

退火温度对LiBaPO₄:Eu³⁺荧光粉的结构及发光性能影响

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摘要: 采用溶胶-凝胶法制备了LiBaPO₄:Eu³⁺荧光粉,通过热重-差热分析(TG-DTA)、傅里叶变换红外(IR)光谱、X射线衍射(XRD)、透射电子显微镜(TEM)、荧光光谱对荧光粉的结构、发光性质进行表征。TG-DTA结果表明在700 °C之后可形成LiBaPO₄相。IR谱图证实了PO₄³⁻离子的存在。XRD结果表明:温度变化会引起衍射峰不同程度的劈裂;Eu³⁺掺杂浓度会对样品晶相有影响,掺杂浓度较小时样品出现杂相,随着掺杂浓度增加,样品为纯相六方晶系LiBaPO₄。TEM结果表明随着浓度的增加,材料颗粒会发生一定程度的团聚。荧光结果表明:由于活化剂在不同温度下的晶体结构和配位环境的差异,制备的LiBaPO₄:Eu³⁺在不同的退火温度下最佳激发波长不同,其主导的能级跃迁也有所差异,且Eu³⁺引起的浓度猝灭情况也随之而变。CIE计算结果表明,随着退火温度升高,样品色纯度逐渐变好。LiBaPO₄:Eu³⁺可被394 nm长波紫外光有效激发,说明其在白光发光二极管领域有潜在的应用价值。

关键词: 溶胶-凝胶法; LiBaPO₄:Eu³⁺荧光粉; 退火温度; 掺杂浓度; 发光性质

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Effect of Annealing Temperature on the Structure and Luminescence Properties of LiBaPO₄:Eu³⁺ Phosphors

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Abstract: The LiBaPO₄:Eu³⁺ phosphors were prepared by the sol-gel method, and the structure and luminescence properties of the phosphors were characterized by thermogravimetric-differential thermal analysis (TG-DTA), Fourier transformation infrared (IR) spectrum, X-ray diffraction (XRD), transmission electron microscope (TEM), and fluorescence spectrum. TG-DTA results showed that the LiBaPO₄ phase can be formed upon 700 °C. IR spectra confirmed the existence of PO₄³⁻ ions. XRD results showed that temperature change can cause different degrees of cleavage of the diffraction peaks. Eu³⁺ doping concentration can affect the crystal phase of the sample, and the samples with a lower doping concentration appeared impurity, as the doping concentration increased, the sample was a pure phase of hexagonal crystals LiBaPO₄. TEM showed that the material particles agglomerated to a certain extent with the increase in concentration. The fluorescence measurement results showed that LiBaPO₄:Eu³⁺ had different optimal excitation wavelengths at different annealing temperatures and its dominant energy level transition is due to the differences in the crystal structure and coordination environment of the activator at different temperatures, and the concentration quenching caused by Eu³⁺ also varied. CIE calculation results showed that the color purity of the sample gradually improved with the increase of annealing temperature. LiBaPO₄:Eu³⁺ can be effectively excited by 394 nm long-wave ultraviolet light, indicating its potential application in the field of white light-emitting diodes.

Keywords: sol-gel method; LiBaPO₄:Eu³⁺ phosphors; annealing temperature; doping concentration; luminescent properties

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0 Introduction

White light-emitting diodes (wLEDs) are currently one of the most efficient light sources in solid-state lighting applications. At present, there are three main ways to realize wLEDs. One is a white light emission composed of blue and yellow light by coating YAG phosphors on the blue LED chip, when the correlated color temperature of the device decreases, its total efficiency will decrease rapidly; And the lack of red light and its poor color rendering make it unsuitable for solid-state lighting; Secondly, red, green, and blue LED chips are mixed in a certain proportion to produce white light; Finally, the LED ultraviolet light chip is coated the trichromatic phosphor. All of those show that red phosphor plays an important role in achieving white LED. Among the various trivalent rare-earth ions, Eu^{3+} is the preferred source of red light due to its simple energy level structure for probing the local environment of Eu^{3+} ions, and Eu^{3+} doping in crystal hosts is widely studied for potentially efficient red light-emitting materials due to its large transitions from 5D_0 excitation level to 7F_J ($J=0, 1, 2, 3, 4$) energy level in the $4f^6$ configuration in the red region^[1-2], such as $\text{NaYGeO}_4:\text{Eu}^{3+}$ ^[3], $\text{Ba}_3\text{B}_6\text{Si}_2\text{O}_{16}:\text{Eu}^{3+}$ ^[4], $\text{LaSrAl}_3\text{O}_7:\text{Eu}^{3+}$ ^[5], etc.

The great interest in phosphors has led to the rapid development of various displays and other related lighting technologies. For general lighting applications, such as UV light-emitting diodes, photoluminescence (PL) bodies, including silicate, aluminate, aluminosilicate, nitride, and borate, all play a vital role as substrates^[6-9]. Among the subjects of these studies, phosphate as the main material has attracted attention due to its ability to provide many crystal field environments imposed at the emission center. ABPO_4 phosphates with a more rigid crystal structure, good thermal stability, and high quantum conversion rate at high temperatures are also a good matrix for fluorescent materials^[10] and one of the most promising phosphor materials for lamps, cathode ray tubes (CRT), and plasma display panels (PDP)^[11]. Among them, the LiBaPO_4 host provides good applicability in luminescence and other fields.

LiBaPO_4 -based phosphors have been reported in previous studies, such as $\text{LiBaPO}_4:\text{Eu}^{3+}$ phosphors prepared by the high-temperature solid-phase method^[12]. However, The emission spectra showed multi-peak characteristics, and the annealing temperature has not been analyzed; the $\text{LiBaPO}_4:\text{Eu}^{3+}$ phosphor was prepared by an improved high-temperature solid-phase method^[13], where only the concentration was explored and its X-ray diffraction (XRD) pattern showed unexplained miscellaneous peaks; The preparation process of the $\text{LiBaPO}_4:\text{Eu}^{3+}$ phosphor prepared by citrate sol method^[14] was complicated and the concentration was explored and its optimal doping concentration (molar ratio) was 1%, etc. Previous studies have not investigated the effect of annealing temperature on the emission intensity of $\text{LiBaPO}_4:\text{Eu}^{3+}$ phosphors prepared by sol-gel method. Herein, a single-doped Eu^{3+} phosphor based on LiBaPO_4 was prepared by the sol-gel method, and the structure and luminescence properties of the materials at different annealing temperatures and doping concentrations were studied in detail.

1 Experimental

1.1 Reagents and instruments

Diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, AR, 99.0%) was purchased from Tianjin Shengao Chemical Reagent Co., Ltd., which was dissolved in distilled water to formulate a $2.00 \text{ mol}\cdot\text{L}^{-1}$ $(\text{NH}_4)_2\text{HPO}_4$. Eu_2O_3 (AR, 99.999%) was purchased from Baotou Research Institute of Rare Earths, which were dissolved in HNO_3 solution to formulate a $0.10 \text{ mol}\cdot\text{L}^{-1}$ $\text{Eu}(\text{NO}_3)_3$ solution. $\text{Ba}(\text{NO}_3)_2$ (AR, 99.0%) and Li_2CO_3 (AR, 99.0%) were purchased from Tianjin Tianda Chemical Experiment Factory and Shanghai Aladdin Biochemical Technology Co., Ltd., respectively. Li_2CO_3 was dissolved in HNO_3 solution to formulate a $1.00 \text{ mol}\cdot\text{L}^{-1}$ LiNO_3 solution. $\text{Ba}(\text{NO}_3)_2$ was dissolved in distilled water to formulate a $0.20 \text{ mol}\cdot\text{L}^{-1}$ $\text{Ba}(\text{NO}_3)_2$ solution. The citric acid ($\text{C}_6\text{H}_8\text{O}_7$, AR, 99.5%) was purchased from Beijing Chemical Works.

The heating rate of thermogravimetric-differential thermal analysis (TG-DTA) by using French Setaram Labsys Evo synchronous thermal analyzer was $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

min⁻¹. The Fourier transformation infrared (IR) spectrum was detected by the KBr compression method using infrared spectrometer Nicolet 6700 with the scanning 32 times. The phase purity and crystal structure of the samples were confirmed by XRD analysis in the range 20°-80° using Japan Ultima VI XRD diffractometer type with a Cu K α radiation of wavelength 0.154 06 nm ($U=40$ kV, $I=40$ mA). The PL spectra were recorded using Japan Model fluorescence spectrometer F-4500, with a scanning speed of 1 200 nm·min⁻¹ and a slit width of 2.5 nm.

1.2 Synthesis

LiBaPO₄:Eu³⁺ phosphors were synthesized by the sol-gel method. Firstly, LiNO₃ (5.00 mL), Ba(NO₃)₂ (25.00 mL), and amount of Eu(NO₃)₃ (The molar fractions related to LiBaPO₄ were 1%, 3%, 5%, 7%, 9%, 11%, 13%) were added to a clean beaker, and the solution was thoroughly stirred. Then citric acid with a molar ratio of 1:1 to rare-earth ions was added and stirred for 30 min. Secondly, (NH₄)₂HPO₄ solution (2.00 mol·L⁻¹) was added and the solution was heated and kept at 80 °C and stirred for 30 min. Thirdly, the obtained solution was placed in a drying oven at 100 °C for 12 h to obtain a gel with a porous structure. Finally, the dried gel was annealed at different temperatures for 2 h to obtain the final samples.

2 Results and discussion

2.1 TG-DTA

Fig.1 shows the TG-DTA curves of the precursors of LiBaPO₄ under gradient annealing. The weight loss and endothermic phenomena in TG and DTA curves before 150 °C are related to the loss of crystal water; The exothermic peak in the DTA curve at 175.39 °C is attributed to the decomposition of nitrate; The exothermic peak at 510.20 °C is due to the residual organic compounds and the combustion reaction between nitrate compounds and citric acid^[15]. Although the material underwent exothermic reaction above 600 °C, its weight loss curve tends to be stable, which is considered to be the formation of the final LiBaPO₄ phase. Above 700 °C, the structure of the material tended to be stable and did not change. Therefore, the prepara-

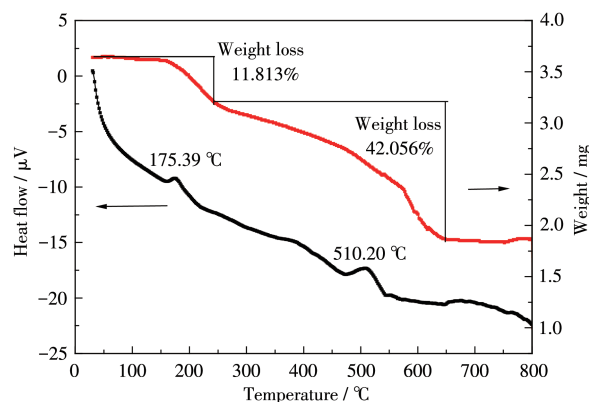


Fig.1 TG-DTA curves of LiBaPO₄ under gradient annealing

tion temperature of the material is above 700 °C.

2.2 IR spectrum

Fig.2 shows the IR spectrum of LiBaPO₄:13%Eu³⁺ in the range of 1 600 to 500 cm⁻¹. The absorption band around 1 386-1 400 cm⁻¹ is caused by the stretching of the P=O along the phosphate chain and the asymmetric stretching of PO₂^[16]. The band at 1 035 cm⁻¹ is caused by PO₄³⁻ symmetric stretching vibration^[17]. The vibration band at 584 cm⁻¹ is attributed to P—O—P asymmetric stretching^[18].

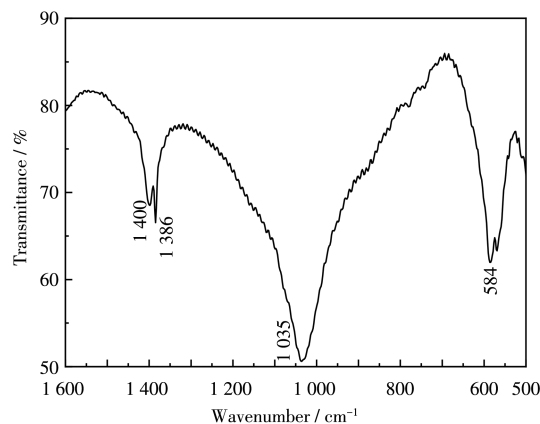


Fig.2 IR spectrum of LiBaPO₄:13%Eu³⁺

2.3 XRD analysis

Fig. 3 shows the XRD patterns of LiBaPO₄ and LiBaPO₄:Eu³⁺. All of the XRD patterns are consistent with the standard card (PDF No. 14-0270). The XRD pattern of LiBaPO₄ annealed at 900 °C shows that LiBaPO₄ belongs to hexagonal crystals, the space group is P6₃, the lattice constants $a=b=0.904$ 6 nm, $c=1.256$ 6 nm, $V=0.391$ 577 nm³, $Z=4$.

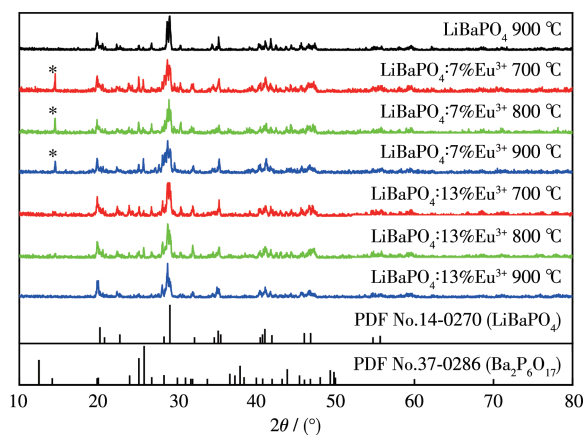


Fig.3 XRD patterns of the LiBaPO_4 and $\text{LiBaPO}_4:\text{Eu}^{3+}$ phosphors

The XRD patterns of $\text{LiBaPO}_4:7\%\text{Eu}$ after annealing at 700, 800, and 900 °C for 2 h are also basically consistent with the standard card (PDF No.14-0270), but the $\text{Ba}_2\text{P}_6\text{O}_{17}$ impurity phase appeared at 15° , and the change of annealing temperature also caused different degrees of splitting of LiBaPO_4 crystal. The weakest degree of splitting was observed when the annealing temperature was 800 °C.

It was found that with the increase of Eu^{3+} doping concentration, the impurity phase of $\text{Ba}_2\text{P}_6\text{O}_{17}$ disappeared at 15° , and the temperature of different degrees of splitting of LiBaPO_4 changed. When the annealing temperature was 900 °C, the splitting degree was the weakest and tended to the pure phase, so 900 °C was selected as the best annealing temperature of the samples. The possible reason is that with the increase of annealing temperature and Eu^{3+} doping concentration, the number of luminescence centers increases, and the molecules or ion groups in the crystal rotate freely, to obtain higher symmetry and make the crystal structure more complete; Or when Eu^{3+} replaces Ba^{2+} , lattice defects are created and more luminescent centers are generated^[19].

2.4 TEM images of $\text{LiBaPO}_4:\text{Eu}^{3+}$

The TEM images of $\text{LiBaPO}_4:\text{Eu}^{3+}$ are shown in Fig.4. It can be seen that $\text{LiBaPO}_4:7\%\text{Eu}^{3+}$ was composed of a circular particle with a particle size of about 200 nm (Fig.4a). Fig.4b shows a representative TEM image of $\text{LiBaPO}_4:13\%\text{Eu}^{3+}$ and it was composed of easily clumped particles with irregular morphology and

partially agglomerated into circular particles (Fig.4c), which may be the reason for the splitting of the XRD peak. The agglomeration of the particles can enhance the electron-hole recombination rate and the luminescence performance of the phosphors^[20-21].

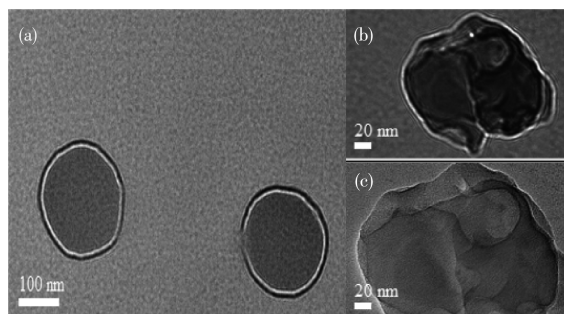


Fig.4 TEM images of $\text{LiBaPO}_4:7\%\text{Eu}^{3+}$ (a) and $\text{LiBaPO}_4:13\%\text{Eu}^{3+}$ (b, c)

2.5 Luminescence properties of $\text{LiBaPO}_4:\text{Eu}^{3+}$

Fig.5 shows the excitation and emission spectra of $\text{LiBaPO}_4:7\%\text{Eu}^{3+}$ phosphors at different annealing temperatures. As shown in Fig.5a, the excitation spectrum was composed of broadband of 200-300 nm and some spikes, where the strongest peak in 200-300 nm broadband was located at 255 nm and belongs to the $\text{O}^{2-}-\text{Eu}^{3+}$ charge transfer band from the ligand to the metal, while the spikes in 300-500 nm correspond to the $f-f$ transition of Eu^{3+} ions, which corresponds to ${}^7F_0-{}^5H_6$ (318 nm), ${}^7F_0-{}^5D_4$ (362 nm), ${}^7F_0-{}^5L_7$ (382 nm), ${}^7F_0-{}^5L_6$ (394 nm), ${}^7F_0-{}^5D_3$ (416 nm), and ${}^7F_0-{}^5D_2$ (465 nm) transitions, respectively^[22]. It is found that the excitation spectra of the samples annealed at 800 and 900 °C were quite different. The optimum excitation wavelength of the sample annealed at 800 °C was 255 nm, and the monitoring wavelength used in the test was 593 nm, while the optimum excitation wavelength of 900 °C annealed samples was 394 nm, and the monitoring wavelength was 615 nm.

As shown in Fig.5b, the emission spectra were composed of peaks in the range of 570-700 nm, which is related to the transition of Eu^{3+} from 5D_0 to 7F_J ($J=0, 1, 2, 3$, and 4) energy levels, attributed to ${}^5D_0 \rightarrow {}^7F_0$ (578 nm), ${}^5D_0 \rightarrow {}^7F_1$ (593 nm), ${}^5D_0 \rightarrow {}^7F_2$ (615 nm), ${}^5D_0 \rightarrow {}^7F_3$ (652 nm), and ${}^5D_0 \rightarrow {}^7F_4$ (688 nm)^[23]. The emission spectra of the samples annealed at 800 °C with 255 or 394 nm as excitation energy showed that

the strongest emission peak appeared at 593 nm, corresponding to the $^5D_0 \rightarrow ^7F_1$ transition, while the peak at 615 nm corresponding to the $^5D_0 \rightarrow ^7F_2$ transition was weak, indicating that Eu³⁺ occupies the center of inversion symmetry and hardly changes with the crystal field strength. The emission spectra of the samples annealed at 900 °C with 394 nm as the best excitation energy showed that the intensity difference between the emission peak at 593 nm corresponding to the $^5D_0 \rightarrow ^7F_1$ transition and the emission peak at 615 nm corresponding to the $^5D_0 \rightarrow ^7F_2$ transition was small and the intensity of the emission peak at 615 nm was slightly stronger, indicating that Eu³⁺ is located in the asymmetric central lattice, and the odd-order term of the crystal field can mix the opposite parity state into the $4f^6$ configuration energy level. At this time, the electric dipole transition is no longer strictly prohibited, Eu³⁺ is mainly emitted by $^5D_0 \rightarrow ^7F_2$ forced electric dipole transition, and the whole material is red light emission^[24]. Combined with the XRD patterns, it is speculated that the existence of the Ba₂P₆O₁₇ phase may be one of the reasons for the energy redistribution of Eu³⁺ between $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions^[25]. These changes showed that the monitored wavelengths varied with annealing temperature and their dominant energy level transitions, which may be related to the crystal structure and coordination environment of the activator at different temperatures^[26].

Generally, the intensity of the charge transfer band was higher than the $f-f$ transition of Eu³⁺, but the LiBaPO₄:Eu³⁺ phosphors annealed at 900 °C have

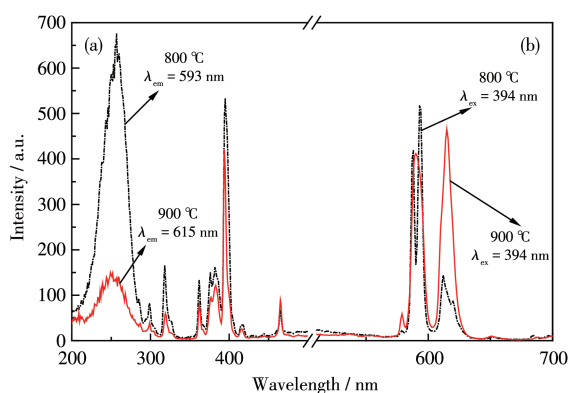


Fig.5 Excitation (a) and emission (b) spectra of LiBaPO₄:7%Eu³⁺ annealed at 800 and 900 °C

observed an experimental phenomenon different from that of 800 °C, that is, the intensity of the $f-f$ transition was stronger than the charge transfer band, which may be related to the fact that the energy of Eu—O electron cloud migration is not enough to effectively reach the luminous center of Eu³⁺^[27]. In the excitation spectrum, the sample annealed at 900 °C shows a small excitation band near 255 nm. The analysis shows that the substitution of Eu³⁺ for Ba²⁺ into the matrix lattice is unequivocal, and interstitial oxygen or vacancy may be generated in the crystal during annealing at 900 °C. This makes it difficult for the 2p electrons of O²⁻ adjacent to Eu³⁺ to migrate to the 4f level of Eu³⁺, resulting in the decrease of charge transition efficiency between O²⁻ → Eu³⁺^[12]. At the same time, the exciting 2p electron of O²⁻ enters the 4f orbital of Eu³⁺, and the energy difference between the 2p valence band of O²⁻ and the 4f orbital of Eu³⁺ determines the position of the charge transfer state (CTS). Although the bonding between Eu³⁺ and ligand O²⁻ is independent of the 4f orbital, the bonding orbital (2p) and anti-bonding orbital (5d) are formed by the interaction between the 5d orbital of Eu³⁺ and the 2p orbital of O²⁻. The longer the Eu³⁺—O²⁻ bond, the smaller the energy difference between the 2p valence band of O²⁻ and the 4f orbital of Eu³⁺. Since the average bond length of Ba—O is greater than that of Li—O, the energy difference between the orbital of Eu³⁺ and the 2p electron of O²⁻ is small. Therefore, the CTS energy of Eu³⁺ occupying the Ba²⁺ lattice is low^[28].

Fig. 6 shows the relationship between emission intensity and the Eu³⁺ doping concentration of LiBaPO₄. During annealing at 800 °C, with the gradual increase of Eu³⁺ concentration, the emission intensity of the sample increased first and then decreased. With the increase of Eu³⁺ concentration, the intensity of the emission peak reached the maximum when the concentration of Eu³⁺ was 7%. The existence of too many luminescent centers of Eu³⁺ makes the distance between Eu³⁺ shorter, and the probability of collision between ions in the excited state increases, so part of the ions in the excited state will lose excitation energy and return to the ground state. So that the phosphor luminous intensity gradually weakened. When the annealing tem-

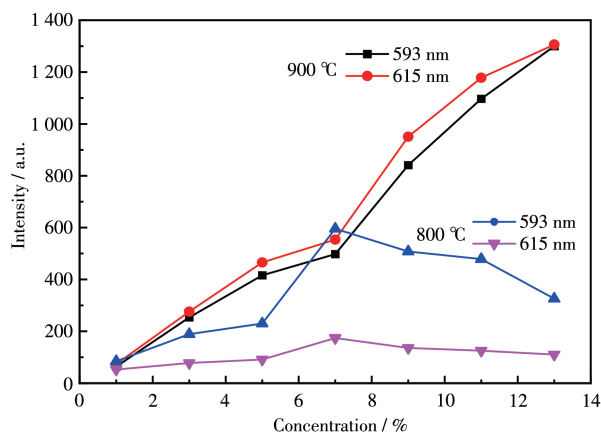


Fig.6 Relationship between emission intensity and the Eu^{3+} doping amount of $\text{LiBaPO}_4:\text{Eu}^{3+}$

perature was 900 °C and the doping concentration reached 13%, the emission peak intensity still showed an upward trend, and the optimal doping concentration was not determined.

Fig. 7 shows the relationship between emission intensity and annealing temperature of the sample. It is determined that the optimal annealing temperature was 900 °C, and only at this annealing temperature, the emission spectrum was dominated by the $^5D_0 \rightarrow ^7F_2$ energy level transition, indicating that the annealing temperature is too high or too low, which is not suitable for the preparation of red phosphors.

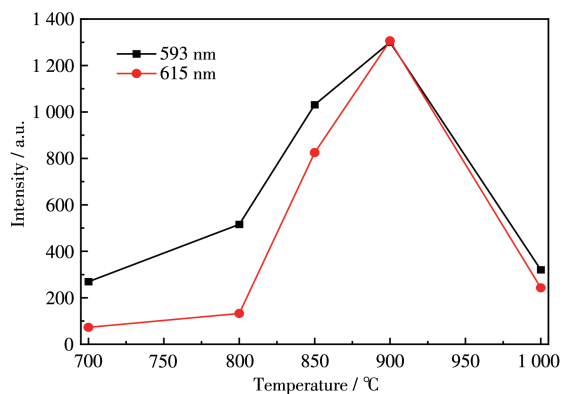


Fig.7 Relationship between emission intensity and annealing temperature of $\text{LiBaPO}_4:13\%\text{Eu}^{3+}$

The difference with the experimental results^[12] is that the optimum doping concentration of the sample synthesized by the high-temperature solid-state method was 5%; Puppallwar et al.^[13] used the improved high-temperature solid-state method, and the optimum doping concentration of the sample was 3%; Game et al.^[14]

the prepared samples by citric acid sol method, the best doping concentration of the samples was 3%. However, the emission peak intensity of the samples prepared by the sol-gel method in this experiment still showed an upward trend when the doping concentration was 13% and the optimal annealing temperature was 900 °C. The results show that the phosphor prepared by the sol-gel method can improve the luminescence efficiency of rare-earth ions more than other methods, and can effectively delay the concentration quenching effect of rare-earth ions. Compared with the Eu^{3+} luminescence properties of other material systems, orange or red phosphors can be prepared at different annealing temperatures. The result is consistent with the XRD result. The sample annealed at 900 °C was a pure phase of LiBaPO_4 with good luminescence. The spectral characteristics of the material show that $\text{LiBaPO}_4:\text{Eu}^{3+}$ can be effectively excited by 394 nm long-wave ultraviolet light, indicating its potential application value in the field of wLEDs.

The critical distance (R_c) corresponding to the critical quenching concentration is defined as the average shortest distance between the nearest Eu^{3+} ions where energy transfer occurs. If the distance between adjacent Eu^{3+} ions is less than 0.5 nm, the energy transfer is mainly realized by exchange interaction, and when the distance is greater than 0.5 nm, the multi-pole interaction is dominant. The critical distance of energy transfer is estimated by the following formula:

$$R_c \approx [3V/(4\pi X_c N)]^{1/3}$$

Where X_c is the critical concentration, N is the number of cations in the unit cell, and V is the volume of the unit cell. According to the crystal structure of the sample, the V and N values were obtained by consulting relevant information, and the X_c values were obtained by analyzing the experimental data ($V=0.391\,577\text{ nm}^3$, $Z=4$, and $X_c=0.07$ (800 °C)/ $X_c=0.13$ (900 °C), respectively). The critical distance of $\text{LiBaPO}_4:\text{Eu}^{3+}$ was calculated to be about 1.387 7 nm/1.128 9 nm, which is greater than 0.5 nm. Therefore, the multipole interaction of the samples annealed at 800 or 900 °C is responsible for the concentration quenching.

Fig.8 shows the simplified energy level diagram

and the proposed relaxation mechanism of Eu³⁺ in LiBaPO₄:Eu³⁺ under excitation at 394 nm. PL emission is due to the transition of electrons between energy levels, involving the excitation of electrons from the ground state to the excitation level ⁵L₆ of Eu³⁺ after absorbing an excited photon, and then non-radiative relaxation to the lower ⁵D₀ energy level of Eu³⁺ ions. The rapid non-radiative (NR) multi-phonon relaxation from the excited state to the ⁵D₀ energy level is followed by the radiative emission corresponding to the ⁵D₀ → ⁷F_{*J*} (*J*=0, 1, 2, 3, 4) transition of Eu³⁺. Taking 394 nm excitation as an example, under the excitation of this wavelength, the electron undergoes a ⁷F₀-⁵L₆ transition, and then transfers to the lower energy level of ⁵D₀ through non-radiative transition, resulting in characteristic emission at 593 and 615 nm (⁵D₀ → ⁷F_{1,2}). The excitation mechanism of other wavelengths is the same. When the annealing temperature was 800 °C, Eu³⁺ occupies the center of inversion symmetry and the ⁵D₀ → ⁷F₁ transition is strong; When annealed at 900 °C, Eu³⁺ is in the central lattice of non-inversion symmetry, and Eu³⁺ is mainly emitted by ⁵D₀ → ⁷F₂ electric dipole transition.

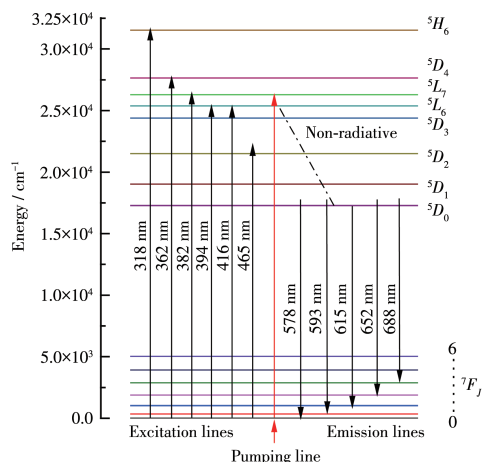


Fig.8 Simplified energy level image of Eu³⁺

2.6 CIE coordinate of LiBaPO₄:Eu³⁺

Fig.9 is the CIE coordinate diagram of LiBaPO₄:7%Eu³⁺ (800 °C) and LiBaPO₄:13%Eu³⁺ (900 °C) phosphors calculated by 1931CIE. The coordinate value of LiBaPO₄:7%Eu³⁺ at 800 °C was (0.457 0, 0.484 4); At 900 °C, the coordinate value of LiBaPO₄:13%Eu³⁺ was (0.576 0, 0.354 6), which are all located in the red-

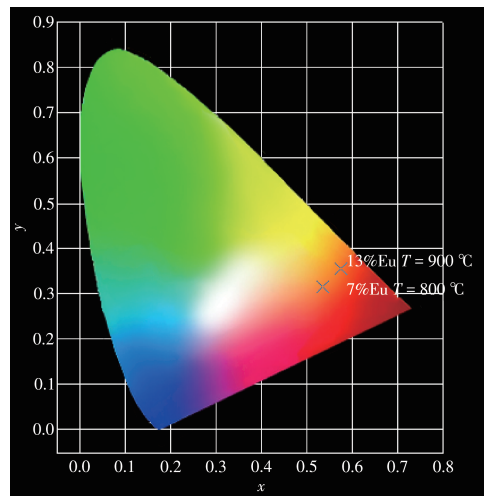


Fig.9 CIE coordinate diagram of the LiBaPO₄:Eu³⁺ phosphors

light region.

3 Conclusions

The LiBaPO₄:Eu phosphors were prepared by the sol-gel method. The results of the TGA showed that the LiBaPO₄ phase could be formed after 700 °C. The absorption peaks obtained in the IR spectra confirmed the existence of PO₄³⁻ and symmetrical and asymmetrical tensile vibrations among P—O in the samples. The XRD results showed that the temperature variations caused the split in varying degrees of diffraction peaks. The doping concentration of Eu³⁺ will affect the structure, and the sample with a small doping concentration appeared heterophase. With the increase of concentration, the sample showed a pure phase. The experimental results show that when the annealing temperature was 800 °C, the charge transfer band was the monitoring wavelength, and the emission spectrum was dominated by the ⁵D₀ → ⁷F₁, indicating that Eu³⁺ occupies the center of inversion symmetry. When the annealing temperature was 900 °C, the *f-f* transition was the monitoring wavelength, and the ⁵D₀ → ⁷F₂ emission of Eu³⁺ in LiBaPO₄ was dominated, indicating that Eu³⁺ is in an asymmetric central lattice. With the change of monitoring wavelength, the dominant energy level transition was different, and the concentration quenching caused by Eu³⁺ also changed. CIE calculation showed that the color purity of the sample became better with the increase in annealing temperature and concentration.

References:

- [1] Pucker G, Gatterer K, Fritzer H P, Bettinelli M, Ferrari M. Optical Investigation of Eu^{3+} in a Sodium Borosilicate Glass: Evidence for Two Different Site Distributions. *Phys. Rev. B*, **1996**, **53**(10):6225-6234
- [2] Yan B, Su X Q. *In Situ* Chemical Coprecipitation Composition of Hybrid Precursors to Synthesize $\text{Y}_x\text{V}_{1-x}\text{O}_4:\text{Eu}^{3+}$ Micron Crystalline Phosphors. *Mater. Sci. Eng. B*, **2005**, **116**(2):196-201
- [3] Han B, Chen Y W, Liu B B, Zhang J Y. Solid State Synthesis and Luminescence Properties of Eu^{3+} Doped NaYGeO_4 Phosphors. *Optik*, **2021**, **242**:167177
- [4] Fan B, Han L M, Zhao W. Luminescence Properties of Novel Red-Emitting Phosphors $\text{Ba}_3\text{B}_6\text{Si}_2\text{O}_{16}:\text{Eu}^{3+}$ for Near - UV Excited LED. *Optik*, **2020**, **207**:164429
- [5] Mendhe M S, Bhure P P, Dhabale P C, Revankar S G, Puppulwar S P. Improvement of Luminescence Properties of $\text{LaSrAl}_3\text{O}_7:\text{Eu}^{3+}$ Phosphor. *Mater. Today: Proc.*, **2019**, **15**:633-637
- [6] Zhou X J, Xiong Z X, Xue H, Lin Y S, Song C X. Hydrothermal Synthesis and Photoluminescent Properties of $\text{Li}_2\text{Sr}_{0.996}\text{SiO}_4:\text{Pr}_{0.004}^{3+}$ Phosphors for White-LED Lightings. *J. Rare Earths*, **2015**, **33**(3):244-248
- [7] Çirçir E, Kalaycioglu N O. Host-Sensitized Phosphorescence of Mn^{4+} , Pr^{3+4+} and Nd^{3+} in $\text{MgAl}_2\text{Si}_2\text{O}_8$. *Mater. Res. Bull.*, **2012**, **47**(5):1138-1141
- [8] Smet P F, Botterman J, Koen V, Korthout K, Poelman D. Persistent Luminescence in Nitride and Oxynitride Phosphors: A Review. *Opt. Mater.*, **2014**, **36**(11):1913-1919
- [9] Mokoena P P, Gohain M, Bezuidenhout B, Swart H C, Ntwaeaborwa O M. Luminescent Properties and Particle Morphology of $\text{Ca}_3(\text{PO}_4)_2:\text{Gd}^{3+}$, Pr^{3+} Phosphor Powder Prepared by Microwave Assisted Synthesis. *J. Lumin.*, **2014**, **155**:288-292
- [10] 李武林. NUV-LED用 ABPO_4 基荧光粉制备与发光特性研究. 重庆: 重庆大学, **2014**:9-10
LI W L. *Preparation and Luminescence Characteristics of ABPO_4 Based Phosphor for NUV - LED*. Chongqing: Chongqing University, **2014**:9-10
- [11] Lin C C, Tang Y S, Hu S F, Liu R S. $\text{KBaPO}_4:\text{Ln}$ ($\text{Ln}=\text{Eu}$, Tb , Sm) Phosphors for UV Excitable White Light-Emitting Diodes. *J. Lumin.*, **2009**, **129**(12):1682-1684
- [12] Li P L, Wang Y Z, Wang Z J, Guo Q L, Yang Z P. Preparation and Luminescence Properties of $\text{LiBaPO}_4:\text{Eu}^{3+}$ Materials. *J. Lumin.*, **2011**, **32**(7):665-669
- [13] Puppulwar S P, Dhoble S J. Photoluminescence Properties of $\text{LiBaPO}_4:\text{M}^{3+}$ Phosphor for Near-UV Light-Emitting Diode ($\text{M}=\text{Eu}$ and Dy). *J. Lumin.*, **2015**, **30**(6):745-750
- [14] Game D N, Palan C B, Ingale N B, Omanwar S K. Synthesis and Photoluminescence Properties of Eu Doped LiBaPO_4 Phosphors for Solid State Lighting. *J. Mater. Sci.: Mater. Electron.*, **2017**, **28**(12):8777-8783
- [15] Keskin İ Ç, Türemiş M, Katı M İ, Gültekin S, Arslanlar Y T, Çetin A, Kibar R. Detailed Luminescence (RL, PL, CL, TL) Behaviors of Tb^{3+} and Dy^{3+} Doped LiMgPO_4 Synthesized by Sol-Gel Method. *J. Lumin.*, **2020**, **225**:117276
- [16] Chengaiah T, Jamalaiah B C, Moorthy L R. Luminescence Properties of Eu^{3+} -Doped $\text{Na}_3\text{Gd}(\text{PO}_4)_2$ Red-Emitting Nanophosphors for LEDs. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, **2014**, **133**:495-500
- [17] Wang L Y, Wang X, Song Q W, Xie T Y, Guo X Q, Wang N, Guang J, Han Y Y. Hydrothermal Synthesis for the Enhanced Red and Green $\text{Sr}_3\text{Y}(\text{PO}_4)_3:\text{Eu}^{3+}$, Tb^{3+} Phosphors. *Mod. Phys. Lett. B*, **2019**, **33**(5):1950048
- [18] Doddaji R, Thummala C. Efficient Blue-White Color Luminescence with Near-Ultraviolet Excitation in $\text{Dy}^{3+}/\text{Tm}^{3+}:\text{Na}_3\text{Gd}(\text{PO}_4)_2$ Nanophosphor for White LEDs. *Solid State Sci.*, **2020**, **101**:106126
- [19] 陈永杰, 左修源, 肖林久, 耿秀娟, 杨英, 张中秋, 申秋, 曹爽. 橙红色荧光粉 $\text{NaBa}_{1-x}\text{PO}_4:x\text{Eu}^{3+}$ 中 Eu^{3+} 的占位情况及光谱性质. 硅酸盐学报, **2019**, **47**(4):494-500
CHEN Y J, ZUO X Y, XIAO L J, GENG X J, YANG Y, ZHANG Z Q, SHEN Q, CAO S. Occupation and Spectral Properties of Eu^{3+} in Red Orange Phosphor $\text{NaBa}_{1-x}\text{PO}_4:x\text{Eu}^{3+}$. *Journal of Chinese Ceramic Society*, **2019**, **47**(4):494-500
- [20] 闫志云. Tb^{3+} 掺杂 SiO_2 核-壳结构材料的制备及发光性能研究. 西安: 西北大学, **2011**:14-39
YAN Z Y. *Preparation and Luminescence Properties of Tb^{3+} -Doped SiO_2 Core-Shell Structured Materials*. Xi'an: Northwestern University, **2011**:14-39
- [21] 井立强, 孙晓君, 蔡伟民, 李晓倩, 付宏刚, 候海鸽, 范乃英. 掺杂 Ce 的 TiO_2 纳米粒子的光致发光及其光催化活性. 化学学报, **2003**, **8**:1241-1245
JING L Q, SUN X J, CAI W M, LI Q Q, FU H G, HOU H G, FAN N Y. Photoluminescence of Ce Doped TiO_2 Nanoparticles and Its Photocatalytic Activity. *Acta Chim. Sinica*, **2003**, **8**:1241-1245
- [22] Tian S H, Li X, Hou Y B, Teng F. Facile Combustion Synthesis and Luminescent Properties of Eu^{3+} Doped Alkali-Alkaline Earth Metal Phosphate Red Phosphor. *Optik*, **2018**, **157**:429-434
- [23] Balakrishna A, Reddy L, Ntwaeaborwa O M, Swart H C. Remarkable Influence of Alkaline Earth Ions on the Enhancement of Fluorescence from Eu^{3+} Ion Doped in Sodiumortho-Phosphate Phosphors. *J. Mol. Struct.*, **2019**, **1203**:127375
- [24] Wu Z C, Liu J, Gong M L, Su Q. Optimization and Temperature-Dependent Luminescence of $\text{LiBaPO}_4:\text{Eu}^{2+}$ Phosphor for Near-UV Light-Emitting Diodes. *J. Electrochem. Soc.*, **2009**, **156**(3):H153-H156
- [25] Long Q W, Xia Y, Huang Y H, Liao S, Gao Y, Huang J M, Liang J Q, Cai J J. Na^+ Induced Electric-Dipole Dominated Transition ($^5D_0 \rightarrow ^7F_2$) of Eu^{3+} Emission in $\text{AMgPO}_4:\text{Eu}^{3+}$ ($\text{A}=\text{Li}^+$, Na^+ , K^+) Phosphors. *Mater. Lett.*, **2015**, **145**:359-362
- [26] Zhang S, Nakai Y, Tsuboi T, Huang Y. Luminescence and Microstructural Features of Eu-Activated LiBaPO_4 Phosphor. *Chem. Mater.*, **2011**, **23**(5):1216-1224
- [27] Lin C C, Liu R S, Tang Y S, Hu S F. Full-Color and Thermally Stable $\text{KSrPO}_4:\text{Ln}$ ($\text{Ln}=\text{Eu}$, Tb , Sm) Phosphors for White-Light-Emitting Diodes. *J. Electrochem. Soc.*, **2008**, **155**(9):J248-J251
- [28] Zhang S, Huang Y, Seo H J. The Spectroscopic Properties and Structural Occupation of Eu^{3+} Sites in LiMgPO_4 Phosphor. *J. Electrochem. Soc.*, **2010**, **157**(5):J186-J190