

# Intense luminescent intensity and adjustable luminescent color in polymethyl methacrylate doped with Tb<sup>3+</sup> ion

MANTING PEI<sup>a</sup>, CHENGGUO MING<sup>b,\*</sup>, YUANXUE CAI<sup>b</sup>, XIAOBIN REN<sup>b</sup>, YUETING QIN<sup>b</sup>, FENGYING YUAN<sup>b</sup>, GANGZHI WANG<sup>b</sup>, LIQUN AN<sup>b</sup>, FENG SONG<sup>c</sup>

<sup>a</sup>*School of Material Science and Chemical Engineering, Tianjin University of Science & Technology, Tianjin 300457, China*

<sup>b</sup>*Physics Department, School of Science, Tianjin University of Science & Technology, Tianjin 300457, China*

<sup>c</sup>*The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, Nankai University, Tianjin 300457, China*

A series of polymethyl methacrylates doped with Tb<sup>3+</sup> and Al<sup>3+</sup> ions were prepared. The excitation and emission spectra of the samples had been studied in details. Strong blue luminescence at ~450 nm is observed in the polymethyl methacrylate undoped with Tb<sup>3+</sup> under 332 nm excitation. With the increasing of Tb<sup>3+</sup> concentration, the luminescent color can vary from blue to green. Our researches are helpful to luminous materials.

(Received October 24, 2017; accepted August 9, 2018)

*Keywords:* Luminescence, Optical materials

## 1. Introduction

The trivalent rare-earth ions doped luminescent materials have been widely studied in both visible and near infrared spectral regions in view of its abundant energy structures [1-6]. And it has been demonstrated to be important in various production or living domains, such as white LED, fluorescent tags, temperature sensors, solid-state lasers [7-10], and so on. The luminescent properties of rare-earth ions depend seriously on the matrix materials. Take the glass and crystal for example, the luminescent of rare-earth ions performs different advantages and disadvantages in these matrix materials [11-16]. So far, the research and applications of the rare-earth ions doped polymethyl methacrylate are rarely reported. In this paper, the preparation of rare-earth ions Tb<sup>3+</sup> doped polymethyl methacrylate has been explored, and the photoluminescence properties have been detailedly analyzed as well.

## 2. Experimental

Polymethyl methacrylates doped with x mol % Tb<sup>3+</sup> (x=0, 0.05, 0.5), 5mol % Al<sup>3+</sup> were synthesized and marked as Tb0, Tb0.05, and Tb0.5, respectively. The preparation procedure is described as follows: Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub> with corresponding mole was completely dissolved in the alcoholic solution. Subsequently, methyl methacrylate was added into the solution with the corresponding mole ratio to methyl

methacrylate. The solution was rapidly stirred with a magnetic stirrer at 300 K for 1h. Benzoperoxide was added into the solution, and then the solution was put into a water bath at 365 K for about ten minutes. The solution was put into a drying cabinet at 320 K for 48 h, when it was relatively viscous like as glycerin. Until the sample becomes a transparent bulk solid, it was taken out. Finally, the sample was incised and surface-polished for optical measurements. The photoluminescence spectra were measured with a model F111AI fluorescence spectrophotometer. The excitation source was a xenon lamp (model Xe900). The visible light was detected by photomultiplier tube detector. The spectral resolution of all spectra is 0.5 nm. The spectral resolution of spectrometer is 0.1 nm. All measurements were taken at room temperature.

## 3. Results and discussion

The excitation spectra of the Tb0, Tb0.05, and Tb0.5 samples in the 290-400 nm wavelength region are shown in Fig. 1, and the monitored peaks had been indicated in the figure. The excitation peak at ~332 nm of Tb0 sample (PMMA undoped with Tb<sup>3+</sup>) should come from the transition of the ligand of PMMA. The excitation peak at ~332 nm of Tb0.5 samples should be from the transition of the ligand of PMMA, however, the excitation peaks at 319, 342, 353, 371, and 380 nm should be attributed to the transitions of Tb<sup>3+</sup> ions: <sup>7</sup>F<sub>6</sub>→<sup>5</sup>H<sub>7</sub>, <sup>7</sup>F<sub>6</sub>→<sup>5</sup>L<sub>3</sub>, <sup>7</sup>F<sub>6</sub>→<sup>5</sup>L<sub>9</sub>, <sup>7</sup>F<sub>6</sub>→<sup>5</sup>G<sub>5</sub>, and <sup>7</sup>F<sub>6</sub>→<sup>5</sup>G<sub>6</sub>. The position and shape of the

excitation peaks of Tb0.05 sample are roughly the same as those of the Tb0.5 sample, besides the intensity.

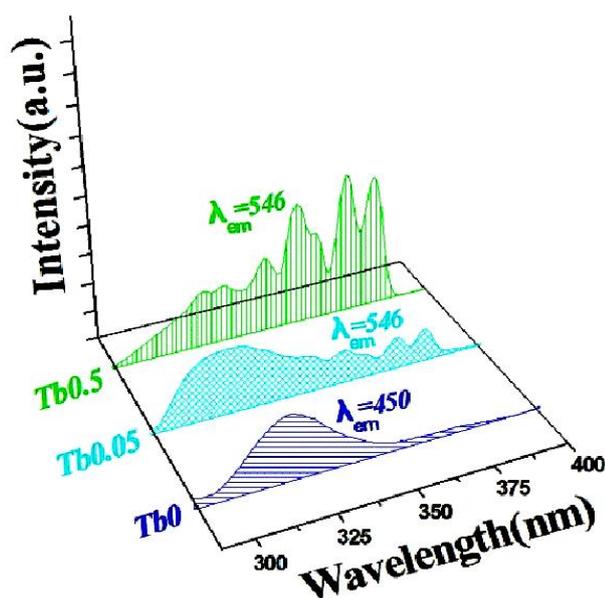


Fig. 1. Excitation spectra of the Tb0, Tb0.05, Tb0.5 samples in the 290-400nm wavelength region

Under 332 nm excitation, the photo-luminescent spectra of the Tb0, Tb0.05, and Tb0.5 samples had been measured in the 380-800 nm wavelength region, and shown in Fig. 2. The emission peak at ~450 nm of Tb0 sample should be from the transition of the ligand of PMMA. The emission peaks at 492, 546, 587, and 625 nm in the Tb0.05, and Tb0.5 samples should come from the transitions of Tb<sup>3+</sup> ions:  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$ ,  $^5D_4 \rightarrow ^7F_4$ , and  $^5D_4 \rightarrow ^7F_3$ . The emission photos of the Tb0, Tb0.05, and Tb0.5 samples were indicated in the inset of Fig. 2. The emission colors of the Tb0, Tb0.05, and Tb0.5 samples are blue, cyan, and green, respectively.

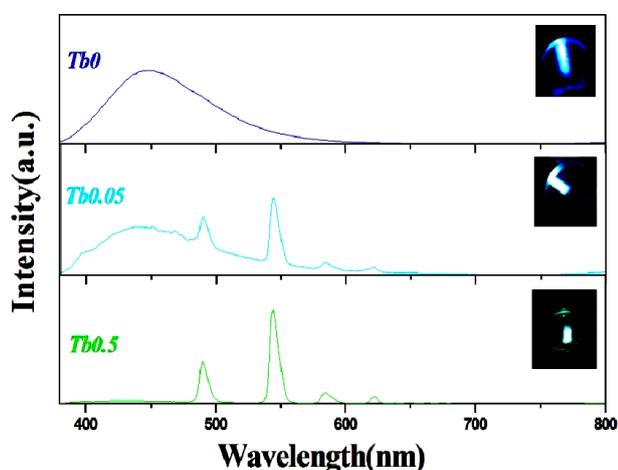


Fig. 2. Emission spectra of the Tb0, Tb0.05, Tb0.5 samples in the 380-800 nm wavelength region under 332 nm excitation

Fig. 3 is the energy level diagrams of PMMA and Tb<sup>3+</sup> ions. The population processes of the 450 nm, 492, 546, 587, and 625 nm emissions can be described as follows: the electron in the valence band (VB) of PMMA can transfer to the conduction band (CB) by absorbing a 332 nm ultraviolet photon; subsequently, the electron comes back to the VB and emit a 450 nm photon; the electron in the CB of PMMA can also release to the VB by non-radiative transition and transfer the energy to the Tb<sup>3+</sup> ion by energy transition; the electron in the ground state  $^7F_6$  can be pumped to the higher excited states ( $^5D_0$ ,  $^5G_5$ ,  $^5D_3$ , etc.), the electron is non-radiatively relaxed to  $^5D_4$  state, from where the 492, 546, 587, and 625 nm emissions arise.

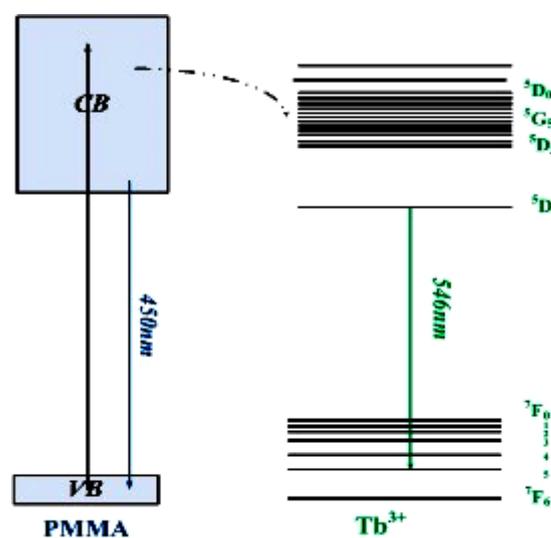


Fig. 3. Energy level diagrams of PMMA and Tb<sup>3+</sup> ions

#### 4. Conclusions

Poly methyl methacrylates doped with Tb<sup>3+</sup> and Al<sup>3+</sup> ions were prepared. For the sample undoped with Tb<sup>3+</sup> ion, the excitation spectrum monitored at 450 nm is measured. A wide excitation band is observed, whose peak value is at ~332 nm. And Strong blue luminescence at ~450 nm is observed under 332 nm excitation. For the samples doped with 0.05 and 0.5 mol% Tb<sup>3+</sup> ion, the emission colors are cyan and green under 332 nm excitation, respectively. Our materials will be hopeful to be applied to luminous technology, like as color displays and light emitting diodes, and so on.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China (nos.11674183, 61405146 and 11304225), the Natural Science Foundation of Tianjin (no.17JJCZDJC37800), the Tianjin Research Program of Application Foundation and Advanced Technology

(no.14CQNJC01700), and the basic research project of Tianjin higher school(no.2017KDYB28).

## References

- [1] H. Du, Y. Lan, Z. Xia, et al., *Mater. Res. Bull.* **44**, 1660 (2009).
- [2] S. Tokito, T. Lijima, T. Tsuzuki, F. Sato, *Appl. Phys. Lett.* **83**, 2459 (2003).
- [3] C. S. Lim, *Mater. Res. Bull.* **47**, 4220 (2012).
- [4] J. Sun, W. Zhang, W. Zhang, et al., *Mater. Res. Bull.* **47**, 786 (2012).
- [5] W. J. Yang, L. Y. Luo, T. M. Chen, N. S. Wang, *Chem Mater.* **17**, 3883 (2005).
- [6] C. G. Ming, F. Song, X. B. Ren, L. Q. An, *Appl. Phys. Lett.* **103**, 041906 (2013).
- [7] C. G. Ming, F. Song, C. R. Li, Y. Yu, G. Zhang, H. Yu, T. Q. Sun, J. G. Tian, *Opt. Lett.* **36**, 2242 (2011).
- [8] B. Dong, D. P. Liu, X. J. Wang, *Appl. Phys. Lett.* **90**, 181117 (2007).
- [9] G. Y. Chen, Y. G. Zhang, G. Somesfalean, Z. G. Zhang, Q. Sun, F. P. Wang, *Appl. Phys. Lett.* **89**, 163105 (2006).
- [10] L. Han, F. Song, S. Q. Chen, *Appl. Phys. Lett.* **93**, 011110 (2008).
- [11] X. J. Li, Q. H. Nie, S. X. Dai, T. F. Xu, L. J. Lu, X. H. Zhang, *J. Alloy. Compd.* **454**, 510 (2008).
- [12] A. H. Li, Z. R. Zheng, T. Q. Lü, Q. Lü, W. L. Liu, *Opt. Express* **17**, 3878 (2009).
- [13] S. Q. Man, H. L. Zhang, Y. L. Liu, J. X. Meng, E. Y. B. Pun, P. S. Chung, *Opt. Mater.* **30**, 334 (2007).
- [14] S. Q. Zeng, G. Z. Ren, Q. B. Yang, *J. Mater. Chem.* **20**, 2152 (2010).
- [15] N. A. Tolstik, A. E. Troshin, S. V. Kurilchik, *Spectroscopy, Appl. Phys. B* **86**(2), 275 (2007).
- [16] G. A. Kumar, R. Riman, S. C. Chae, Y. N. Jang, I. K. Bae, H. S. Moon, *J. Appl. Phys.* **95**(7), 3243 (2004).

---

\*Corresponding author: mingchengguo1978@163.com