

# Clustering study in $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped polymer optical fibers by optical properties and near-field scanning microscopy

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The clusters of  $\text{Eu}^{3+}$  ion in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped polymethyl methacrylate (PMMA) have been studied by three means. The relative fluorescence intensity ratio of the  ${}^5D_0 \rightarrow {}^7F_2$  to  ${}^5D_0 \rightarrow {}^7F_1$  transitions with different concentrations of  $\text{Eu}^{3+}$  in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA and metastable-state ( ${}^3D_0$ ) lifetime dependence on  $\text{Eu}^{3+}$  concentration are analyzed. The analysis indicates that there are no clustering effects in  $\text{Eu}^{3+}$  ions of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA when the  $\text{Eu}^{3+}$  doping concentration is up to 1.0 wt.-%. At the same time, the clustering effect has not been observed by the scanning near-field optical microscopy (SNOM) in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA with 1.0 wt.-% of  $\text{Eu}^{3+}$  ions. The analysis reveals that a high concentration of  $\text{Eu}^{3+}$  can be incorporated into polymer optical fiber (POF) without clustering effect.

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There has been an increasing interest in rare-earth-doped polymer optical fiber (POF) because of its applications in optical communication systems and optical sensors, especially in local networks and data communications<sup>[1]</sup>. In recent years, much work has been done on rare-earth-doped POFs, such as  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Er}^{3+}$ -doped POFs<sup>[2-5]</sup>. Amplified spontaneous emission (ASE) was found in  $\text{Nd}^{3+}$ -doped POFs<sup>[2]</sup> and  $\text{Eu}^{3+}$ -doped graded index POFs<sup>[6]</sup>. However the clusters of rare-earth ions exist in the  $\text{RE}(\text{OA})_3$ -doped POF (RE is rare-earth ion) when  $\text{Eu}^{3+}$  doping concentration is about 0.08 wt.-% and  $\text{Nd}^{3+}$  doping concentration is 0.02 wt.-%<sup>[7,8]</sup>. Ions within a cluster are subject to a fast cross relaxation process that causes a loss of population inversion. It is detrimental to fiber lasers and amplifiers, for example in the former an increase in threshold and a reduction in conversion efficiency, and in the latter an increase in the power requirement<sup>[9]</sup>. Furthermore, since clusters tend to be formed more readily at high rare-earth ion concentrations, the maximum concentration is limited, which can be achieved in practice to values well below what is required to make very short device. The source of loss of population inversion can be minimized in rare-earth-doped systems by using a low-dopant concentration and a long fiber length. But the loss of rare-earth-doped POF is larger than that of silica optical fiber<sup>[10]</sup>, the POF laser and amplifier require high dopant concentration because the device length must be kept short. Therefore we hope to find a new material that can be doped to high concentration in polymer systems without quenching, providing the means for short-length amplification devices.

In this letter, the clusters of the  $\text{Eu}^{3+}$  ion in the  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped polymethyl methacrylate (PMMA) have been studied by the scanning near-field optical microscopy (SNOM), fluorescence spectra analysis, and metastable-state ( ${}^5D_0$ ) lifetime measurements. The result indicates that there are no clustering effects in  $\text{Eu}^{3+}$  ions of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA when the

$\text{Eu}^{3+}$ -doping concentration is up to 1.0 wt.-%.

The  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped POF preforms and  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped POFs have been fabricated using the same method as described in Ref. [3].  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped POF preforms with different  $\text{Eu}^{3+}$  concentrations are grinded and polished into 1-mm-thick slices and used as measured sample. Fluorescence spectrum and fluorescence decay curve of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA are recorded on fluorescence spectrophotometers (Shimadzu RF-5301 and Edinburgh FL/FS 920), respectively.

Figure 1 shows the fluorescence spectrum of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA from 550 to 700 nm at excitation wavelength of 355 nm using a xenon lamp. The four emission peaks at 580, 591, 613, and 651 nm are assigned to the transitions from  ${}^5D_0$  to the four levels of the ground  ${}^7F$  manifolds, i.e.,  ${}^7F_0$ ,  ${}^7F_1$ ,  ${}^7F_2$ , and  ${}^7F_3$ , respectively. The  ${}^5D_0 \rightarrow {}^7F_2$  transition being electric dipole is hypersensitive transition and its intensity is very sensitive to the local environment<sup>[11]</sup>. The  ${}^5D_0 \rightarrow {}^7F_1$  transition being magnetic dipole transition has intensity independent of the environment and thus can be used

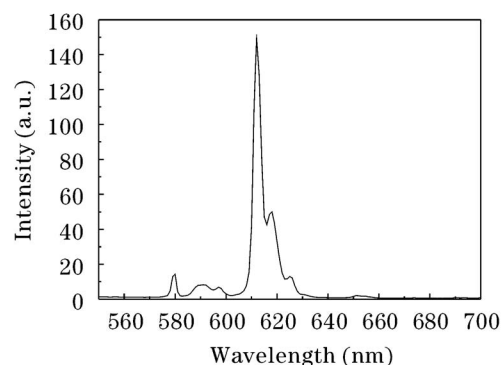


Fig. 1. Fluorescence spectrum of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA.

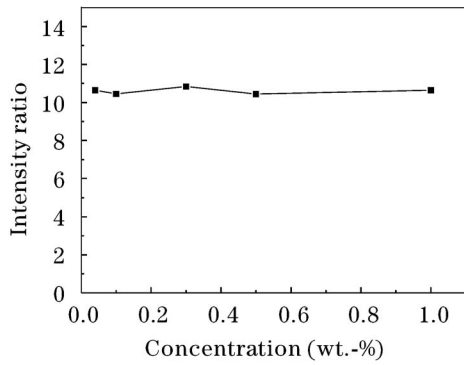


Fig. 2. Relationship between the fluorescence intensity ratio and  $\text{Eu}^{3+}$  doping concentration.

as a reference. The relative fluorescence intensity ratio of the  ${}^5D_0 \rightarrow {}^7F_2$  to  ${}^5D_0 \rightarrow {}^7F_1$  transition is very sensitive to structural change in the vicinity of  $\text{Eu}^{3+}$  ions. The relative fluorescence intensity ratio decreases with increasing rare-earth ion concentration as the existence of clustering in close ions. The relative fluorescence intensity ratio of different  $\text{Eu}^{3+}$  doping concentrations is shown in Fig. 2. From Fig. 2, the relative fluorescence intensity ratio has little difference when the  $\text{Eu}^{3+}$  ion concentration increases to 1.0 wt.-%. This indicates no clustering existence when the  $\text{Eu}^{3+}$  doping concentration is up to 1.0 wt.-%.

The optical property usually affected by ion-ion interaction is the metastable-state lifetime, and the lifetime decreases with increasing rare-earth ion concentration as the existence of clustering in close ions<sup>[12]</sup>. The 613-nm fluorescence decay curve of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA is shown in Fig. 3. The concentration of  $\text{Eu}^{3+}$  ions is 0.5 wt.-%. The measured lifetime of the  ${}^5D_0$  level determined by exponential fitting is 396  $\mu\text{s}$ . Figure 4 displays the metastable-state ( ${}^5D_0$ ) lifetime dependence on the concentration of  $\text{Eu}^{3+}$  in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA. There is no decrease in the  ${}^5D_0$  level lifetime up through 1 wt.-% of  $\text{Eu}^{3+}$  ions. This indicates that no concentration quenching takes place to the high  $\text{Eu}^{3+}$  doping concentration in the system.

We used a commercial SNOM from RHK Technology (USA) to achieve a high spatial resolution optical contrast and simultaneously measure the sample (1 wt.-% of  $\text{Eu}^{3+}$  ions) topography. The SNOM has been operated in illumination mode. The light from argon ion laser is

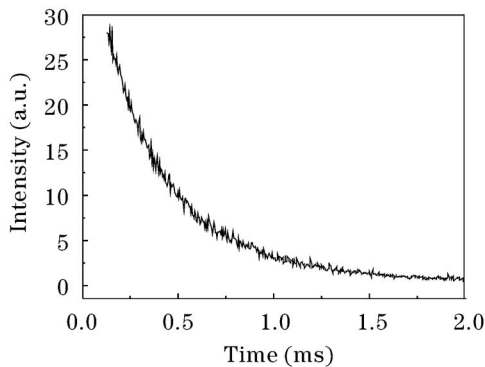


Fig. 3. Fluorescence decay curve (at 613 nm) of  ${}^5D_0$  level of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA.

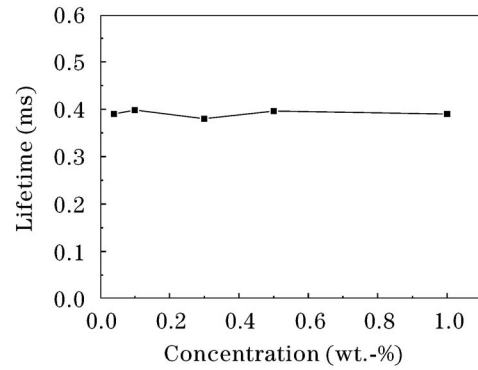


Fig. 4. Metastable-state ( ${}^5D_0$ ) lifetime dependence on doping concentration of  $\text{Eu}^{3+}$  in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA.

coupled into a very small aluminum-coated quartz single-mode glass fiber tip with a 50-nm aperture. The transverse resolution decided by the aperture of tip is 50 nm. The tip illustrates the sample and scans near the sample surface of interest. The transmitted light of sample is detected through the objective by a photon counting avalanche photodiode. On the other hand, the light intensity is relevant to the dwell time of tip at each scanning point. Typical pixel dwell time in our images is 10 ms. Images are acquired and processed by the software SPM325.06 version (RHK, USA).

The experiment results are shown in Figs. 5(a) and (b). Figure 5(a) is the topography of the sample surface, decided by the voltage difference of four-phase detector under the constant separation mode of SNOM. Figure 5(b) is the transmitted light intensity of the sample scanned by the tip, given by a photon counter. To give out a more intuitionistic and quantitative result, we use SNOM software to mark a light line in the corresponding locations of Figs. 5(a) and (b) and obtain the average surface height (Fig. 6(a)) and the corresponding transmitted light intensity (Fig. 6(b)) as a function of distance.

From Fig. 6, we can see the difference of surface height of the sample is large and the difference of the transmitted light intensity of the sample is very large and obvious. Note that the transmitted light intensity is largest in the smallest surface height and the transmitted light intensity is smallest in the largest surface height. The change of characteristic of the transmitted light intensity is opposed to surface height. This implies that the difference of the transmitted light intensity is caused by the difference of surface height of the sample. Therefore it is concluded that the clustering effect has not been observed by using SNOM with a resolution of 50 nm in

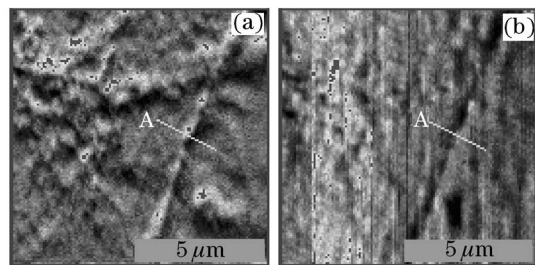


Fig. 5. (a) Near-field topography of the sample surface, (b) transmitted light intensity of the sample.

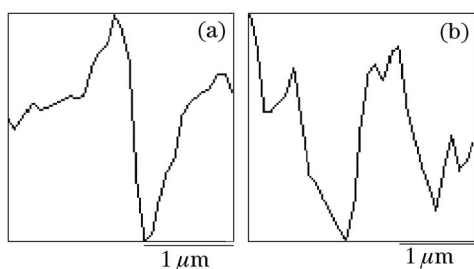


Fig. 6. (a) Average surface height profile of the sample along a line indicated in Fig. 5(a), (b) transmitted light intensity of profile along a line indicated in Fig. 5(b).

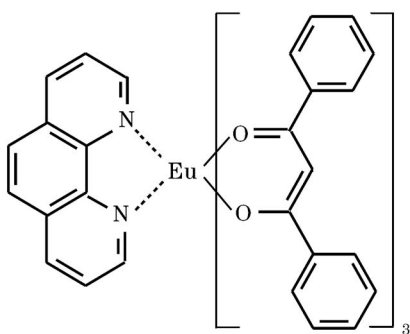


Fig. 7. Chemical structure of  $\text{Eu}(\text{DBM})_3\text{Phen}$ .

$\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA with 1.0 wt.-% of  $\text{Eu}^{3+}$  ions.

The main reason for clustering stems from a lack of nonbridging oxygen atoms to which the rare-earth ions coordinate. Rare-earth ions typically prefer to coordinate with approximately eight oxygen atoms<sup>[12]</sup>. Because of the deficiency of available oxygen atoms in silica fiber and waveguide, the rare-earth ions cluster together to share the sites, which suffer from clustering with quenching concentration as low as 0.1 wt.-%. The molecular structure of  $\text{Eu}(\text{DBM})_3\text{Phen}$  is shown in Fig. 7. The central  $\text{Eu}^{3+}$  ion is bound by three dibenzoylmethane (DBM) ligands and one phenanthroline (Phen) ligand. Each  $\text{Eu}^{3+}$  ion is completely coordinated with eight atoms of the surrounding ligands (six oxygen atoms and two nitrogen atoms) and hence does not need to cluster with another ion to fill the coordination. Furthermore, the presence of the surrounding ligand acts as a physical buffer between the rare-earth ions and the other ions. It is therefore concluded that there is no clustering effect in this organic system.

In conclusion, the clusters of  $\text{Eu}^{3+}$  ion in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA have been studied by three means. The relative fluorescence intensity ra-

tio of the  ${}^5D_0 \rightarrow {}^7F_2$  to  ${}^5D_0 \rightarrow {}^7F_1$  transition with different  $\text{Eu}^{3+}$  doping concentrations and metastable-state ( ${}^5D_0$ ) lifetime dependence on the concentration  $\text{Eu}^{3+}$  in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA are analyzed. The result indicates no clustering effect in  $\text{Eu}^{3+}$  ions of  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA when the  $\text{Eu}^{3+}$  doping concentration is up to 1.0 wt.-%. At the same time, the clustering effect has not been observed by using SNOM in  $\text{Eu}(\text{DBM})_3\text{Phen}$ -doped PMMA with 1.0 wt.-% of  $\text{Eu}^{3+}$  ions. The analysis shows that a high concentration of  $\text{Eu}^{3+}$  can be incorporated into POF without clustering effect, providing the means for short-length amplification devices.

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