Luminescence Properties of Tungstate Phosphors Doped with Rare-Earth Ion

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Abstract The preparation of red phosphor in the phosphor-converted white LED is indispensable, and plays a very important role in improving the color rendering index. As a newly developed kind of red phosphor, $LiEuW_2O_8$ shows great potential. The luminescence properties of $LiEuW_2O_8$ phosphor doped with rare-earth ions are studied. $LiEu_{1-x}RE_xW_2O_8$ (RE=La and Sm) series red phosphors are produced by the high-temperature solid-phase synthesis method. When La^{3+} and Sm^{3+} replace Eu^{3+} in $LiEuW_2O_8$, both of them transfer energy to Eu^{3+} through reabsorption and thus realizing sensibilization of Eu^{3+}. After being doped with La^{3+} and Sm^{3+}, the excitation and emission peaks of $LiEuW_2O_8$ and the crystal structure do not change; however, the luminescence intensity is improved. With the addition of La^{3+} and Sm^{3+} of 3% and 4% (molar fraction), respectively, the luminescence intensity reaches the maximum.

Key words materials; $LiEuW_2O_8$; tungstate phosphor; white LED

OCIS codes 160.2540; 160.4670; 160.4760

稀土离子掺杂对钨酸盐荧光粉发光性能的研究

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摘要 红色荧光粉的在制备荧光转换型白光LED时是不可或缺的，因为红色荧光粉在制备高显色指数白光LED中发挥着重要的作用。$LiEuW_2O_8$是最近几年最新发展起来的一种很有潜力的红色荧光粉。主要研究了稀土离子掺杂对$LiEuW_2O_8$发光性能的影响。采用高温固相法制备钨酸锂铕系列红色荧光粉。La^{3+}和Sm^{3+}取代$LiEuW_2O_8$中的Eu^{3+}，La^{3+}和Sm^{3+}通过再吸收的方式将能量传递给Eu^{3+}，实现对Eu^{3+}的敏化作用。La^{3+}和Sm^{3+}的掺杂并没有改变样品的激发和发射峰，也没有改变晶体结构，但是掺入后能显著提高样品的发射强度。La^{3+}的最佳掺杂量(物质的量分数)为3%，Sm^{3+}的最佳掺杂量为4%。

关键词 材料；$LiEuW_2O_8$；钨酸盐荧光粉；白光LED

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1 Introduction

With the rapid increase of LED efficiency and the continuous declination of LED cost, especially with the advent of white LED, the application areas of LED have expanded from displays and indicators to lighting[1]. Compared with traditional lighting, white LED has several advantages, including power consumption, long life, environmental protection, and fast response. LED represent a new lighting generation after incandescent and fluorescent light. It is the most promising high-tech area in the 21st century. The preparation of red phosphor in the phosphor-converted white LED is indispensable, and plays a very important role in improving the color rendering[2]. However, red phosphor has low luminescence efficiency and poor stability at present. Therefore, red phosphor that can be excited by blue and ultraviolet (UV) chips is a key factor in the development of white LED.

As a newly developed kind of red phosphor, $LiEuW_2O_8$ shows great potential compared with traditional red phosphors for LED. The biggest disadvantage of $LiEuW_2O_8$ phosphor is its low luminescence efficiency. However, the biggest advantages of $LiEuW_2O_8$ red phosphor are a simple synthesis process, easy industrialization, and the fact that it can be applied in near-UV chips. It this current paper, we study the properties of $LiEuW_2O_8$ phosphor doped with rare-earth ion[3].

2 Experiments

We adopt the high-temperature solid-phase synthesis method to prepare $LiEu_{1-x}RE_xW_2O_8$ (RE = La and Sm) red phosphor. The raw materials used in this experiment are $LiCO_3$ (purity 99.5%), Eu_2O_3 (99.99%), WO_3 (99.5%), La_2O_3 (99.9%), and Sm_2O_3 (99.9%).

The first step of the experiment is to determine the temperature (Fig. 1). Here, 880 ℃ is defined as the best temperature. The second step is to determine the amount of Eu^{3+} (Fig. 2), after which the effects of the cosolvent on the luminescent properties of $LiEuW_2O_8$ are discussed (Fig. 3).

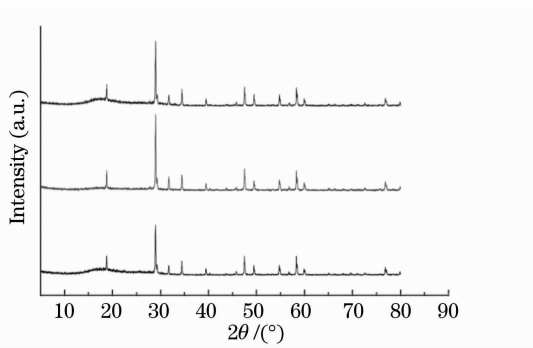

Fig. 1 XRD pattern of $LiEuW_2O_8$ at different temperatures

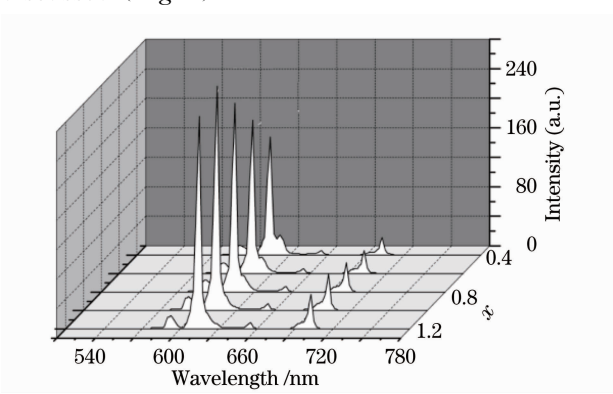

Fig. 2 Emission intensity of $Li_{4-3x}W_2O_8:Eu_x$ for different amounts of Eu

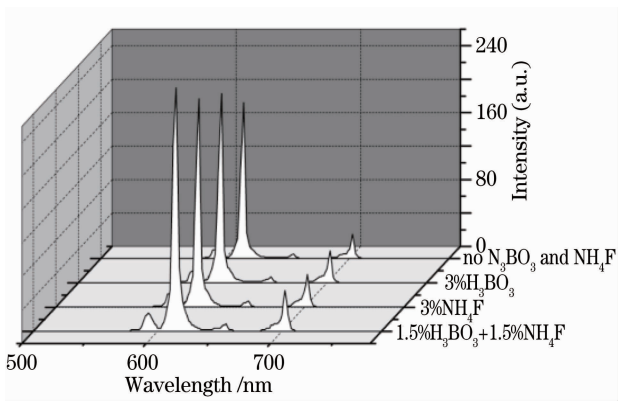

Fig. 3 Cosolvent effect on the luminescent properties of $LiEuW_2O_8$

Raw materials are weighed according to a certain stoichiometric ratio, then ground uniformly in an agate mortar. The raw materials are then placed in alumina crucible. The crucible is placed in the furnace for 3 h, and temperature is set as between 800 ℃ and 900 ℃.

The structure of sample is tested by X-ray power diffraction using Cu Kα radiation on a RIGAKUD max/RB X-ray diffractometer. The Donan 98B (Southeast University, China) phosphor test system is used for spectral analysis of phosphor, using a xenon lamp excitation source. The test results are corrected automatically.

3 Results and discussion

3.1 XRD analysis of $LiEuW_2O_8$ phosphor doped with rare-earth ion

Fig. 4 shows the XRD patterns of $LiEuW_2O_8$. $LiEuW_2O_8$ has a scheelite structure with space group $I4_1/a$. Its major peak 2θ is 29°, with other peaks at 18.8°, 31.7°, 34.4° and 47.5°. The unit cell parameters are $a=0.05201$ nm and $c=0.11253$ nm. Its parameters are close to the standard pattern JCPDS48-886 ($NaYW_2O_8$, $a=0.05208$ nm, and $c=0.11282$ nm). Compared with the standard pattern JCPDS48-886 ($NaYW_2O_8$), replacing Eu^{3+} with La^{3+} and Sm^{3+} does not alter the crystal system and cell structure significantly. Due to the doping of rare-earth ions, the X-ray (XRD) diffraction peak intensity of $LiEuW_2O_8$ doped with rare-earth ions is greater than that of the undoped $LiEuW_2O_8$.

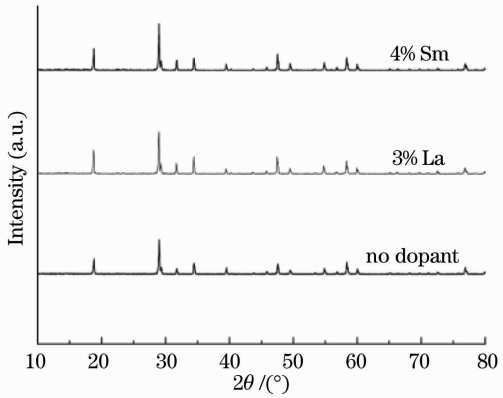

Fig. 4 XRD patterns of $LiEuW_2O_8$ doped with La^{3+} and Sm^{3+}

3.2 Luminescence properties of $LiEuW_2O_8$ phosphor doped with La^{3+}

If the outermost layer of ion is a saturated sp track or fully filled internal track, using an activator is difficult because it has a very stable electronic configuration. As shown in Fig. 5, other ions are doped into the matrix. Except for the activator ion, the ions are able to absorb excitation radiation energy, which is then transferred to the activator. When part of the emission spectrum of Sm^{3+} and the excitation spectrum of Eu^{3+} overlap, the conditions of resonance energy transfer from Sm^{3+} to Eu^{3+} are met. The Sm^{3+} ion replaces the Eu^{3+} ion of $LiEuW_2O_8$. The Sm^{3+} ion plays the role of sensitizer. In this case, the ion that absorbs radiation energy is called the sensitizer[4,5].

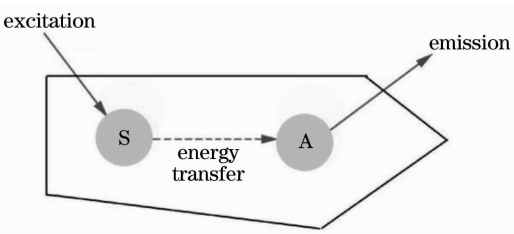

Fig. 5 Energy transfer from S (sensitization) to A (activation)

The outermost three-electron shell structure of La atom is $4s^24p^64d^{10}4f^05s^25p^65d^16s^2$. The La atom loses two 6s electrons and one 5d electron, creating a stable trivalent cation. The outermost electron shells, $5s^2$ and $5p^6$, of the La ion and its internal shells are saturated; thus, it is in a very stable state. The 5p electron has difficulty in transiting through the valence band into the forbidden band; therefore, it is unable to create the necessary condition for fluorescence. We can conclude that the La^{3+} ion is optical inert, and can thus be applied as the matrix material or sensitizer. The La^{3+} ion replaces the Eu^{3+} ion of $LiEuW_2O_8$, and the La^{3+} ion plays the role of sensitizer at this time. By way of reabsorption, the La^{3+} ion transfers the energy to the Eu^{3+} ion.

The chemical formula of the phosphor is $LiEu_{1-x}La_xW_2O_8$. The effects of doping concentration x on the experimental results are as follows. We began from an x value of 0.01, increased it to 0.01, and again gradually increased it to 0.06. The mixed raw materials were calcined at 850 ℃ for 3 h, after which the changes in emission spectra were tested. Emission spectral test results are shown in Table 1.

Table 1 Luminescence properties of $LiEu_{1-x}La_xW_2O_8$ phosphors

Chemical formula	Luminescence intensity	Emission peak /mm	Color coordinate (x, y)
$LiEuW_2O_8$	210	615	0.6678, 0.3315
$LiEu_{0.99}La_{0.01}W_2O_8$	214	615	0.6674, 0.3318
$LiEu_{0.98}La_{0.02}W_2O_8$	219	615	0.6672, 0.3315
$LiEu_{0.97}La_{0.03}W_2O_8$	225	615	0.6678, 0.3322
$LiEu_{0.96}La_{0.04}W_2O_8$	212	615	0.6675, 0.3321
$LiEu_{0.95}La_{0.05}W_2O_8$	207	615	0.6678, 0.3315
$LiEu_{0.94}La_{0.06}W_2O_8$	204	615	0.6675, 0.3312

Fig. 6 and Fig. 7 are the excitation and emission spectra, respectively, of $LiEuW_2O_8$ doped with different contents of La^{3+}. The two figures show that the excitation and emission peak positions of $LiEuW_2O_8$ doped with La^{3+} remain unchanged. $LiEuW_2O_8$ can be excited effectively by 395 nm UV and can emit 615 nm red light. However, as the doping amount of La^{3+} increases, the emission intensity of $LiEuW_2O_8$ phosphor also increases. As the concentration of La^{3+} ion increases, the main emission peak intensity at 615 nm increases. When x is 0.03 (i.e., the molar fraction of La^{3+} is 3%), the emission intensity of $LiEuW_2O_8$ reaches its maximum. When x is greater than 0.05, the emission intensity decreases significantly. Because under a small doping amount, La^{3+} ions play a role as sensitizing agent, the luminescence intensity of $LiEuW_2O_8$ increases. However, when the doping amount of La^{3+} increases, concentration-quenching phenomenon occurs because the concentration of La^{3+} increases continually, resulting in a declination in luminescence intensity. The energy transfers enhanced from La^{3+} to La^{3+}, resulting in a sensitizing effect from La^{3+} to Eu^{3+}.

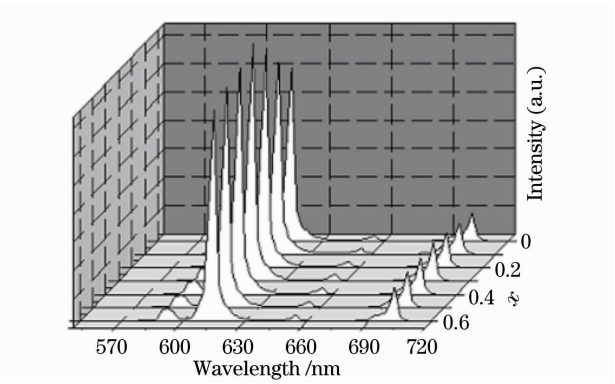

Fig. 6 Emission spectra of $LiEu_{1-x}La_xW_2O_8$ doped with La^{3+}

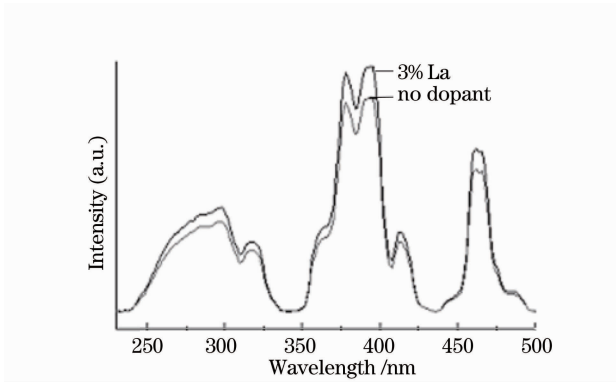

Fig. 7 Excitation spectra of $LiEu_{1-x}La_xW_2O_8$ doped with La^{3+}

3.3 Luminescence properties of $LiEuW_2O_8$ phosphor doped with Sm^{3+}

A strong absorption peak is present between 350 and 410 nm, which belongs to the $^6H_{5/2} \rightarrow {}^4K_{11/2}$ transition of Sm^{3+}. It is a good match with near-UV chips. In addition, the emission spectrum of Sm^{3+} and excitation spectrum of Eu^{3+} more or less overlap, meeting the transfer condition of resonance energy from Sm^{3+} to Eu^{3+}. The chemical formula of the phosphor is $LiEu_{1-x}Sm_xW_2O_8$. The effects of doping concentration x on the experimental results are as follows. We began from an x value of 0.01, increased it to 0.01, and again gradually increased it to 0.07. The mixed raw materials were calcined at 850 ℃ for 3 h, after which the changes in emission spectra were tested. Emission spectral test results are shown in Table 2.

Table 2 Luminescence properties of $LiEu_{1-x}Sm_xW_2O_8$ phosphors

Chemical formula	Luminescence intensity	Emission peak /nm	Color coordinate (x, y)
$LiEuW_2O_8$	210	615	0.6672, 0.3317
$LiEu_{0.99}Sm_{0.01}W_2O_8$	212	615	0.6671, 0.3315
$LiEu_{0.98}Sm_{0.02}W_2O_8$	214	615	0.6682, 0.3311
$LiEu_{0.97}Sm_{0.03}W_2O_8$	217	615	0.6667, 0.3327
$LiEu_{0.96}Sm_{0.04}W_2O_8$	223	615	0.6670, 0.3315
$LiEu_{0.95}Sm_{0.05}W_2O_8$	219	615	0.6657, 0.3321
$LiEu_{0.94}Sm_{0.06}W_2O_8$	211	615	0.6664, 0.3319
$LiEu_{0.93}Sm_{0.07}W_2O_8$	205	615	0.6672, 0.3317

Fig. 8 and Fig. 9 are the excitation and emission spectra, respectively, of $LiEuW_2O_8$ doped with different contents of Sm^{3+}. The figures show that the excitation and emission peak positions of $LiEuW_2O_8$ doped with Sm^{3+} remain unchanged. $LiEuW_2O_8$ can be excited effectively by 395 nm UV and can emit 615 nm red light. Fig. 8 shows that the characteristic excitation peak of Sm^{3+} transition from $^6H_{5/2} \rightarrow {}^4K_{11/2}$ does not exist. The characteristic excitation peak of Sm^{3+} transitioning from $^6H_{5/2} \rightarrow {}^4K_{11/2}$ can match near-UV

chips. In addition, part of the emission spectrum of Sm^{3+} and the excitation spectrum of Eu^{3+} overlap, thereby meeting the conditions of resonance energy transfer from Sm^{3+} to Eu^{3+}. Sm^{3+} ion replaces the Eu^{3+} ion of $LiEuW_2O_8$, and plays the role of sensitizer at this time. By way of reabsorption, the Sm^{3+} ion transfers the energy to the Eu^{3+} ion; thus, the characteristic excitation peak of Sm^{3+} transition from $^6H_{5/2}$ to $^4K_{11/2}$ does not exist. The position of the $LiEuW_2O_8$ emission peak does not change; however, the emission intensity is significantly enhanced after doping. When the concentration of Sm^{3+} ion is increased, the emission intensity at 615 nm increases. When x is 0.04 (i.e., the molar fraction of Sm^{3+} is 4%), the emission intensity of $LiEuW_2O_8$ reaches its maximum. When x is greater than 0.04, the emission intensity decreases. The concentration quenching phenomenon occurs because of the concentration of Sm^{3+} increases continually, resulting in a declination in luminescence intensity. The energy transfer is enhanced from Sm^{3+} to Sm^{3+}, resulting in a sensitizing effect from Sm^{3+} to Eu^{3+}. Fig. 7 and Fig. 9 are nearly the same because La^{3+} and Sm^{3+} merely play the roles of sensitizers. Thus, they are unable to change the emission spectra peak, and merely increase the emission intensity, which is a relative value.

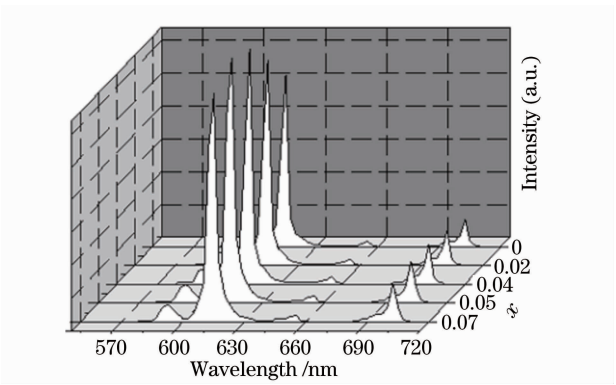

Fig. 8 Emission spectra of $LiEu_{1-x}La_xW_2O_8$ doped with Sm^{3+}

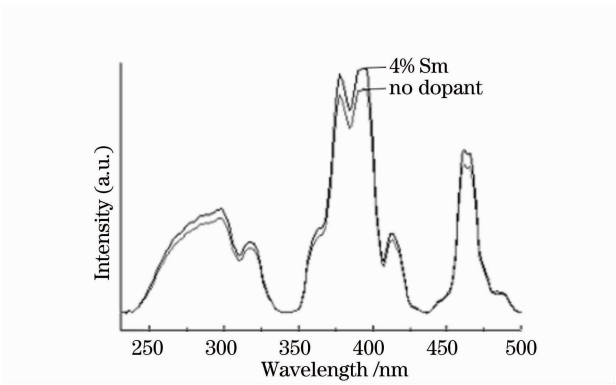

Fig. 9 Excitation spectra of $LiEu_{1-x}Sm_xW_2O_8$ doped with Sm^{3+}

4 Conclusions

We adopt high-temperature solid phase synthesis method to prepare $LiEu_{1-x}RE_xW_2O_8$ (RE = La and Sm) red phosphor. La^{3+} and Sm^{3+} replace the Eu^{3+} of $LiEuW_2O_8$, and both of them transfer energy to Eu^{3+} through reabsorption, thereby realizing the sensitization of Eu^{3+}. After doping, the positions of excitation and emission peaks, as well as the crystal structure do not change; however, the luminescence intensity is improved. With the addition of La^{3+} and Sm^{3+} of 3% and 4% (molar fraction), respectively, the luminescence intensity reaches the maximum.

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