparticles have been presented in a recent review [16].

Optimizing the content and ratio of Er/Yb dopants is of major importance because these parameters will define the total effectiveness of the device which may explore the Er–Yb co-doped material. In this work, we have prepared transparent glass-ceramics samples doped with different content and ratio of Er^{3+}/Yb^{3+} dopants dispersed in the PbF_2 nanocrystals embedded in the oxyfluoride glass host. The content and ratio have been optimized for the purpose of enhancement of the up- and down-conversion luminescence of the dopants aiming in particular at the, respectively, efficient up- and down-conversion of solar spectrum for enhancement of light-to-current conversion efficiency of solar cells. The rise and decay times for the population of the excited levels of Er^{3+} and Yb^{3+} have been studied and fitted and the mechanisms for the $Er \leftrightarrow Yb$ energy transfers have been suggested.

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2. Experimental

The nano-scaled oxyfluoride glass-ceramics co-doped with Er^{3+} and Yb^{3+} ions, have been obtained on heat treatment of their precursor glasses with chemical formula $33(SiO_2)9(AlO_{1.5})32(CdF_2)22(PbF_2)4.0(ZnF_2):x(ErF_3):z(YbF_3)$, mol%; the preparation procedure for these oxyfluoride glass-ceramics has been described elsewhere [17]. When progressively doping with x and z mol% of ErF_3 and YbF_3, respectively, other chemical components in the precursor glass formula were decrease proportionally. The obtained glass-ceramics will be further identified according to the doping levels x and z of their precursor glasses as xEr:zYb, respectively.

Fig. 1(a) shows a photograph of several pieces of bulk glass-ceramics and Fig. 1(b,c,d) depict transmission electron microscope images (TEM) of three glass-ceramics with post-signed doping levels. The pink color of glass-ceramics is due to Er dopant. The black spots in TEM images correspond to PbF_2 based nanocrystals co-doped with Er and Yb, as they have been identified by the selected area electron diffraction (SAED) patterns and TEM energy dispersion X-ray spectroscopy (TEM EDX); examples are given in [13,17,18]. The doping level of the nanocrystals, when dispersed within the glass-ceramics, has been estimated to be about three times higher than in the precursor glasses [13,18] because the rare-earth dopants nucleate the growth of the PbF_2 nanocrystals on heat treatment of the precursor glasses [17] and aggregate only within these nanocrystals while being homogeneously dispersed in the precursor glasses [13,17,18 and Refs. therein]. The refractive index of these tiny PbF_2-based nanocrystals matches the refractive index of glass-ceramics at about $n=1.75$. Due to the matching and small diameter of the nanocrystals, below 10 nm, these glass-ceramics are highly transparent [17].

The nanocrystals are random and homogeneously dispersed in Fig. 1(b,c) whilst the nanocrystals tend to make larger clusters in more heavily doped sample in Fig. 1(d). Also, increasing of total doping level results in a reduction of the nanocrystals size, from Fig. 2(b)–(d). This reduction is ascribed here to the decrease in superionic conductivity of PbF_2 by progressive doping with rare-earth ions, which results in shortening of the diffusion length of fluorine ions in the PbF_2 matrix, while this diffusion length determines the size of the PbF_2 nanocrystals [15,19 and Refs. therein]. The clustering of PbF_2 nanocrystals observed in Fig. 1(d) may be due to increase in the surface tension with decrease in the diameter of the nano-crystals, which is relaxed by formation of larger clusters of nanocrystals.

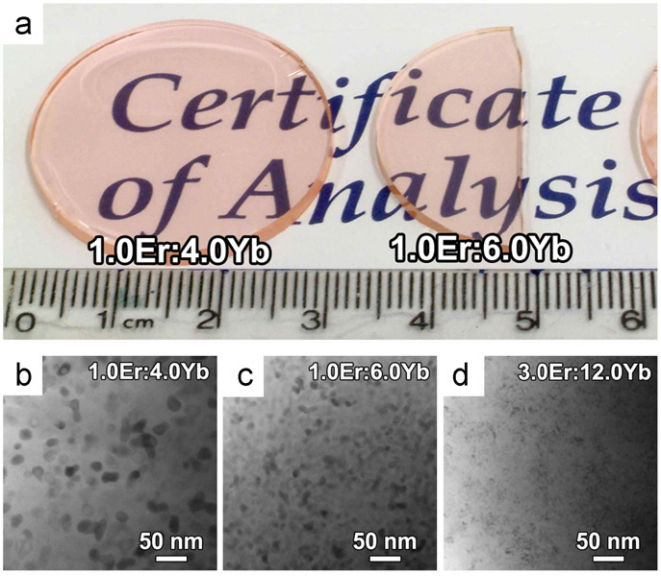

Fig. 1. (a) Photograph of pieces of glass-ceramics and (b, c, d) TEM images of the fragments of the glass-ceramics with post-signed co-doping levels.

The steady-state and transient luminescence experiments have been carried out using the Edinburgh 920S and SPEX 1680 spectrometers, and visible and infrared photomultipliers, as described elsewhere [4,9 and Refs. therein]. The sample size was typically about $3\times1\times0.1$ cm^3, their area was larger than the diameter of excitation beam and they all were measured in the same experimental geometry ensuring the option to compare the relative intensities of the different samples. The spectral response of the setups has been taken into account.

The quantum efficiency of luminescence of Yb^{3+} and Er^{3+} dopants in this glass-ceramics host was estimated by comparison with the efficiency of a "standard" rare-earth ion Eu^{3+} doped in the same glass-ceramics host; the respective Eu^{3+} spectra were shown in our previous work [20]. The Eu^{3+} standard phosphor is well known to have a quantum yield of about 75% independent of the hosting material due to very large energy gap between the involved energy levels of Eu^{3+}, e.g. in [20 and Refs. therein]. We have found that, when doped in our glass-ceramics host, the red standard, "phosphor", emission bands of Eu^{3+} have the similar intensity to the 1.0 μm emission band of Yb^{3+} in the Er–Yb co-doped glass-ceramics (a spectral response of equipment was taken into account, see further in Fig. 4(a)). In both cases, pumping was done at similar wavelengths of 390 (for Eu^{3+}) and 378 (for Er^{3+}) nm to ensure similar absorption coefficients for the incident light for these two dopants. This experimental result indicates that the total yield in the 1.0 (Yb^{3+}) and 1.5 (Er^{3+}) μm emission bands in the Er–Yb co-doped glass-ceramics is higher than 140%, because they have the similar intensities at such pump, Fig. 4(a). Taking into account that, at the pump of 378 nm, the Er–Yb co-doped glass ceramics does also emit third emission band in the red at about 660 nm, with intensity similar to the 1.0 and 1.5 μm emission bands, Fig. 4(a), the total quantum yield for the emission of Er–Yb glass-ceramics approached 200% at such pump, in agreement with other estimates presented further in this paper.

It is worth noting that the Eu^{3+} doped polymer film developed at Hitachi and Mitsubishi Co, Ref. [7], did already experimentally show an extra current in Si solar cells due to down-conversion of solar spectrum by this Eu^{3+} doped polymer film deposited on the top of the Si solar cell. The above comparison and notification indicate that the Er–Yb co-doped glass-ceramics reported in this paper can be used for enhancement of the energy conversion efficiency of Si solar cells due to down-conversion of solar spectrum.

3. Results and discussion

3.1. Up-conversion luminescence spectra

Fig. 2(a) shows up-conversion luminescence spectra of glass-ceramics with different Er/Yb contents and ratio, when pumped at about 980 nm by a weak monochromatic radiation of unfocused Xe-lamp formed by a monochromator of Edinburgh FS920 spectrometer with a spectral band width of 10 nm. Such radiation of Xe-lamp produces the pump power density of about 1 mW/cm^2 [5], which is similar to the power density of solar radiation in the same spectral range and width, e.g. in [2]. This pump occurs mostly into absorption band $^2F_{7/2}\rightarrow{}^2F_{5/2}$ of Yb^{3+}, as shown in diagram of Fig. 2(b), and to the much lower degree into absorption band $^4I_{15/2}\rightarrow{}^4I_{9/2}$ of Er^{3+}. It is because the absorption cross-section of the former band of Yb^{3+} is several times larger than for