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Structure, luminescence and energy transfer of $LiLa(MoO_4)_2$:Dy^{3+}, Eu^{3+} crystal

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ABSTRACT

$LiLa(MoO_4)_2$: Dy^{3+} and $LiLa(MoO_4)_2$: Dy^{3+}, Eu^{3+} phosphors were successfully synthesized by conventional solid state reaction method. The crystal structure, luminescent properties and energy transfer mechanism of the samples were researched. The optimal Dy^{3+} doping concentration of $LiLa(MoO_4)_2$ (LLM) excited by ultraviolet was 5 mol%. Upon 454 nm excited, the energy transfer mechanism between Dy^{3+} and Eu^{3+} in co-doped LLM phosphors was identified as dipole-dipole interactions. The energy transfer efficiency from Dy^{3+} to Eu^{3+} and the CIE coordinates of LLM: Dy^{3+}, Eu^{3+} crystals have been calculated. The results show that the energy transfer from Dy^{3+} to Eu^{3+} in the system is efficient and the sample colors are changed in the greenish yellow region.

1. Introduction

In recent years, with the development of purification process of rare earth (RE) ions, based on lanthanide doped particles, these luminescent materials, such as white light emitting diodes (LEDs), pulsed lasers, fluorescent probes and bioimaging have attracted considerable attention to the advantages of high conversion efficiency, narrow-band emission, long lifetimes, and good photostability [1]. Because 4f electrons of lanthanide ions are shielded by the electrons of $5s^2 5p^6$, there are a large number of energy levels and the electron transition between 4f-4f electrons. RE ions are suitable for the activator and the sensitizer as the luminescent center of phosphors. In lanthanide families, Eu^{3+} and Dy^{3+} can emit red, blue and yellow lights due to the ${}^5D_0 \rightarrow {}^7F_2$, ${}^4F_{9/2} \rightarrow {}^6H^{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively. They usually serve as the doping ions for phosphors to obtain white light. At present, there are many reports that the tunable color of Dy^{3+}/Eu^{3+}co-doped phosphors has been discussed by energy transfer mechanism [2–4]. It seems that Dy^{3+}/Eu^{3+}co-doped phosphors have been a hot area of research in this field.

As we all know, the structure and properties of phosphors depend on the host materials. Therefore, it is very important to choose an acceptable host material for rare earth ions doping. There are a variety of host materials, such as molybdates [5], vanadates [6], tungstates [7], phosphates [8] and niobates [9]. Among these molybdates, double alkaline rare earth molybdates with the general formula $MRE(MoO_4)_2$ (M = alkali metal ions, RE = rare earth ions) seem to be potential candidates as luminescent host materials because of their excellent thermal and chemical stability [10]. In the big family of the double alkaline rare earth molybdates, LLM has the scheelite structure with the space group $I_{41/a}$, in which the four oxygen atoms are located around the Mo^{6+} ions to form a tetrahedral structure, while both Li^+ and La^{3+} are eight coordinated [11]. What's more, $MoO_4{}^{2-}$ also has strong absorption in NUV region and exhibits broad charge transfer band because of the charge transfer from O^{2-} to Mo^{6+}, which can effective transfer the absorbed energy to the activator ions to enhance luminescent intensity [12]. Therefore, LLM has attracted particular interest in the laser host and the crystal fiber in recent years [13–15]. However, there are few reports on the research of LLM phosphor.

In this paper, a series of different rare earth doped LLM crystals were prepared with a conventional solid-state reaction method. The x-ray diffraction and fluorescence spectroscopy were used to analyze the crystal structure and photoluminescence properties of the samples, respectively. In addition, the energy transfer process of LLM: Dy^{3+}, Eu^{3+} phosphor was investigated in detail.

2. Experimental

Dy^{3+}/Eu^{3+} co-doped LLM crystals were prepared using a traditional solid-state reaction. Lithium carbonate (Li_2CO_3, AR), lanthanum oxide (La_2O_3, AR), molybdenum oxide (MoO_3, AR), dysprosium oxide (Dy_2O_3, AR) and europium oxide (Eu_2O_3, AR) were used as starting materials. Firstly, all the raw materials were weighed stoichiometrically. The raw materials were then thoroughly ground in an agate mortar and the mixture was stirred for at least 20 min to obtain a

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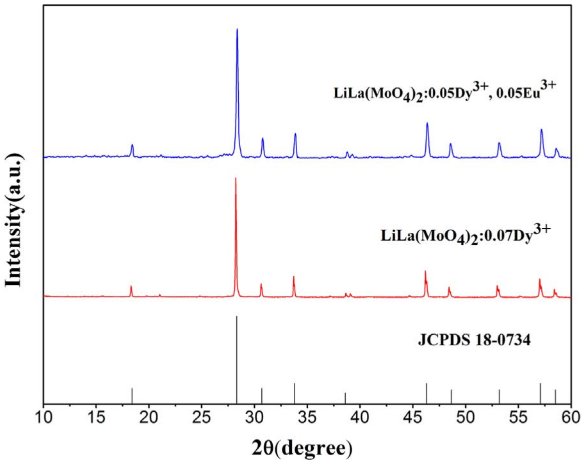

Fig. 1. X-ray diffraction patterns of $LiLa(MoO_4)_2$:$0.07Dy^{3+}$ and $LiLa(MoO_4)_2$:$0.05Dy^{3+}$, $0.05Eu^{3+}$ phosphors.

homogeneous mixture. After that, the mixture was placed in a corundum crucible. Finally, the corundum crucible was heated from room temperature to 800 °C in a high temperature electric furnace, and the solid state reaction was carried out at this temperature for 4 h. After the reaction, the samples were taken out at room temperature.

The crystal phase of LLM crystal was characterized by X-ray diffraction on a Bruker D8-Advance diffractometer. The structural parameters were refined by the GSAS program using the XRD data of the powder. The emission spectra were measured on a fluorescence spectrophotometer (Hitachi F-4600, Japan) with a xenon lamp as the excitation source. The Edinburgh integrating sphere of the fluorescence spectrometer was used to measure photoluminescence quantum yield of the samples. All measurements were performed at room temperature.

3. Results and discussion

3.1. Phase characterization and crystal structure analyses

The XRD patterns of LLM: Dy^{3+} and LLM: Dy^{3+}, Eu^{3+} crystals are shown in Fig. 1. The patterns of them have a number of peaks that can be indexed to the pure tetragonal phase of LLM (the space group: $I_{41/a}$), and the intensities of the diffraction peaks have no obvious changes with different doping ions. This fact indicates that the doping ions have few effects on the crystal structure of the synthetic products.

The Rietveld refinement of XRD patterns of Dy^{3+} single-doped LLM phosphor is performed by using the GSAS program to investigate the structure and lattice parameters. Fig. 2 shows the observed (thin-cross), calculated (red line) and difference patterns (blue line) of the samples. It is shown that the observed are matched well with the calculated patterns. The reliability values of refinement are $R_{wp} = 9.37\%$, $R_p = 6.96\%$ and $\chi^2 = 2.969$. The lattice parameters of the LLM are refined to be $a = b = 5.3062$ Å, $c = 11.651$ Å, $\alpha = \beta = \gamma = 90°$ and lattice volume (V) is 328.036 $Å^3$. The crystal structure model of LLM is modeled by Rietveld refinement parameters with a Diamond software (see Fig. 3). It is obvious that Li^+ and La^{3+} ions occupy the same site, and the surrounding oxygen atoms and La-O bonds form polyhedrons in the lattice. The polyhedrons are connected with the MoO_4^{2-} tetrahedral to form a stable structure filled with the entire lattice. Furthermore, because Dy^{3+}, Eu^{3+} and La^{3+} have the similar ionic radii, Dy^{3+} and Eu^{3+} will be likely to occupy the La^{3+} site in the lattice [16].

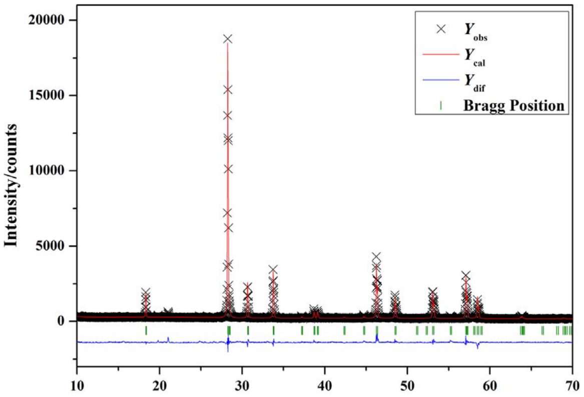

Fig. 2. Observed, calculated and difference XRD patterns of $LiLa(MoO_4)_2$:$0.07Dy^{3+}$ powder.

3.2. Photoluminescence (PL) properties of LLM: Dy^{3+}

Fig. 4a shows the photoluminescence excitation spectra of LLM: $0.05Dy^{3+}$ phosphor monitoring at 576 nm. The excitation spectra show some absorption peaks at 353, 367, 389, 428, 454 and 476 nm due to the $^6H15/2 \rightarrow {}^6P_{7/2}$, $^6H_{15/2} \rightarrow {}^6P_{5/2}$, $^6H_{15/2} \rightarrow {}^4I_{13/2}$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$, $^6H_{15/2} \rightarrow {}^4I_{15/2}$, and $^6H_{15/2} \rightarrow {}^4F_{9/2}$ transitions of Dy^{3+} ions, respectively. The intensity of $^6H_{15/2} \rightarrow {}^4I_{13/2}$ at 389 nm is maximum among the transitions. Upon excitation at 389 nm, the emission spectra of LLM: xDy^{3+} (x = 0.01, 0.03, 0.05, 0.07, 0.09 and 0.11) are shown in Fig. 4b (Schematic energy level diagram is shown in Fig. 8). It is found that the emission peaks located at 487, 576 and 667 nm are corresponding to the magnetic dipole transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$, electric dipole transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ of Dy^{3+} ions, respectively. It is obvious that the electric dipole transition intensity is higher than the other two. The result implies that the doping Dy^{3+} ions occupy a lower symmetry in the lattice [16]. This is supported by the La^{3+} sites with no inversion centers in LLM crystal lattice (Fig. 3).

As shown in the inset of Fig. 4b, it is observed that with the increase of the Dy^{3+} concentration from 0.01 to 0.11, the luminescent intensity of emission peaks offers upgrade firstly than descending latter tendency. When the Dy^{3+} doping concentration increased to 0.05, the intensity of the emission peaks achieves a maximum. But when the Dy^{3+} concentration is higher than 5 mol%, the emission intensity declines dramatically owing to concentration quenching [17]. It is natural to conclude that Dy^{3+} has an optimum dopant concentration of 0.05 and it will be used in the following experiments.

3.3. Photoluminescence properties and energy transfer of LLM: Dy^{3+}, Eu^{3+} crystals

Fig. 5 shows the excitation and the emission spectra of LLM: $0.05Dy^{3+}$, $0.05Eu^{3+}$ phosphor. When the monitoring wavelength is 576 nm, the photoluminescence excitation spectra of (blue line) LLM: $0.05Dy^{3+}$, $0.05Eu^{3+}$ are similar to those of LLM: $0.05Dy^{3+}$ phosphor (compared with Fig. 4a). Meanwhile, the excitation spectra of (red line) LLM: $0.05Dy^{3+}$, $0.05Eu^{3+}$ monitoring at 618 nm exhibit a strong absorption peak at 465 nm. It is ascribed to $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} ion. In general, the energy transfer phenomenon in co-doped phosphors would take place if the activator ions and the sensitizer ions have the same wavelength range of the excitation band. From the excitation spectra, it can be seen that the phosphor has the stronger absorption at 454 nm (monitored at 576 nm), but there is little absorption while monitored at 618 nm. The emission spectra of LLM: Dy^{3+}, Eu^{3+} phosphor excited by 454 nm show some emission peaks at 487, 576 and 618 nm (characteristic emission of Eu^{3+}), which are ascribed to the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ of Dy^{3+} ions and $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ions. It indicates that a possible energy transfer phenomenon happens between Dy^{3+} ions and Eu^{3+} ions in co-doped LLM phosphors [18].

To further research the energy transfer mechanism of Dy^{3+} to Eu^{3+} and the sensitization of Dy^{3+} in co-doped LLM phosphors, a series of