

Multicolor emission of Tb³⁺/Eu³⁺ co-doped poly(methyl methacrylate) for optical fibre technology

P. Miluski,^{*1} M. Kochanowicz,¹ J. Zmojda¹, and D. Dorosz²

¹*Faculty of Electrical Engineering, Bialystok University of Technology, Wiejska 45D, 15-351 Bialystok, Poland,*

²*Faculty of Materials Science and Ceramics, AGH University of Science and Technology, 30 Mickiewicza Av., 30-059 Krakow, Poland*

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Abstract—The article presents multicolor emission observed in poly(methyl methacrylate) specimens co-doped by trivalent terbium and europium ions. Bright luminescence was obtained using organometallic complexes of lanthanides and energy transfer antenna effect. Spectroscopic characterization exhibits a wide excitation spectrum according to the chelating structure of used complexes and characteristic Tb³⁺ and Eu³⁺ emission peaks in luminescence spectra. The calculated CIE 1931 chromaticity coordinates confirm that colorful emission from green to red can be obtained using the proposed materials.

The luminescent polymers are attractive for new photonic applications. Numerous constructions of organic light emitting diodes (OLEDs), solar cells (OPVs) sensing structures, wavelength shifters, amplifiers, and lasers have been investigated so far [1–6]. A wide range of amorphous thermoplastic optical polymers: poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonate (PC), and acrylic polymers with substituted hydrogen ions by heavier ions, e.g. fluorine (CYTOP) and deuterium (ZEONEX) have been successfully applied in optoelectronic devices constructions [7–9]. High transparency and thermoplasticity of poly(methyl methacrylate) make it a suitable candidate for fabrication of luminescent structures (solid, thin film, fibers) for visible spectrum range applications [4]. Several methods of PMMA host doping (e.g. direct, solvent, and copolymerization) can be used for incorporation of luminescent complexes in a polymer chain structure and uniform dopant distribution can be easily achieved [10–12]. The well-defined luminescence spectrum shapes of trivalent lanthanides ions are attractive for multicolor light emission. Unfortunately, the absorption spectra of rare earth ions are very narrow according to defined energy level transition and effective excitation require well spectral aligned sources. This disadvantage can be overcome by using organometallic structure complexes. The surrounding of lanthanide ion organic ligand acts as wide an absorption band antenna. Moreover, it also allows shielding of a luminescent ion from non-radiative deactivation of the excited state by polymeric host

vibrational overtones. The excited ligand can transfer energy through its triplet state to the lanthanide ion and radiative transition is possible according to allowed transitions of rare earth ions. In fact, the ligand choice is a crucial issue in obtaining effective luminescence of lanthanides in an organic host [13–15]. The absorption and emission spectra of rare earths are well separated and the reabsorption effect can be minimised. So far there have been reported several single lanthanide doped polymeric fibres [16–20]. Among different rare earths, the intense luminescence can be obtained for terbium [16] and europium [17–18] complexes. Therefore, the spectroscopic characterisation of lanthanides co-doped poly(methyl methacrylate) significantly extends the potential applications field of polymeric optical fibers. The article presents trivalent terbium and europium doped PMMA for multicolor light emission.

The specimens were fabricated in Bialystok University of Technology laboratory. The methyl methacrylate (MMA), Benzoyl Peroxide (BP), and lanthanides Terbium(III)-tris-(2,2,6,6-tetramethyl-3,5-heptanedionate) and Europium(III)-tris-(2,2,6,6-tetramethyl-3,5-heptanedionate) were supplied by Sigma-Aldrich with standard >99% purity. The chemicals were used without additional purification except MMA (the stabilizer agent was removed before polymerization). A free radical polymerization process (34h at 65–80°C) was used for specimens fabrication. The chelate doping process was performed directly during PMMA polymerization in 8mm diameter glass test tubes. The concentrations of lanthanide complexes used in the experiment are presented in Tab. 1. A uniform dopant distribution with no PMMA defects was observed in the fabricated specimens. Next, PMMA specimens were prepared by cutting and polishing into 3.0 mm thick discs. The luminescence of chosen Tb³⁺/Eu³⁺ co-doped PMMA specimens is presented in Fig. 1.

* E-mail: p.miluski@pb.edu.pl

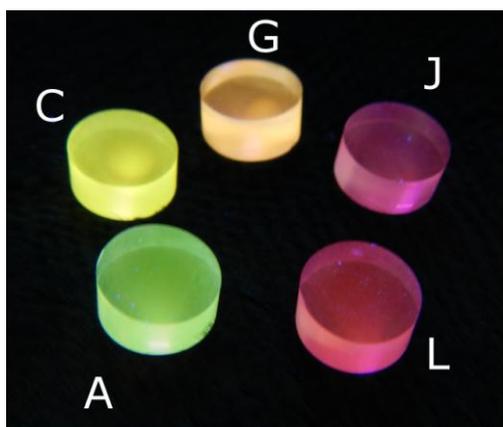


Fig. 1. The photo of the fabricated specimens under 365nm excitation (mercury vapor black light).

The excitation and emission spectra of bulk specimens were measured using a xenon lamp (450W) and a steady state spectrofluorometer (Horiba Fluorolog 3). The measurements were performed at a temperature of 20°C.

Tab. 1. The concentrations of lanthanides used in experiment.

Specimen	Tb(tmhd) ₃ molar concentration ·10 ⁻³	Eu(tmhd) ₃ molar concentration ·10 ⁻³
A	1.13	0
B	1.14	0.08
C	1.14	0.15
D	1.13	0.45
E	1.15	0.98
F	1.13	1.17
G	0.82	1.16
H	0.60	1.14
I	0.44	1.18
J	0.20	1.16
K	0.09	1.22
L	0	1.20

The recorded excitation spectrum (Fig. 2a) is a composition of trivalent terbium and europium ions transitions. The direct terbium absorption peaks according to ${}^7F_6 \rightarrow {}^5D_3$ (378nm), ${}^7F_6 \rightarrow {}^5D_4$ (486nm), and europium ${}^7F_0 \rightarrow {}^5L_6$ (392nm), ${}^7F_0 \rightarrow {}^5D_3$ (412nm), and ${}^7F_0 \rightarrow {}^5D_2$ (462nm) are noticeable. Additionally, a high intensity, wide ligand absorption band is noticeable at 312nm. The excitation spectrum shape confirms the possibility of efficient excitation of lanthanides by the using antenna effect.

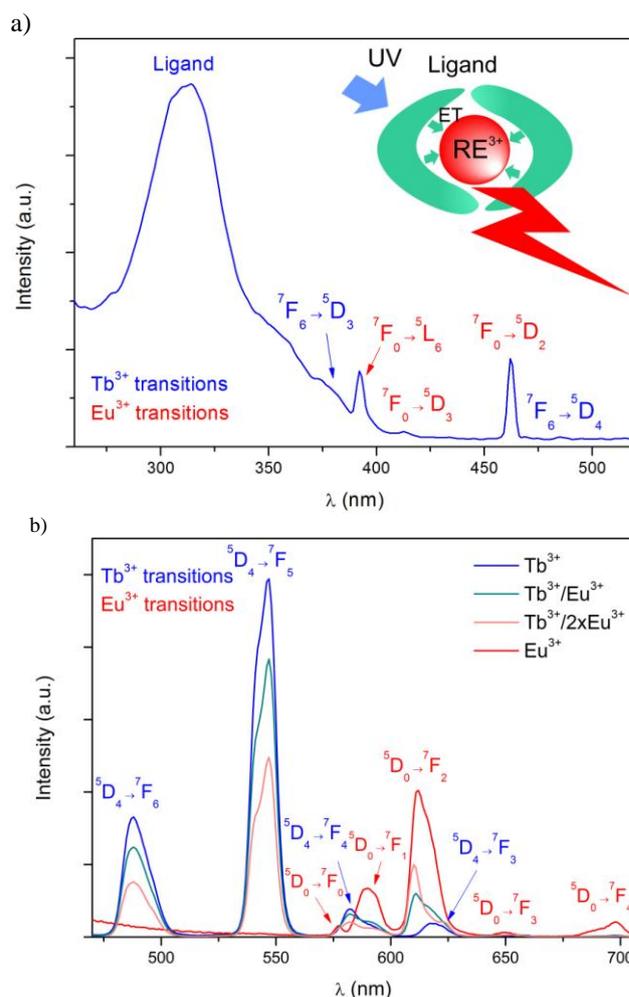


Fig. 2. The Tb³⁺/Eu³⁺ doped PMMA: a) excitation spectrum, monitoring at 610nm, specimen G, inset the antenna effect, b) emission spectra at excitation 355nm.

The recorded luminescence spectra (at excitation 355nm) are presented in Fig. 2b. The luminescence spectra of rare earth observed in PMMA are similar to those reported in glass matrices. Identified energy state transitions are marked blue and red color for terbium and europium ions accordingly. The emission peaks related to terbium luminescence: ${}^5D_4 \rightarrow {}^7F_6$ (486nm), ${}^5D_4 \rightarrow {}^7F_5$ (547nm), ${}^5D_4 \rightarrow {}^7F_4$ (582nm), ${}^5D_4 \rightarrow {}^7F_3$ (629nm), and europium ${}^5D_0 \rightarrow {}^7F_0$ (577nm), ${}^5D_0 \rightarrow {}^7F_1$ (590nm), ${}^5D_0 \rightarrow {}^7F_2$ (612nm), ${}^5D_0 \rightarrow {}^7F_3$ (649nm), and ${}^5D_0 \rightarrow {}^7F_4$ (697nm), are noticeable. Opposite to fluorescent organic dyes, lanthanides assure a significant shift between absorption and emission spectra. Therefore, low reabsorption effects are expected in the polymeric optical fibre structure. The ratio of lanthanides concentration of Tb³⁺ and Eu³⁺ can be used for luminescence spectrum modification. This phenomenon can be used to obtain a desired luminescence color. For this reason, the chromaticity coordinates CIE 1931 were calculated and presented in Fig. 3.

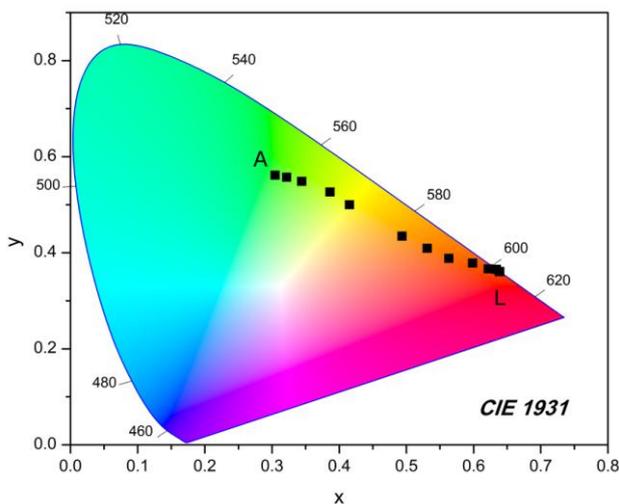


Fig. 3. The chromaticity coordinates of Tb^{3+}/Eu^{3+} doped PMMA, excitation 355nm

The presented results show luminescence color modification from green, through amber to red. The chosen excitation wavelength (355nm) can be successfully used as a compromise to relatively low absorption of PMMA and high excitation of terbium and europium chelate ligands.

In summary, the multicolor emission observed in poly(methyl methacrylate) specimens co-doped by of Tb^{3+}/Eu^{3+} has been characterized in terms of excitation and luminescence spectrum shape. Additionally, the CIE 1931 chromaticity coordinates were presented. Intense luminescence from green to red color (at 355nm excitation) was obtained using energy transfer from an organic ligand to rare earths. The presented properties of lanthanides co-doped PMMA are important for the development of new applications in optical fibre technology.

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