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Ultraviolet to near-infrared downconversion in Yb^{3+}–Na^{+} codoped Sr_2CaWO_6

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HIGHLIGHTS

- Yb^{3+}–Na^{+} codoped Sr_2CaWO_6 powders were prepared by solid-state reaction.
- The phosphor possesses a broadband absorption in the UV region.
- Ultravoilet to near-infrared downconversion was observed.
- Theoretical quantum efficiency can reaches up to 190%.
- The phosphor is a promising quantum-cutting material for its application in solar cells.

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ABSTRACT

This study investigated photoluminescent properties of Sr_2CaWO_6:Yb^{3+}, Na^{+} phosphor. The samples were successfully synthesized via a solid-state reaction method with various doping concentrations. The phosphor can efficiently absorb ultraviolet photons of 250–350 nm and transfer its absorbed photon energy to Yb^{3+} ions. Then subsequent quantum cutting between WO_6 groups and Yb^{3+} ions takes place, downconverting an absorbed ultraviolet photon into two photons of 1007 nm radiations. Analyses of decay curves of different samples reveal an efficient energy transfer from WO_6 groups to Yb^{3+} ions. Cooperative energy transfer from host to Yb^{3+} ions is responsible for downconversion via lifetime analysis. Quantum efficiencies were calculated, and estimated maximum efficiency reached 190%. These phosphors combine wide wavelength absorption in the ultraviolet range with high quantum efficiency, enabling potential application of efficiency enhancement of Si solar cell.

1. Introduction

Downconversion (DC) materials have drawn much attention owing to their potential photovoltaic applications. Photovoltaic efficiency of crystalline silicon (c-Si) solar cells can be enhanced by modifying solar spectrum [1–8]. Spectrum modulation could be achieved via DC material to reduce the mismatch between incident solar spectrum and response curve of c-Si solar cells. DC process can cut one photon in the ultraviolet (UV) region into two low-energy photons in the near infrared (NIR) region whose energy is just above the band gap of the c-Si solar cell [3]. Through NIR DC process, energy loss due to thermalization of electron-hole pairs in c-Si solar cells could be mitigated significantly [4]. It is possible to break classical efficiency limit of c-Si solar cells through doubling the incident photons. An ideal DC layer overlying surface of the solar cell can improve solar cell efficiency from the Shockley–Queisser limit of 30% to 40% [1]. Rare-earth (RE) doped DC materials have been reported in many systems in recent years, such as Tb^{3+}–Yb^{3+} [2], Pr^{3+}–Yb^{3+} [9], Ho^{3+}–Yb^{3+} [10], Er^{3+}–Yb^{3+} [11], and Tm^{3+}–Yb^{3+} [12]. Among these studies, Yb^{3+} ion is selected as the luminescent center due to its excellent properties. It can emit photons usually at about 1000 nm with high quantum efficiency. The photons can be efficiently absorbed by the c-Si solar cell. Various trivalent RE ions, such as Tb^{3+}, Pr^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} are selected as sensitizers for Yb^{3+} ions to realize DC process. However, major limitation for those systems is weak absorption strength of UV sunlight due to forbidden transitions between 4f

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levels. In order to solve this, broadband sensitization of Yb^{3+} has attracted much attention. RE ions and the transition metal ions with broadband absorptions of f–d transition such as Ce^{3+} [13,14], Eu^{2+} [15], and Yb^{2+} [16] and d–d transition such as Bi^{3+} [17], and Cr^{3+} [18], respectively, are chosen as the energy donors for Yb^{3+}. The host-sensitized NIR DC phosphor which can realize broadband spectral conversion was firstly reported by Wei in YVO_4 systems [19]. Henceforce, investigation on this kind of systems aroused more interests because they can possess many properties such as broadband absorption, and high quenching concentration for Yb^{3+} NIR emission. An in-depth investigation on different sensitized NIR DC phosphors is necessary for their potential application.

Both intense blue emission and broadband absorption in the UV region were observed in $Sr_2CaW(Mo)O_6$ host reported by Zhou [20]. These luminescent properties match well with demands of efficient NIR DC materials described previously. Therefore, Yb^{3+} doped Sr_2CaWO_6 can serves as a promising material combined with solar cells to improve energy-conversion efficiency. However, the luminescent properties of Yb^{3+} doped Sr_2CaWO_6 are not thoroughly explored yet to the best of authors' knowledge. In this paper, NIR DC of Yb^{3+}-doped Sr_2CaWO_6 phosphor is investigated.

2. Experimental procedure

2.1. Sample synthesis

Yb^{3+} and Na^+ co-doped Sr_2CaWO_6 powders were prepared by conventional solid-state reaction. Raw materials were $SrCO_3$(99%), $CaCO_3$ (99%), $H_{40}N_{10}O_4W_{12}$ (99%),Yb_2O_3 (99.99%), and Na_2CO_3 (99%). They were mixed through grinding in an agate mortar according to stoichiometric ratio. To decompose the carbonates, the mixtures firstly reacted at 700 °C for 2 h in air. Thus obtained samples were thoroughly ground and mixed again, and calcined at 1200 °C for 5 h. The final products appeared to be white.

2.2. Sample characterization

Phase purities of Sr_2CaWO_6:Yb^{3+}, Na^+ phosphors were gained using powder X-ray diffraction (XRD) analysis on an X-ray Diffractometer (Max 18 XCE, Japan) with a Cu Ka source (λ = 0.154056 nm) at a scanning speed of 3 min^{-1} in the range of 10–80° for 2θ.

Both Photoluminescence excitation (PLE) and photoluminescence (PL) spectra in visible regions were measured with a Jobin-Yvon Fluorolog 3 system, while those in infrared regions were recorded with a FLS 9200 fluorescence spectrophotometer (A 450 W Xe lamp was used as the excitation source). For lifetime measurements, a Q-switched frequency-quadrupled (266 nm) Nd:YAG laser with a pulse duration of 10 ns was used and the signal was analyzed with a Tektronix TDS2024digital storage oscilloscope. The visible emission was dispersed by Jobin-YvonHRD1 double monochromator and detected by Hamamatsu R928 photomultiplier, NIR emission by Zolix SBP750monochromator and Acton ID-441-CInGaAs NIR detector, respectively. The signal was analyzed by anEG&G7265 DSP lock-in amplifier and stored into computer memories. The spectra of samples doped with different Yb^{3+}content were recorded under identical conditions to be compared. All the measurements were carried out at room temperature.

3. Results and discussion

XRD patterns of $Sr_2Ca_{1-2x}Yb_xNa_xWO_6$ are shown in Fig. 1. It can be seen that there is no obvious impurity phase except at

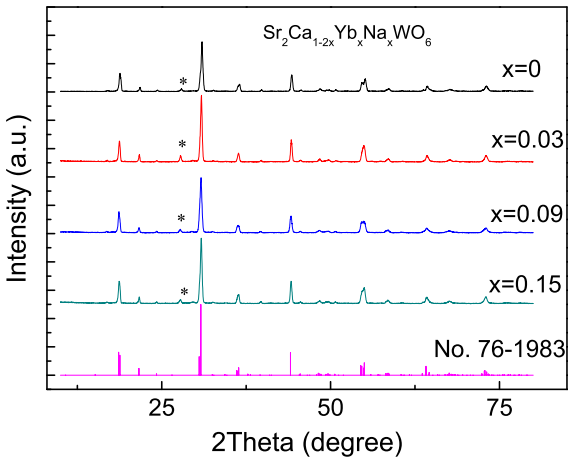

Fig. 1. Powder XRD patterns of sample $Sr_2Ca_{1-2x}Yb_xNa_xWO_6$ with different doping contents (x = 0, 0.03, 0.09, 0.15, "$*$" belong to $SrWO_4$ impure phase, other diffraction peaks belong to Sr_2CaWO_6 phase).

2θ = 27.8°, assigned to SrWO4 (JCPDS No. 080490). All other diffraction peaks for the samples are in accordance with JCPDS Card (No. 76-1983) for Sr_2CaWO_6. Isovalent substitution of two Ca^{2+} ions with ion pairs of Yb^{3+}–Na^+ has negligible influence on crystal phases. No obvious change or peaks shifting can be observed at different doping levels, indicating doping ions Yb^{3+} and the charge compensator ions Na^+ have been incorporated into the lattice, and the introduction of Yb^{3+} and Na^+ ions does not change obviously the crystal structure of the powder due to their close ionic radii (Yb^{3+}, r = 87 pm; Na^+, r = 102 pm; Ca^{2+}, r = 100 pm for 6-fold coordination; Sr^{2+}, r = 144 pm for 12-fold coordination). It has been reported that the crystal structure of Sr_2CaWO_6 is double-perovskite with space group $P2_1/n$. The Sr site with symmetry C_1 is 12-coordinated by oxygen, while the Ca site with symmetry C_i is 6-coordinated [20–22]. One can imagine that the dopant Yb^{3+} ion refers to occupying the Ca^{2+} site in the present host since the ionic radii of Yb^{3+} and Na^+ are closer to that of Ca^{2+}. However, according to Wang's reports, Yb^{3+} ions preferentially and mostly occupy the Ca^{2+} site. Only a few amounts of Yb^{3+} occupy Sr^{2+} site [23].

Fig. 2 shows PLE and PL spectra of $Sr_2Ca_{1-2x}Yb_xNa_xWO_6$ with x = 0.15 sample. Broad blue emission from 350 to 650 nm is observed with a maximum at 430 nm under excitation of UV light

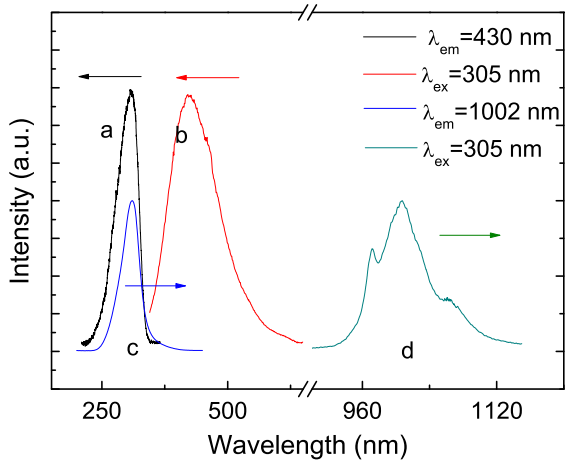

Fig. 2. PLE and PL spectra of $Sr_2Ca_{1-2x}Yb_xNa_xWO_6$ with x = 0.15. ((a) Monitored at 430 nm; (b) excited at 305 nm; (c) monitored at 1002 nm; (d) excited at 305 nm.)