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Near-infrared downconversion through host sensitized energy transfer in Yb^{3+}-doped $Na_2YMg_2(VO_4)_3$

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ABSTRACT

Host sensitized near-infrared emitting phosphor $Na_2YMg_2(VO_4)_3$:Yb^{3+} was fabricated by a sol–gel method. Efficient broad emission is observed under ultraviolet excitation ranging from 240 nm to −400 nm and this luminescence originates from ligand–metal charge transfer of *2p* of O^{2-} to *3d* of V^{5+}. Under excitation of ultraviolet light in the broad absorption band, intense near-infrared emission of Yb^{3+} around 974 nm is observed for Yb^{3+}-doped $Na_2YMg_2(VO_4)_3$. Through study of photoluminescence spectra, fluorescence decay curves and concentration-dependent luminescence, mechanism of energy transfer from VO_4 group to Yb^{3+} was proposed to rationalize the downconversion process. This phosphor with performance of ultra-violet to near-infrared downconversion could have potential application in improving efficiency of silicon-based solar cell.

1. Introduction

Owing to the mismatch between the solar spectrum and spectral responses of the crystal silicon solar cell, thermalization of charge carriers generated by absorption of high-energy photons, is one mechanism of the major energy losses. These energy losses can be efficiently reduced by spectrum modification. Adapting the solar spectrum through downconversion would be an optimizing scheme to exceed the Queisser–Shockley limit from 29% to 38.6% [1]. Absorbed by suitable downconversion phosphors, a photon with twice energy of band gap of c-Si can be down-converted into two photons with exact energy of the band gap, resulting in a great improvement in conversion efficiency of Si solar cell [2].

Due to their abundant energy levels, Rare earth (RE) ions are optimal candidates for downconversion. Up to now, downconversion in the near-infrared region has been identified in RE^{3+}–Yb^{3+} systems including Tb^{3+}–Yb^{3+} [3], Pr^{3+}–Yb^{3+}[4], Tm^{3+}–Yb^{3+} [5], Ho^{3+}–Yb^{3+} [6], Dy^{3+}–Yb^{3+} [7], and Er^{3+}–Yb^{3+} [8]. Trivalent Yb^{3+} plays a significant role in producing near-infrared (NIR) photons in the 900–1100 nm spectrum region (just above the band edge of crystalline Si) and serves as luminescence sensitizers in these RE dual ions-activated phosphors for downconversion. It has been reported to achieve quantum efficiency as great as 190% in some systems [8]. However, the low-absorption cross sections of these RE ions arising from parity-forbidden *4f*–*4f* transitions inhibit them from absorbing a large part of solar radiation. Then the system of broadband absorption in the ultraviolet region has been exploited such as Ce^{3+}–Yb^{3+} [9] and Eu^{2+}–Yb^{3+} [10]. In this case, Ce^{3+} or Eu^{2+} couples are good alternatives since Ce^{3+} and Eu^{2+} have strong *f*–*d* absorbing transitions in the desired spectral region. It was confirmed that the cooperative downconversion mechanism, based on one donor exciting two acceptors simultaneously, is responsible for the energy transfer (ET) process from Ce^{3+} or Eu^{2+} to Yb^{3+}. Recently a novel downconversion phosphor YVO_4:Yb^{3+} was reported to display strong NIR emission through energy transfer from host to Yb^{3+}. Calculated quantum efficiency can reach as high as 185.7% for the host-sensitized NIR downconversion phosphor [11]. After that, investigation on this kind of systems drew more attention because they could provide many advantages such as broad band absorption and high quenching concentration for the Yb^{3+} NIR emission.

In this paper, in order to make use of the broad ultraviolet (UV) high-energy region of solar spectrum, $Na_2YMg_2(VO_4)_3$ (NYM) doped with Yb^{3+} ions is proposed as a potential spectral-modified material for enhancing silicon photovoltaic efficiency. To the best of our knowledge, it is firstly reported of visible and NIR emission under UV excitation in NYM host. The dependence of visible and NIR emission and decay lifetime on the Yb^{3+} doping concentration has been investigated. The possible mechanism involved and relevant discussions on the NIR downconversion phenomenon have been presented. Remarkably, it was found that host could absorb broadband light in the UV region and convert one UV photon into

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two NIR photons via the cooperative energy transfer (CET) process.

2. Experimental

Yb^{3+}-doped NYM samples were all prepared by the sol–gel method. Firstly, standard solutions, $Y(NO_3)_3$ (1 mol/L) and $Yb(NO_3)_3$ (0.1 mol/L), were obtained through dissolving rare earth oxides in diluted HNO_3 solution. Then nitrates NH_4VO_3 (A.R.), $MgNO_3$ (A.R.) and $NaNO_3$ (A.R.) were mixed with rare earth nitrate solutions in an appropriate ratio. Next, a certain citric acid (molar ratio of citric acid to total metal cation was 2:1) and distilled water were added to the mixed nitrate solution. The resultant mixture was stirred at 60 °C until homogeneous sol formed. After being dried, the gels were heated at 400 °C for 2 h in air, and then the precursors were fully ground and sintered at 700 °C for 1 h. Until cooling down naturally to room temperature, white powder samples were obtained.

The phase structures of the samples were identified by powder X-ray diffraction (XRD) measurement, which were recorded by an X-Ray Diffractometer (Max 18 XCE, Japan) using Cu Kα irradiation ($\lambda = 0.154056$ nm). Thermal gravimetric (TG) of the precursors was conducted from room temperature to 900 °C on a thermal analyzer (TA-50, SHIMADZU) with a heating rate of 10 °C/min. Morphology and sizes of the samples were examined with scanning electron microscope (SEM).

Photoluminescence excitation (PLE) and photoluminescence (PL) spectra in both visible and infrared regions were recorded by using a FLS 9200 fluorescence spectrophotometer. Fluorescence decay curves of green emission were measured under excitation of third harmonics 355 nm of a pulsed YAG:Nd laser with a pulse duration of 10 ns. The visible emission was dispersed by a Jobin-Yvon HRD1 double monochromator and detected by a Hamamatsu R928 photomultiplier. It was similar for NIR emission by a Zolix SBP750 monochromator and an Acton ID-441-C InGaAs NIR detector. Decay signal was analyzed with a Tektronix TDS2024 digital storage oscilloscope. All spectra were recorded under identical conditions. Characteristics of the samples with different Yb^{3+} dopant concentrations can be compared. All measurements were carried out at room temperature.

3. Results and discussion

To examine the conversion process and elucidate phase transformation of NYM host during calcinations, TG analysis was conducted for the precursor. This precursor was obtained after gels were heated at 400 °C for 2 h. As shown in Fig. 1, the change of weight loss is not obvious. The weight loss (5.2%) before 200 °C is mainly attributed to elimination of physically-absorbed water. The weight loss between 200 °C and 560 °C is ascribed to decomposition of residual citric acid. Then crystallization of NYM gradually formed.

Fig. 2 shows the obtained XRD patterns of NYM doped with different Yb^{3+} contents and the data JCPDS card No. 490412 for NYM as a reference. The XRD patterns match well with phase of NYM. It is indicated that only phase-pure NYM crystallites are obtained. Partial substitution of Yb^{3+} for Y^{3+} does not affect the structure of NYM phase, and no additional peaks of other phases have been found, indicating that Yb^{3+} ions are effectively doped into the host lattice at the Y^{3+} sites. To estimate the crystallite size, the SEM image of NYM phosphor is presented in Fig. 3. It could be seen that NYM powder consists of stable agglomerates of nanocrystalline particles with sizes ranging from about 100 nm to 1000 nm, and shows an irregular shape.

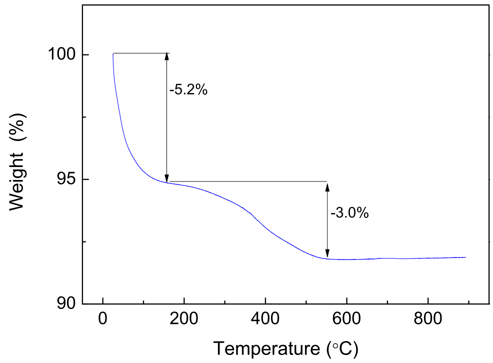

Fig. 1. Thermal behaviors of precursor obtained after gels were heated at 400 °C for 2 h.

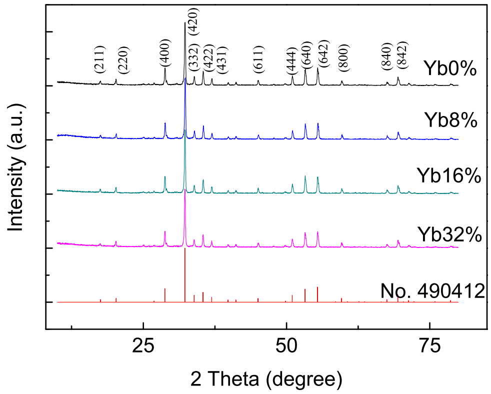

Fig. 2. XRD patterns of $Na_2YMg_2(VO_4)_3$ powders doped with x mol% ($x=1, 4, 8, 16, 32$), as compared with the standard pattern of JCPDS 490412.

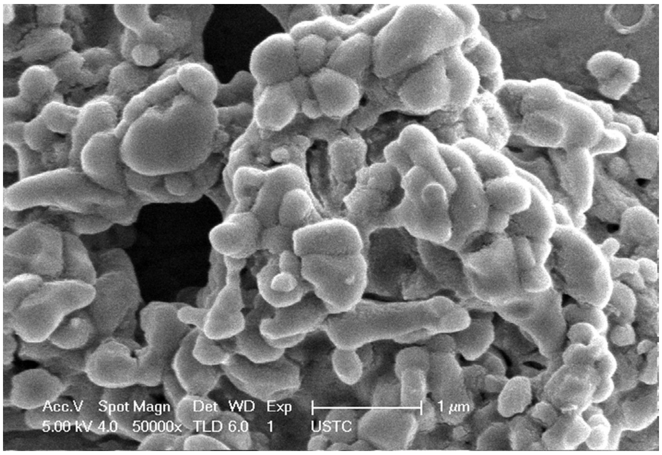

Fig. 3. SEM image of $Na_2YMg_2(VO_4)_3$ powders prepared at 700 °C.

PL and PLE spectra of NYM:Yb^{3+}15% on visible and NIR wavelength regions are presented in Fig. 4. Under excitation at 350 nm, both a broad and intense green emission centered at about 521 nm and a typical infrared one from Yb^{3+} were observed. The green emission in the region from 400 nm to 750 nm is a kind of luminescence of complexes, consisting of a central highly-charged transition metal ion without d electrons surrounded by a number of oxygen ions, which is well understood now [12]. The metal ion V^{5+} (in isolated $[VO_4]$) completely occupies the fourfold T_d site [13]. The ground state molecular orbital for the V^{5+} ion (d°) with T_d symmetry is represented as $^1A_1$ state, and the excited states are represented as $^1T_1$, $^1T_2$, $^3T_1$ and $^3T_2$ states [14]. The observed emission band could be assigned to the ligand–metal charge transfer transitions of *2p* of O^{2-} to *3d* of V^{5+} within