

Properties of Epoxy Novolak Resin Layers Doped with Bismuth for Photoluminescence Near 1300 nm

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ABSTRACT: In this article, we report on the optical properties of bismuth ions doped epoxy novolak resin (ENR). The polymer layers containing 1–20 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. Absorption spectra were taken in the range from 350 to 800 nm. Optical band gap E_g was determined from the absorption coefficient values using Tauc's procedure, i.e., from the relationship $\alpha h\nu = A(h\nu - E_g)^2$ and the obtained values varied from 2.94 to 3.23 eV depending on the amount of bismuth ions involved in the samples. Photoluminescence spectra around 1300 nm were recorded

by using excitation of semiconductor lasers operating at 808 nm ($E_x = 500$ mW). Optical properties of bismuth-doped ENR were evaluated on the bases of the concentration of the bismuth ions involved in the samples and showed, e.g., close relations between concentration of the dopants and intensity of the luminescence band at 1300 nm. IR spectra showed only negligible changes in the original substrate resin. Our results proved that the bismuth-doped ENR have a potential for utilization in photonic devices. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1608–1612, 2010

Key words: optical materials and properties; polymers; epoxy novolak resin; bismuth

INTRODUCTION

Almost all optical communication systems throughout the world use silica-based optical fibers and operate in two bands: at 1550 nm and 1300 nm. To obtain active photonics function in that spectral region, the materials used for construction of the pertinent devices must be doped with suitable lasing ions. For the 1550 nm region, which is so called third telecommunications window (due to minimal optical losses in silica fibers^{1–3}), the erbium ions have been the mostly used and well-established dopant that is currently a matter of interest for application as optical amplifiers and optical sources.

However, the 1300 nm region is even more interesting than the former, mainly because there the dispersion of silica is minimum and hence many fiber communications systems are being optimized for this wavelength. This fact gave rise to research for

suitable lasing dopants as well as for suitable hosting materials well compatible with the already existing communication systems. There have been three main approaches to meet these systems: the neodymium (Nd^{3+}) doped amplifier, the praseodymium (Pr^{3+}) doped amplifier, and the Raman amplifier.^{4–8} However, all of them have appeared to be rather complicated and costly.

Recently, a new dopant came into the focus of the researches in the field of active photonics devices operating at 1300 nm: bismuth ions. The first demonstration of amplification phenomenon at 1300 nm in bismuth photonics materials was reported in Ref. 9 in bismuth-doped silica glass. Except bismuth luminescence in silica glass,^{10–14} it was also reported on optical properties of Bi-doped germanium oxide glasses,^{15,16} Bi-doped borosilicate glasses,¹⁷ Bi-doped aluminosilicate glasses,¹⁸ etc.^{19–22}

In our research, we combined two main principles—the sought luminescence of bismuth ions and not yet widely used though promising polymer as the hosting material. The idea to dope polymer matrix with bismuth ion has been already presented for using as the passive waveguides in Ref. 23. In this article, epoxy novolak resin (ENR) polymer was chosen for its excellent properties (optical losses 2 dB cm^{-1} at 980 nm, 0.77 dB cm^{-1} at 1310 nm, and 1.71 dB cm^{-1} at

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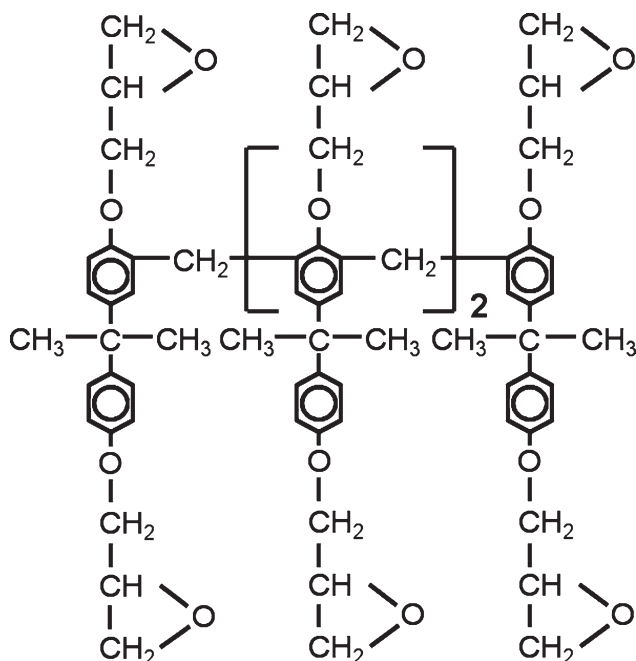


Figure 1 Structure of the epoxy novolak resin polymer.

1500 nm)^{24,25} and feasible fabrication process. Results of the research with special regards to photoluminescence properties important for potential using the formulated material as optical amplifier will be presented for the first time.

EXPERIMENTAL

Preparation of the samples

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 mold placed on a quartz substrate and let to dry in air. Chemical structure of ENR polymer is shown in Figure 1.

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. Bismuth chloride (BiCl₃) was dissolved in 1-methyl-2-pyrrolidinone (C₅H₉NO) or dimethyl sulfoxide (C₂H₆OS) (Sigma-Aldrich), so that the concentration of bismuth in the solutions ranged from 1 to 20 at. %. For the doping, the solutions were added to the polymer prior to the deposition of the samples.

Measurement

After the deposition, the samples were characterized by several methods. Absorption measurements in the spectral range from 350 to 800 nm were performed using a Varian Cary 50 spectrometer (Varian) and the optical band gap was determined from the

analysis of the spectral dependence of the absorption near the absorption edge shown in Figure 2. Semiconductor laser POL 2100 excitation at $\lambda_{\text{ex}} = 808$ nm ($E_{\text{ex}} = 150$ mW, room temperature) was used to measure photoluminescence spectra (PL) in the range from 1200 to 1400 nm. The fabricated samples were characterized by Fourier transform infrared (FTIR) spectroscopy using the 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).

RESULTS AND DISCUSSION

Absorbance spectra

The absorption spectra of the bismuth-doped samples are shown in Figure 2. The figure shows that with the increasing level of the doping, the absorption edge shifts to the higher wavelengths. Absorption spectra were measured to determine optical band gap of ENR samples doped with bismuth ions.

Optical band gap

The absorption coefficient α is well described by the equation²⁶

$$\alpha(\nu) = A(h\nu - E_g^{\text{opt}})^r/h\nu$$

where $h\nu$ is the energy of incident photons, E_g^{opt} is the value optical band gap between the valence band and the conduction band, x is parameter that gives the type of electron transition. Specifically, r is $\frac{1}{2}$, $\frac{3}{2}$, 2, and 3 for transitions direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively. The factor A depends on transition probability and can be assumed to be constant

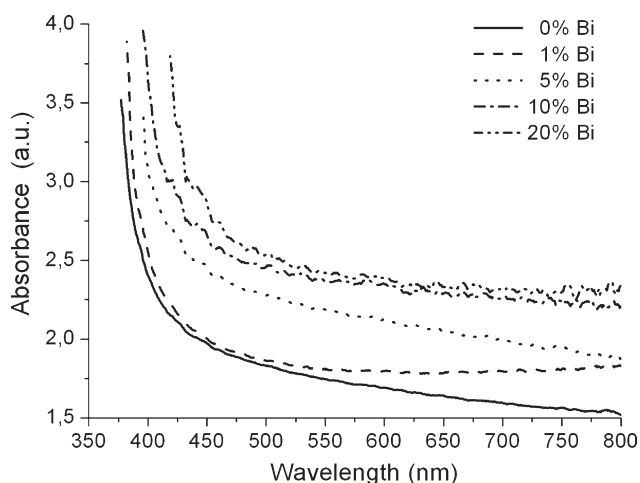


Figure 2 Absorbance spectra of ENR samples doped with bismuth ions.

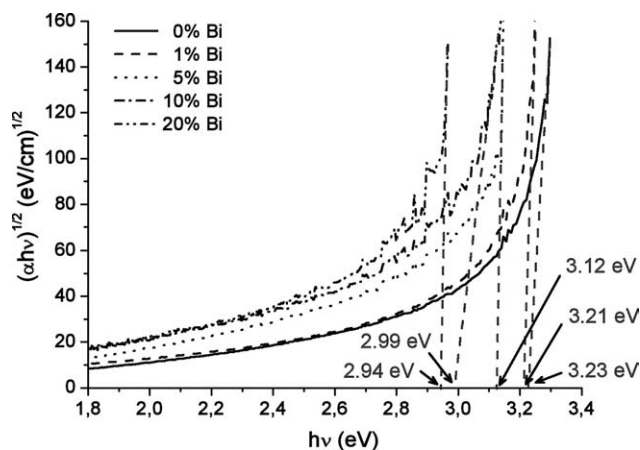


Figure 3 Optical band gap of ENR samples doped with bismuth ions.

within the optical frequency range. The usual method for the determination of the value of E_g^{opt} involves plotting $(\alpha hv)^{1/r}$ against hv .²⁷ Figure 3 shows plots of $(\alpha hv)^{1/2}$ versus hv near the absorption edge of ENR with different contents of bismuth ions. Figure 3 shows that increasing content of bismuth

ions caused decreasing hv . The value of the optical band gap was highest in the undoped sample (3.23 eV), while the lowest value was found with the sample having the highest used concentration of bismuth (2.94 eV for 20 at. % of Bi).

Similar effect, which is closely associated with the hosting matrix, has been already described and explained in Ref. 27 for poly(methyl methacrylate) doped with metal chlorides.

Photoluminescence

Figure 4 gives photoluminescence spectra of ENR layers doped with four different amount of bismuth (1 at. %, 5 at. %, 10 at. %, and 20 at. %).

The photoluminescence around 1330 nm is undoubtedly caused by the Bi(III) transition (it did not appeared in the virgin novolak sample), and its intensity increased with the increasing concentration of the dopant from 1 to 10 at. %. The wavelengths of the PL maxima shifted with the concentration of the dopant from 1334 nm (1 at. %) to 1327 nm (5 and more at. %). However, there is a sudden fade away of the luminescence band in the sample containing

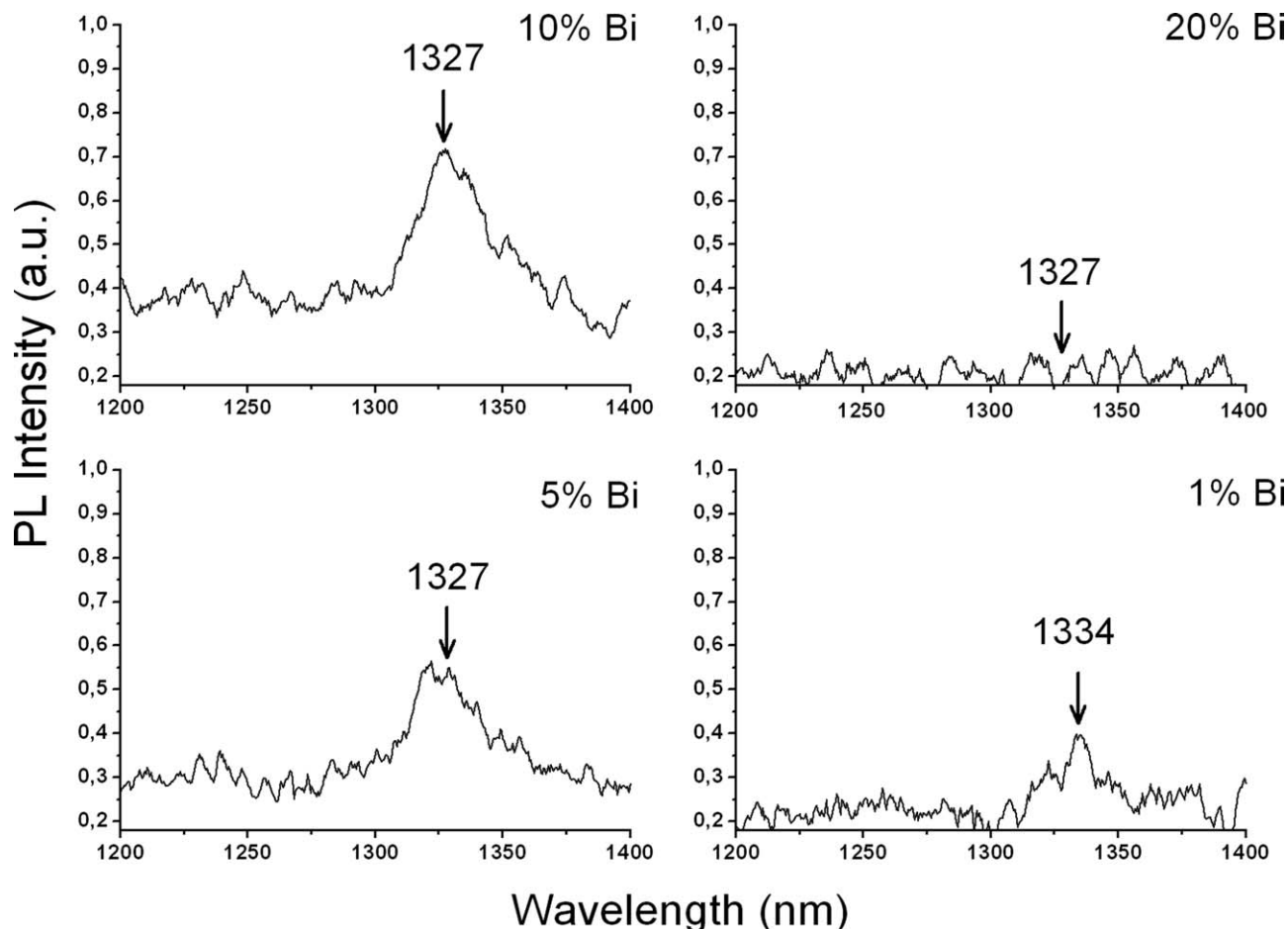


Figure 4 Photoluminescence spectra of ENR polymer doped with bismuth ions ($\lambda_{\text{ex}} = 808$ nm, under room temperature).

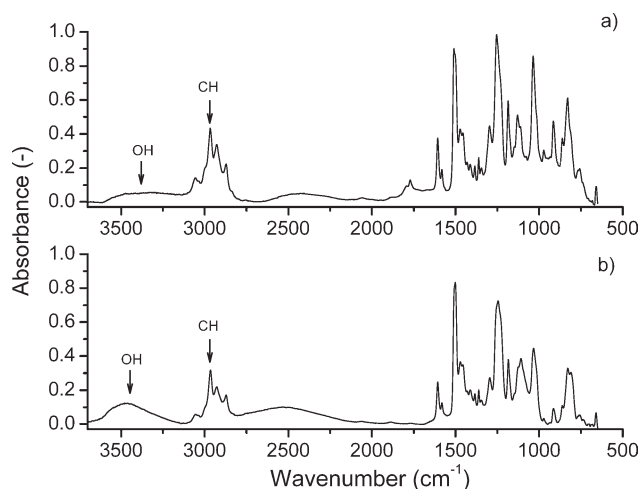


Figure 5 Infrared spectra of the ENR samples: (a) undoped sample and (b) the sample doped with 20 at. % of Bi^{3+} .

20 at. % of the bismuth ions. As we are sure that it was not caused by any experimental error that feature can be attributed to the so called “concentration quenching effect,” which is a well-known phenomenon, e.g., for the Er^{3+} doped materials (see, e.g., Refs. 1 and 28). 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. This very interesting result will be further followed in details.

The increasing concentration of bismuth had positive influence also on the full width at half maximum (FWHM), which can be considered as one of the figures of merit for the utility of the optical active materials. Although the FWHM is rather small (about 10 nm) in the samples containing less than 1 at. % of bismuth, in the samples containing 10 at. % of the bismuth the FWHM reaches up to 30 nm.

Infrared spectroscopy

In Figure 5(a,b), there are displayed the IR spectra in the range 500 cm^{-1} to 3800 cm^{-1} for the virgin [Fig. 5(a)] and one of the bismuth-doped [Fig. 5(b)] samples. Evidently, there are only negligible differences in the spectra before and after the doping. The virgin resin already revealed weak broad absorption of the OH groups (stretching O—H) in the region around 3360 cm^{-1} , which got more pronounced in the doped samples, but their intensities and shapes indicated only some humidity rather than absorbed water or created OH-bonds due to the Bi-doping. The calculated integral intensities of the O—H stretching bands in the Bi-doped samples did not revealed any obvious dependencies with the concentration of the bismuth dopants, so that we may assume that the increase of the O—H absorption is an essential event closely connected with an acciden-

tal event and not the effect closely connected with the presence of the dopant. However, as there is no coincidence of the wavelength of the absorption of the OH groups and any pumping wavelength needed for the Bi^{3+} luminescence at 1300 nm, so the problem with the eventual presence of the OH groups seems to be marginal.

There are slight changes in the region of the C—H stretching vibration ($2800\text{--}3100\text{ cm}^{-1}$), but again, as the pertinent absorption band do not collide with the pumping wavelength. We do not expect any serious impact on the potential function of the Bi^{3+} doped photonic device.

The disappearance of the 1750 cm^{-1} bands attributed to the coband may be explained this way: as C—O often acts as an electron donor (Lewis base) and Bi^{3+} as the acceptor of electrons (Lewis acid), it might happen that there will be a bonding interaction resulting in the heavier Bi—O(C) units that will shift the pertinent band forward the lower wavenumbers in the IR spectra. What concerning directly the Bi^{3+} vibrations in the IR spectra—the only expected vibrations can be the Bi—O ones, but they would occur in the farer IR region and could not be detected this way. On the other side, the Bi^{3+} emission bands showed very close relations with their concentration in the samples, so that it gives a good reason to interpret the obtained results as that the novolak resin acts as a matrix and the same time the carrier of the incorporated ions of the dopants. As only minor changes occurred in the matrix of the resin, it makes it a good material for potential utilization in the construction of a cheap and well functioning active photonic device.

CONCLUSION

Fabrication and properties of the ENR polymer doped with bismuth ions were demonstrated. Higher content of the bismuth ions makes the absorption edge shifted to the higher wavelengths.

Optical band gap E_g was determined from the absorption coefficient values using Tauc's procedure and the value of the optical band gap was highest in the undoped sample (3.23 eV), while the lowest value was found with the sample having the highest used concentration of bismuth (2.94 eV for 20 at. % of Bi).

The emission around 1300 nm with 30 nm of FWHM was observed in the doped polymer films under 808 nm laser excitation and revealed a close connection with the concentration of the dopant. The maximum PL intensity was found with the sample containing 10 at. % bismuth showing thus possibility of concentration quenching effect. This phenomenon will be further investigated. IR spectra showed that the doping has only marginal effect on the structure of the virgin substrate and that all the possible

absorptions occurred out of the pumping as well as emission wavelengths.

The results of our research proved that the doping bismuth ions in widely used polymer is a viable material to make a new photonic device usable in 1300 nm region.

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