Luminescent properties of a novel green phosphor CePO₄-6LaPO₄:Tb³⁺

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Abstract: 6LaPO₄-CePO₄:Tb³⁺ phosphors were synthesized by coprecipitation-high temperature solid phase methods. The structure and luminescence properties of phosphors were tested and analyzed by XRD, IR and fluorescence spectroscopy. The XRD pattern showed that the phosphors were LaPO₄ and CePO₄ of monoclinic; the FT-IR spectrum showed the same results as the XRD results; the fluorescence spectrum showed that the phosphors emitted green light at 544 nm, which corresponded to the transitions ⁵D₄-⁷F₅ of Tb³⁺.

1. Introduction
At present, phosphors are generally composed of luminescent center and matrix materials. The rare earth ion Tb³⁺ emitting excellent green light under the excitation of light, and is an ideal green light illuminating center[1-3]. It is well known that due to the f-f forbidden transition of rare earth ions, the absorption efficiency is low, so it is necessary to find some methods to enhance the absorption efficiency. The method commonly used to enhance the absorption efficiency is to dope rare earth ions as an activator and select a suitable matrix material. The energy absorbed by the matrix material can transmit to the activation center effectively to improve the luminous efficiency. This shows the choice of matrix materials is crucial. Phosphates have excellent thermal stability, high chemical stability and other excellent properties[4-7]. So, phosphates have become an important matrix materials. Studying on CePO₄ or LaPO₄ as matrix materials are very common[1,2,8-10], but it is not common about CePO₄ and LaPO₄ as composite matrix. Therefore, 6LaPO₄-CePO₄:Tb³⁺ phosphors were prepared by coprecipitationl-high temperature solid-phase methods. The structure and luminescence properties of the phosphors also were investigated.

2. Experiments
2.1 Synthesis of samples
CePO₄-6LaPO₄:Tb³⁺ green phosphors were synthesized by co-deposition and high temperature solid state methods. Firstly, La(NO₃)₃ (the concentration of La(NO₃)₃ solution is 0.16 mol/L, measured 9 mL of this solution), Ce(NO₃)₃ (the concentration of Ce(NO₃)₃ solution is 0.16 mol/L, measured 1.5 mL of this solution) and TbCl₃ 5% (mol) were added to clean beaker, which was stirred for 5 min. Then H₃PO₄ (the concentration of H₃PO₄ solution is 0.16 mol/L, measured 10.5mL of this solution) was added to clean beaker, which was stirred for 5 min. Then H₃PO₄ (the concentration of H₃PO₄ solution is 0.16 mol/L, measured 10.5mL of this solution) was added to stir for 30 min, and formed white precipitations. Secondly, NH₃⋅H₂O was added to adjust pH to 1, 3, 5, 7, 9,
11, and stirred about 2 hours in room temperature. Thirdly, the white precipitations were filtered from the mixed solution, which was washed several times with ethanol and deionized water and dried at room temperature about 1 day. Then the samples were annealed at 800 °C for 17 hours. Finally, the samples were obtained.

3. Results and discussion

3.1. XRD study

Fig.1 XRD pattern of CePO₄-6LaPO₄:6(mol)% Tb³⁺ at different pH conditions

Fig.1 showed that the XRD patterns of CePO₄-6LaPO₄:6(mol)% Tb³⁺ phosphors at different pH conditions. It could be seen from the fig.1 that all the diffraction peaks of the sample showed very similar profiles, and were agreed with the standard card (No. 32-0493 and No. 46-1326), which means that monoclinic phase LaPO₄ and CePO₄ was predominant.

3.2. IR study

Fig.2 FT-IR spectrum of CePO₄-6LaPO₄:6(mol)% Tb³⁺ at different pH conditions

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Fig. 2 showed that FT-IR spectrum of CePO₄·6LaPO₄·6(mol)% Tb³⁺ phosphors at different pH conditions. It can be seen from Fig. 2 that the phosphors had a similar infrared characteristic absorption band in the range of 1600-400 cm⁻¹. The absorption peak at 1107, 1063, and 1016 cm⁻¹ belonged to asymmetric stretching vibration peak of P-O; 952 cm⁻¹ belonged to symmetrical stretching vibration of P-O; the peak at 626 cm⁻¹ belonged to the bending vibration peak of O=P-O; The peak at 575, 559, and 535 cm⁻¹ were the bending vibrations of O-P-O [8,9]. The absorption of N-H was not observed in the FT-IR spectrum, which showed that ammonia volatilized completely. The result indicated the sample was phosphate, which was consistent with XRD study.

3.3. Luminescence study

3.3.1. Excitation and emission spectra of CePO₄·6LaPO₄·Tb³⁺

Fig. 3 Excitation spectrum of phosphors at different pH conditions (λ_em=544nm)

Fig. 3 showed that the excitation spectra of CePO₄·6LaPO₄·Tb³⁺ phosphors at different pH conditions. The excitation spectra consisted of a broad peaks at 286 nm, and the peaks corresponded to the charge transfer band of O²⁻·Tb³⁺(CT). It could be seen from the excitation spectrum that the phosphors of pH value was 1 gave the strongest absorption peak at 286 nm.

Fig. 4 Emission spectrum of phosphors at different pH conditions (λ_exc=286nm)

Fig. 4 showed that the emission spectra of CePO₄·6LaPO₄·Tb³⁺ phosphors at different pH conditions. The emission spectra consisted of a broad peaks at 286 nm, and the peaks corresponded to the charge transfer band of O²⁻·Tb³⁺(CT). It could be seen from the emission spectrum that the phosphors of pH value was 1 gave the strongest emission peak at 386 nm.
Fig. 4 showed that the emission spectra of CePO₄·6LaPO₄:Tb³⁺ phosphors at different pH conditions (λₑₓ=286nm). The emission peaks of 544 and 588 nm corresponded to the transitions from ⁵D₄ to ⁷F₅ (544 nm) and ⁷F₄ (588 nm), respectively, which gave the strongest emission intensity at 544 nm (⁵D₄→⁷F₅).

The excitation and emission spectrum showed that the emission of green light gradually decreases with the increase of pH, and the phosphors was benefited to emit a strongest green light when pH=1. With the pH increases, the phosphors would exist in the form of basic phosphates, which is not conducive to luminescence of the sample. Therefore, the optimal pH was 1.

3.3.2. Luminescent properties of CePO₄·6LaPO₄:x% (mol)Tb³⁺

Fig. 5 showed that the Emission spectrum of CePO₄·6LaPO₄:x% (mol)Tb³⁺. It showed that the mutual exchange effect increase with Tb³⁺ concentration, which resulted in luminescence quenching[8]. The result indicated that optimal Tb³⁺ concentration was 6% (mol), which was most favorable for green luminescence.

The phosphor synthesized at the above optimal conditions was most beneficial to green light emission. This is due to the formation of isoelectronic trap. The analysis is as follows:

The difference in covalent radius and electronegativity between Tb³⁺ and La³⁺, which produce an impurity potential dominated by short-range effects, which can trap holes and easily form isoelectronic traps[11]. In the paper, Tb³⁺ was equivalently substituted for La³⁺/Ce³⁺ to form an isoelectronic trap, which combined with the intrinsic defects in the matrix to form a defect complex (i.e.:Tb³⁺ isoelectronic trap and phosphate group PO₄³⁻), and the emission peaks were located at 544 and 588 nm, which was also showing the characteristics of electron traps such as Tb³⁺.

4. Conclusion

A series of CePO₄·6LaPO₄:Tb³⁺ green phosphors were synthesized by coprecipitation-high temperature solid phase methods, which ensured the uniformity of Tb³⁺ doping in the phosphors. The results showed that the optimal Tb³⁺ concentration was 6 mol%, the optimum pH was 1, and the optimal excitation wavelength was 286 nm. The green phosphors were synthesized at above conditions, the sample emitted strong green light and was a good candidate for green phosphors.
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