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Photosensitivity in Ce^{3+}-doped optical fibers

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A UV-induced absorption change has been studied in Ce^{3+}-doped preforms and fibers made by a solution-doping modified-chemical-vapor-deposition technique. A reduction in the Ce^{3+} concentration and the creation of a broad absorption band extending from the UV to the IR were seen on UV exposure. In addition, a peak in the absorption band is created at 245 nm, attributed to Ce^{4+}. The reduction in Ce^{3+} concentration was observed to remain for at least 3 months, whereas the created broad absorption bands at 632.8 nm recovered by 90% in 2 h. Large UV-induced refractive-index changes (10^{-4}) in Ce^{3+}-doped fibers are also demonstrated. A linear dependence on the average UV intensity is found below 4 kW/m², above which saturation occurs. The index change also increases with increasing Ce^{3+} concentration, again saturating at high levels. A decrease in magnitude with increasing wavelength is observed, but the index change at 1.55 μm is still more than 50% of that at 0.5 μm, demonstrating the potential of the technique for producing gratings with optical communication applications.

The photosensitive response of optical fibers has been the focus of many researchers, primarily because of its potential in the manufacture of efficient gratings within fibers. In certain fiber cores, the axial index may be periodically perturbed by exposure to an interference pattern from a suitable laser,[1,2] and the resultant gratings have many applications, including single-mode fiber lasers, wavelength-dispersion-multiplexing telecommunications, and fiber sensors. The gratings have many advantages over their conventional bulk counterparts, being compact and easy to align, with low insertion losses.

Photoinduced index changes are well known in germanosilicate fibers on exposure to both blue (480 nm) and UV (240 nm) light.[3-5] Although the exact cause of the change is still debated, it is generally believed to be associated with germanium ions. To increase the photosensitivity, more germanium should be incorporated into the fiber core, but this, of course, alters the fiber index profile. The aim of our research is to find an improved fiber for efficient fiber gratings, in which the photosensitive core dopant may be changed without altering the guiding properties of the fiber. It is known that other glasses, including a cerium-doped sodium silicate glass,[6] suffer large absorption changes on exposure to certain wavelengths; hence index changes might be expected. The absorption changes induced in fiber cores composed of SiO_2, P_2O_5, Al_2O_3, and Ce_2O_3 on exposure to pulsed UV light at 266 and 355 nm was therefore investigated, and an index change of 1.4×10^{-4} was recorded at 1.064 μm, with the potential of further improvements with increased doping level. The conventional modified-chemical-vapor-deposition method combined with the solution-doping technique developed by Townsend *et al.*[7] was used to fabricate the fibers.

Cerium ions can exist in two ionic valency states in a glass matrix, cerous (Ce^{3+}) and ceric (Ce^{4+}). The equilibrium between the two states depends on the basicity of the glass matrix and the glass preparation condition. A photoinduced absorption change in cerium-doped glasses has been attributed to Ce^{3+} ions in the glass,[8] which are photoionized to form Ce^{4+} ions on UV exposure. P_2O_5 and Al_2O_3 were therefore used as codopants to favor the formation of the Ce^{3+} instead of the Ce^{4+} state.[9] A SiO_2/P_2O_5 layer deposited at a relatively low temperature (~1300°C) on the inside of a silica tube was solution doped with $AlCl_3 \cdot 6H_2O$ and $CeCl_3 \cdot 7H_2O$, with water as a solvent. Four fiber preforms were made in this way, with similar $AlCl_3 \cdot 6H_2O$ concentrations but different $CeCl_3 \cdot 7H_2O$ concentrations to vary the Ce^{3+}-doping level: one had no $CeCl_3 \cdot 7H_2O$ to clarify the effect of alumina. The soaking time in each case was 1 h, and the preforms were subsequently dried by heating to 600°C for 1 h. Nitrogen instead of the usual oxygen was used in the following collapse process to encourage the formation of Ce^{3+} ions further.

The parameters of the resultant preforms are listed in Table 1. The P_2O_5 concentration was estimated by using the data given by Hammond and Norman.[10] Absorption spectra are shown in Fig. 1; they were measured with a Perkin-Elmer recording spectrophotometer of the type EPS-ST. Polished thin slices of preform (180 to 480 μm thick) were used because of the high UV loss. A small aperture ensured that light could pass only through the preform core region, and to improve sensitivity we focused the collimated beam of the spectrophotometer to a size slightly larger than the aperture. Insertion losses were corrected by comparisons with data measured at 600 nm in a fiber drawn from the same preform by a cutback technique. The error in these measurements is less than ±1 dB/mm.

The Ce^{3+} ion has a $4f$–$5d$ electric dipole transition with a corresponding absorption peak, the position of which is highly dependent on the glass composition. In similar glasses, it has been centered in the 276–306-nm region.[9,11] The Ce^{4+} ion, meanwhile, has a charge transfer band, which should appear as a peak at a slightly shorter wavelength. Only one peak in the absorption spectra is observed, however, as shown in Fig. 1, and this is confirmed to be due to Ce^{3+} ions by the observation of strong fluorescence centered around 420 nm, a Ce^{3+} characteristic. In

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Table 1. Fiber Characteristics

Preform Number	N.A.	Ce^{3+} Concentration (ppm)	P$_2$O$_5$ Concentration (mol. %)	Al$_2$O$_3$ · 6H$_2$O Concentration in Solution (M)
1	0.13	11700	12	3.62
2	0.19	5800	23	2.49
3	0.18	1900	22	2.49
4	0.17	0	21	3.77

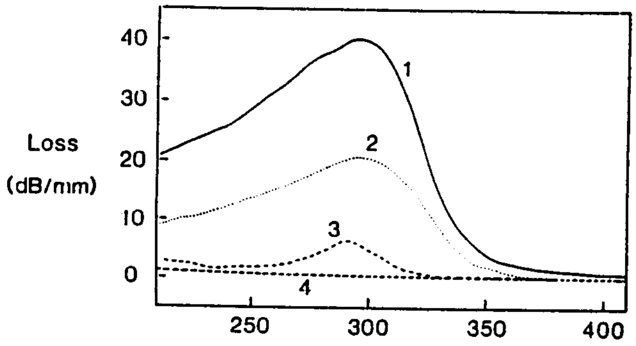

Fig. 1. Absorption spectra of cerium-doped preforms. Curves 1, 2, 3, and 4 are the spectral loss of preforms 1, 2, 3, and 4, respectively.

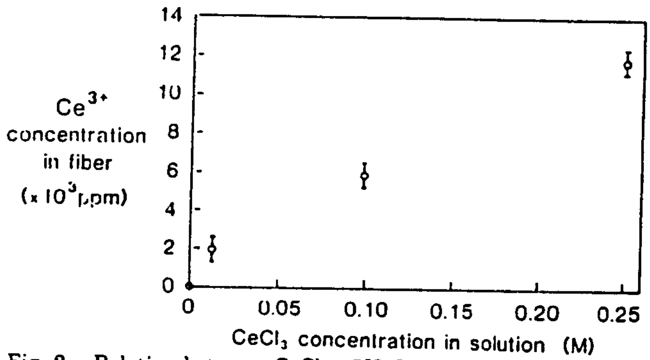

Fig. 2. Relation between CeCl$_3$ · 7H$_2$O solution concentrations and Ce^{3+}-doping level in the preforms.

the absence of any significant additional Ce^{4+} peak, it is assumed that most of the cerium ions must be in the Ce^{3+} state. The concentration is determined by comparison with Ce^{3+} absorption data given by Laczka and Stoch[11] for a glass composed of SiO$_2$ + 0.05Al$_2$O$_3$, giving 11,700, 5800, and 1900 parts in 10^6 (ppm) for preforms 1, 2, and 3, respectively (±300 ppm in each case is due to loss measurement error). The additional rising loss trend at short wavelengths in preforms 3 and 4 is attributed to the UV edge of the glass, which is not visible in heavily doped preforms 1 and 2, because of the dominant Ce^{3+} peak. The relationship between this dopant level and the CeCl$_3$ · 7H$_2$O solution concentrations is shown in Fig. 2. This level is found to have only a slight sign of saturation at high concentrations, indicating the possibility of producing preforms with a higher Ce^{3+} dopant level. Fibers drawn from all preforms have a relatively low loss of ~150 dB/km at the important communication wavelength of 1.55 μm.

Changes in the absorption spectrum of preform 2 on exposure to pulsed 266-nm radiation from a frequency-quadrupled YAG laser (pulse width 8–9 ns, 30-Hz repetition rate, and average intensity of 4 kW/m^2) for 1 min are shown in Fig. 3. Curve 1 is the original loss spectrum, and curves 2, 3, and 4 were measured 10 min, 109 h, and 82.2 days, respectively, after exposure. It can be seen from curve 2 that the Ce^{3+} absorption peak at 290 nm has been greatly reduced on UV exposure, indicating a reduction of Ce^{3+} concentration. A broad absorption band extending over both sides of the Ce^{3+} peak has appeared, which may be attributed to photoelectrons trapped at various defect centers. The induced broad band shows signs of recovering in curve 3, with total recovery by curve 4. The reduction in the Ce^{3+} absorption peak remains, however, even after 82 days (curve 4), and the anticipated Ce^{4+} absorption band resulting from Ce^{3+} ions losing electrons can also be seen near 245 nm.

The recovery process of the broadband loss was further investigated at 632.8 nm in fiber drawn from the preform, with a single-mode cutoff of 590 nm and an intrinsic loss of 200 dB/km at 632.8 nm. The fiber was laterally exposed to 266-nm light with an average intensity of 4 kW/m^2, while it was probed with 632.8-nm light propagating through the fiber. On exposure, the fiber loss increased almost immediately to a high level and stabilized at that level, provided the UV intensity remained constant. The loss varied linearly with UV intensity, indicating a single photon process (Fig. 4). The loss mentioned here is the actual material loss calculated by taking into account the fact that only a fraction of the light propagates in the fiber core. When the UV was blocked, a reversal of the loss was observed, as shown in Fig. 5. After 7 h, the loss had dropped to 8.3% of its original value. Also shown in the figure is a good fit to the data, consisting of the summation of three exponential decays, $\Sigma_{i=1}^{3} A_i \exp(-\alpha_i t)$, where $A_1 = 0.586$, $A_2 = 0.0955$, $A_3 = 0.129$, $\alpha_1 = 0.0291$, $\alpha_2 = 0.00210$, and $\alpha_3 = 0.0000213$. Three different processes are therefore involved, with time constants of 34 s,

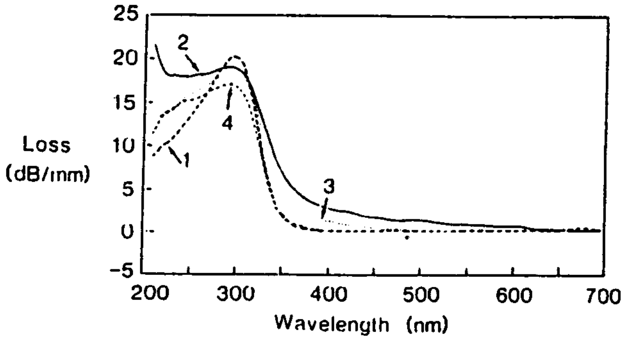

Fig. 3. Absorption spectra of preform 2 before and after exposure to UV light of 4 kW/m^2 for 1 min. Curve 1 is the original loss, and curves 2, 3, and 4 are the spectral loss changes approximately 10 min, 109 h, and 82.2 days, respectively, after UV exposure.

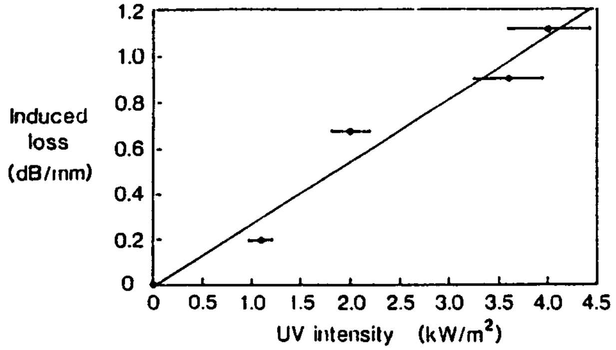

Fig. 4. UV intensity dependence of the induced loss at 632.8 nm in a fiber containing 5800 ppm Ce^{3+} ions.

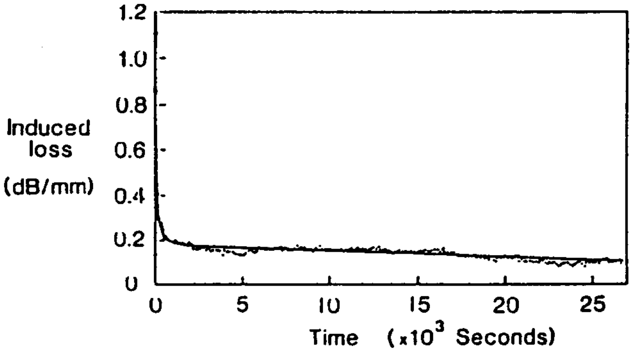

Fig. 5. Fiber loss recovery process at 632.8 nm after exposure to UV light of 4 kW/m².

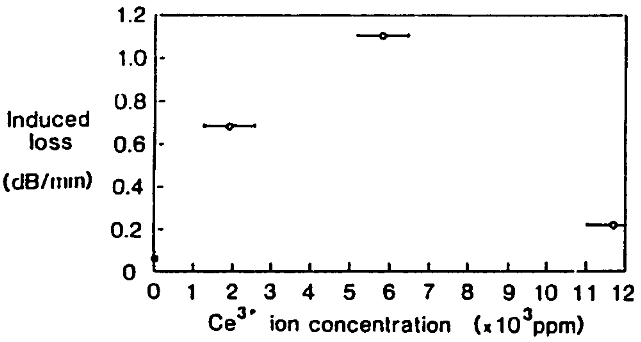

Fig. 6. Induced fiber loss at 632.8 nm during UV exposure of 4 kW/m² versus Ce^{3+} concentration.

8 min, and 13 h, respectively, indicating that different types of defect center are formed. The induced losses measured during UV exposure of 4 kW/m² in fibers drawn from the other three preforms are plotted for comparison in Fig. 6. As expected, no induced loss was observed in the fiber doped only with alumina, indicating that the mechanism is Ce related. There is, however, a significant reduction in loss at high concentrations. The reason is speculated to be that at a high concentration the Ce^{3+} ions start to cluster, which may lead to a reduction of Ce^{3+} concentration in the unclustered region, causing a decrease of the induced defect centers associated with the loss increase. The induced loss measured 4 h after exposure of 4 kW/m² at the important fiber communications window, 1.55 μm, was found to be only 3.1 dB/m, negligible for typical fiber grating lengths (1 cm long).

Fibers were also exposed to pulsed 355-nm light from a frequency-tripled YAG laser. Similar changes in absorption were noted, but 19 times the average intensity was required for the changes to be of identical magnitude. This is not surprising, given that the Ce^{3+} absorption strength at this wavelength is only one 1/15 of that at 266 nm.

In order to produce a reliable and repeatable technique for measuring refractive index change, we fabricated four dual-core fiber preforms, each containing one phosphosilicate core and a core from each of the four preforms. The dual-core preforms were numbered 1, 2, 3, and 4 and contained 11,700, 5800, 1900, and 0 ppm Ce^{3+} ions, respectively. The respective fibers drawn from them are referred to as DC1, DC2, DC3, and DC4. Three fibers with different diameters were drawn in each case to give single-mode operation over a wide range of probe wavelengths. In all fibers the cores are sufficiently spaced to preclude any significant coupling between them.

The experimental arrangement used to measure the index change is depicted in Fig. 7. A probe beam is weakly focused onto a cleaved end of the test dual-core fiber, launching equal intensities into both cores. At the far cleaved end of the fiber, the two cores act as point light sources a few micrometers apart, with the transmitted light interfering to give large fringes in the far field. The lateral position of the fringes depends on the optical path difference between light propagating in the two cores, and so a change in index in only one core will cause fringe movement. A narrow slit is placed in the fringe pattern, allowing only a small part of a fringe to be transmitted onto a photodiode and monitored on a chart recorder. A coating-stripped section of this fiber is then laterally exposed to pulsed 266-nm UV light from a frequency-quadrupled, pulsed Nd:YAG laser. Previous experiments have demonstrated that no index change occurs in the pure-phosphosilicate core, so any fringe movement that occurs on exposure must simply be the result of an index change in the cerium-doped core. The best measurement accuracy can be achieved by exposing a long length of fiber, but this accuracy is limited, particularly at shorter wavelengths, by the UV-induced loss, which has the effect of reducing fringe contrast. We therefore exposed lengths between 5 and 15 cm by scanning the beam repeatedly along the fiber until the fringe position stabilized, typically after 1 min. The fringes were found to be stable for at least 30 min after UV exposure, dissociating the index

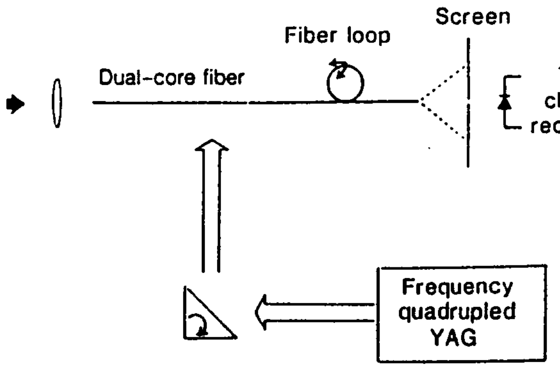

Fig. 7. Experimental setup for measuring UV-induced index change.

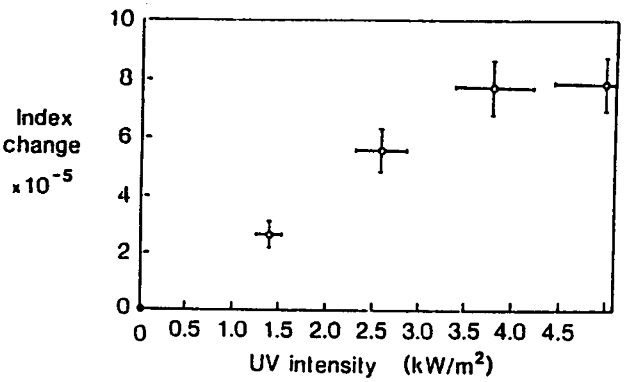

Fig. 8. UV intensity dependence of induced index change at 784 nm in a fiber doped with 5800 ppm Ce^{3+} ions.

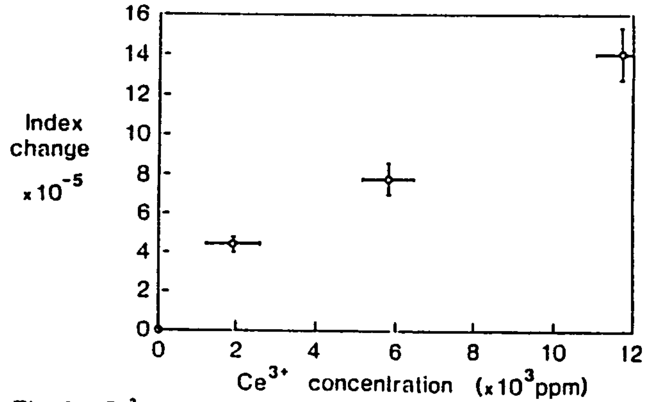

Fig. 9. Ce^{3+} concentration dependence of UV-induced index change at 1.06 μm with UV light of 4 kW/m^2.

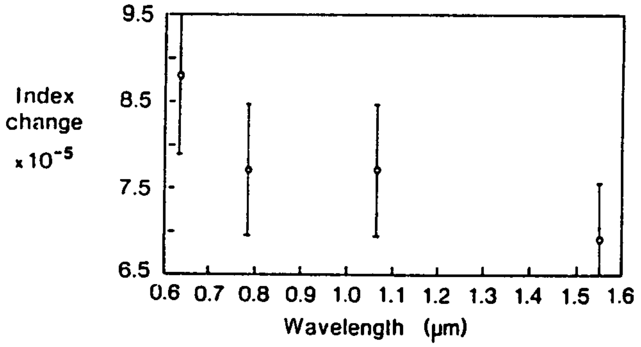

Fig. 10. Wavelength dependence of UV-induced index change with UV light of 4 kW/m^2 in a fiber doped with 5800 ppm Ce^{3+} ions.

change mechanism from the fast recovery process of the induced loss at IR wavelengths. We could then calculate the core material refractive-index change from the number of fringes shifted and the exposed fiber length by taking into account the fact that only a proportion of the optical power propagates in the fiber core.

The variation of refractive-index change in DC2 with average UV intensity was investigated at 784 nm (Fig. 8). The curve shows a nearly linear response at low average UV intensities, indicating that the index change mechanism is dependent on a single-photon process, but a saturation trend appears above 4 kW/m^2. We also measured the dependence of the induced index change on Ce^{3+} concentration at 1.064 μm, using fibers from the four different preforms. The results are shown in Fig. 9 for an average UV intensity of 4 kW/m^2. As expected, no index change was seen in DC4, in which the core is doped only with Al_2O_3, demonstrating that Ce^{3+} is necessary for the refractive-index change. Rather than being a simple linear function of Ce^{3+} concentration, however, the index change appears to be limited by another mechanism, predominant even at low concentration levels.

We investigated the wavelength dependence of the induced index change by comparing measurements in DC2 at 632.8 nm (helium–neon laser) and 1550 nm (laser diode) with those already made at 784 and 1.064 μm for the same average UV intensity of 4 kW/m^2, as shown in Fig. 10. In contrast to the low wavelength dispersion observed with germanosilicate fibers,[4,5] however, a drop in the induced index change with increasing wavelength was observed. Despite this, though, the index change at the important communication wavelength of 1.55 μm is still 6.8×10^{-5}, large enough to give a 90% efficiency reflection grating, if the index change is induced periodically over a length of 13 mm. Pulsed 355-nm light (frequency-tripled Nd:YAG) was found to produce an equivalent effect but required an average intensity greater by a factor of 4.

To summarize, a UV-induced absorption change in a selection of Ce^{3+}-doped glass preforms and fibers has been studied. The Ce^{3+} ion concentration is reduced, and a broad absorption band extending up to IR wavelengths is created on UV exposure. Eighty-two days after exposure the change in Ce^{3+} concentration remained, but the induced broadband absorption had totally recovered. Further investigation revealed three distinct recovery time constants of the order of a few tens of seconds, a few minutes, and a few hours. The induced broad absorption band is attributed to defect centers formed by trapping photoelectrons released by Ce^{3+} ions. The anticipated Ce^{4+} absorption resulting from Ce^{3+} ions losing electrons, observed by Stroud,[6] was also seen. The UV-induced loss at 632.8 nm during UV exposure was found to stay at a constant level and depend linearly on average UV intensity. The loss was also observed to increase with Ce^{3+} ion concentration for low concentration levels but to decrease at higher levels. 355-nm light was found to give similar absorption changes at 632.8 nm but required an average intensity 19 times that at 266 nm.

Large average index changes are also induced in Ce^{3+}-doped optical fibers on exposure to pulsed 266-nm UV light. A linear dependence on UV intensity indicates a single photon process caused by Ce^{3+} absorption. The fact that the index change is stable for at least 30 min after exposure disassociates it from the fast recovery loss process. Similar effects are seen at 355 nm, but the required average intensity is four times higher; however this is much less than that required to produce the same induced loss at 632.8 nm (19 times), additional evidence dissociating the two processes. The saturation trends of both the UV intensity and Ce^{3+} concentration dependence may be explained by a lack of electron-trapping defect centers associated with the index change mechanism, indicating that an increased index change is achievable if this defect center concentration can be increased, probably by a higher Al^{3+} doping level. Recently the formation of refractive gratings in Ce^{3+}-doping silica optical fibers was demonstrated by Broer *et al.*[12]

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