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Synthesis and near-infrared luminescence properties of LaOCl:Nd^{3+}/Yb^{3+}

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HIGHLIGHTS

- Near-infrared emitting phosphors LaOCl:Nd^{3+}/Yb^{3+} were prepared.
- LaOCl:Nd^{3+}/Yb^{3+} samples show strong near-infrared emission lines in the region of 1060–1150 nm and 980–1050 nm.
- The possible energy transfer mechanism between Nd^{3+} and Yb^{3+} was discussed.

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ABSTRACT

Near-infrared emitting phosphors LaOCl:Nd^{3+}/Yb^{3+} were prepared by the solid-state method, and their structures and luminescent properties were investigated by using X-ray diffraction and photoluminescence analysis, respectively. The studies shows that tetragonal LaOCl:Nd^{3+}/Yb^{3+} can be synthesized by the solid-state reaction at 600 °C for 3 h. Upon 353 nm UV excitation, LaOCl:Nd^{3+}/Yb^{3+} sample shows strong near-infrared emission lines in the region of 1060–1150 nm (corresponding to $^4F_{3/2} \rightarrow {}^4I_{J'}$ transition of Nd^{3+}, J' = 9/2, 11/2, 13/2, 15/2) and 980–1050 nm (corresponding to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+}). The decreasing emission intensity of Nd^{3+} with increasing doping concentration of Yb^{3+} proved the energy transfer in LaOCl:Nd^{3+}/Yb^{3+}. The possible near-infrared emission and energy transfer mechanism between Nd^{3+} and Yb^{3+}, as well as the energy transfer efficiency of LaOCl:Nd^{3+}/Yb^{3+} were discussed.

1. Introduction

Some possible strategies exploring green and sustainable energy through solar photovoltaic technology have drawn great attention in the past decades, and silicon solar cells become a hot issue in these years. However, obvious spectral mismatch existed in the process of the emission of the sunlight and the absorption of the silicon solar cells: low energy photons cannot be used efficiently by the solar cells, while the majority of high energy photons are wasted by solar cells [1–3]. The spectral mismatch caused great losses of solar energy, which in turn leads to the limitation of the efficiency of the solar photovoltaic [4,5]. Rare earth (RE) ions doped luminescence materials are supposed to solve this problem because of their feature of spectral modification [6,7]. According to Stokes law, high energy photons can be “cut” into two or more low energy photons through quantum cutting process, and it is also verified that luminescence materials in combination with solar cells can greatly eliminate the spectral mismatch and enhance the utilization of solar energy [8–11], therefore it can indirectly improve the photovoltaic efficiency of solar cells. RE ion co-doped materials converting short-wave photons into long-wave photons have been confirmed by some experimental results [12–16]. Accordingly, developing efficient solar spectral modification materials is a necessary.

Down-conversion materials of lanthanide ions doped phosphors for solar cells can absorb the ultraviolet/visible (UV/VIS) photons in sunlight and emit near-infrared (NIR) photons for the absorption of the solar cells, and an alternative access to achieve down-conversion luminescence originates from the energy transfer and quantum cutting by using RE ions. Among them, Nd^{3+} ion has rich energy level structures, and it shows rich absorption line in the UV/VIS region [1–3,8,17]. Yb^{3+} has only two energy levels of $^2F_{5/2}$ and $^2F_{7/2}$, and the transition between them corresponds to strong near-infrared emission around 1000 nm, therefore Yb^{3+} can act as excellent luminescent centers as activator [3–5,9,11,15]. Some previous researchers found that there is efficient energy transfer between Nd^{3+} and Yb^{3+} couples and strong near-infrared emission can be found [3,10].

The host material plays an important role in the luminescence property of down-conversion materials [8,18]. In order to elevate the near-infrared emission intensity, LaOCl was focused on as a host material in the present study. LaOCl is a tetragonal rare earth oxychloride which has a layer structure, the $(LaO)^+$ layers are separated by Cl^- in the direction to the *c* axis, and the RE ions are surrounded by four O^{2-} and four Cl^- ions with the C_{4v} symmetry [19–21]. The unique lattice structure of LaOCl determines that a fine crystal field for luminescence can be provided when formulating

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the solid solution with different doped RE anions. Besides, LaOCl has characteristics of both low phonon energy of chlorides and high stability of oxides [22,23]. In this study, we investigated the near-infrared emission of Nd^{3+} and Yb^{3+} codoped LaOCl, and the studied samples was synthesized by the traditional solid-state method. The phase structure formation, photoluminescence properties and the energy transfer mechanism were discussed in detail.

2. Experimental

The starting materials include La_2O_3, Nd_2O_3, Yb_2O_3 and NH_4Cl. All chemicals were of analytical grade and were used directly without further purification. All the compounds were synthesized by a solid-state method, and the details were as follows: La_2O_3, Nd_2O_3, Yb_2O_3 powder were weighted according to the given molar ratio and mixed thoroughly. Then normal or excessive molar ratio of NH_4Cl was added into the mixture, mixing them again until the new mixture distributed well. The obtained mixtures were sintered at different temperature and grinded those in an agate mortar, the sample powders were obtained. The heating rate is 5 °C/min and the holding time is 3 h. After that, the samples were washed for three times by the water and dried for the following measurement.

X-ray powder diffraction (XRD) patterns were recorded on Shimadzu XRD-6000 diffraction apparatus with Cu Kα radiation (λ = 0.15406 nm, 40 kV, 30 mA), and collected in the 2θ range between 10° and 60°, with a scanning speed of 4°/min. The excitation, emission spectra and fluorescence decay curves were recorded on a FL3-21 spectrofluorometer made by Jobin Yvon Company, and the R1033P photomultiplier for the near-infrared signal detection. All the measurements were carried out at room temperature.

3. Results and discussion

By doping different contents of NH_4Cl (100%, 150%, 200%, 300% of the molar ratio) and using different sintering temperatures (600–1000 °C), the optimum synthesis route of RE doped LaOCl was determined. However, all the XRD patterns of LaOCl:$0.02Nd^{3+}/0.02Yb^{3+}$ prepared in different adding contents of NH_4Cl and sintering temperatures were found to possess a single phase structure of LaOCl, even if they were sintered at a relatively low temperature of 600 °C. Fig. 1 gives the XRD patterns of LaOCl:$0.02Nd^{3+}/0.02Yb^{3+}$ sintered at 600 °C with different molar ratio of NH_4Cl. As is shown in Fig. 1, the obtained XRD patterns are matched well with the standard data of JCPDS Card No. 88-0064 for LaOCl. The phase structures of those samples substantially have no changes with the addition of different NH_4Cl content. Thus, crystallization of pure-phase LaOCl was successfully achieved. It is believed that some excessive NH_4Cl can be eliminated by the washing. Furthermore, it can be seen that 2% addition of Nd_2O_3 and 2% addition of Yb_2O_3 have no effect on the phase structure, and it should be ascribed to that La^{3+}, Nd^{3+} and Yb^{3+} all belong to lanthanide ions with similar ion radius and the same charge.

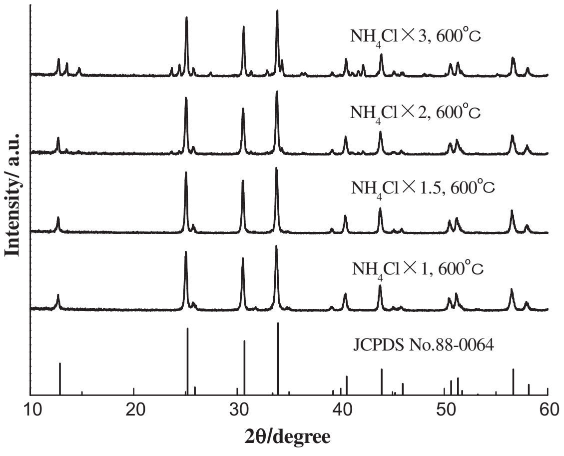

Fig. 1. XRD patterns of LaOCl sintered at 600 °C with different NH_4Cl adding contents and the standard JCPDS Card No. 88-0064 is also given as a comparison.

As shown in Fig. 2a, the emission spectra of LaOCl:$0.05Nd^{3+}$, LaOCl:$0.05Yb^{3+}$ and LaOCl:$0.05Nd^{3+}/0.05Yb^{3+}$ under 353 nm excitation were selected for the comparison. Fig. 2b illustrates the excitation spectra of these samples. It can be seen from the two figures: (1) the emission spectra of Nd^{3+} single doped sample LaOCl:$0.05Nd^{3+}$ exhibit broad near-infrared emission bands (1060–1150 nm) with peaks at 1079 nm and 1370 nm, which correspond to the characteristic emissions of transitions $^4F_{3/2} \rightarrow {}^4I_{J'}$ (J' = 9/2, 11/2, 13/2, 15/2) of Nd^{3+} [2,3,16], and these emission lines are ascribed to energy attenuations of Nd^{3+} when it is excited. In the excitation spectrum of LaOCl:$0.05Nd^{3+}$, monitored at 1079 nm (Nd^{3+}:$^4F_{3/2} \rightarrow {}^4I_{11/2}$), many excitation lines in the range of 350–850 nm are observed, and all those excitation lines originate from the transitions of ground state to the excited states of Nd^{3+} ions corresponding to $^4I_{9/2} \rightarrow {}^4D_{3/2}$, $^4G_{9/2}$, $^4G_{11/2}$, $^4F_{7/2}$, as shown in the figure [13]. (2) The observed emission intensity is very low in the emission spectrum of LaOCl:$0.05Yb^{3+}$. A tiny emission band of 980–1050 nm with the strongest peak at 1017 nm can be assigned as the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} [5,8–11]. It is known that the excitation spectrum of LaOCl:$0.05Yb^{3+}$ could not be detected in the region of 300–800 nm. (3) Apparent near-infrared emission in the region of 980–1050 nm (characteristic Yb^{3+} emission) and 1060–1150 nm (characteristic Nd^{3+} emission) have been gained in Nd^{3+}/Yb^{3+} co-doped LaOCl:$0.05Nd^{3+}/0.05Yb^{3+}$. The emission intensity of LaOCl:$0.05Nd^{3+}/0.05Yb^{3+}$ was enhanced greatly compared with that of the single doped samples, especially in the region of 980–1050 nm. The excitation spectra of LaOCl:$0.05Nd^{3+}$ and LaOCl:$0.05Nd^{3+}/Yb^{3+}$ are generally the same, no matter the monitored emission is 1079 nm or 1017 nm. Such an obvious match indicates the possible energy transfer between Nd^{3+} and Yb^{3+}. Accordingly, Fig. 2 also indicates that Nd^{3+} can show near-infrared emission by its own energy attenuations; however, Yb^{3+} achieved the strong down-conversion near-infrared emission when it is co-doped with Nd^{3+}. The phenomenon indicated the energy transfer between Nd^{3+} and Yb^{3+} in LaOCl:$0.05Nd^{3+}/0.05Yb^{3+}$, and the proper process of down-conversion near-infrared emission was as follows: Nd^{3+} absorb high energy photons when excited by UV and visible light, and Yb^{3+} realized strong near-infrared emission as getting energy from Nd^{3+} by energy transfer.

In order to further prove the energy transfer of $Nd^{3+} \rightarrow Yb^{3+}$ in LaOCl:Nd^{3+}/Yb^{3+}, the emission spectrum of LaOCl:$0.05Nd^{3+}/yYb^{3+}$ (y = 0.01, 0.03, 0.05, 0.1, 0.2) were measured under 353 nm excitation, and the variation of Yb^{3+} and Nd^{3+} emission intensities (peak at 1017 nm and 1079 nm, respectively) was also shown in Fig. 3. Near-infrared emissions in the range of 980–1050 nm and 1060–1150 nm are observed in all the samples. When the Yb^{3+} concentration is 0.01, Nd^{3+} has a relative high concentration, thereby strong interaction with Nd^{3+} ions results in the concentration quenching [8,11]. With the Yb^{3+} concentration increased from 0.03 to 0.2 and the Nd^{3+} doping concentration is fixed at 0.05, the emission intensity of Nd^{3+} decrease and that of Yb^{3+} increase, which is another evidence of the energy transfer from Nd^{3+} to Yb^{3+}.

Fig. 4 shows the proposed near-infrared emission and energy transfer mechanism in LaOCl:Nd^{3+}/Yb^{3+} system: intricate energy level structure of Nd^{3+} determines the good absorption of Nd^{3+} in UV–VIS region, corresponding to Nd^{3+} ground state absorption (GSA) of $^4I_{9/2} \rightarrow {}^4D_J$ (J = 1/2, 3/2), $^4I_{9/2} \rightarrow {}^4G_K$ (K = 11/2, 9/2, 7/2, 5/2) and $^4I_{9/2} \rightarrow {}^4F_L$ (L = 7/2, 5/2, 3/2), which transitions causing