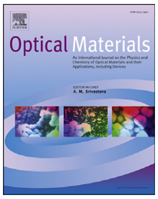
Optical Materials 75 (2018) 465–470

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Photoluminescence properties of Mn^{2+}/Yb^{3+} co-doped oxyfluoride glasses for solar cells application

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ARTICLE INFO

Article history:
Received 3 July 2017
Received in revised form
31 October 2017
Accepted 6 November 2017

Keywords:
Mn^{2+}/Yb^{3+}
Down-conversion
Energy transfer
Oxyfluoride glasses
Solar cells

ABSTRACT

Mn^{2+}/Yb^{3+} co-doped oxyfluoride glasses were facilely synthesized in the SiO_2–Al_2O_3–Na_2O–CaF_2 system. Partial crystallization processed during the preparation of the glasses, by which small amounts of CaF_2 nano-crystals were formed. Under ultraviolet and blue (370–500 nm) light excitation, an efficient down-conversion involving the emission of near-infrared is realized in the Mn^{2+}/Yb^{3+} co-doped oxyfluoride glasses. The near-infrared emission peaks mainly at 976 nm and secondarily at 1020 nm, which is a comfortable match with the band gap of c-Si. The variation in visible and near-infrared spectra and the decay curves of Mn^{2+}:$^4T_1 \rightarrow {}^6A_1$ emission have been investigated to verify the possible energy transfer from Mn^{2+} ions to Yb^{3+} ions. On analyzing the energy transfer processes theoretically and experimentally, we propose that quantum cutting and down-shifting processes may occur simultaneously in the samples. We suggest that the Mn^{2+}-Yb^{3+} co-doped materials can provide a novel direction to realize UV–Vis to NIR down-conversion for Si solar cells.

1. Introduction

The worldwide long-term energy demand, together with the decreasing supply of fossil fuels has driven the development of energy from renewable sources, such as wind, solar, geothermal heat and so on [1–3]. As solar resource is affordable, inexhaustible and clean, the development of solar energy technologies will have huge longer-term advantages. Photovoltaic solar cells can directly convert the solar energy into electricity based on the photovoltaic effect, which represents a promising approach to sustainable energy generation [4–6]. At present, the commercial crystalline silicon (c-Si) solar cell only has an efficiency of 18%. The spectral mismatch between the response solar spectrum and the band gap of the semiconductor silicon is one of the most important reasons. While the maximum response to silicon solar cell is around 800–1100 nm, the response of shorter wavelength region becomes quite weak, especially in the 300–500 nm region. However, the solar energy intensity is still very strong in this region, even stronger than the near-infrared (NIR) region. An ability to use this part of the radiation to convert to the NIR could effectively improve the efficiency of a single junction c-Si solar cell up to 40%, well over the efficiency limit (29%) estimated by Shockley and Queisser [7].

A promising way towards attaining this goal is by using the NIR down-conversion (DC) materials. Based on whether the quantum efficiency can be higher than 100%, down-conversion process can be reached by two possible routes, i.e. down-shifting (DS) and quantum cutting (QC). By combining DC layers with the solar cell, the cell can absorb additional energy that down converting from higher energy UV and visible (Vis) photons into NIR lower energy photons [8]. There are numerous efforts reported for NIR QC, such as rare-earth (RE) -Yb^{3+} co-doped systems (RE = Tm^{3+}, Tb^{3+}, Pr^{3+}, Ho^{3+}, Er^{3+} or Nd^{3+}) or Ce^{3+}/Eu^{2+}-Yb^{3+} co-doped materials [8–13], in which RE^{3+} or Ce^{3+}/Eu^{2+} ions act as donors to UV–Vis and transfer their energy to Yb^{3+} to produce near-infrared emission. However, the sensitizers (Tb^{3+}, Tm^{3+}, Pr^{3+}, Ho^{3+}, Er^{3+} and Nd^{3+}) exhibit naturally narrow absorption bands and weak absorption cross-section in the UV/blue region, due to the characteristic forbidden 4f-4f transitions. Ce^{3+} and Eu^{2+} ions might be a good broadband sensitizer for Yb^{3+}, yet the DC process may be complicated as the energy transfer (ET) from Ce^{3+}, Eu^{2+} to Yb^{3+} is possibly a metal-to-metal charge transfer through a facile redox reaction [14,15]. Thus, the NIR emission may weak due to the presence of reduction states like Yb^{2+}.

As one of the transition metal ion, Mn^{2+} ions play an important role in inorganic phosphors. It can produce a broad emission owing to the forbidden d–d transition from $^4T_1$–$^6A_1$ level. The emission

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https://doi.org/10.1016/j.optmat.2017.11.009

color varies from green to red, affecting by the crystal field strength and the coordination number of Mn^{2+} in host materials. At present, many Ce^{3+}/Mn^{2+} and Eu^{3+}/Mn^{2+} co-doped red luminescence materials have been studied, such as phosphors, glass or glass-ceramics materials [16–20]. Furthermore, Mn^{2+}/Yb^{3+} co-doped phosphors have also been reported and led to some results in the search for novel UC materials and process [21–24]. Gao et al. reported that Mn^{2+} can be an efficient sensitizer for intense NIR emission of Yb^{3+} in the Zn_2GeO_4 host lattice [25]. But there is little report about Mn^{2+}/Yb^{3+} co-doped transparent glass serving as DC layer for c-Si solar cells.

Herein, we report on the preparation and measurement of Mn^{2+}/Yb^{3+} co-doped SiO_2–Al_2O_3–Na_2O–CaF_2 glasses. Among the glasses systems, the oxyfluoride glasses have the advantages of high chemical and mechanical stabilities and the balance of the relative low phonon energy and good stability. A broadband UV–Vis (370–500 nm) to NIR DC phenomenon can be achieved by ET from Mn^{2+} to Yb^{3+}. The possible existence of ET from Mn^{2+} to Yb^{3+} has been proposed by the excitation spectra, Vis and NIR emission spectra, and luminescence decay curves of Mn^{2+}. The involved ET mechanism and possible transfer routine have been analyzed. The highest quantum efficiency (QE) approached up to 145.3%.

2. Experimental

The glasses with composition of $55SiO_2$-$20Al_2O_3$-$5Na_2CO_3$-$20CaF_2$ (in mol%) was prepared by melt-quenching method. The starting materials used for the preparation of the oxyfluoride glasses were analytical grade reagents (99.0% pure) of SiO_2, Al_2O_3, Na_2CO_3 and CaF_2. Mn^{2+} and Yb^{3+} ions were introduced by $MnCO_3$ (99.9% pure) and Yb_2O_3 (99.99% pure). The $MnCO_3$ doped content was set as 0.5 mol%. The Yb^{3+} concentration changed from 0, 0.5, 1, 2 and 4 mol%, and the corresponding samples were named by G:Mn0.5-Yb0, 0.5, 1, 2, and 4 respectively.

The glasses were fabricated by the conventional melt-quenching method with the following procedure. The chemicals were weighed in 10 g batch and thoroughly mixed using an agate mortar with a pestle. Then each of those was collected into an alumina crucible for sintering them in muffle furnace in air for 100 min at 1450 °C. The glass melts were subsequently poured in the pre-heated copper mold (two smooth surface brass plates) and then pressed to a thickness of slightly thicker than 2 mm. The glasses rapidly came into shape. The glasses were subsequently annealed at 500 °C for 180 min to avoid undesirable thermal stresses. The glasses had the potential to form glass-ceramics through crystallization after reheat treatment. Yet the glass-ceramics samples became less transparency than the corresponding precursor glass samples. Apart from simplification of the preparation process, the glass samples had a higher transparency and absorption efficiency, compared with glass-ceramics. Thus, we chose the precursor samples here for further discussions.

Every obtained glass was double-side polished for further optical measurement. The absorption spectra of glass in the UV–Vis–NIR region were recorded by a UV–Vis–NIR spectrometer (CARY5000). The crystalline phase of the samples was characterized by using X-ray diffraction spectroscopy (XRD, DX-2700) with monochromatized Cu Kα irradiation at 40 kV and 25 mA. The 2θ scan range was 10°–80° with a step size of 0.03° (2θ). FTIR transmission spectra were carried out on the MAGNA-560 spectrometer in the range of 400–4000 cm^{-1} with 4 cm^{-1} resolution using KBr tablets. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by a Tau-3 fluorescence spectrophotometer (Jobin Yvon-Inc, France). Decay curve measurements were obtained using a FLS980 spectrometer (Edinburgh Instruments Ltd., Livingston, U.K.) with excitation of microsecond flashlamps. All the measurements were performed at room temperature.

3. Results and discussion

The XRD profile for the glasses (sample G:Mn0.5-Yb2) is shown in Fig. 1(a), and it is representative for all samples in this study. The XRD patterns mainly show the typical broad diffuse scattering by the amorphous glass matrix. The large broad peak around 15°–35° (2θ) is a typical feature of silicate glass. We can also observe some narrow diffraction peaks from XRD patterns, which would be indicative of partial crystallization during the sample preparation. When Mn^{2+} and Yb^{3+} ions are introduced to the precursor glasses, these ions preferentially enrich into the crystallized nanocrystals with low phonon energy. The low phonon energy of these precipitated nanocrystals can reduce the multi-phonon non-radiative relaxation rate, and enormously enhance the emission efficiency of Yb^{3+} ions. The relative intense diffraction peaks could be seen at 2θ angles of 28.2°, 47.0° and 55.8°, which would be identified as the CaF_2 crystalline phase (JCPDS No. 27-0462).

The FTIR spectrum of in the 400–4000 cm^{-1} region of is shown in Fig. 1(b). The spectra exhibited a conventional band associated with Si–O–Si and Si–O–Al symmetric stretching between the tetrahedrons in the region of 600–800 cm^{-1}. Another band is

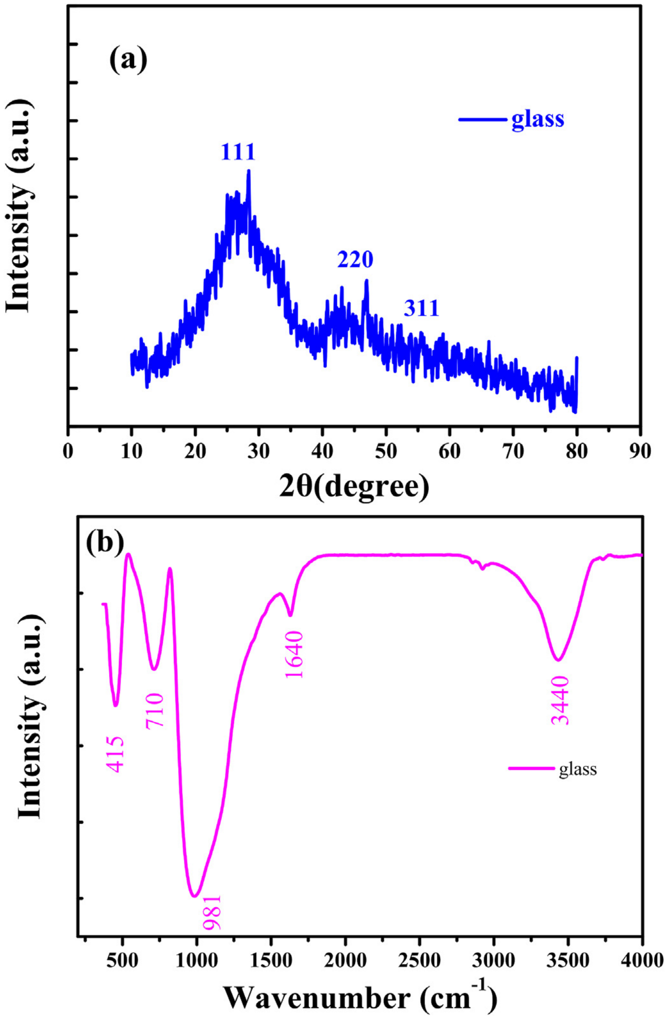

Fig. 1. (a) The X-ray diffraction scan and (b) FTIR spectrum of the glasses.