

VISIBLE LUMINESCENCE FROM Pr-DOPED POLY(METHYL METHACRYLATE)

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Judd-Ofelt parameters (Ω_2 , Ω_4 , Ω_6) were calculated on the basis of the absorption spectrum of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ (DBM: dibenzoylmethane, TOPO: trioctylphosphine oxide) doped poly(methyl methacrylate) (PMMA) by both including and excluding the hypersensitive transition $^3\text{H}_4 \rightarrow ^3\text{P}_2$. Room-temperature visible luminescence from Pr-doped PMMA is reported. The luminescent properties of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ were also predicted according to the Judd-Ofelt theory. The values of the fluorescence branching ratio and the emission cross section of $^3\text{P}_0 \rightarrow ^3\text{F}_2$ fluorescence transition indicates the potential of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA as an efficient luminescent material.

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1. Introduction

Recent decades have witnessed a growing interest in the investigation of spectroscopic properties of rare-earth because of their potential applications in optical devices [1-13]. Among the rare earth ions, praseodymium ion Pr^{3+} ($4f^2$) has been intensively studied due to the fact that its emission spectra have been extended from the blue to the near infrared region [1-8]. However, the optical properties of praseodymium ion in polymer are scarcely studied.

The Judd-Ofelt theory [14,15] is a widely used and remarkably successful theory for quantitative characterization of optical $4f$ transitions in rare-earth doped glasses and crystals. However, it was found that in many cases application of Judd-Ofelt theory to Pr^{3+} activated system yielded poor results in comparison with experimental observations [1-3,5]. To overcome these difficulties, it is customary to simply remove from the fit the $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transition, although the reason is not clearly established [1,2].

In this paper, a spectroscopic study of Pr-doped poly(methyl methacrylate) (PMMA) is reported. PMMA was selected as the matrix for its low optical absorption, simple synthesis and low cost. These characteristics make it suitable as a polymer matrix material for rare earth ions doping. With the help of the standard Judd-ofelt theory, Judd-Ofelt parameters were calculated by both including and excluding the hypersensitive transition $^3\text{H}_4 \rightarrow ^3\text{P}_2$. The prediction of the line strength on the basis of the Judd-Ofelt theory is in good agreement with the experimental results. Visible luminescence from Pr-doped PMMA was reported and the radiative properties of the doped material were also predicted.

2. Experimental

$\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ was prepared by the method reported before [16]. Its molecular structure is shown in the inset of Fig.2. The central Pr^{3+} ion is bound to three DBM and two TOPO ligands.

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Two TOPO act as synergic shielding ligands, which produce antisymmetrical structures that promote faster radiation rates, because the coordination of phosphine oxide molecules can prevent the coordination of water or solvent molecules and lower vibrations ($\text{P}=\text{O}:1125\text{ cm}^{-1}$) [17].

$\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ containing MMA solution was prepared by dissolving $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ in purified MMA. To prepare $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA, 30mg 2,2-Azoisobutyronitrile (AIBN) as an initiator was added to the above 20ml Pr-MMA solution and pre-polymerized at $85\text{ }^\circ\text{C}$ for 30 min, the pre-polymerized solution was then poured into a model. The polymerization of the model was carried out at $50\text{ }^\circ\text{C}$ for 24 h and additionally heated at $90\text{ }^\circ\text{C}$ until solidification was fulfilled. The sample was cut and polished for optical measurements.

The absorption spectrum was recorded with a UV-VIS-NIR spectrophotometer (Perkin Elmer Lambda 900) at room temperature. The fluorescence spectrum of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA was excited with the 476.5 nm line of an Ar^+ laser and recorded using a Jobin Yvon HRD monochromator in the spectral region 550-700 nm. The refractive index was measured using an Abbé refractometer.

3. Results and discussion

3.1. Absorption spectrum and Judd-Ofelt analysis

Fig. 1 shows the absorption spectrum of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA in the wavelength range 400–2200 nm at room temperature. All the absorption bands are attributed to the excitation from the ground state, $^3\text{H}_4$, to various excited states and the assignments of the bands are given in the figure. Because of inhomogeneous broadening, the Stark structure is poorly resolved. Adjacent energy levels often overlap and appear in the spectrum as one.

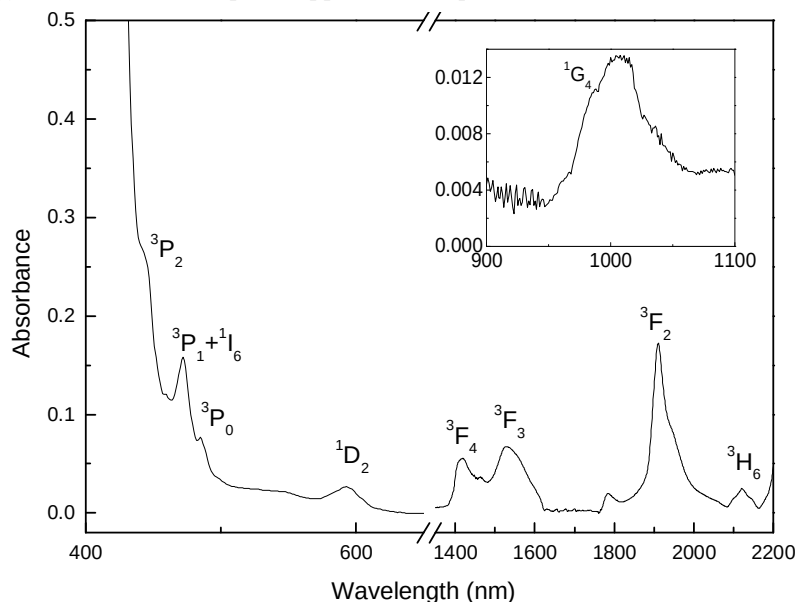


Fig. 1. Absorption spectrum of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA.

The Judd-Ofelt parameters of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA were calculated by two fits: (a) Nine transition fits were used in the fitting procedure, the transitions included were $^3\text{H}_4 \rightarrow ^3\text{H}_6, ^3\text{F}_2, ^3\text{F}_3, ^3\text{F}_4, ^1\text{G}_4, ^1\text{D}_2, ^3\text{P}_0, ^3\text{P}_1 + ^1\text{I}_6$ and $^3\text{P}_2$.

(b) Eight transitions, by excluding the hypersensitive transition $^3\text{H}_4 \rightarrow ^3\text{P}_2$ from the data of fit (a).

The experimental and calculated line strengths for the absorption bands, Judd-Ofelt parameters and RMS deviations of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA obtained by the two fits are listed in Table 1.

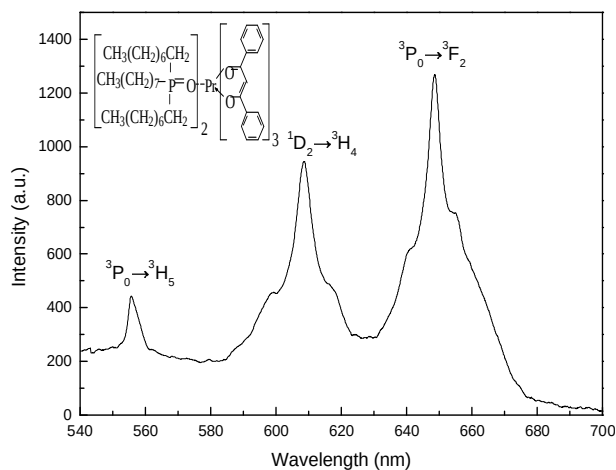
Table 1. Experimental and calculated line strengths and Judd-Ofelt parameters of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA.

Excited states	Line strength S (10^{-20} cm^2)		
	S_{exp}	$S_{\text{cal}}^{\text{a}}$	$S_{\text{cal}}^{\text{b}}$
$^3\text{H}_6$	0.804	0.396	0.383
$^3\text{F}_2$	7.600	7.586	7.591
$^3\text{F}_3$	3.235	3.425	3.366
$^3\text{F}_4$	1.273	1.333	1.286
$^1\text{G}_4$	0.187	0.092	0.090
$^1\text{D}_2$	0.715	0.195	0.190
$^3\text{P}_0$	0.141	0.671	0.676
$^3\text{P}_1 + ^1\text{I}_6$	1.534	1.015	1.019
$^3\text{P}_2$	0.832	0.399	--
RMS deviations (10^{-20} cm^2)		0.451	0.454
Ω_2 (10^{-20} cm^2)		11.39	11.40
Ω_4 (10^{-20} cm^2)		3.88	3.91
Ω_6 (10^{-20} cm^2)		1.91	1.81

It's generally believed that the application of the Judd-Ofelt theory to Pr^{3+} has problems [1-3,5]. If all transitions are used in the intensity fitting, the hypersensitive transition $^3\text{H}_4 \rightarrow ^3\text{P}_2$, especially, is stimulated badly. But in this work, the overall agreement between the experimental and calculated line strengths for the other transitions in fit (a) is very close to that in fit (b). At the same time, the Judd-Ofelt parameters obtained by the two fits are nearly similar. Also with and without the hypersensitive transition $^3\text{H}_4 \rightarrow ^3\text{P}_2$ from the fitted transitions, the RMS deviations are almost the same and comparable with previous studies of other praseodymium systems [1-3,5]. This phenomenon is due to the fact that the line strength of the hypersensitive transition $^3\text{H}_4 \rightarrow ^3\text{P}_2$ is not the strongest, and therefore does not have a significant influence on the values of the Judd-Ofelt parameters. Here, the Judd-Ofelt parameters calculated by fit (a) were used to predict the radiative properties of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA.

3.2. Radiative Properties

The fluorescence spectrum of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA was excited with the 476.5 nm line of an Ar^+ laser and is shown in Fig. 2. There are three main peaks and the wavelength centered at 556 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_5$), 592 nm ($^1\text{D}_2 \rightarrow ^3\text{H}_4$) and 632 nm ($^3\text{P}_0 \rightarrow ^3\text{F}_2$), respectively.

Fig. 2. Fluorescence spectrum of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA.

After the Judd-Ofelt parameters have been determined, the radiative lifetimes and the fluorescence branching ratios can be calculated with the obtained fluorescence spectrum. The radiative lifetimes of the 1D_2 and 3P_0 states are 238 and 22.2 μs , respectively. The fluorescence branching ratios of $^3P_0 \rightarrow ^3H_5$, $^1D_2 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3F_2$ are 0, 8.52 and 60.52, respectively. Since the fluorescence branching ratio of $^3P_0 \rightarrow ^3H_5$ is zero, this transition is not accounted by the Judd-Ofelt theory in the Pr^{3+} ion. The presence of $^3P_0 \rightarrow ^3H_5$ can be accounted by considering the J-J' mixing, which is not taken into account in this calculation.

The emission cross section, σ_p , can be related to the radiative transition probability using the formula [18]:

$$\sigma(J \rightarrow J') = \frac{\lambda_p^4}{8\pi n^2 c \Delta\lambda_{\text{eff}}} A(J \rightarrow J') \quad \text{where} \quad \Delta\lambda_{\text{eff}} = \frac{\int I_e(\lambda) d\lambda}{I_e^{\text{peak}}} \quad (1)$$

where λ_p is the mean wavelength of the transition, A is the spontaneous emission probability, c is the velocity of light, n is the refraction index which is 1.495, $I_e(\lambda)$ is the fluorescence intensity of the corresponding band and I_e^{peak} is the peak fluorescence intensity of the band. Using Eq. (1), the emission cross sections of $^1D_2 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3F_2$ are calculated and the results are 0.22×10^{-20} and $18.18 \times 10^{-20} \text{ cm}^2$, respectively.

The luminescence branching ratio is a critical parameter, because it characterizes the possibility of attaining stimulated emission from any specific transition. It has already established that an emission level with β value near 50% becomes a potential laser emission transition [19]. The fluorescence branching ratio of $^3P_0 \rightarrow ^3F_2$ is 60.52%. The emission cross section σ_p is one of the most important parameters for luminescent material. The emission cross section σ_p of $^3P_0 \rightarrow ^3F_2$ fluorescence transition of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA is $18.18 \times 10^{-20} \text{ cm}^2$, which is comparable with those shown by glasses used in the solid state laser applications [3,5].

From the magnitude of the fluorescence branching ratio and the emission cross section of $^3P_0 \rightarrow ^3F_2$ fluorescence transition it can be concluded that $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA is a promising candidate for an efficient luminescent material.

4. Conclusions

In this paper, visible luminescence from Pr-doped PMMA was reported. Judd-Ofelt parameters (Ω_2 , Ω_4 , Ω_6) were obtained from the absorption spectrum by both including and excluding the hypersensitive transition $^3H_4 \rightarrow ^3P_2$ and the values of Judd-Ofelt parameters obtained by the two fits are nearly similar, especially the Ω_2 . This phenomenon can be explained by the fact that the line strength of the hypersensitive transition $^3H_4 \rightarrow ^3P_2$ is not the strongest, and, therefore, does not have a significant influence on Ω_2 value. The evaluation of the radiative properties of the $^3P_0 \rightarrow ^3F_2$ transition indicates the potential of $\text{Pr}(\text{DBM})_3(\text{TOPO})_2$ doped PMMA as an efficient luminescent material.

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References

- [1] J. Hormadaly, R. Reisfeld, J. Non-Cryst. Solids **30**, 337 (1979).
- [2] P. Goldner, F. Auzel, J. Appl. Phys. **79**, 7972 (1996).
- [3] Y. K. Sharma, S. P. Tandon, S. S. L. Surana, Mater. Sci. Eng. B **77**, 167 (2000).
- [4] A. Jouini, J. C. Gâcon, M. Ferid, M. Trabelsi-Ayadi, Opt. Mater. **24**, 175 (2003).
- [5] D. K. Sardar, F. Castano, J. Appl. Phys. **91**, 911 (2002).
- [6] M. Yu. Sharonov, Z. I. Zhmurova, E. A. Krivandina, A. A. Bystrova, I. I. Buchinskaya, B. P. Sobolev, Opt. Commun. **124**, 595 (1996).

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- [7] M. Malinowski, M. Kowalska, R. Piramidowicz, T. Lukasiewicz, M. Swirkowicz, A. Majchrowski, *J. Alloy. Compd.* **323**, 214 (2001).
 - [8] G. Jose, P. R. Biju, N. V. Unnikrishnan, *Phys. Chem. Glasses* **45**, 57 (2004).
 - [9] X. Y. Chen, W. Zhao, E. Cook, G. K. Liu, *Phys. Rev. B* **70**, 205122 (2004).
 - [10] L. N. Sun, H. J. Zhang, Q. G. Meng, F. Y. Liu, L. S. Fu, C. Y. Peng, J. B. Yu, G. L. Zheng, S. B. Wang, *J. Phys. Chem. B* **109**, 6174 (2005).
 - [11] X. S. Xu, H. Ming, Q. J. Zhang, *Opt. Commun.* **199**, 369 (2001).
 - [12] B. Chen, N. Dong, Q. J. Zhang, M. Yin, J. Xu, H. Liang, H. Zhao, *J. Non-Cryst. Solids* **341**, 53 (2004).
 - [13] X. Y. Dong, H. Y. Tam, B. O. Guan, C. L. Zhao, X. Y. Dong, *Opt. Commun.* **224**, 295 (2003).
 - [14] B. R. Judd, *Phys. Rev.* **127**, 750 (1962).
 - [15] G. S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).
 - [16] H. Liang, Z. Q. Zheng, Q. J. Zhang, H. Ming, B. Chen, *phys. stat. sol. (b)* **241**, 1149 (2004).
 - [17] Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, *J. Phys. Chem. A* **107**, 1697 (2003).
 - [18] W. F. Krupke, *IEEE J. Quantum. Electron.* **QE-10**(4), 450 (1974).
 - [19] V. Ravi Kumar, N. Veeraiah, B. Appa Rao, S. Bhuddudu, *J. Mater. Sci.* **33**, 2659 (1998).