Defect production in silica fibers doped with Tm^{3+}

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Irradiation of Tm^{3+} fibers with blue light at 476 nm induces a broad-bandwidth loss in these fibers. We have measured the spectral dependence of the loss for both silica–germania and silica–alumina fibers and show through micro-Raman studies of the core regions of the fibers that this induced loss is correlated with the production of structural defects in the glass host.

Defects in undoped germanosilicate fibers have a profound effect on optical properties in the visible region of the spectrum. Photoexcitation of these defects can produce a refractive-index change, which in turn can be used for many useful purposes, including the formation of gratings and second-harmonic generation in fibers. The defects responsible for this behavior have been associated with the germanium doping present in the core.[1–4]

Glasses doped with rare-earth ions also show photochromic effects on excitation with blue light.[5] Cerium- and europium-doped fibers have both shown photochromic effects, which have been used for photoinduced second-harmonic generation[6] and to produce distributed-feedback gratings.[7] Photochromic effects in thulium-doped germanosilicate fibers have been observed by Millar *et al.*,[8] who observed changes in the optical absorption of the Tm^{3+}-doped fibers on irradiation with light at 476 nm. These effects were monitored by measurement of induced absorption at 514.5 and 633 nm before and after irradiation with light at 476 nm. 476-nm light is resonant with the $^1G_4$ level of thulium, and it is also close to the wavelength observed to produce photochromic effects in undoped germanosilicate fibers through two-photon absorption, 488 nm. The absorption bands were observed to appear on irradiation at 476 nm and disappear on irradiation with 514.5-nm light.

In this Letter we describe further experiments on thulium-doped silicate fibers. We have measured the spectrum of the induced absorption on irradiation at 476 nm for Tm^{3+}-doped silica–germania and silica–alumina fibers. We have also studied the vibrational spectrum of these glasses both before and after photochromic effects occur and find that the Raman spectra show significant changes on irradiation. Peaks appear at 495 and 606 cm^{-1}. These peaks are associated with defects in the silica network structure itself. These photochromic effects occur in both silica–alumina and silica–germania fibers, showing that the defects are not associated with the presence of germanium in the glass structure.

We prepared the fibers used in these experiments, using modified chemical vapor deposition, and doped them with thulium using solution doping.[9] The concentrations of rare earth were 1000 parts in 10^6 (ppm) in the aluminosilicate fiber and 3000 ppm in the germanosilicate fiber, determined from optical absorption measurements based on cross sections determined by Smith and Cohen.[10] Raman spectra of the core regions of the fibers were taken with a Jobin-Yvon S3000 micro-Raman spectrometer. The pump wavelength for Raman measurements was 488 nm, and all spectra were taken in a backscattering geometry. The pump light used for Raman scattering slowly erased the changes in the glass, so care was taken to irradiate the fibers for the shortest possible time when spectra were taken. The micro-Raman geometry permits accurate coupling into the fiber, and in all cases the coupling was not changed between spectra taken before and after 476-nm irradiation.

Absorption spectra were taken with a standard spectrometer/photomultiplier combination, with a Hamamatsu S1 photocathode photomultiplier and photon-counting electronics. The 476-nm pump light and white light were counterpropagated, which allowed us to measure the absorption spectra without ever changing the coupling of the white-light source, guaranteeing that the changes measured were real effects and not just artifacts of changes in the fiber coupling.

Figure 1 shows the Raman spectrum of a germanosilicate fiber doped with 3000 ppm of thulium before and after irradiation with ~50 mW of light at 476 nm for 1 min. As can be seen from the figure, peaks at 495 and 606 cm^{-1} were enhanced by the irradiation. On further irradiation with ~100 mW of 514.5-nm light, these peaks reduced in magnitude, although they did not return to their former size. A similar effect was seen in the aluminosilicate fiber, although in this fiber the effect was less pronounced because peaks at these frequencies are already present in the vibrational spectrum of aluminosilicate glass before irradiation.

Trace (a) of Fig. 2 shows the change in the absorption spectrum of the germanosilicate fiber before and after irradiation with 476-nm light. A broad absorption band across most of the visible spectrum

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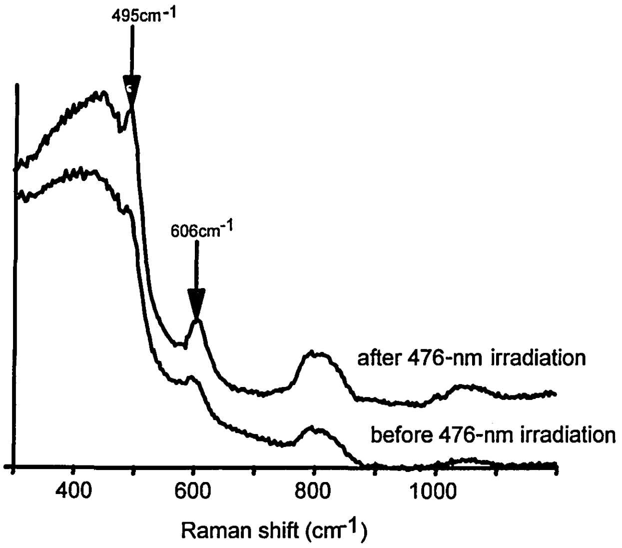

Fig. 1. Raman spectrum of germanosilicate fiber core before and after irradiation with 476-nm light. Increases in the peak heights at 495 and 606 cm^{-1} are clearly visible in the postirradiation spectrum.

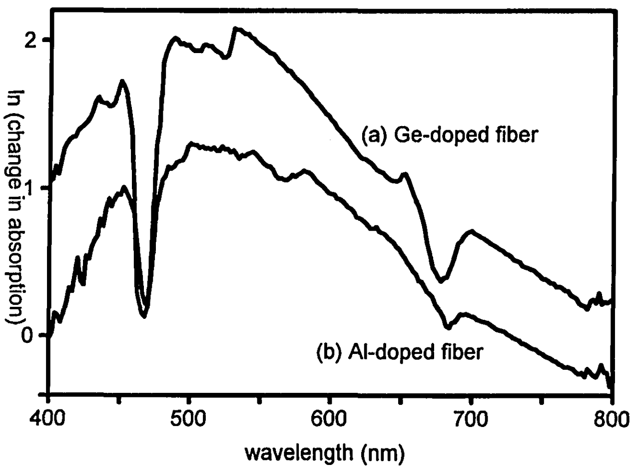

Fig. 2. Natural log of the change in absorption on irradiation of a 1-m length of Tm^{3+}-doped germanosilicate [trace (a)] and aluminosilicate [trace (b)] fibers. The two spectra are similar, indicating that the interaction between thulium and the silica host is most likely to be responsible for the defect that creates the absorption.

is induced on irradiation; its peak is at ~500 nm. As with the induced Raman peaks, the induced absorption could be reduced to ~10% of its maximum size by irradiation with light at 514.5 or 488 nm. Trace (b) of Fig. 2 shows the equivalent spectrum for a thulium-doped aluminosilicate fiber. As can be seen from Fig. 2, the induced absorption spectra for the germania-doped and the alumina-doped fibers are similar, indicating that the presence of germanium is not necessary for the formation of this band. A reduction in the absorption at the Tm^{3+} absorption peaks is also seen in both cases.

The defects responsible for the Raman peaks at 495 and 606 cm^{-1} in pure silica have been the subject of much discussion in the literature. Chmel *et al.*[11] note that there is substantial agreement between experimentalists that the assignment of the 495-cm^{-1} peak to a four-membered siloxane ring is correct but disagreement as to the origin of the 606-cm^{-1} peak, which was assigned by Grissberger and Galeener[12] to be a three-membered siloxane ring. Chmel *et al.* assign this 606-cm^{-1} defect to be a partially broken bond. Both defects are removed by the addition of fluorine and created by neutron irradiation.[10] However, their sensitivities to each treatment are different. Their activation energies, as measured by annealing, are also different. The four-membered ring is thought to be isolated from the main silica network, either by the presence of partially broken bonds or by some other means.[13] In previous work, Gabriagues and Fevrier[14] studied the Raman spectra of a fiber that showed good second-harmonic generation efficiency in comparison with that of standard telecommunications fiber. They noted that the peaks at both 495 and 606 cm^{-1} showed significant differences between the two fibers. Those authors went on to suggest that the presence of the defects responsible for the 495- and 606-cm^{-1} Raman lines was beneficial to the changes necessary for one to see second-harmonic generation in germanium-doped fibers not containing rare-earth ions. It appears from our Raman data that the numbers of both of these defects are increased when 476-nm light is absorbed by the thulium ion and that either the defects or the complex produced in this process has an absorption band in the visible region of the spectrum. Resonance with the thulium $^1G_4$ absorption is obviously critical, because 488-nm light, which is not strongly resonant with any levels of Tm^{3+}, causes the removal of the defects. How this process occurs is by no means clear, and the interaction of the thulium ion with the defects is the subject of further investigation at present. Both cerium and europium ions are known to exist in several ionization states in oxide glasses, and so oxidation or reduction of the rare earth is a possible cause of changes in absorption and thus in refractive index in fibers doped with these ions. Thulium occurs in the form Tm^{2+} in CaF_2 but to our knowledge has never been reported in an oxide glass. Thus a change of ionization state of the thulium ion is less likely than in the case of cerium or europium. It is interesting to note that in the study reported in Ref. 3 the fibers thought to be doped only with cerium were later found to contain a small amount of Tm^{3+}, which may have contributed to the photochromic effect.

We also note that the presence of germanium-related defects in the glass is not necessary in this case for the production of photochromic defects.

In summary, we have measured both an induced absorption band and a change in the vibrational spectrum of thulium-doped germanosilicate and aluminosilicate optical fibers on irradiation with light resonant with a thulium absorption at 476 nm. This process is evidence that a fundamental structural change of the glass network is involved in photoinduced phenomena in rare-earth-doped fibers and that this change is not associated with the presence of germanium in the glass. It may have serious repercussions for the production of devices that use Tm^{3+} in the visible region of the spectrum but may shed some light on experiments in which the presence of the rare-earth ion enhances the nonlinear properties.

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