Accurate determination on luminescence intensity of luminous materials

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Under 360 nm excitation, we measured the luminescent spectrum of the Tm^{3+}-doped phosphate glass in the temperature range from 300 K to 440 K. The 452 nm blue luminescence (Tm^{3+}: $^1D_2 \rightarrow {}^3F_4$) was observed. By comparing the luminescence intensity of the 452 nm emission to that of the pumping light, the accurate thermal stability of the luminescence had been discussed.

(Received October 1, 2022; accepted June 6, 2023)

Keywords: Luminescence materials, Optical characteristics, Glass

1. Introduction

Luminescence intensity of luminous material is related to two main factors. One is the external factors, such as excitation power, excitation wavelength, and sample temperature [1-6], and so on. Another is the internal factors, such as crystal field environment, host component, concentrations of activated and sensitized ions, and so on [7-13]. For example, the luminescence intensity of the luminous material will be possibly different with varying of the activated or sensitized ion concentration [14-18]. To study the relation of the luminescence intensity and the activated or sensitized ion concentration, the measurement conditions of the samples are very harsh. It is necessary that the size and shape, the location of placement of different samples should be the same. However, during the spectral measurement, the location, the size and shape of the sample possibly change, which will cause the relative big error. Especially, when we measure the relation of the luminescence intensity and sample temperature, the sample volume will vary with the temperature, which will effect the intensity of the signal light. If we directly use the result of the measured signal light, the error will be larger. For decreasing the measurement error and obtaining the realer result, in this work, the Tm^{3+} -doped phosphate glass was prepared. The luminescence intensity at different temperature was studied. We attempted a new method to measure the signal light.

2. Experimental

Using high-temperature melting method, the phosphate glass doped with Tm^{3+} ion was synthesized [19]. Its chemical composition is $70P_2O_5$-$10Na_2O$-$8CaO$-$2MgO$-$9Al_2O_3$-$1Tm_2O_3$ (mol%). The raw materials are $NH_4H_2PO_4$, Na_2CO_3, $CaCO_3$, $MgCO_3$, Al_2O_3, and Tm_2O_3. According to predetermined proportion, the raw materials were weighted by a electronic scale (accuracy: 0.0001 g). They were grounded in an agate mortar for 30 minutes, until the mixture became uniform fine powder. Then, the powder was moved into a corundum crucible, and put into a high-temperature furnace. Initially, the furnace was heated to 673 K at the rate of 1 K • min^{-1} and held at the temperature for 1 h to release the volatile components. Then, the furnace temperature was raised to 1700 K at the rate of 2 K • min^{-1} and kept the temperature for 3 h to melt the raw materials completely. A clear, viscous melted liquid was poured in air onto a preheated stainless-steel plate, which was preheated at 450 ℃ for 3 h in the air. The excitation and emission spectra were recorded with a HORIBA Fluorolog-3 luminescence spectrometer (Horiba Jobin Yvon, Edison, USA). The excitation sources are a xenon lamp (model Xe 900). The spectral resolution of the excitation and emission spectra is 0.5 nm. The spectral resolution of luminescence spectrometer is 0.1 nm. And the sample temperature was monitored by a T1000 thermodetector (XIATECH, China), whose precision is ±0.01 ℃.

3. Results and discussion

Under 360 nm excitation, the luminescent temperature spectra of the Tm^{3+}-doped phosphate glass had been measured. Fig. 1 is the corresponding luminescent spectra at eight different temperatures from 300 K to 440 K (the

temperature values indicated in the figure). In the 425 nm-750 nm wavelength region, two emission peaks were observed. The emission peak at 452 nm should be from the transition of Tm^{3+} ion: $^1D_2 \rightarrow {}^3F_4$. The emission peak at 720 nm should come from the second harmonics of the pumping light. Under different environmental temperatures, the peak positions of the emissions are almost the same. However, the peak intensities are different, which become smaller and smaller with increase of the temperature. The luminous intensities of 452 nm and 720 nm emissions vs environment temperature for the Tm^{3+}-doped phosphate glass are shown in Fig. 2. As a result, the intensity of the 452 nm luminescence will obviously decrease will the increase of the temperature.

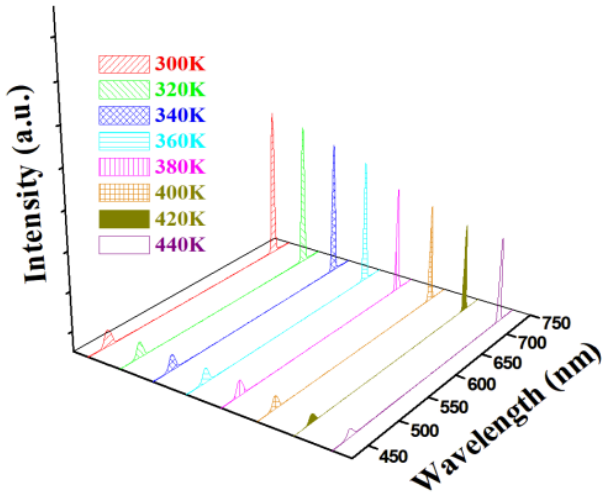

Fig. 1. Luminescent spectra of the Tm^{3+}-doped phosphate glass at different temperature under 360 nm excitation (color online)

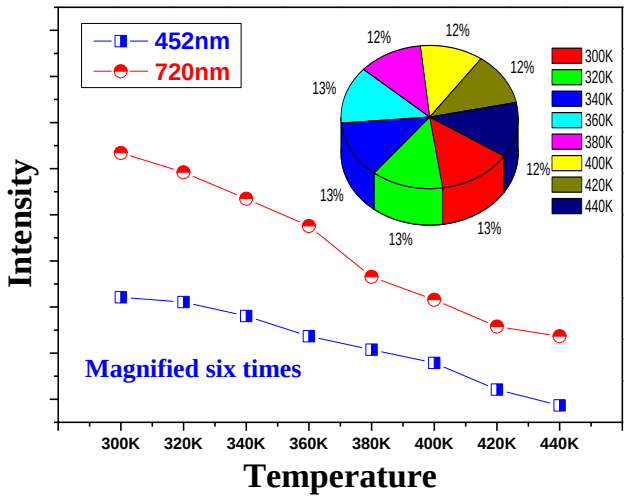

Fig. 2. Curve graphs of luminescent intensities at 452 nm and 720 nm vs environment temperature for the Tm^{3+}-doped phosphate glass; the inset is the intensity ratios of the 452 nm blue emission to the pumping light at different temperature (color online)

However, by measuring the intensity ratio of the 452 nm light to the 720 nm pumping light, we found that the intensity of the 452 nm light almost keeps unchanged with the increase of the temperature, seen in the inset of Fig. 2. Under 360 nm excitation, the energy diagram of the trivalent Tm^{3+} ion is shown in Fig. 3. The particles in the $^3H_6$ state can be excited to the $^1D_2$ state by absorbing the energy of the pumping light. Then, by radiative transition: $^1D_2 \rightarrow {}^3F_4$, the 452 nm blue light arises. At the same time, the nonradiative transition form the high energy level to low energy level will also happen, which can decrease the luminescence intensity. The multi-phonon relaxation is related to the temperature, phonon energy, and the energy gap. The equation can be given by: $W_p = C\left[1 + \frac{1}{\exp(h\nu/KT-1)}\right]^p \exp(-m\Delta E) = W_0 \exp(-m\Delta E)$[20], where C is a constant, ΔE is the energy gap of high level and low level, $p=\Delta E/h\nu$, and $m = -\ln\left(W_p / W_{p-1}\right) / h\nu$. The nergy gap of between $^1D_2$ and $^1G_4$ is about 6200 cm^{-1}. The phonon energy of the glass material is about 1100 cm^{-1}. The multi-phonon relaxation from $^1D_2$ to $^1G_4$ is five/six phonon process. Thus, with increase of the sample temperature, multi-phonon relaxation effect will be weaker. The population of $^1D_2$ state will change very small. The 452 nm blue light should be stabler with the changing of the temperature.

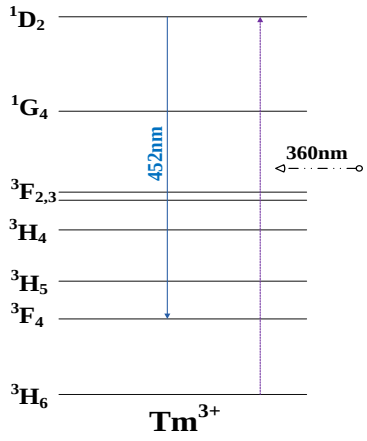

Fig. 3. Energy diagram of the trivalent Tm^{3+} ion

4. Conclusions

Using high-temperature melting method, the Tm^{3+}-doped phosphate glass had been prepared. The luminescence spectra of the glass sample had been measured under 360 nm excitation. The 452 nm blue luminescence was observed, which should come from the transition of Tm^{3+} ion: $^1D_2 \rightarrow {}^3F_4$. Under 360 nm excitation, we also studied the temperature spectrum of the glass sample in the temperature range from 300 K to 440 K. As a result, the intensity of the 452 nm luminescence decreases with the increase of the temperature. However, the intensity ratio of the 452 nm light to 720 nm pumping light is almost invariable. By comparing the 452 nm emission and the pumping light, the luminescence characteristics of the 452 nm emission had been discussed. Using above method, the accurate luminescence characteristics can be obtained.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 12174206), the National Key R&D Plan (Grant No. 2021YFB3502701).

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