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Fluorescent Temperature Characteristics of CaMoO4:5%Tb^{3+} Based on Variable Temperature Excitations

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Abstract: This study focuses on the fluorescent thermometric properties of CaMoO4:5%Tb3+ under different temperature excitations. At the detection wavelength of 544 nm, with the temperature varying from 293 K to 563 K, there is a broadband absorption peak in the range of 250 nm to 350 nm. The results indicate that this phenomenon is caused by the superposition of the 4f-5d transition of Tb3+ and the O2--Mo6+ charge transfer. It is considered that as the temperature rises, the luminescent intensity of the material shows an obvious continuous decreasing trend, which reflects a significant luminescent thermal quenching trend; thus, this quenching belongs to the "strong coupling" type. Based on the excitation spectrum results, two excitation wavelengths, 312 nm and 338 nm, were specifically selected to excite the samples, which correspond to the top of the charge transfer band, the redshift intersection of the charge transfer band, and the edge of the charge transfer band at 293 K, respectively.

Keywords: Strong coupling; Fluorescent temperature characteristics; Excitation

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1. Introduction

Rare earth elements have unfilled 4f5d electron configurations shielded from the external environment, thus possessing abundant electronic energy levels and long-lived excited states, which can generate a variety of radiation absorption and emission. Luminescence is a phenomenon in which an object directly converts internally absorbed energy (in some way) into non-equilibrium radiation without going through a thermal stage. Molybdate-based tricolor phosphors have attracted widespread attention due to their advantages, such as low sintering temperature, stable properties, high color rendering, good thermal stability, adjustable light color and color temperature, uniform light color that does not change with current, etc. Therefore, molybdate phosphors are regarded as a very promising fluorescent material. When Tb^{3+} is at the inversion symmetry center of the calcium molybdate lattice, atoms transition photons outward in the form of magnetic dipoles, and the magnetic dipole transition does

not change with the intensity of the crystal field around Tb^{3+}. According to the Judd-Ofelt theory [1], when Tb^{3+} deviates from the inversion symmetry center of the calcium tungstate-molybdate lattice, atoms transition photons outward in the form of electric dipoles. Since the system is composed of two point charges with equal magnitude and opposite signs, the electric dipole rotates under the action of torque in the external electric field, causing the electric dipole moment to turn to the external electric field. Therefore, the luminescent intensity increases with the increase of the distortion degree of the crystal field around Tb^{3+}. The electric dipole transition is affected by the local electric field and is very sensitive to the symmetry around Tb^{3+}. This paper takes tungstate-molybdate as the main matrix; the other part is a small amount of component doped into the matrix, called the activator. The activator plays an important role in luminescent properties, and can even affect the luminescent color, brightness, and other characteristics, so it is also called the luminescent center. This study investigates the influence of doped Tb^{3+} ions on their luminescent properties and the energy transfer mechanism. Calcium molybdate belongs to the tetragonal scheelite structure, with advantages such as good thermodynamic and chemical stability, excellent luminescent properties, and low synthesis temperature. It is widely used in fluorescent lamps, display panels, solid-state lasers, etc., and is regarded as a perfect fluorescent matrix material [2].

In this study, rare earth molybdate materials with a scheelite structure were designed and selected, and the $^5D_4$–^7F energy level of Tb^{3+} was chosen as the research object. The CaMoO4:5%Tb^{3+} material was synthesized by the high-temperature solid-state method [3]. Through variable-temperature excitation spectra, excitation strategies with wavelengths of 312 nm and 338 nm were designed to excite molybdate, and then variable-temperature excitation spectra were obtained. It was found that the four energy levels of Tb^{3+} ions, i.e., $^5D_4$–$^7F_3$ emission, $^5D_4$–$^7F_4$ emission, $^5D_4$–$^7F_5$ emission, and $^5D_4$–$^7F_6$ emission, showed different changes with temperature, and the sources of these different changes were pointed out. By fitting the change trends of different behaviors, the fitting curves applicable to temperature measurement were obtained. The thermal population of the matrix ground state was explored to construct the opposite change trend of fluorescent intensity, realizing high-sensitivity temperature measurement, and a theoretical explanation was given.

2. Experiment

Samples of MoO_3, CaO, and Tb_4O_7 were weighed according to different stoichiometric ratios, respectively dissolved in an appropriate amount of distilled water, and stirred until completely dissolved. Then, rare earth ions were added to the sodium molybdate solution to allow the solution to fully react. After centrifugation, washing, drying, and grinding, $CaMoO_4$ powder doped with rare earth ions was obtained, which was calcined in a muffle furnace at 600°C for 3 hours. A series of $CaMoO_4$:5%Tb^{3+} samples with a Tb doping concentration of 5% was obtained.

3. Results and discussion

3.1. Temperature-dependent excitation spectra

When $CaMoO_4$:5%Tb^{3+} was excited using the energy levels corresponding to the matrix absorption and the $^5D_4$–^7F transition absorption of Tb^{3+} [4], the effect of different temperatures on the emission spectrum of the $CaMoO_4$:5%Tb^{3+} luminescent material at a Tb^{3+} concentration of 5% was investigated. As shown in **Figure 1**, at a detection wavelength of 544 nm and with the temperature varying from 293 K to 563 K, there is a broad absorption peak in the range of 250 nm to 350 nm, which is caused by the superposition of the 4f-5d transition of

Tb^{3+} and the O^{2-}-Mo^{6+} charge transfer. It is worth noting that as the temperature increases, the luminescent intensity of the material shows a very obvious continuous decreasing trend, indicating a significant luminescent thermal quenching trend. Therefore, this quenching [5] belongs to the "strong coupling" type.

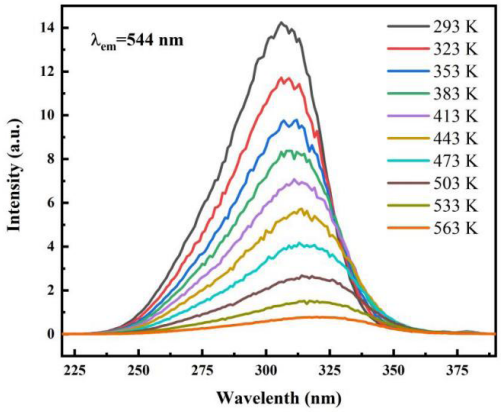

Figure 1. Temperature-dependent excitation spectra at a wavelength of 544 nm

As shown in the figure, the temperature-dependent excitation spectra at a wavelength of 544 nm were detected in the temperature range of 293 K to 563 K, corresponding to the characteristic emission of the $^5D_4 \rightarrow ^7F$ transition. With the gradual increase in temperature, the excitation spectrum exhibits obvious characteristics: it shifts toward longer wavelengths (i.e., the wavelength increases and the frequency decreases), and the spectral lines weaken simultaneously. This indicates that in the temperature range of 293 K to 563 K, the Mo-O charge transfer weakens as the temperature rises. This is because the non-radiative process of the $^5D_4 \rightarrow ^7F$ energy level is enhanced with increasing temperature, leading to a reduction in particles at the energy level and a consequent decrease in the characteristic emission of $^5D_4 \rightarrow ^7F$. The laser spectrum of Tb^{3+} includes a strong absorption near 245 nm and weak absorptions in the range of 290 nm to 390 nm. Due to the overlap between the Mo-O charge absorption band and the charge absorption band of Tb^{3+} [6], no obvious charge absorption peak of Tb^{3+} was observed.

3.2. Temperature-dependent emission spectra excited at 312 nm and thermal coupling properties

Based on the excitation spectrum results, two excitation wavelengths, 312 nm and 338 nm, were selectively chosen to excite the samples. These wavelengths correspond to the top of the charge transfer band, the redshift intersection of the charge transfer band, and the edge of the charge transfer band at 293 K, respectively. We hypothesize that the redshift characteristic of the charge transfer band edge can be utilized to construct three opposite thermal behaviors in a single material, thereby exploring the influence of excitation light on thermal coupling [7].

To verify this hypothesis, the samples were excited at 312 nm and 338 nm, respectively. **Figure 2** shows the temperature-dependent emission spectra excited at 312 nm. The main emission peak near 545 nm corresponds to the $^5D_4 \rightarrow ^7F_5$ transition emission. In addition, the emission at 488 nm corresponds to $^5D_4 \rightarrow ^7F_6$, 585 nm to $^5D_4 \rightarrow ^7F_4$, and 620 nm to $^5D_4 \rightarrow ^7F_3$. With increasing temperature, all emissions corresponding to the $^5D_4 \rightarrow ^7F_5$ energy level show a decreasing trend, as do those at 488 nm, 585 nm, and 620 nm. The emission intensity reaches the maximum when the calcination temperature is 293 K.

No emission from the $^5D_3 \rightarrow ^7F_j$ transition was observed, which is attributed to the cross-relaxation effect between

Tb^{3+} ions. This process can be expressed as: Tb^{3+} ($^5D_3$) + Tb^{3+} ($^7F_6$) → Tb^{3+} ($^5D_4$) + Tb^{3+} ($^7F_0$). Additionally, it may be due to the large phonon energy of the molybdate material, where multi-phonon relaxation causes the quenching of the $^5D_3 \rightarrow {}^7F_j$ transition. **Figure 2** more intuitively shows the electric dipole transitions at 293 K and 563 K.

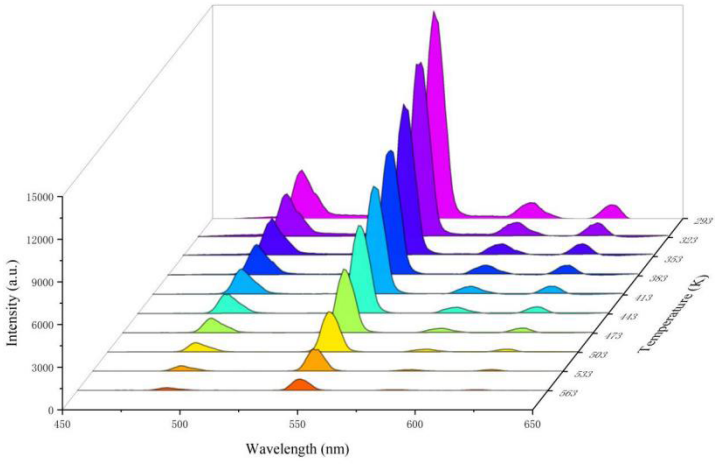

Figure 2. Temperature-dependent emission spectra with an excitation wavelength of 312 nm

To better observe the variation trend of fluorescence intensity and the thermal coupling properties of the two energy levels, further processing was performed on the emission spectral data. **Figure 3** shows the temperature-dependent integrated emission intensity under an excitation wavelength of 312 nm, where the marked points correspond to the emission from the $^5D_4 \rightarrow {}^7F_5$ transition. The two characteristic emission energy levels were fitted using Formula (1):

$$R=B\exp\left(-\frac{\Delta E}{kT}\right) \quad (1)$$

In formula (1), R is the fluorescence intensity ratio, B is a constant representing the energy level difference between two thermally coupled energy levels, k is approximately 0.695, which is the Boltzmann constant [8], and T is the thermodynamic temperature.

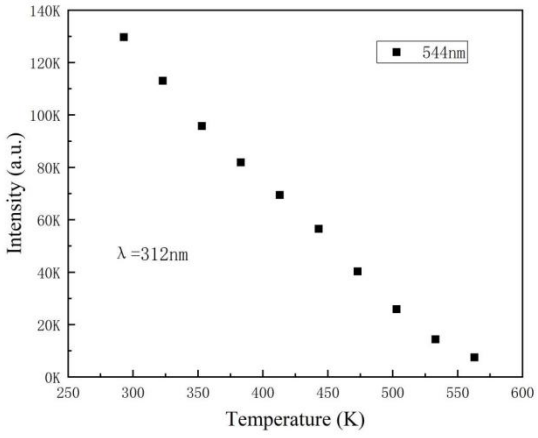

Figure 3. Temperature-dependent emission integrated intensity with an excitation wavelength of 312 nm

3.3. Temperature-dependent emission spectra under 338 nm excitation and thermal coupling properties

To construct the same thermal quenching behavior by utilizing the characteristic of red shift at the edge of the charge transfer band, temperature-dependent emission spectrum tests were also conducted with an excitation wavelength of 338 nm, as shown in **Figure 4**. The characteristic emission with the main emission peak around 545 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition emission. With the increase of temperature, the emissions at 488 nm, 585 nm, and 620 nm first enhance and then weaken. **Figure 5** shows the emission spectra under an excitation wavelength of 338 nm at 293 K and 593 K. The emission at the left 1 with a central wavelength of 488 nm corresponds to the $^5D_4 \rightarrow {}^7F_6$ transition emission; the emission at the left 2 with a central wavelength of 545 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition emission; the emission at the left 3 with a central wavelength of 585 nm corresponds to the $^5D_4 \rightarrow {}^7F_4$ transition emission; and the emission at the right with a central wavelength of 620 nm corresponds to the $^5D_4 \rightarrow {}^7F_3$ transition emission.

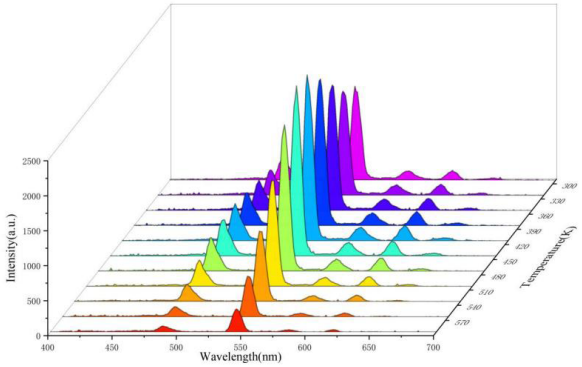

Figure 4. Temperature-dependent emission spectra with an excitation wavelength of 338 nm

The excitation at 345 nm shows an opposite thermal quenching behavior compared to that at 312 nm. To further verify whether different excitations affect the thermal coupling trend and alter the relative sensitivity of fluorescence thermometry [9], the fluorescence emission spectral data under 338 nm excitation were also processed and analyzed. As shown in **Figure 5**, the black markers in the temperature-dependent integrated emission intensity under 338 nm excitation correspond to the emission from the $^5D_4 \rightarrow {}^7F_5$ transition. With the increase in temperature, the emission from the $^5D_4 \rightarrow {}^7F_5$ transition first increases and then decreases, among which the emission at 544 nm rises rapidly, while the emissions from the other three emission peaks increase slowly.

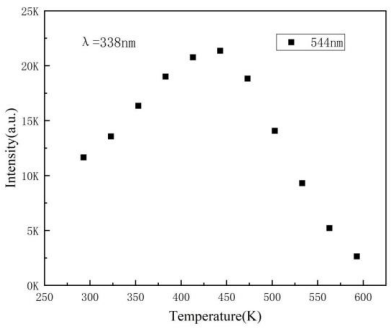

Figure 5. Temperature-dependent emission integrated intensity with an excitation wavelength of 338 nm

3.4. Temperature measurement sensitivity

The relative sensitivity S_r can describe the temperature sensing sensitivity more accurately than S. It can be expressed by formula (2):

$$S_r = \frac{1}{R}\frac{dR}{dT} \times 100\% \quad (2)$$

Relative sensitivity refers to the percentage change in the initial R value per unit temperature. When evaluating the performance of temperature-sensing materials [10], it is more meaningful to use relative sensitivity as a parameter. **Figure 6** below shows the relative sensitivity of the ratio of 338 nm to 312 nm. At 303 K, the relative sensitivity S_r reaches a maximum of 1.3%K^{-1}, and it is more sensitive at low temperatures.

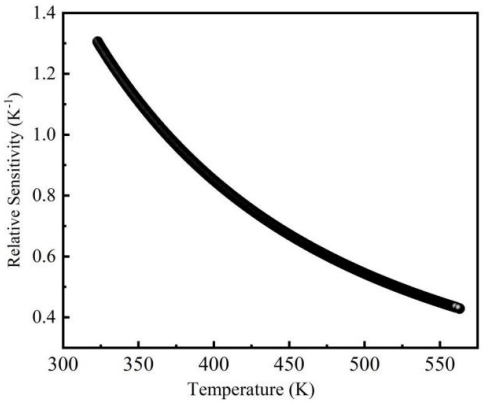

Figure 6. Sensitivity curves of excitation wavelengths

4. Conclusion

In this work, we designed and selected the $^5D_4$ energy level transition of Tb^{3+} ions as the research object. The CaMoO4:5%Tb^{3+} material was synthesized by the high-temperature solid-phase method. Through variable-temperature excitation spectroscopy, two excitation strategies were designed to excite the charge transfer band of MoO_4^{2+}. Furthermore, by measuring the variable-temperature emission spectra, it was found that the emissions of Tb^{3+} ions, i.e., $^5D_4$–$^7F_6$, $^5D_4$–$^7F_5$, $^5D_4$–$^7F_4$, and $^5D_4$–$^7F_3$, show different changes with the increase of temperature, and the sources of these different changes were pointed out. By fitting the trends of the two thermal behavior changes, the fitting curves applicable to temperature measurement were obtained. When the temperature is 303 K, the relative sensitivity of temperature measurement using thermally coupled energy levels reaches the maximum, and the maximum relative sensitivity of the ratio of the two excitations at 312 nm and 338 nm is 1.3%K^{-1}. The influence of matrix thermal population on the fluorescence intensity ratio was explored. The opposite trend of fluorescence intensity was constructed by using the thermal population of the matrix ground state, realizing high-sensitivity temperature measurement, and a theoretical explanation was given. This study may have certain reference value for the dual-excitation temperature measurement method based on thermally opposite behaviors.

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Disclosure statement

The authors declare no conflict of interest.

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