

Optical Properties of Erbium and Erbium/Ytterbium Doped Polymethylmethacrylate

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In this paper we report on the fabrication and properties of Er^{3+} and Er^{3+}/Yb^{3+} doped Polymethylmethacrylate (PMMA) layers. The reported layers were fabricated by spin coating on silicon or on quartz substrates. Infrared spectroscopy was used for an investigation of O-H stretching vibration. Measurement were made of the transmission spectra in the wavelength ranges from 350 to 700 nm for the Er^{3+} doped samples and from 900 to 1040 nm for the Yb^{3+} doped samples. The refractive indices were investigated in the spectral range from 300 to 1100 nm using optical ellipsometry and the photoluminescence spectra were measured in the infrared region.

Keywords: polymer, polymethylmethacrylate, Erbium, Ytterbium, optical properties.

1 Introduction

In recent years, Rare Earth (RE) ions containing photonics materials have attracted much attention for their potential applications for full color displays, optical sources and laser systems such as optical amplifiers [1–6]. A list of the RE elements with some of their basic properties is shown in Table 1.

Most research has focused on RE ions which can emit in the visible region. Steckl et al. reported in [7] about the properties of GaN layers doped with Eu^{3+} , Er^{3+} , and Tm^{3+} ions. They obtained (for the first time) photoemission from higher excited RE states in GaN covering the entire visible spectrum: light emission in the green (from Er at 537/558 nm), red (Pr at 650 nm and Eu at 621 nm), and blue (Tm at 477 nm) spectral regions. A second major field of study deals with RE ions which can emit in the infrared region. For these purposes, the RE ions are most often studied for telecommunication systems. For telecommunication systems operating at 1300 nm investigations are made of RE ions such as Nd^{3+} , Pr^{3+} and Dy^{3+} [8–11]. For telecommunications applications at 1530 nm, investigations are made of Er^{3+} and Tm^{3+} ions [12–14]. In the last decade there have also been investigations of sensitizers to produce more efficient RE doped sources. The most often used sensitizer is Yb^{3+} for Er^{3+} -doped optical amplifiers [15, 16]. In addition to Yb^{3+} other RE ions are nowadays examined as sensitizers, such as Ho^{3+} for Tm^{3+} [17, 18] or Ho^{3+} for Yb^{3+} [19] doped photonics materials, etc. [20].

Optical materials such as semiconductors, glass and optical crystals doped with RE ions are conventional materials for accomplishing lasing action. Recently there has been considerable interest in the development of new photonics materials such as polymers [21, 22], which have better properties and a lower price.

In this paper, we present the fabrication and properties of Er and Er/Yb doped polymer layers. As a polymer material we chose Polymethylmethacrylate (PMMA), due to its low optical absorption, simple synthesis and low cost. These characteristics make it a suitable host material for RE ions [23, 24]. Er^{3+} ions were chosen due to fact that Er^{3+} ions now play a key role in long-distance optical communication systems. Yb^{3+} co-

Table 1: The rare earth elements and some of their properties

Atomic number	Element	Electron configuration RE^{3+}	Ground term RE^{3+}
58	Cerium – Ce	$4f^1 5s^2 5p^6$	$^2F_{5/2}$
59	Praseodymium – Pr	$4f^2 5s^2 5p^6$	3H_4
60	Neodymium – Nd	$4f^3 5s^2 5p^6$	$^4I_{9/2}$
61	Promethium – Pm	$4f^4 5s^2 5p^6$	5I_4
62	Samarium – Sm	$4f^5 5s^2 5p^6$	$^6H_{5/2}$
63	Europium – Eu	$4f^6 5s^2 5p^6$	7F_0
64	Gadolinium – Gd	$4f^7 5s^2 5p^6$	$^8S_{7/2}$
65	Terbium – Tb	$4f^8 5s^2 5p^6$	7F_6
66	Dysprosium – Dy	$4f^9 5s^2 5p^6$	$^6H_{15/2}$
67	Holmium – Ho	$4f^{10} 5s^2 5p^6$	5I_8
68	Erbium – Er	$4f^{11} 5s^2 5p^6$	$^4I_{15/2}$
69	Thulium – Tm	$4f^{12} 5s^2 5p^6$	3H_6
70	Ytterbium – Yb	$4f^{13} 5s^2 5p^6$	$^2F_{7/2}$

-doping was applied because it was previously shown that the addition of ytterbium ions increased the intensity of the luminescence at 1530 nm [16].

2 Experiment

Small pieces of PMMA (Goodfellow) were left to dissolve in chloroform for a few days before being used in the fabrication of PMMA layers. The PMMA layers were fabricated by spin coating on silicon substrates or the polymer was poured into a bottomless mold placed on a quartz substrate and left to dry. For RE doping anhydrous $ErCl_3$ and $YbCl_3$ or ErF_3 and YbF_3 or erbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedio-

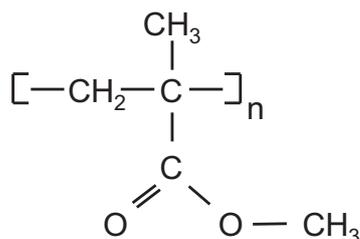


Fig. 1: Molecular structure of PMMA

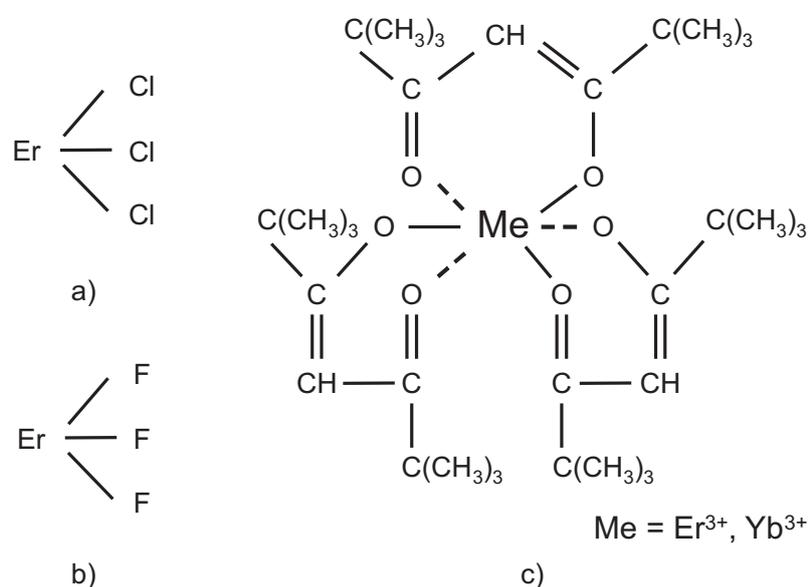
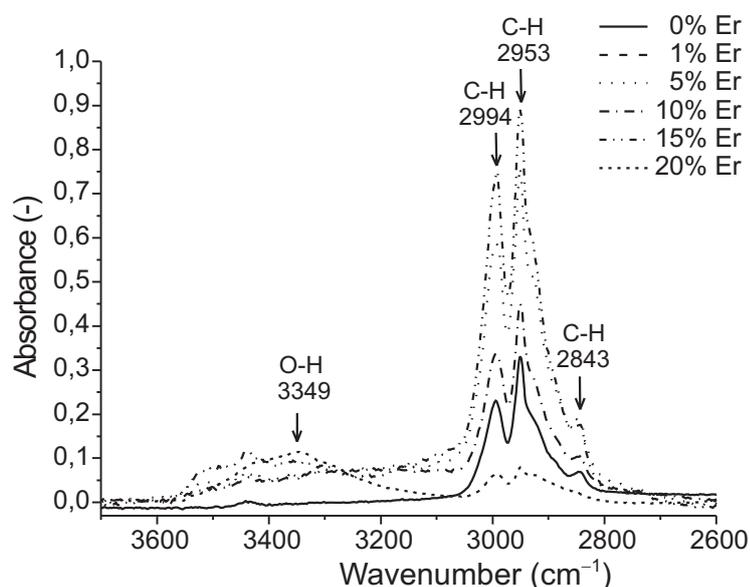
nate) (Sigma-Aldrich) and ytterbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) (Goodfellow) were dissolved in C_5H_9NO or C_2H_6OS (Sigma-Aldrich).

The layers were fabricated in such a way that the content of erbium in the solutions varied from 1.0 at. % to 20.0 at. %, and were then added to the polymer. The samples containing

1.0 at. % of erbium were co-doped with ytterbium (Er^{3+}/Yb^{3+} samples) in amounts varying from 1.0 at. % to 20.0 at. %. The molecular structure of PMMA is shown in Fig. 1. The molecular structure of $ErCl_3$ shown in Fig. 2a, the structure of ErF_3 in Fig. 2b, and that of erbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) and ytterbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) are shown in Fig. 2c.

3 Results and discussion

The samples were characterized by infrared spectroscopy (FT-IR) using a Bruker IFS 66/v FTIR spectrometer equipped with a broadband MCT detector, to which 128 interferograms were added with a resolution of 4 cm^{-1} (Happ-Genzel apodization). Fig. 3 displays the FT-IR spectra of PMMA layers doped with Er^{3+} ions ($ErCl_3$) in the wavelength range from 4000 to 2600 cm^{-1} .

Fig. 2: Molecular structure of a) $ErCl_3$, b) ErF_3 and c) erbium(III) and ytterbium(III) ionsFig. 3: Infrared spectra of PMMA samples doped with Er^{3+} using $ErCl_3$

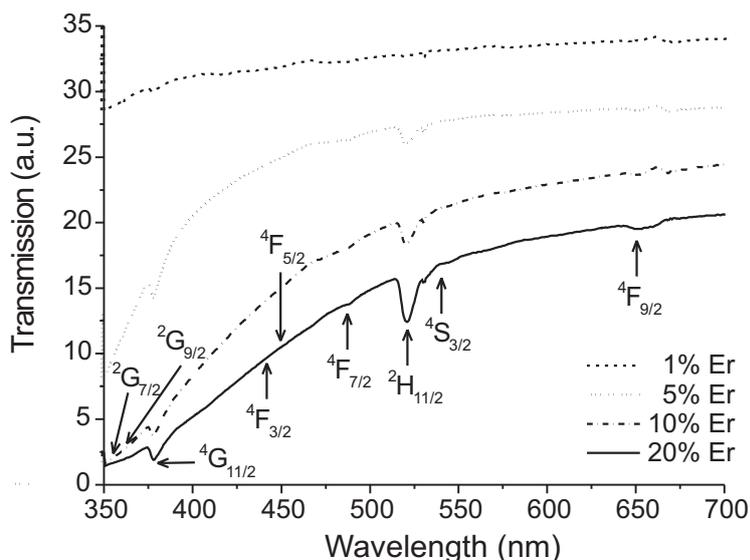


Fig. 4: Transmission spectra of the Er^{3+} doped PMMA using erbium(III)

The three strong broad bands occurring at 2994 cm^{-1} , 2953 cm^{-1} , 2843 cm^{-1} correspond to the aliphatic C-H bands. These bands are assigned to the stretching vibrations of CH_3 and CH_2 , and indicate a high content of hydrogen-rich CH_x . The absorption band at 3349 cm^{-1} corresponds to the O-H stretching vibrations of the PMMA layers. Fig. 3 also shows that increasing the Er^{3+} content also increased the intensity of the O-H vibrations. This can be explained by the fact that ErCl_3 , as very hygroscopic substance, not only dopes the polymer samples also but bring a certain amount of water. It is a well-known fact that the presence of O-H groups in a matrix containing rare earth ions unfortunately causes problems by hindering emission in the infrared region.

The transmission measurements were performed using a UV-VIS-NIR Spectrometer (UV-3600 Shimadzu) in the spectral range from 350 to 700 nm. The transmission spectra of

the Er^{3+} doped polymer (erbium(III)) in the spectral range from 350 nm to 700 nm are shown in Fig. 4. In the samples containing 10.0 at. % of Er^{3+} , two bands appeared that were attributed to the following transitions: $^4\text{G}_{11/2}$ (377 nm) and $^2\text{H}_{11/2}$ (519 nm). In the samples containing 20.0 at. % of Er^{3+} one more band appeared at $^4\text{F}_{9/2}$ (650 nm). We did not observe bands $^2\text{G}_{7/2}$ (355 nm), $^2\text{G}_{9/2}$ (363 nm), $^2\text{H}_{9/2}$ (405 nm), $^4\text{F}_{3/2}$ (441 nm), $^4\text{F}_{5/2}$ (448 nm), $^4\text{F}_{7/2}$ (485 nm) and $^4\text{S}_{3/2}$ (539 nm). The same results were obtained for samples doped with ErCl_3 and ErF_3 solution.

The transmission spectra of the Er^{3+} (1.0 at. %) doped polymers co-doped with Yb^{3+} ions using erbium(III) and ytterbium(III) (from 1.0 at. % to 20.0 at. %) in the spectral range from 900 nm to 1040 nm are shown in Fig. 5. The sample containing 20.0 at. % of Yb^{3+} ions has a typical $\text{Yb}^{3+} \ ^2\text{F}_{5/2}$ transition with maxima at 977 nm. The samples

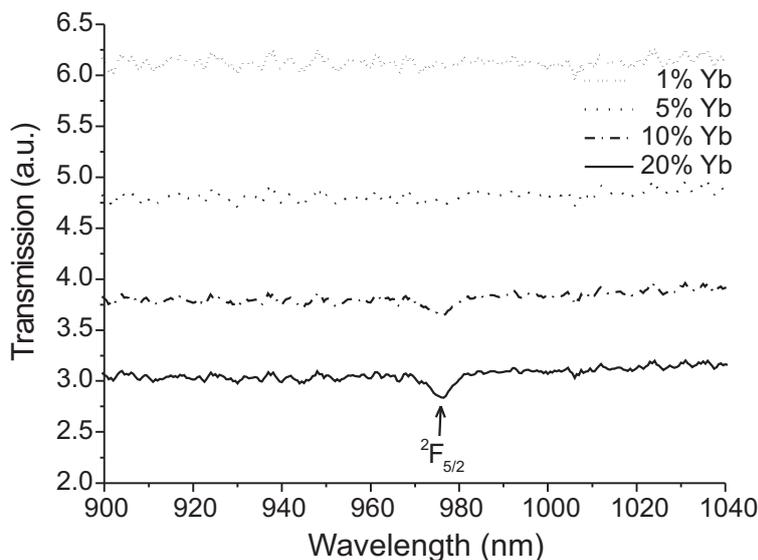


Fig. 5: Transmission spectra of Er^{3+} (1.0 at.%) doped PMMA co-doped with Yb^{3+} using erbium(III) and ytterbium(III) ions

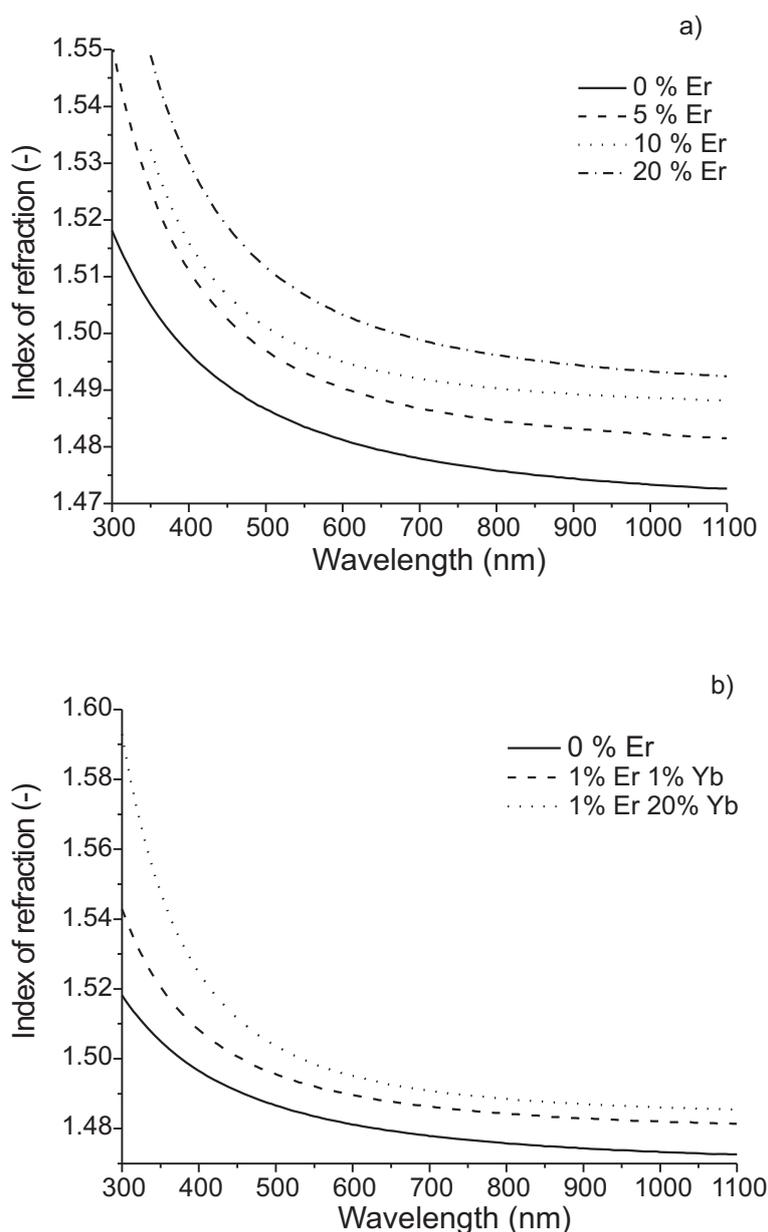


Fig. 6: Wavelength dependence of the refractive indices a) of the Er³⁺ and b) Er³⁺+Yb³⁺ doped PMMA layers using erbium(III) and ytterbium(III)

with a lower concentration have a weaker $^2F_{5/2}$ transition, and the samples with concentration 1 at. % Yb³⁺ ions have no visible Yb³⁺ ($^2F_{5/2}$) transition.

The refractive indices were measured using variable angle spectroscopic ellipsometry (VASE, J.A.Woollam & co.) working in rotating analyzer mode. The measurements were carried out in the spectral range from 300 to 1100 nm. Fig. 6a shows the dependence of the refractive indices of the Er³⁺ doped PMMA (erbium (III)), and Fig. 6b shows the dependence of the refractive indices of the 1at. % Er³⁺ (erbium (III)) doped PMMA with Yb³⁺ co-doping (ytterbium (III)). It is obvious that increasing the content of Er³⁺ and Er³⁺+Yb³⁺ increases the refractive indices of the material.

The refractive index value is, also a matter of the polarizability of the ions present in the material [26]. Polarizability

(or ion deformation) is understood as a function of the size of the ions – the larger the size, the larger the polarizability, and vice versa. The presence of larger cations in the substance (in this case rather large Er³⁺ and/or Yb³⁺ the thin layer of polymer) usually raises the refractive index. The results are not surprising, but what is important is the exact refractive index value (of course depending on the wavelength) of the deposited material.

Semiconductor laser excitation (P4300 operating at $\lambda_x = 980$ nm with $E_{ex} = 500$ mW; room temperature) was used to detect sample luminescence in the range from 1450 to 1650 nm. The photoluminescence spectra of the Er³⁺ doped samples (erbium (III)) are given in Fig. 7a, and the Er³⁺ doped samples (ErF₃) are given in Fig. 7b. In the case of erbium (III) only the samples with higher Er³⁺ concentra-

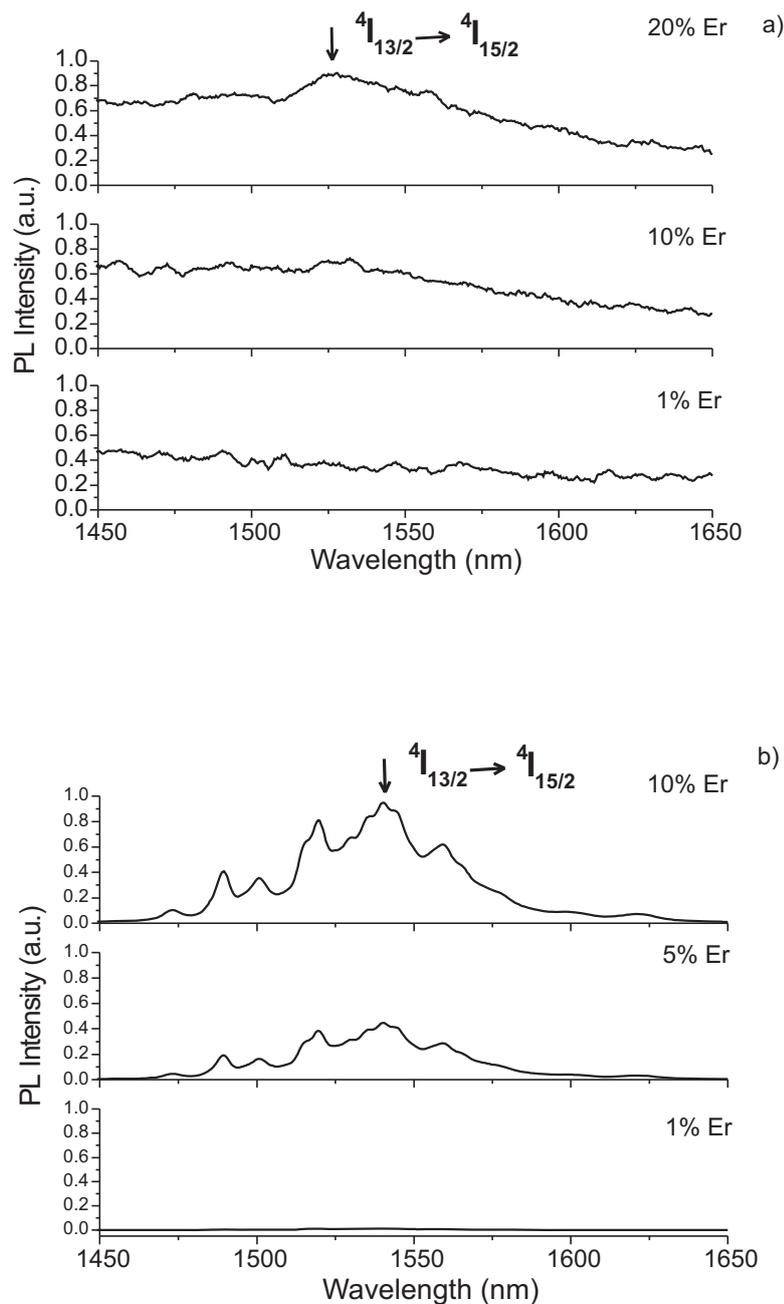


Fig. 7: Photoluminescence spectra of Er^{3+} doped PMMA layers a) (erbium(III)), b) ErF_3 ($\lambda_{\text{ex}} = 980 \text{ nm}$ with $E_{\text{ex}} = 500 \text{ mW}$; room temperature)

tions showed very weak photoluminescence bands at 1530 nm attributed to the erbium transition $4I_{13/2} \rightarrow 4I_{15/2}$. In the case of ErF_3 , the emission intensity is higher than that of erbium (III) (See Fig. 7). The highest emission intensity was found in sample (ErF_3), which contained 10.0 at. % erbium.

Fig. 8 shows the infrared emissions obtained for samples doped with 1.0 at.% erbium and co-doped with ytterbium ions in amounts varying from 1.0 at. % to 10.0 at. % (Fig. 8a erbium(III), ytterbium(III) and Fig. 8b ErF_3 , YbF_3). The samples showed very weak emission at 1530 nm. Therefore co-doping with ytterbium ions had only a weak effect on the photoluminescence spectra.

4 Conclusion

We have reported on the fabrication process and the properties of PMMA layers doped with Er^{3+} and Er^{3+} ions co-doped with Yb^{3+} ions.

- Polymer layers were fabricated by spin coating or by pouring the polymer into a bottomless mould placed on a glass substrate.
- We observed the FTIR absorption band at around 3349 cm^{-1} corresponding to the O-H vibrations and three bands at 2994 cm^{-1} , 2953 cm^{-1} and 2843 cm^{-1} corresponding to the aliphatic C-H bands.

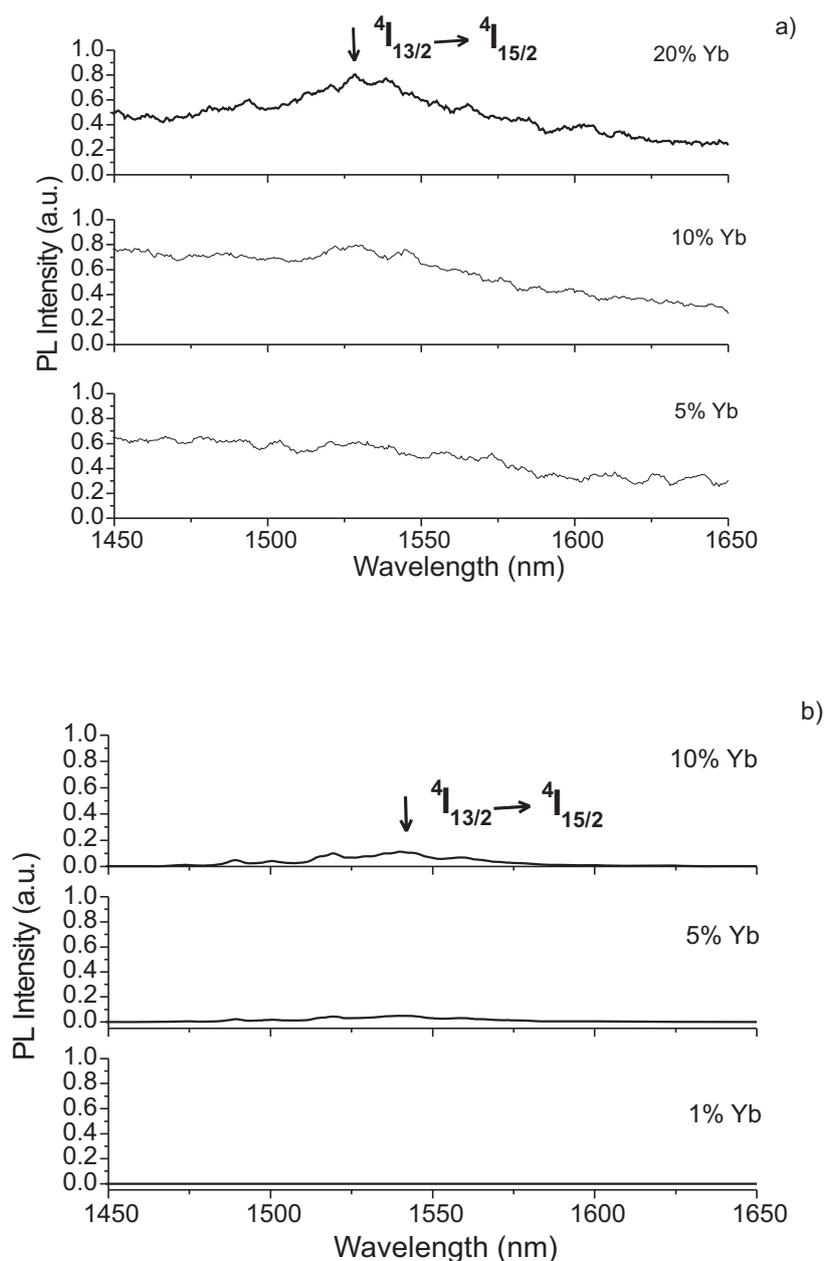


Fig. 8: Photoluminescence spectra of $\text{Er}^{3+}+\text{Yb}^{3+}$ doped PMMA layers (1.0 at. % Er) a) (erbium(III), ytterbium(III)), b) ErF^{3+} , YbF^{3+} ($\lambda_{\text{ex}} = 980 \text{ nm}$ with $E_{\text{ex}} = 500 \text{ mW}$; room temperature)

- The content of Er^{3+} and $\text{Er}^{3+} + \text{Yb}^{3+}$ ions had a significant effect on the transmission spectra. We observed three bands corresponding to the Er^{3+} ions (${}^4\text{G}_{11/2} - 377 \text{ nm}$, ${}^2\text{H}_{11/2} - 519 \text{ nm}$, ${}^4\text{F}_{9/2} - 650 \text{ nm}$) and one band corresponding to the Yb^{3+} ions (${}^2\text{F}_{5/2} - 977 \text{ nm}$). These bands we observed in the samples doped with a higher Er and Yb concentration, and they almost disappeared in the background in the case of samples with a low Er and Yb concentration.
- The refractive indices were investigated by spectroscopic ellipsometry and we found that increasing the content of the Er^{3+} and Yb^{3+} ions increases the refractive indices of the material.
- The Er^{3+} doped PMMA samples exhibited a typical emission at 1530 nm, due to the Er^{3+} intra- $4f$ ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ only at samples with higher content of Er^{3+} ions. The highest emission intensity was found in sample (ErF_3) containing 10.0 at. % erbium. It was also found that the addi-

tion of ytterbium did not substantially affect the 1530 nm luminescence.

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