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Wavelength conversion of Yb^{3+}-activated $Y_4CdMo_3O_{16}$ from near UV-region to IR emission

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HIGHLIGHTS

- The structural refinements of the Yb^{3+}-doped phosphors were completed.
- The charge transfer of the molybdate to Yb^{3+} ions is efficient.
- Efficient conversion from near UV light to Yb^{3+} IR emission was demonstrated.
- This is an excellent candidate for enhancement of spectral response of Si-based solar cells.

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ABSTRACT

Yb^{3+} (0.5–30 mol %) activated $Y_4CdMo_3O_{16}$ phosphors have been prepared by the traditional solid-state reaction method. The phase formation was investigated by the XRD structural refinements. The surface properties of the powder phosphors were verified by SEM, TEM and EDS measurements. The optical properties were evaluated by the reflectance spectra, photoluminescence excitation and emission spectra, decay curves (lifetimes), and the absolute quantum efficiency (QE). Under the excitation of UV light, Yb^{3+}-activated $Y_4CdMo_3O_{16}$ shows the efficient near-infrared (NIR) emission bands (900–1100 nm), which is ascribed to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions of Yb^{3+} ions. The NIR emission intensity shows a dependence on Yb^{3+} contents, which has an optimal doping of 25 mol %. The energy transfer (ET) from MoO_4 to Yb^{3+} ions in the lattices was discussed. The NIR emission around 1000 nm just corresponds to the optical response of Si-based solar cells. Consequently, the efficiency could be enhanced by arranging luminescent layers mixed with $Y_4CdMo_3O_{16}$:Yb^{3+} phosphors and transparent matrix in the front surface of Si solar cells.

1. Introduction

Yb^{3+} ion has a simple 4f energy level, i.e., two electronic manifolds with a ground $^2F_{7/2}$ and an excited $^2F_{5/2}$ state, which consequently processes some specialties such as no excited state absorption and no cross-relaxation process etc [1]. Yb^{3+}-activated materials have been given wide investigations on the potential applications such as CW and pulsed solid-state laser hosts, scintillators, medical NIR radiation therapy, structural probes in solids, and sensitizer in up-conversion for Er^{3+}-co-doped systems, etc [2,3].

Recently Yb^{3+}-doped phosphors have been widely investigated as spectral converters to improve photovoltaic (PV) conversion efficiency [4–7]. This is based on two facts. Firstly, the silica used in solar cell has a band gap of 1.1 eV (1120 nm). The optical absorption of the Si-solar cells is much efficient in the NIR band, but it is very weaker in the wavelength below 400 nm [4,8]. Secondly, the separation between $^2F_{7/2}$ ground states and $^2F_{5/2}$ excited states of Yb^{3+} ion corresponds to a wavelength of approximately 1000 nm, which well matches the optical absorption of Si-based solar cells [9,10].

One of the strategies for increasing the efficiency of solar cells is

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so-called down-conversion phosphors as luminescent layers (phosphor nanoparticles incorporated into a transparent matrix) in the front surface of solar cells. The down-conversion mechanism is shown in Fig. 1. In this process, hosts absorb UV/visible photons and then transfer the energy to Yb^{3+} ions, which realize emission of Yb^{3+} ions. It is well-known that Yb^{3+} ions have no optical absorption in the visible range, so the selection of the host is very important. The preferable candidates are host-sensitized phosphors, in which the matrix has intrinsic absorption in blue-to-UV region and intrinsic (exciton) emission in the blue-to-green region [11]. In recent years, Yb^{3+}-doped phosphors have been widely reported in enhancing the efficiency of solar cells. For example, tungstates, molybdates [12], aluminates [13], oxide [14], vanadates [11], and niobate [15], etc. Among these materials, molybdates have been confirmed to be one of the most classic hosts. The host can efficiently absorb UV or blue light by charge transfer state (CTS) in MoO_x groups and then transfer the energy to Yb^{3+} ions.

In this work, Yb^{3+}-doped $Y_4CdMo_3O_{16}$ was selected as a phosphor to investigate the near IR emission due to the motivations as follows. $Y_4CdMo_3O_{16}$ has a cubic fluorite-like structure, which has a space group of Pn-3n (222) [17]. The optical absorption of molybdates is from the charge transfers (CT) due the Mo-O polyhedral. Compared with the other oxides such as tungstates, molybdates usually have efficient optical absorption with the CT band extending to near-UV or blue region [16]. In cubic $Y_4CdMo_3O_{16}$, Mo^{6+}-O^{2-}-Yb^{3+} bond angle is close to 180°, which can get the maximum wave-function overlap and energy transfer by orientation factors in the Foerster energy transfer mechanism [18]. In Yb^{3+}-activated $Y_4CdMo_3O_{16}$ phosphors, efficient energy transfer from Mo-O complex to Yb^{3+} ions could be expected.

Yb^{3+}-activated $Y_4CdMo_3O_{16}$ phosphors were prepared by conventional solid state reaction. The detailed phase formations were characterized by XRD structural refinements. The photoluminescence excitation spectra, emission spectra, the lifetime and the absolute quantum efficiency (QE) were reported. The efficient energy transfer from molybdate host to Yb^{3+} ions was discussed. The emission has a potential application in Si-based solar cell devices.

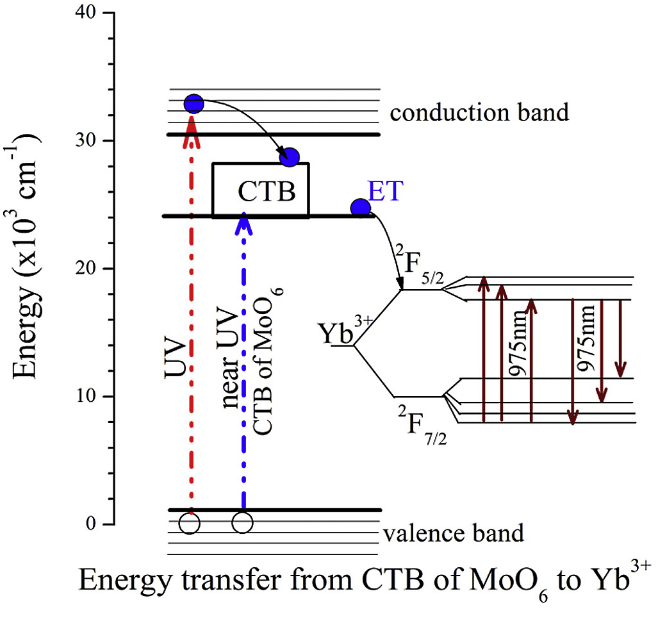

Fig. 1. The scheme of the suggested energy transfer from $Y_4CdMo_3O_{16}$ host to Yb^{3+} ions.

2. Experimental

The $Y_{4-4x}Yb_{4x}CdMo_3O_{16}$ ($x = 0.005–0.3$) phosphors were synthesized via the solid-phase reaction. The starting raw materials were the stoichiometric mixtures of the reagent gradeY_2O_3, Yb_2O_3, $Cd(NO_3)_2 \cdot 4H_2O$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. Firstly, the stoichiometric mixtures were pre-heated at 350 °C for 3 h. Secondly the obtained powders were mixed again and then heated up to 1000 °C for 6 h in air atmosphere. The final products could be obtained by maturely cooling to room temperature.

X-ray diffraction profiles were taken by the Rigaku D/Max diffractometer (40 kV, 30 mA) equipped with Cu Kα as an incident radiation. Morphology of the products was investigated by field-emission scanning electron microscope (SEM, Hitachi S-4700, Japan) operated at 30 kV (back-scatter detector) with a resolution of 4.0 nm. The SEM is equipped with energy dispersive spectrometer (Thermo-Noran, USA) and time-of-flight secondary ion mass spectrometry ToF-SIMS IV (ION-TOF GmbH, Germany). Before SEM-EDS investigations, the samples were placed on carbon plasters and coated with Pt targets using Cressington 208 HR system (Cressington Scientific Instruments Ltd., UK). Low-magnification TEM was carried out on a HT7700 microscope using an accelerating voltage of 120 kV. HRTEM images and SAED patterns were obtained on a Tecnai G2F20 at an accelerating voltage of 200 kV. The diffuse reflection spectra (DRS) were taken on the Cary 5000 UV–Vis-NIR spectrophotometer by using $BaSO_4$ powder as a standard reference.

The photoluminescence spectra of the Yb^{3+}-doped samples were completed on a Spex-Fluorolog DM 3000F spectrophotometer under the excitation of a 500 W Xe-lamp. The infrared luminescence spectra (900–1100 nm) were measured on a Jobin-Yvon DSS-IGA020L InGaAs photo-diode. The resolution of the spectral measurements is 0.1 nm. The decay curves were recorded using a LeCroy 9350A 500 MHz digital oscilloscope and the exciting laser beam was the YAG:Nd laser.

3. Results and discussions

3.1. The phase formation and structure

The phase formations of $Y_{4-4x}Yb_{4x}CdMo_3O_{16}$ ($x = 0.005–0.3$) phosphors were confirmed by XRD patterns, which keep the same profile. No impurity diffraction lines were observed even in the 30mol % Yb-heavily doped sample. This can be understood by the fact that Yb^{3+} (0.985 Å) and Y^{3+} (1.019 Å) have the similar radius in the eight-coordination.

The experimental XRD pattern $Y_4CdMo_3O_{16}$ was given Rietveld refinement via the GSAS (General Structure Analysis System) program [19]. All the samples can be well indexed to the cubic structure. The representative refinements for $x = 0.005$ and 0.3 were shown in Fig. 2. The refined parameters are presented in Table 1. And Table 2 lists the refined atom positions of $Y_4CdMo_3O_{16}$. The phosphors well crystallize in a cubic space group of Pn-3n (222) with $Z = 4$.

Fig. 3 (a) is the schematic structural view of $Y_4CdMo_3O_{16}$ along [001]-direction modelled by the refined atomic coordinate parameters in Table 2. The structure can be regarded as a derivative of a fluorite-like structure. The Mo^{6+} ions are in the 48(i) sites in the presence of a fluorite-type sublattice [17]. There are two kinds of Y^{3+} ions in the deformed cubic coordination (Fig. 3 b). The Y(1) cations fully occupy 48i sites, while Y(2) ions are statistically distributed with Cd^{2+} in the 2a cation sites in $Y_4CdMo_3O_{16}$ lattices.

The surface morphological characteristics of the powder samples were investigated by the SEM measurement. Fig. 4 (a, b) is the typical SEM images of Yb^{3+}-doped $Y_4CdMo_3O_{16}$, which presents many ball-like particles. The average size estimated by the SEM