

Optical Properties of Bi-Doped Epoxy Novolak Resin Containing Ce, Dy, and Y Ions

Václav Prajzler,¹ Oleksiy Lyutakov,² Ivan Hüttel,² Jarmila Špírková,² Jirí Oswald,³ Vladimír Machovic,² Vítězslav Jerábek¹

¹Department of Microelectronics, Faculty of Electrical Engineering, Czech Technical University, Technická 2, 166 27 Prague, Czech Republic

²Department of Solid State Engineering, Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic

³Department of Solid State Engineering, Institute of Physics of the ASCR, v.v.i., Cukrovarnická 10, 162 00 Prague, Czech Republic

Received 9 March 2011; accepted 23 May 2011

DOI 10.1002/app.34945

Published online 27 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this article, we report on the optical properties of Bismuth doped Epoxy Novolak Resin (ENR) co-doped with Dysprosium, Cerium, and Yttrium ions. The polymer layers containing 1.0 to 20.0 at % of Bismuth were fabricated by spin-coating onto silicon or quartz substrates. The properties of the material were studied using several methods with special regards to its potential utilization in photonics devices. Transmission spectra were taken in the range from 350 to 1600 nm, while photoluminescence spectra around 1300 nm were recorded by using excitation of semiconductor lasers operating at 808 nm and at 980 nm ($E_x = 250$ mW). Optical properties of the samples were eval-

uated on the bases of the concentration of the Bismuth ions as well as on the concentrations of the co-doping ions and showed close relations between concentration of the dopants and intensity of the luminescence band at 1300 nm. Our results proved that the Bismuth doped ENR has a strong potential for application in active photonics structures, as it has excellent optical properties and very easy and not demanding fabrication procedures. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 710–715, 2012

Key words: photoluminescence; polymers; epoxy novolak resin; bismuth

INTRODUCTION

Long-haul operation communication systems using silica fiber use two bands at 1550 nm and 1300 nm, which coincide with two silica fiber low optical loss windows: one between 1200 to 1350 nm and the second one from 1450 to 1550 nm. Erbium-doped optical fiber amplifiers have been extensively used for optical amplification in telecom systems for the 1550 nm, but the majorities of the worldwide optical telecommunication networks were optimized for 1300 nm for two reasons: low optical losses and no chromatic dispersion of silica fiber at this wavelength. Therefore, there exists a strong requirement for optical sources and amplifiers operating at this wavelength. However, there has not been any key breakthrough for optical amplification at 1300 nm, although praseodymium

and neodymium-doped optical amplifiers are intensively studied, and some of them are commercially available.^{1–4} It is due to these that the amplifiers have small low-quantum efficiency and higher noise.

Recently, a new dopant came into the focus of the researches in the field of active photonics devices operating at 1300 nm. As Fujimoto and Nakatsuka⁵ reported about 1300 nm emission from Bi-doped silica glass a research activity has been stimulated with focusing also study on luminescence properties of other Bismuth doped materials.⁶ Till date, several papers have been presented on photoluminescence (PL) spectra of the Bi doped optical glasses^{7–12} though no but one paper done by us reported about 1300 nm PL of Bi doped polymer materials.¹³

Nowadays, a possibility of enhancing the near-infrared emission of the Bi doped glasses by co-doping them with transition metal ions such as Ytterbium (Yb^{3+}),¹⁴ Dysprosium (Dy^{3+}),¹⁵ Thulium (Tm^{3+}),¹⁶ and Nickel¹⁷ has appeared. In this article, we are going to report about PL properties of Bi doped Epoxy Novolak Resin (ENR) and co-doped with Cerium (Ce^{3+}), Dysprosium (Dy^{3+}), and Yttrium (Y^{3+}) ions, as they, according to the published literature might have some co-activating potential.

Polymers, in general, open new options for construction a new promising family of optical-

Correspondence to: V. Prajzler (xPrajzlv@feld.cvut.cz).

Contract grant sponsor: Czech Science Foundation; contract grant number: 102/09/P104.

Contract grant sponsor: Czech Technical University; contract grant number: MSM6840770014.

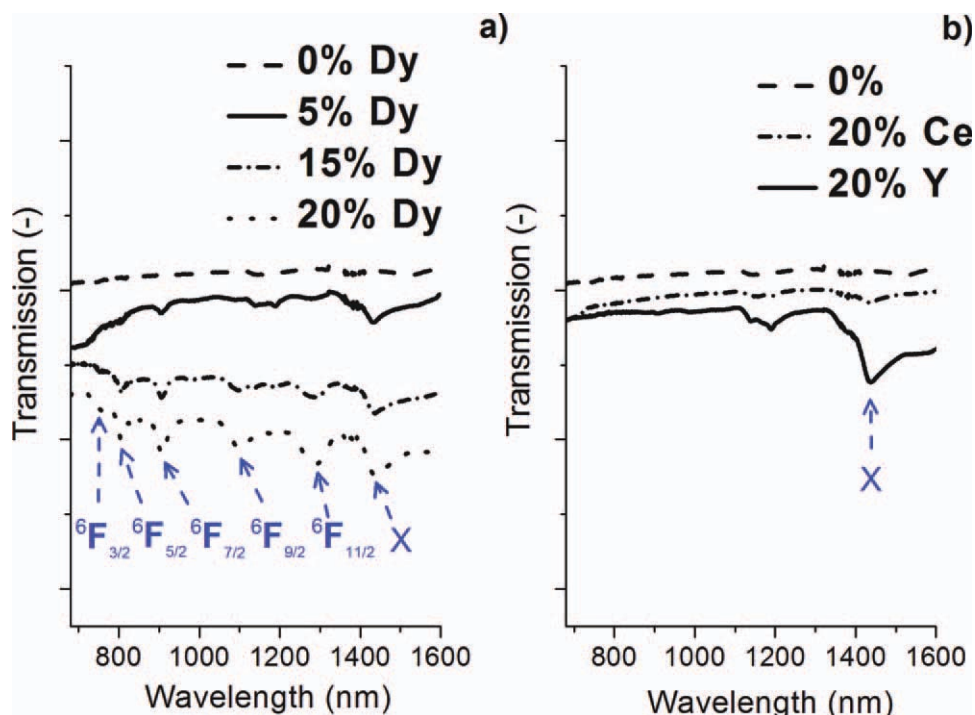


Figure 1 (a) Transmission spectra of Bi (1.0 at %)-doped and Dy-co-doped ENR samples. (b) Transmission spectra of Bi (1.0 at %)-doped and Y (20.0 at %) and Ce (20.0 at %)-co-doped ENR samples. The X-labeled bands cannot be attributed neither Dy neither Y, though it does not belong to the ENR substrate either, so that the origin of the band remains elusive [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

photonics components using their feasible fabrication processes and low cost and among them a special interest is paid to ENR polymer as it revealed low optical losses at 1300 nm ($0.77 \text{ dB}\cdot\text{cm}^{-1}$ at 1310 nm),^{18,19} which makes it a material with high application potential.

We have already dealt with the ENR polymer in our article.¹³ The article gave the results of our pilot experiments on the Bi-doping into ENR in concentration range from 1.0 at % to 20 at %. The PL spectra showed that the optimal concentration of the dopant should not exceed 15.0 at %, as at the higher concentration of the Bi ions caused the undesired concentration quenching effect. The results also showed that the PL emission around 1300 nm below that critical value depends strongly on the concentration of the Bi. However, high concentration of the doping ions may cause troubles with solubility of the precursors. Also, bismuth compounds are known for their tendency to hydrolyze, which makes the fabrication processes rather environment and health unfriendly, so it would be reasonable to keep their concentration involved in the fabrication processes as low as possible. For that, the photoluminescence-enhancing potential of the rare earths would be a good option.

In this article, we are going to describe the influence of the PL sensitizers Ce^{3+} , Dy^{3+} , and Y^{3+} ions, on the possible amplification of the 1300 nm emission of the Bi-doped ENR, with the aim to lower the concentra-

tion of the Bi ions as much as possible without a significant deterioration of the amplifying effect, optimally down to 1.0 at %, which will be a concentration of the amplifying ion currently used in other dielectric materials. This will be done with help of the luminescence-enhancing ions (for the explanation of the energy transfer processes see Refs. 20,21).

EXPERIMENTAL

Polymer layers were fabricated by the spin coating of ENR (NANOTM Su-8) polymer (Micro Resist Technology GmbH) on silicon substrate, or, the polymer was poured into a bottomless mould placed on a quartz substrate and let to dry in air.

The ENR solution with bismuth, cerium, dysprosium or yttrium was spin coated on the silicon substrate (1500 rpm, 12 min). After the deposition the samples were baked at 90°C for 45 min, and then, ultraviolet (UV) light was used for hardening it. Finally, hard baking at 90°C for 60 min was applied. Bismuth chloride (BiCl_3) was dissolved in 1-methyl-2-pyrrolidinone ($\text{C}_5\text{H}_9\text{NO}$) or dimethyl sulfoxide ($\text{C}_2\text{H}_6\text{OS}$) (Sigma-Aldrich) so that the concentration of Bismuth in the solutions ranged from 1.0 to 20.0 at %. For the doping, the solutions were added to the polymer before the deposition of the samples. Deposition process of the Bismuth doped ENR layers have been already described in Ref. 16. The co-doping with other

TABLE I
Comparison of Transmission Levels of Dy³⁺ in our Epoxy Novolak Resin Polymer Containing Bi(1.0 at. %) and Dy³⁺ (20.0 at %) and in Dy³⁺-containing Fluoride Glass²²

Transition	Wavelength (nm)	
	Fluoride glasses	ENR
⁶ H _{15/2} → ⁶ H _{13/2}	2830	nm
⁶ H _{11/2}	1695	nm
⁶ F _{11/2}	1280	s
⁶ F _{9/2}	1100	s
⁶ H _{5/2}	973	no
⁶ F _{7/2}	906	vs
⁶ F _{5/2}	804	vs
⁶ F _{3/2}	752	vw

nm, not measured; no, not observed; vw, very weak; w, weak; s, strong.

trivalent transition metal (Ce, Dy and Y) ions was performed by the same way as the Bismuth doping, i.e., adding the chloride of the pertinent metal dissolved in the aforementioned solvents into the Bismuth doped ENR precursor and depositing the layers by the procedure described above.

RESULTS

Transmission spectra

Transmission measurements were performed using a UV-VIS-NIR Spectrometer (UV-3600 Shimadzu) in

the spectral range from 350 to 1600 nm. In our previous article,¹³ we have already mentioned that the absorption spectra of the Bi-doped ENR polymer increasing level of the doping shifted the absorption edge to the longer wavelengths. Similar dependence appeared also now where ENR polymer was co-doped with any of three—Cerium, Dysprosium, and Yttrium ions. The transmission spectra of the samples co-doped with Dy³⁺ are shown in Figure 1(a).

Table I display the spectral data shown in Figure 1 and compares our transmission bands with the data attributed to pertinent transitions in dysprosium-doped fluoride glass as reported in Ref. 22. The content of Dy³⁺ ions had a significant effect on the occurrence of the bands attributed to the Dy³⁺ transitions: while they were rather strong in the samples with higher Dy³⁺ concentration, they almost vanished in the background in the case of the samples with low Dy³⁺ concentration. We found five bands that corresponded to Dy³⁺ ions in the samples containing 20.0 at % of Dy³⁺. Two very strong bands corresponded to ⁶F_{5/2} (804 nm) and ⁶F_{7/2} (906 nm), but we did not find any band, which could be attributed to ⁶H_{5/2} at 973 nm. However one peak, which has not been ever seen before now appeared at 1436 nm (labeled with X in the figure). It evidently had a connection with the Dy-doping, as its intensity increased with the increasing Dy concentration, though in the moment we are not able to attribute it to any known Dy-transition. However, we are going to follow this new feature in our next research.

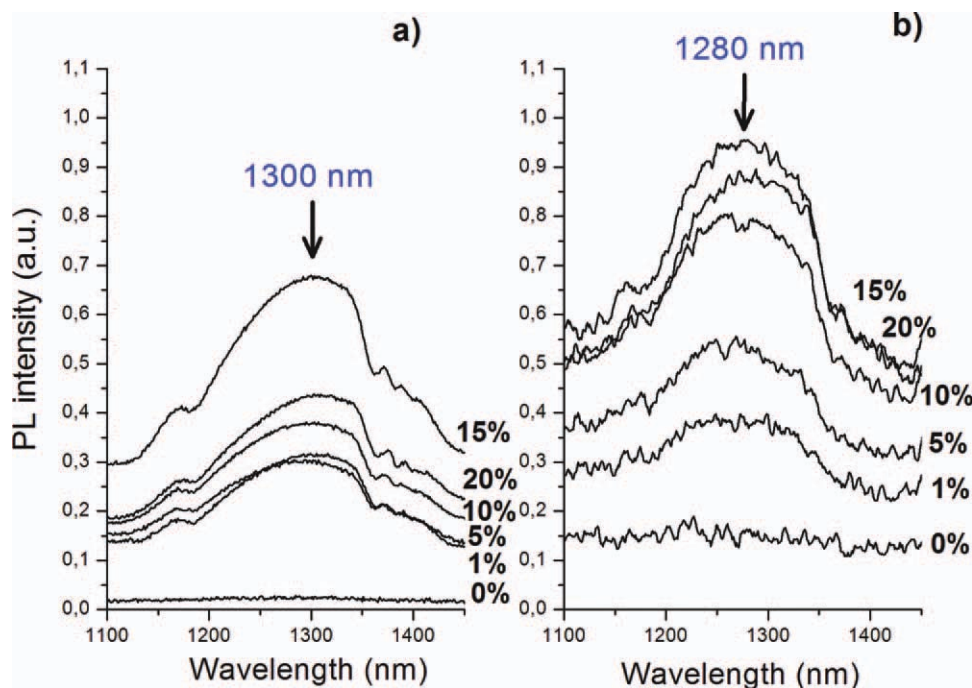


Figure 2 PL spectra of ENR polymer doped with Bismuth ions measured at room temperature and using pumping wavelength: (a) $\lambda_{\text{ex}} = 980$ nm and (b) $\lambda_{\text{ex}} = 808$ nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

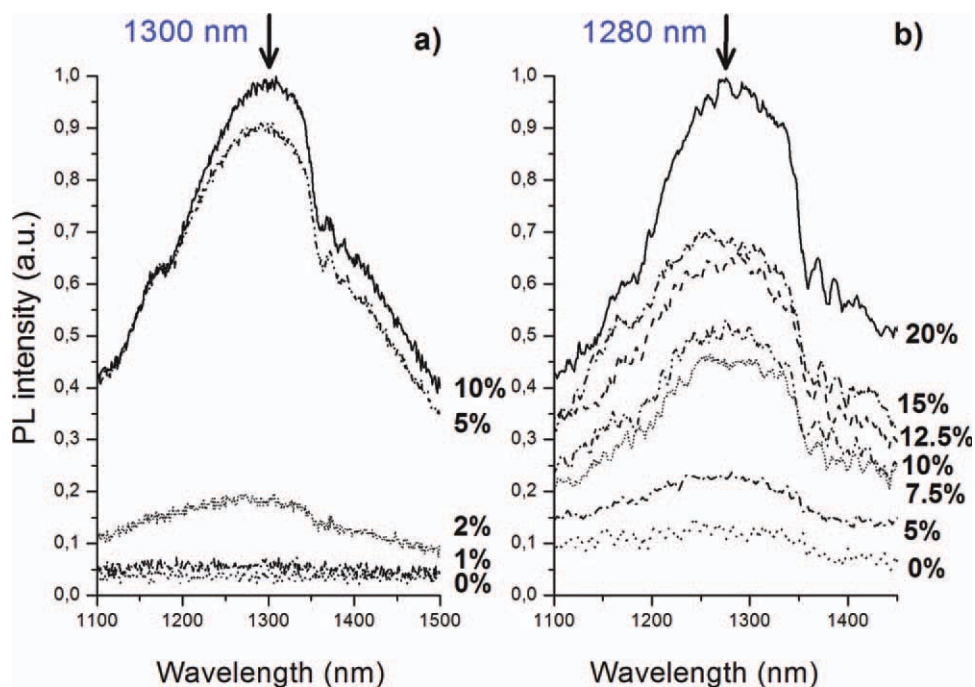


Figure 3 PL spectra of Bi (1.0 at %) doped-ENR co-doped with Ce³⁺ at room temperature and using pumping wavelength: (a) $\lambda_{ex} = 980$ nm and (b) $\lambda_{ex} = 808$ nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We also measured transmission spectra of the Cerium and Yttrium co-doped samples, but as expected, we did not see any bands as these ions do not have any transition between 700 and 1600 nm [see Fig. 1(b)].

Photoluminescence

Semiconductor laser POL 4300 with excitation (pumping wavelength) at $\lambda_{ex} = 980$ nm (250 mW) and laser LD 808 with excitation (pumping

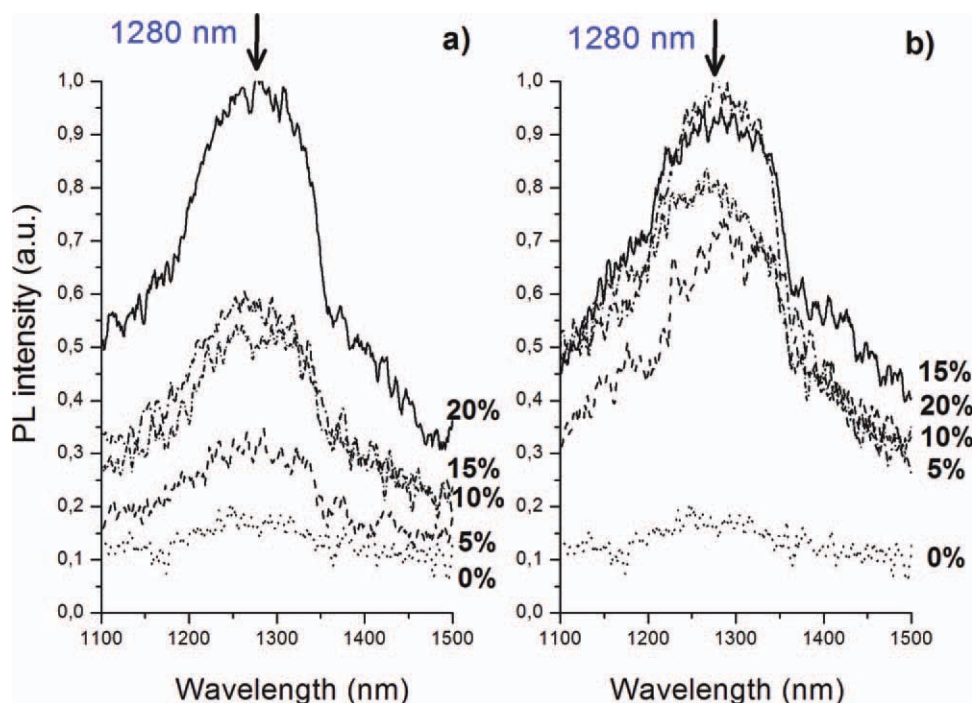


Figure 4 PL spectra (pumping wavelength— $\lambda_{ex} = 808$ nm, room temperature) of ENR polymer doped with 1.0 at % Bismuth ions co-doped with (a) Dy³⁺ and (b) Y ions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

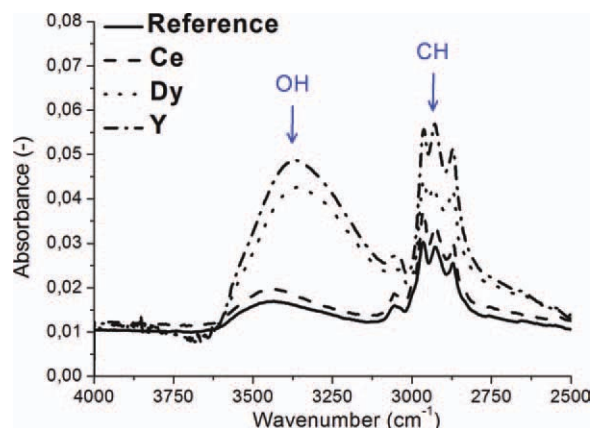


Figure 5 Infrared spectra of the Ce, Dy, and Y-doped (20.0 at %) ENR samples compared with the reference (undoped ENR) sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wavelength) at $\lambda_{\text{ex}} = 808$ nm (250 mW) was used to measure PL spectra in the range from 1200 to 1500 nm. Figure 2 gives PL spectra of ENR layers doped with different amount of Bismuth. Figure 2(a) shows PL spectra obtained at 980 nm excitation, and Figure 2(b) shows PL spectra obtained at 808 nm excitation.

The PL around 1300 nm is undoubtedly caused by the Bi^{3+} ions, and the maximum intensity was observed with the samples containing 15.0 at % Bi^{3+} . However, there is a sudden drop of the luminescence band in the sample containing 20.0 at % Bi, and this was found for both excitation wavelengths. It seems to be a consequence of the so-called “concentration quenching effect,” which is a well-known phenomenon of the rare earth doped materials.^{20,21} It was found that this effect has a close connection not only with the higher concentration of the dopants but also with chemical composition and structure of the hosting material materials.^{20,21}

Figure 3 gives PL spectra of Bi (1.0 at %) doped-ENR layers and co-doped with different amount of Ce^{3+} ions. Figure 3(a) shows PL spectra obtained at excitation wavelength 980 nm while Figure 3(b) shows them at excitation at 808 nm. No concentration quenching was observed neither at 980 nm excitation neither at 808 nm excitation, which indicates that the concentration of the co-doping Cerium could be possibly even higher than 20.0% without deterioration of the PL properties of the doped ENR.

The spectra given in Figures 2 and 3 illustrate also another finding, i.e., the longer the excitation wavelengths the longer the wavelengths of the emission and vice versa.

Figure 4 shows PL spectra of the ENR layers doped with 1.0 at % Bismuth ions and co-doped with Dy^{3+} ions [Fig. 4(a)] and Y ions [Fig. 4(b)]. The PL spectra were measured at 808 nm excitation at room temperature. Figure 4(a) shows that the PL

intensity increased with increasing concentration of the co-dopant and maximum intensity of the luminescence was obtained with the sample containing the highest used concentration (20.0%) of the Dy^{3+} ions.

The intensity of the PL for the layers co-doped with Y ions increased with the increasing concentration of the Y ions but in the samples containing 20.0 at % Y ions the PL intensity decreased to the value similar to that of the samples doped with 15.0 at % Y [see Fig. 4(b)]. Obviously, the concentration-quenching effect here appeared again. Why it appears with some of the dopant and does not do with others we are not able to understand now, but we are going to pay to that feature special attention in future, as it appears to be a key-factor for obtaining the optimal performance of the photonics device.

Infrared spectroscopy

One of the frequently occurred impurities in the photonics materials, that can cause some troubles, is presence of OH groups coming from the omnipresent traces of water. Especially, when one of the precursors is hygroscopic, as in our case the rare-earth chlorides, the presence of water may be a serious obstacle in obtaining a good function of the actual realized device. To assess a measure of that nasty problem the IR spectroscopy is a suitable tool, as the fundamental stretching vibrations of water $\nu(\text{OH})$ occur in the region around 3500 cm^{-1} , i.e., they are easily accessible in the mid-IR region of the spectra.

Figure 5 shows the infrared spectra of the Ce, Dy, or Y co-doped ENR samples containing 1.0 at % of Bismuth ions in the range where the undesired OH absorptions may appear. Apparently, there are weak broad absorption bands belonging to the symmetric

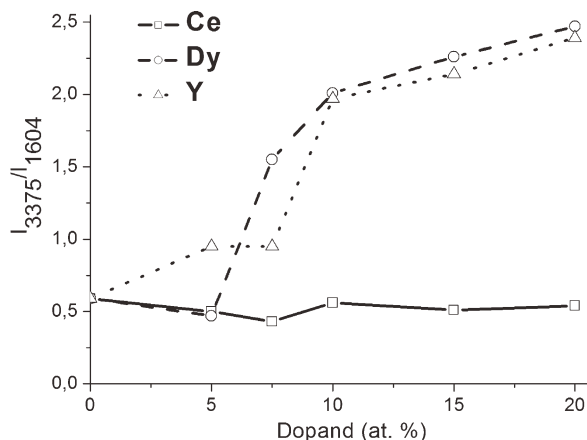


Figure 6 Intensity of the stretching O-H absorption bands (represented as ratio of the intensity of the 3375 cm^{-1} band to intensity of the band at 1604 cm^{-1}) vs. concentration of the Ce, Dy, or Y dopants.

and antisymmetric stretching O-H bands $\nu(\text{OH})$. Character of the bands indicates that they come from the slight moisture of the samples that could be adsorbed during the measurement rather than from the OH groups incorporated in the network structure. From Figure 6 showing the dependence of the intensity of the OH absorption bands (normalized to the intensity of the bands occurring at 1604 cm^{-1} , intensity of which were the same in the all measured samples) on the concentration of the dopants it follows that (with exception of Y) the higher concentration of the dopant the higher intensity of the $\nu(\text{OH})$. It appears to point to the fact that the moisture comes from the chlorides of the doping elements, which are strongly hygroscopic. Similar effect has been already mentioned also in our previous article.¹³ In any case, the intensities of the OH absorption bands are so low, that they do not bring about any serious problem for practical applications of these materials.

CONCLUSION

Fabrication and properties of the ENR polymer doped with Bismuth ions and co-doped with Ce^{3+} , Dy^{3+} , and Y^{3+} ions were demonstrated. We measured transmission spectra of the samples and found that higher content of Bismuth ions makes the transmission edge shifted to the higher wavelengths. We also found five bands that correspond to Dy^{3+} ions at the samples containing 20.0 at % of Dy ions while other co-doping ions did not reveal any transitions in the characterized spectral region.

PL spectra in the range from 1200 to 1500 nm with excitation at $\lambda_{\text{ex}} = 808\text{ nm}$ and $\lambda_{\text{ex}} = 980\text{ nm}$ showed the maximum PL intensity with the sample containing 15.0 at % of Bismuth indicating thus possibility of concentration quenching effect. Co-doping with Ce^{3+} , Dy^{3+} , and Y^{3+} ions increased intensity of the PL, and we found its maximal value with the samples containing 20.0 at % of the co-doping Ce and Dy ions. Concentration quenching effect appeared in the case of the samples co-doped with Y ions (20.0 at %), where the maximum of the PL intensity was found at the concentration of 15.0 at %

of Y. The small amount of moistening water does not mean any serious problem for practical use.

The results of our research proved that the Bismuthdoped polymer can be viable material to make a new photonics device usable in 1300 nm region and that co-doping with transition metal ions may improve intensity of the thought emission.

References

1. Miniscalco, W. J.; Andrews, L. J.; Thompson, B. A.; Quimby, R. S.; Vacha, L. J. B.; Drexhage, M. G. *Electron Lett* 1988, 24, 28.
2. Brierley, M. C.; Millar, C. A. *Electron Lett* 1998, 24, 438.
3. Ohishi, Y.; Kanamori, T.; Kitagawa, T.; Takahashi, S.; Snitzer, E.; Sigel, G. H. *Opt Lett* 1991, 16, 1747.
4. Man, S. Q.; Pun, E. Y. B.; Chung, P. S. *Opt Commun* 1999, 168, 369.
5. Fujimoto, Y.; Nakatsuka, M. *Jpn J Appl Phys Part 2-Lett* 2001, 40, L279.
6. Qian, Q.; Zhang, Q. Y.; Yang, G. F.; Yang, Z. M.; Jiang, Z. H. *J Appl Phys* 2008, 104, 043518.
7. Seo, Y. S.; Fujimoto, Y.; Nakatsuka, M. *IEEE Photon Tech Lett* 2006, 18, 1901.
8. Sokolov, V. O.; Plotnichenko, V. G.; Dianov, E. M. *Opt Lett* 2008, 33, 1488.
9. Peng, M. Y.; Wang, C.; Chen, D. P.; Qiu, J. R.; Jiang, X. W.; Zhu, C. S. *J Non-Cryst Solids* 2005, 351, 2388.
10. Zhou, S. F.; Feng, G. F.; Bao, J. X.; Yang, C.; Qiu, J. R. *J Matter Res* 2007, 22, 1435.
11. Qiu, J. R.; Peng, M. Y.; Ren, J. J.; Meng, X. G.; Jiang, X. W.; Zhu, C. S. *J Non-Cryst Solids* 2008, 354, 1235.
12. Dianov, E. M.; Melkumov, M. A.; Shubin, A. V.; Firstov, S. V.; Khopin, V. F.; Guryanov, A. N.; Befetov, I. A. *Quantum Electron* 2009, 39, 1099.
13. Prajzler, V.; Lyutakov, O.; Huttel, I.; Spirkova, J.; Oswald, J.; Machovic, V.; Jerabek, V. *J Appl Polym Sci* 2010, 17, 1608.
14. Ruan, J.; Wu, E.; Zeng, H. P.; Zhou, S. F.; Lakshminarayana, G.; Qiu, J. R. *Appl Phys Lett* 2008, 92, 101121.
15. Yang, G.; Chen, D. P.; Ren, J.; Xu, Y. S.; Zeng, H. D.; Yang, Y. X.; Chen, G. R. *J Am Ceram Soc* 2007, 90, 3670.
16. Ruan, J.; Dong, G. P.; Liu, X. F.; Zhang, Q.; Chen, D. P.; Qiu, J. R. *Opt Lett* 2009, 34, 2486.
17. Wu, B. T.; Ruan, J.; Qiu, J. R.; Zeng, H. *J Phys D: Appl Phys* 2009, 42, 135110.
18. Beche, B.; Pelletier, N.; Gaviot, E.; Zyss, J. *Opt Commun* 2005, 230, 91.
19. Tung, K. K.; Wong, W. H.; Pun, E. Y. B. *Appl Phys A: Mater Sci Proc* 2005, 80, 621.
20. A. Polman, A. *J Appl Phys* 1997, 82, 1.
21. Kenyon, A. J. *Progr Quantum Electron* 2002, 26, 225.
22. Digonnet, J. F. M. *Rare-Earth-Doped Fiber Lasers and Amplifiers*; Marcel Dekker Inc.: Stanford, California, 1993, p 473.