Optical and Spectroscopic Properties of Polymer Layers Doped with Rare Earth Ions

Vaclav Prajzler¹, Oleksiy Lyutakov², Ivan Huttel², Jiri Oswald³ and Vitezslav Jerabek¹

¹Czech Technical University in Prague, Department of Microelectronics
Technicka 2, 166 27 Prague 6,
²Institute of Chemical Technology in Prague
Technicka 2, 166 28 Prague 6,
³Institute of Physics of the Academy of Sciences Czech Republic v.v.i.
Cukrovarnicka 10, 162 00 Prague,
Czech Republic

1. Introduction

This chapter deals with description properties of a number of Rare-Earth (RE) ions in polymer materials. The list of the RE elements with some of its basic properties are shown in Table 1. The electronic structure of each trivalent RE element consists of partially filled 4f subshell, and outer 5s² and 5p⁶ subshell. With increasing nuclear charge electrons enter into the underlying 4f subshell rather than the external 5d subshell. Since the filled 5s² and 5p⁶ subshells screen the 4f electrons, the RE elements have very similar chemical properties. The screening of the partially filled 4f subshells, by the outer closed 5s² and 5p⁶ subshell, also gives rise to sharp emission spectra independent of the host materials. The intra-subshell transitions of 4f electrons lead to narrow absorption peaks in the ultra-violet, visible, and near-infrared regions.

<table>
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<tr>
<th>Atomic number</th>
<th>n⁺</th>
<th>Element</th>
<th>Electron configuration RE³⁺</th>
<th>Ground term RE⁵⁺</th>
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<td>Ytterbium - Yb</td>
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*nNumber of electros (n) in the 4f shell of three-valence Rare Earth ions.

Table 1. The Rare Earth elements and some of its properties

Trivalent RE ions can be used for many photonics applications. Erbium (Er), neodymium (Nd), praseodymium (Pr) ions are well-known, because these elements have transitions used in telecommunications systems. Except these RE ions other elements are intensively studied. Europium (Eu), terbium (Tb) and cerium (Ce) produce red, green and blue light which is used for full colour displays. Thulium (Tm) and holmium (Ho) lasers has received a large amount of interest during last ten years because these elements are the best candidates for a wide range of applications including medicine and eye-safe remote sensing systems such as laser ranging, coherent Doppler lidar for wind sensing, wind-shear detection and etc (Kenyon A.J.; 2002; Bourdet et al. 2000).

The choice of host materials for RE ions hardly influences the energy levels of the RE ions. Therefore in principle any materials that have little absorption at the pump and emission wavelength can be used. Up to now there have been published many papers describing properties of RE-doped with many different materials. Photonics materials such as glasses, optical crystals (LiNbO$_3$, Al$_2$O$_3$, Y$_2$O$_3$) and semiconductors (Si, SiGe, SiC, GaN, etc.) are conventional materials for accomplishing lasing action (Polman A; 1997; Wong, et al. 2002; Zavada, et al. 1995). Recently there has been considerable interest in the development of new photonics materials such as polymers which have better properties and a lower price. It is due to fact that a number of properties make polymers attractive hosts for RE ions including high transparency in the visible and near-infrared spectra, well controlled refractive indices, good thermal stabilities, offering simple fabrication process and low cost (Liang et al., 2003; Slooff et al., 2002; Sosa et al., 2003; Tung et al., 2005).

Polymers doped with RE-ions are still a new area and there is only a small number of groups active in this field as for example: L.H. Slooff from the FOM Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands, W.H. Wong from the Department of Electronic Engineering and Department of Physics and Material Sciences, City University of Hong Kong, H. Liang from Structure Research Laboratory and Department of Polymer Science and Engineering, University of Science and Technology of China and X. Xu from Optical Physics Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing, China.

For our research we chose two types of polymers. As first polymer we chose Polymethylmethacrylate (PMMA) polymer because it is the most common used polymer and we also used new of type polymer Epoxy Novolak Resin (ENR) due to its low optical losses 0.2 dB/cm at 1090 nm, 0.77 dB/cm at 1310 nm, 1.71 dB/cm at 1550 nm and due to easy fabrication process (Beche et al., 2005). We doped these two polymers with erbium (Er), ytterbium (Yb), europium (Eu), neodymium (Nd), thulium (Tm), holmium (Ho), praseodymium (Pr) and dysprosium (Dy) ions (Prajzler et al., 2007; Prajzler et al., 2008). We chose these RE ions because Er$^{3+}$ doped materials can emit at 1530 nm and Tm$^{3+}$ doped photonics materials can have emission bands around 1470 nm and from 1600 to 2100 nm. Yb$^{3+}$ and Ho$^{3+}$ ions were used as co-dopants. Tm$^{3+}$ doped polymers were co-doped with Ho$^{3+}$ ions and Er$^{3+}$ doped polymers were co-doped with Yb$^{3+}$ ions. Trivalent Dy$^{3+}$ ions are studied for emission at 1300 nm. Other RE ions were chosen for photoluminescence study in visible region.

2. Experimental part
2.1 PMMA layers
Fabrication process of PMMA layers doped with RE ions is following: 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 layers were formed by the solution either being spin-coated onto silicon and glass substrates or by being poured into bottomless molds placed on a glass substrate and left to dry. For RE doping, solutions whose content ranged from 1.0 at. % to 20.0 at. % RE-ions were added to the PMMA. For RE co-doping rare earth chloride or Rare Earth fluoride were together dissolved in \( \text{C}_5\text{H}_9\text{NO} \) or \( \text{C}_2\text{H}_6\text{OS} \). Samples containing 1.0 at. % erbium were co-doped with ytterbium in amounts also ranging from 1.0 at. % to 20.0 at. %.

### 2.2 Epoxy Novolak Resin

Commercially available polymer Epoxy Novolak Resin (NANO™ Su-8 10) supported by Micro Resist Technology GmbH was used for fabrication of the RE doped samples. Chemical structure of Epoxy Novolak Resin (ENR) polymer is shown in Fig.1.

![Chemical Structure of Epoxy Novolak Resin](image)

Fig. 1. Structure of the Epoxy Novolak Resin polymer

Polymer layers were formed by the solution either being spin-coated onto silicon or by being poured into bottomless molds placed on a quartz substrate and let to dry. After the deposition the samples were baked at 90°C for 45 min and then UV light was used for hardening. Finally hard baking at 90°C for 60 min was applied. The doping occurred using anhydrous RE chloride or RE fluoride dissolved in \( \text{C}_2\text{H}_6\text{OS} \) (Sigma-Aldrich). For the doping, solutions where the RE content ranged from 1.0 at. % to 20.0 at. % were added to the ENR polymer.

### 3. Results and discussion

#### 3.1 Infrared spectra

The fabricated samples were investigated by infrared spectroscopy (FT-IR). Infrared reflectance and ATR spectra were obtained 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. 2a displays the FT-IR spectra of PMMA layers doped with \( \text{Er}^{3+} \) ions. Fig. 2b shows the FT-IR spectra of ENR layers doped with \( \text{Nd}^{3+} \) ions in the wavelength range from 3900 to 2600 cm\(^{-1}\).
Fig. 2a shows the three strong broad bands occurring at 2843 cm\(^{-1}\), 2953 cm\(^{-1}\), 2994 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. 2a also shows that increasing the Er\(^{3+}\) content also increases 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 but also brings 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.

Fig. 2b shows also three strong broad bands occurring at 2873 cm\(^{-1}\), 2930 cm\(^{-1}\) and 2965 cm\(^{-1}\) correspond to aliphatic C-H bands while that one corresponding to aromatic C-H band is at 3060 cm\(^{-1}\). 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 bands at 3380 cm\(^{-1}\) correspond to the O-H stretching vibrations of the ENR layers. Similar results were obtained for all the samples with the only difference that the O-H stretching bands were for particular rare
earth's slightly shifted (while the C-H stretching bands remained un-affected). Fig. 2b also shows that increasing RE content caused the O-H vibrations intensity increased as well. This can be explained by the fact that RE chloride and fluoride are very hygroscopic substances.

3.2 Transmission spectra

The transmission measurements were performed using a UV-VIS-NIR Spectrometer (UV-3600 Shimadzu) in the spectral range from 350 to 1800 nm. The transmission spectra of the Er$^{3+}$ doped PMMA layers in the spectral range from 350 nm to 700 nm are shown in Fig.3a and the transmission spectra of the Er$^{3+}$ (1.0 at.%) doped polymers co-doped with Yb$^{3+}$ ions in the spectral range from 900 nm to 1040 nm are shown in Fig. 3b.

Samples contain 5.0 at. % of Er$^{3+}$, two bands appeared that were attributed to the following transitions: $^4G_{11/2}$ (377 nm) and $^2H_{11/2}$ (519 nm). Samples contain 20.0 at.% of Er$^{3+}$ another band appeared at $^4F_{9/2}$ (650 nm). We did not observe bands $^2G_{7/2}$ (355 nm), $^2G_{9/2}$ (363 nm), $^2H_{9/2}$ (405 nm), $^4F_{3/2}$ (441 nm), $^4F_{5/2}$ (448 nm), $^4F_{7/2}$ (485 nm) and $^4S_{5/2}$ (539 nm). Sample contains 20.0 at. % of Yb$^{3+}$ ions has a typical Yb$^{3+}$ $^2F_{5/2}$ transition with maximum at 977 nm. Samples with a lower concentration have weaker $^2F_{5/2}$ transition, and the samples with concentration 1 at.% Yb$^{3+}$ ions have no visible Yb$^{3+}$ ($^2F_{5/2}$) transition.

Transmission spectra of the Ho$^{3+}$ doped ENR layers are shown in Fig. 4. Fig. 4a shows transmission spectra in spectral range fr om 400 nm to 1000 nm and samples contain 10.0 at.% of Ho$^{3+}$ appeared following three strong bands $^5G_6$ (448 nm), $^5F_4$ (535 nm) and $^5F_5$ (639 nm). Fig. 4a also shows three week bands $^5G_5$ (415 nm), $^5F_2$ (466 nm), and $^5F_3$ (482 nm), which can be assigned to the holmium ions. Fig. 4b shows transmission spectra in spectral range from 900 nm to 1300 nm and we found out band at 1152 nm corresponds to $^5I_6$ transitions. Transmission spectra of ENR polymer doped with Ho$^{3+}$ ions co-doped with Tm$^{3+}$ ions are shown in Fig. 5. Fig. 5a shows four bands $^1G_4$ (463 nm), $^3F_2$ (658 nm), $^3F_3$ (683 nm), and $^3H_4$ (790 nm), and Fig. 5b shows one band $^3I_6$ (1210 nm) corresponds to Tm$^{3+}$ ions. Fig. 5a also shows tree bands $^3G_6$ (448 nm), $^5F_4$ (535 nm), and $^5F_5$ (639 nm) correspond to Ho$^{3+}$ ions.

ENR polymer doped with Nd$^{3+}$ and Dy$^{3+}$ ions is shown in Fig. 6. Fig. 6a shows four strong bands corresponding to the Nd$^{3+}$ transitions: $^5G_{5/2}$ (574 nm), $^4F_{2/2}$ (740 nm), $^4F_{5/2}$ (794 nm), $^4F_{7/2}$ (865 nm) and Fig. 6b shows six bands corresponds to the Dy$^{3+}$ ions. We observed transitions $^6F_{3/2}$ (758 nm), $^6F_{5/2}$ (807 nm), $^6F_{7/2}$ (906 nm), $^6F_{9/2}$ (1100 nm), $^6F_{11/2}$ (1280 nm) and $^6H_{11/2}$ (1685 nm).
Fig. 4. Transmission spectra of ENR polymer doped with Ho\(^{3+}\) ions (1.0 at.%) and co-doped with Tm\(^{3+}\) ions a) 10.0 at.% Tm\(^{3+}\), b) 20.0 at.% Tm\(^{3+}\)

Fig. 5. Transmission spectra of ENR polymer doped with Ho\(^{3+}\) ions (1.0 at.%) and co-doped with Tm\(^{3+}\) (20.0 at.%) ions

Fig. 6. Transmission spectra of ENR polymer doped with a) Nd\(^{3+}\) ions and b) Dy\(^{3+}\) ions

The obtained transmission spectra of the ENR layers doped with Eu\(^{3+}\) ions are shown in Fig. 7a and ENR polymer doped with Pr\(^{3+}\) is shown in Fig. 7b.
Fig. 7. Transmission spectra of ENR polymer doped with a) Eu$^{3+}$ ions and b) Pr$^{3+}$ ions

Fig. 7a shows only two weak bands correspond to Eu$^{3+}$ ions – $^5D_3$ (393 nm) and $^5D_2$ (464 nm). Fig. 7b shows four bands correspond to Pr$^{3+}$: $^3I_2$ (443 nm), $^3P_1$ (466 nm), $^3P_0$ (479 nm) and $^1D_2$ (587 nm) in the sample containing 10.0 at.% Pr$^{3+}$. We found out very strong bands at 1440 nm and at 1540 nm, which correspond to $^3F_4$ and $^4F_4$ bands, respectively. The bands at 1950 nm and at 2340 nm (that would be attributed to $^3F_2$ and $^3H_6$ transitions) did not appear not even in the sample with the highest Pr$^{3+}$ concentrations (20.0 at.%).

3.3 Photoluminescence

Semiconductor lasers (operating at $\lambda_{ex}$ = 980 nm, $\lambda_{ex}$ = 827 nm) and He-Ne laser excitation ($\lambda_{ex}$ = 632.8 nm) were used to detect sample luminescence in the range from 1450 nm to 1650 nm.

Fig. 8 shows Photoluminescence spectra (PL) of ENR layers doped with Dy$^{3+}$ ions. Fig. 8a shows PL spectra pumped at 632.8 nm (6 mW) under temperature of 4 K and this Fig. clearly shows the band at 1340 nm caused by the Dy$^{3+}$ transition $^6H_{9/2} - ^6F_{11/2} \rightarrow ^6H_{15/2}$. This transition appeared only in the samples containing 10 at.% of dysprosium. Photoluminescence of the samples with higher content (15 at.%) of dysprosium is much weaker. Fig. 8a also shows that maximum is around 1340 nm and Fig. 8b shows PL spectra
obtained by using optical pumping at 827 nm (temperature 4 K). PL spectra caused by Dy$^{3+}$ ions was observed only at samples containing 15 at.% and PL maximum was found out around 1310 nm. Measurements at two additional excitations – 827 nm and 980 nm – were also applied but the photoluminescence occurred only on the background level.

Fig. 9a shows photoluminescence spectra of ENR layers doped with Tm$^{3+}$ ions is spectral range from 1000 nm to 1200 nm. Fig. 9b shows PL spectra of ENR doped with Tm$^{3+}$ ions in spectral range from 1300 nm to 1600 nm under excitation 632.8 nm (He-Ne laser) under temperature 4 K. Fig. 9a shows maximum PL intensity around 1047 nm and Fig. 9b shows maximum PL intensity around 1420 nm but this photoluminescence is very weak.

Fig. 9. Photoluminescence spectra of Tm$^{3+}$ doped ENR

Fig. 10 shows photoluminescence spectra of ENR layers doped with Er$^{3+}$ (Fig.10a) and Er$^{3+}$ doped ions co-doped with Yb$^{3+}$ ions (Fig.10b) in spectral range from 1450 nm to 1650 nm. Fig. 10a shows that only the samples with higher Er$^{3+}$ concentrations showed strong photoluminescence bands at 1530 nm attributed to the erbium transition $4I_{13/2} \rightarrow 4I_{15/2}$. The highest emission intensity was found out in the sample containing 10.0 at.% erbium. Fig. 10b shows typical 1530 nm Er$^{3+}$ emission but co-doping with ytterbium ions had no effect on the photoluminescence spectra at all.

Fig. 10. Photoluminescence spectra of ENR layers doped with a) Er$^{3+}$ ions and b) Er$^{3+}$ ions co-doped with Yb$^{3+}$ ions
Fig. 11 shows photoluminescence spectra of PMMA layers doped with Er$^{3+}$ (Fig.11a) and Er$^{3+}$ doped ions co-doped with Yb$^{3+}$ ions (Fig.11b) under excitation 980 nm using semiconductor laser under room temperature. Fig. 11a shows the typical photoluminescence bands around 1540 nm attributed to the erbium transition $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ and Fig. 11a also shows that the increasing content of Er$^{3+}$ ions increases also the photoluminescence intensity. The highest PL intensity observed so far had the sample containing 10.0 at.% of erbium. Fig. 11b shows that Yb$^{3+}$ co-doping have positive influence.

![Photoluminescence spectra of PMMA layers doped with a) Er$^{3+}$ ions and b) Er$^{3+}$ (1.0 at.%) ions co-doped with Yb$^{3+}$ ions](image)

4. Conclusion

We report on spectroscopic properties of the Polymethylmethacrylate and Epoxy Novolak Resin polymer doped with Rare Earth ions. Polymer layers were fabricated by a spin coating or by pouring the polymer into a bottomless mould placed on a quartz substrate. The fabricated polymer layers doped with RE ions were examined by infrared spectroscopy and IR spectroscopy of the samples revealed absorption bands corresponding to the O-H vibrations in the region from 3340 cm$^{-1}$ to 3380 cm$^{-1}$. Transmission measurements were performed in the spectral range from 350 nm to 1800 nm. The content of RE ions had a significant effect on the occurrence of the bands attributed to the RE transitions: while they were rather strong in the samples with higher RE concentration they almost vanished in the background in the case of the samples with low RE concentration.

We observed photoluminescence bands around 1300 nm of the ENR samples doped with Dy$^{3+}$ ions caused by the dysprosium transition. ENR and PMMA layers doped with Er$^{3+}$ ions had typical 1 530 nm emission due to the $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transition. It was also found out that the addition of ytterbium did not substantially affect at PL spectra at ENR layers. One possibility how to explain this result is the presence of the O-H groups. The O-H groups are well-known as strong quencher of the Er$^{3+}$ photoluminescence and fabrication samples with lower content of O-H groups will be the aim of the future research.

5. References


Lasers and electro-optics is a field of research leading to constant breakthroughs. Indeed, tremendous advances have occurred in optical components and systems since the invention of laser in the late 50s, with applications in almost every imaginable field of science including control, astronomy, medicine, communications, measurements, etc. If we focus on lasers, for example, we find applications in quite different areas. We find lasers, for instance, in industry, emitting power level of several tens of kilowatts for welding and cutting; in medical applications, emitting power levels from few milliwatt to tens of Watt for various types of surgeries; and in optical fibre telecommunication systems, emitting power levels of the order of one milliwatt. This book is divided in four sections. The book presents several physical effects and properties of materials used in lasers and electro-optics in the first chapter and, in the three remaining chapters, applications of lasers and electro-optics in three different areas are presented.

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