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Near-infrared emission of Yb^{3+} sensitized by Mn^{4+} in La_2MgTiO_6

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ABSTRACT

Mn^{4+}/Yb^{3+} co-doped La_2MgTiO_6 near infrared phosphor were prepared by co-precipitation technique. The La_2MgTiO_6: Mn^{4+}, Yb^{3+} phosphors can convert the short-wavelength sunlight in 250–550 nm spectral region into near infrared emission at 990 nm, which matches well with the high photosensitive region of Si-based solar cells. The mechanisms for the $Mn^{4+}\rightarrow Yb^{3+}$ have been discussed based on the Mn^{4+} and Yb^{3+} concentration dependent steady-state and transient luminescence properties. The energy transfer efficiency is 31% in the $La_{1.91}MgTi_{0.998}O_6$: 0.002Mn, 0.09Yb sample with the maximal 990 nm emission intensity. It is found that phonon-assisted energy transfer plays an important role in sensitization process from Mn^{4+} to Yb^{3+} in the Mn^{4+}/Yb^{3+} co-doped La_2MgTiO_6.

1. Introduction

The conversion from sunlight to electricity using solar cell devices represents a promising approach to green and renewable energy [1–5]. Despite relevant technology having been around for more than half a century, solar energy remains non-price-competitive with traditional fossil fuels, mainly owing to the low energy conversion efficiencies of solar cells [6]. State-of-the-art commercial crystalline Si (c-Si) solar cells with operating energy efficiencies only around 15% dominate the present photovoltaic technologies [3]. Nevertheless, the theoretical maximum conversion efficiency of Si-based solar cells is higher than 30% [7,8]. To enhance the efficiency of the Si-based solar cell, down-shifting is a promising technique by which short-wavelength sunlight can be converted to light in near-infrared (NIR) region where the photovoltaic solar cell is more sensitive. Lanthanide ions are usually used to obtain NIR light by down-shifting because of their rich energy-level structure permitting abundant NIR emission. Among the lanthanide ions, Yb^{3+} is particularly noteworthy since its NIR emission locates at around at 980 nm, which is just above the band edge of Si semiconductor where the solar cell exhibits excellent spectral response. However, the Yb^{3+} ions exhibit weak and narrow absorption due to their parity-forbidden 4–4f transitions, and as a result, only a small part of ultraviolet and visible sunlight can be converted into NIR emission. Sensitization is an important approach to enhance the absorption efficiency of Yb^{3+} ions and thus increase Yb^{3+} ions emission intensity.

In recent years, tetravalence manganese ion (Mn^{4+}) doped luminescent materials have been investigated and attracted much attention [9–18]. The $^4A_2 \rightarrow {}^4T_1$, $^4A_2 \rightarrow {}^4T_2$ spin-allowed d–d transitions of Mn^{4+} exhibit a strong and continuous UV and visible absorption, which indicates the possible application for broadband light conversion [10]. For Mn^{4+}-activated oxide phosphors, aluminates are investigated as major hosts, such as $CaAl_4O_7$, $Sr_4Al_{14}O_{25}$, $Ca_{14}Zn_6Al_{10}O_{35}$ and $LaAlO_3$ [10,18–20]. However, it is noted recently that some titanates can also act as phosphor host for Mn^{4+} ions because of the advantage characteristics including the similarity of ionic radius between Ti^{4+}(60.5 pm) and Mn^{4+}(53 pm) and non-necessity of cosubstitution for charge compensation owing to the same oxidation number. Especially, the perovskite-type titanates are attractive because the six-coordination sites in which are more favorable for Mn^{4+} luminescence [21]. On the other hand, the La^{3+} sites can be replaced by Yb^{3+} ions because of their similar ion radius and thus energy transfer from Mn^{4+} to Yb^{3+} is expected to take place in the La_2MgTiO_6 matrix. Hence the Mn^{4+}, Yb^{3+} co-doped double perovskite compound La_2MgTiO_6 promises to be broadband spectral converters to obtain efficient NIR emission (around 1000 nm).

In this work, therefore, the Mn^{4+}-Yb^{3+} co-doped La_2MgTiO_6 materials have been prepared by co-precipitation technique and the luminescence properties and energy transfer mechanism between Mn^{4+} and Yb^{3+} ions have been discussed in detail.

2. Experimental

2.1. Materials synthesis

Co-precipitation method is an excellent technique for preparation of luminescent material with relatively high melting point. It can make the

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raw material refining and homogeneous mixing, lower the calcinations temperature and reduce the calcinations time [22]. Considering that conventional solid state reaction method for preparing La_2MgTiO_6 powder requires up to 1773 K of synthesis temperature [23], $La_{2-x}MgTi_{1-y}O_6$:Mny,Ybx(x = 0.03, 0.06, 0.09, 0.12, 0.15, 0.18; y = 0.002, 0.004, 0.006, 0.008, 0.010) were prepared with co-precipitation technique in this work. The raw materials are La_2O_3, MgO, Ti$(SO_4)_2$, $MnCO_3$, Yb_2O_3, HNO_3, $NH_3{\cdot}H_2O$ and HBO_3. All the reagents were of the analytical purity. The procedure for the samples synthesis of $La_{2-x}MgTi_{1-y}O_6$:Mny,Ybx are simply described as follows: firstly, La_2O_3, MgO, $MnCO_3$, Yb_2O_3, were weighted according to the stoichiometric ratio and completely dissolved in dilute nitric acid under condition of stirring and heating, respectively. Then a certain amount of de-ionized water was added to obtain $La(NO_3)_3$, $Mg(NO_3)_2$, Mn$(NO_3)_2$ and $Yb(NO_3)_3$ solution with concentration of 1 mol/L. $Ti(SO_4)_2$ was also dissolved in de-ionized water to obtain the H_2TiO_3 solution. Subsequently, these solutions were mixed with proper ratio according to the designed target product, and stirred for 0.5 h to obtain a new homogeneous solution. The white precipitate was formed by slowly dropping $NH_3{\cdot}H_2O$ with magnetic stirring. The precipitate was filtrated and washed four times with de-ionized water, and then twice with ethyl alcohol, and followed by drying at 200 °C for 24 h to obtain precursors. The precursors was pre-sintering at 550 °C for 3 h to remove the organic matter, and then 1% wt boric acid additive as flux was added to the cooled precursors. After grinding, the powders were pre-sintered at 1000 °C for 3 h again and then cooled to room temperature for regrinding. In the end, the powders were further calcined at 1300 °C for 3 h. The final products were obtained after the furnace cooled down to room temperature.

2.2. Characterization

The structure of the samples was identified by X-ray diffraction (XRD) on a Bruker D8 advance equipment using Cu tube with Cu/K (k = 0.1541 nm) radiation. The excitation spectra and visible-near-infrared photoluminescence (PL) spectra were measured with a monochromator (Zolix Instrument, Omni-λ320i) coupled with photomultiplier (PMTH-S1-CR131) and NIR sensitive detector (DInGaAs 2600-TE), in which a monochromator (Zolix Instrument Omni-λ320) coupled with a 150 W xenon lamp was used to provide the monochromatic exciting light. The luminescence decay curves of 710 nm was measured by PTI QM 40 spectrofluorometer using a pulse xenon lamp as the excitation source. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 portrays the powder X-ray diffraction patterns of the $La_{2-x}MgTi_{0.998}O_6$: $Mn_{0.002}$, xYb (x = 0.03, 0.06, 0.12, 0.18) powders. As a reference, the X-ray diffraction patterns of La_2MgTiO_6 from the Joint Committee on Powder Diffraction Standards (JCPDS No. 70-4252) are also shown. According to the JCPDS card (No. 70-4252), La_2MgTiO_6 crystallizes in the monoclinic structure with the space group P 2_1/c. The diffraction peaks of the as-prepared products keep the same patterns as those of the sample La_2MgTiO_6, indicating that the additive Mn^{4+} and Yb^{3+} ions were successfully incorporated into crystal lattice.

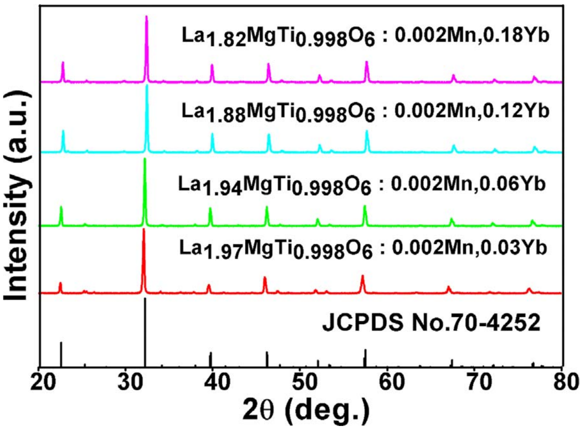

Fig. 1. Powder x-ray diffraction patterns of the $La_{2-x}MgTi_{0.998}O_6$: $Mn_{0.002}$, xYb (x = 0.03, 0.06, 0.12, 0.18) powders.

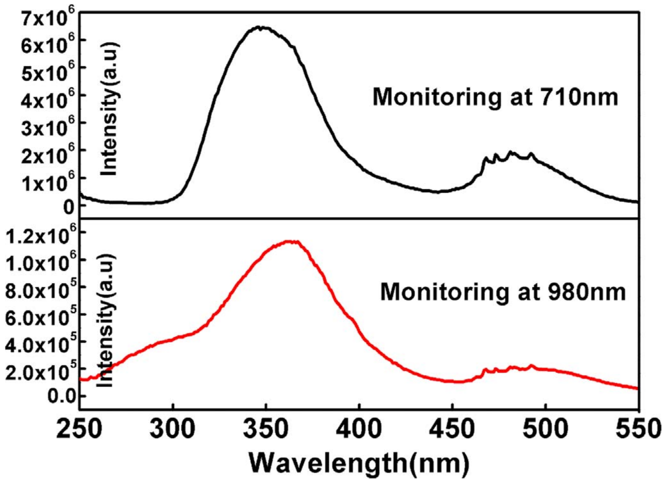

Fig. 2. Excitation spectra of the Mn^{4+} monitored at 710 nm and Yb^{3+} monitored at 980 nm in $La_{1.91}MgTi_{0.998}O_6$: $Mn_{0.002}$, $Yb_{0.09}$ sample.

Fig. 2 shows the excitation spectra of the Mn^{4+} ions monitored at 710 nm and Yb^{3+} ions monitored at 980 nm in $La_{1.91}MgTi_{0.998}O_6$: $Mn_{0.002}$, $Yb_{0.09}$ sample, respectively. Broad excitation bands from 250 nm to 550 nm corresponding to the absorptions involving transitions from the $^4A_2$ to the $^4T_1$ and $^4T_2$ states of Mn^{4+} can be observed in sample. It is interesting to find that the excitation spectra monitored at 980 nm of Yb^{3+} emission is similar with that monitored at 710 nm of Mn^{4+} emission in $La_{1.91}MgTi_{0.998}O_6$: $Mn_{0.002}$, $Yb_{0.09}$ sample. This clearly proves that an energy transfer from Mn^{4+} to Yb^{3+} takes place when Mn^{4+} ion is excited in the Mn^{4+}/Yb^{3+} co-doped sample. The $Mn^{4+}\rightarrow Yb^{3+}$ energy transfer makes the 980 nm emission of Yb^{3+} easily to be performed by pumping with light in wide wavelength range of 250–550 nm.

Fig. 3(a) exhibits the emission spectra in range of 900–1100 nm of the $La_{1.91}MgTi_{0.998}O_6$: $Mn_{0.002}$, $Yb_{0.09}$ sample pumped by 460 nm light. The Mn^{4+}/Yb^{3+} co-doped phosphor shows a strong NIR emission band with the highest peak at 990 nm, which is imputed to Yb^{3+} ions $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition. The relationship of Yb^{3+} ions 990 nm emission intensities tendency with Yb^{3+} ions concentrations are also given in the inset of Fig. 3. It is found that the integrated intensity of the NIR emission band centered at 990 nm increases at first with the increase of the concentrations of Yb^{3+} ions, reaching the maximum at x = 0.09, and then decreases gradually as the result of the concentration quenching. At the optimal concentration of Yb^{3+} for 990 nm emission (x = 0.09), the intensity of the Yb^{3+} at 990 nm can be further enhanced by increasing Mn^{4+} content and the strongest emission appears at y = 0.006, just as show in Fig. 3(b). It is found that the luminescence intensity of 990 nm after optimization of the Mn^{4+} concentration is further increased by about 1 time. At higher Mn^{4+} doped contents, however, the concentration quenching also occurs and the 990 nm emission intensity begins to decrease.

According to the excitation and emission properties of Mn^{4+}/Yb^{3+} co-doped phosphors, an energy transfer sensitization mechanism is proposed and depicted in Fig. 4. The energy transfer efficiency depends on how well the acceptor energy levels match the frequencies of the donor emission. From Fig. 4, and we can see that there is relatively large energy gap between the Mn^{4+}: ^2E level and Yb^{3+}: $^2F_{5/2}$ level. It