Gamma radiation-induced refractive index change in Ge- and N-doped silica

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We measured the change of the refractive index over a wide wavelength range in Ge- and N-doped high purity (fiber optics grade) silica glasses subjected to gamma irradiation. The radiation-induced change of the refractive index tends to be greater in the infrared part of the spectrum compare to the values measured in the UV-visible part of the spectrum. By means of the Kramers–Kronig relations, we estimate that a weak broadening of the optical vibration band of the silica network adds to this effect. The paper also discusses the difference observed in the spectral behavior of the induced refractive index change for both types of doped glass. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2885116]

I. INTRODUCTION

In the context of the radiation resistance of glass material, we investigated the variation of the optical refractive index properties of doped bulk glasses subjected to ionizing radiation. Usually, the best radiation resistance in glasses is first of all achieved by selecting a glass material as pure as possible. In the case of continuous irradiation, the best radiation resistance occurs in the step index fibers. However, a certain number of applications call for the use of graded refractive index profiles, which therefore requires the doping of the glass, as, for example, the case of Ge-doped optical fibers. Because of Ge doping, such fibers cannot be qualified as radiation resistant. However, a certain degree of radiation hardness can be achieved by substituting the germanium by nitrogen. This fiber technology is therefore viewed as an alternative to germanosilicate one for applications in radiation environments.[1]

The radiation resistance of an optical fiber is primarily assessed by the magnitude of the radiation-induced attenuation (RIA). The RIA occurs because of the defect creation induced by the action of the radiation on the silica. These defects, also often called color centers, develop specific absorption bands in the optical spectrum of the silica glass. The origin and concentrations of these defects strongly depend on the glass composition. In particular, Ge admixture is the main source of radiation-induced color centers in standard telecommunication optical fibers.[2]

Besides the RIA effect, high energy particles or ionizing radiation can also induce a refractive index change that may introduce severe aberrations in precise optical instruments.[3] One physical reason for the index change was attributed to a radiation-induced densification of the glass. Primak[4] reported experimental observations of such compaction effect in neutron irradiated bulk silica. In such a case, high energy neutrons directly interact with the atomic network to produce displacements. The bulk sample densification was also reported in silicate glass proton irradiation experiments.[5] In the case of ionizing radiation high energy photons, extra electron transitions are created and triggered by optically active point defect formations resulting from the breaking of atom-to-atom chemical bonds. Interestingly, a certain number of recent experimental studies also revealed the existence of a densification mechanism in amorphous silicon dioxide films[6] and bulk samples[7] under intense excimer of 5–6.4 eV photon energy laser light exposures.

Although the radiation stimulated atomic reconstruction of the SiO_2 glass network was discussed in literature,[8,9] its microscopic mechanisms remain in many aspects unclear. Obviously, they depend on the type of irradiation. In the case of the sub-band-gap photon irradiation, like UV radiation, many-photon absorption processes dominate and the light intensity is of paramount importance. In the case of gamma irradiation, the energy of one photon is more than sufficient for breaking Si–O bonds. Dopants and intrinsic defects play an essential role in the glass network modification processes for all types of irradiation.[10,11]

This work aims to evaluate, by means of direct measurements, the gamma radiation-induced change of the refractive index $n(\omega)$ in silicate glasses as a function of the frequency. Basically, we applied the same methodology as presented in Ref. 12 referring to the case of excimer laser irradiations (UV irradiation). Through the Kramers–Kronig relations, the absorption behavior can be related to the refractive index change. The refractive index dispersion in the high-frequency region of the transparency window reflects electronic transitions, while lattice vibration processes occur in the low-frequency region of the spectrum. This methodology represents an attempt to separate and estimate the radiation-induced material disordering in electron and phonon glass subsystem modifications.[13]

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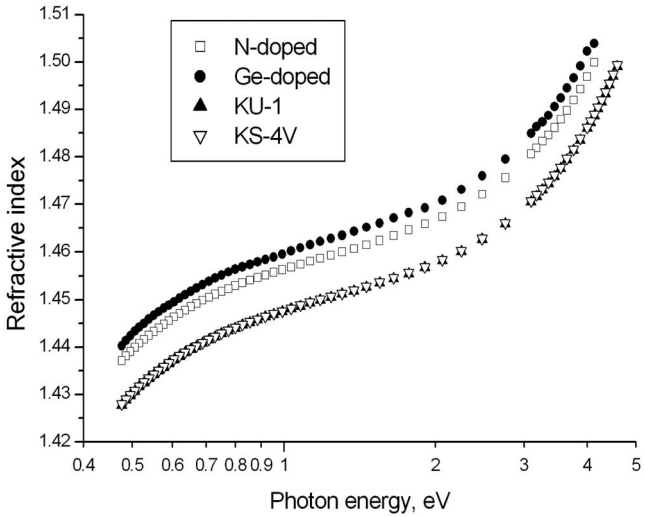

FIG. 1. Initial $n(\omega)$ dependencies for Ge- and N-doped silica samples used in the irradiation experiments. The refractive index dispersion of pure silica glass KU1 and KS4V is also displayed for comparison.

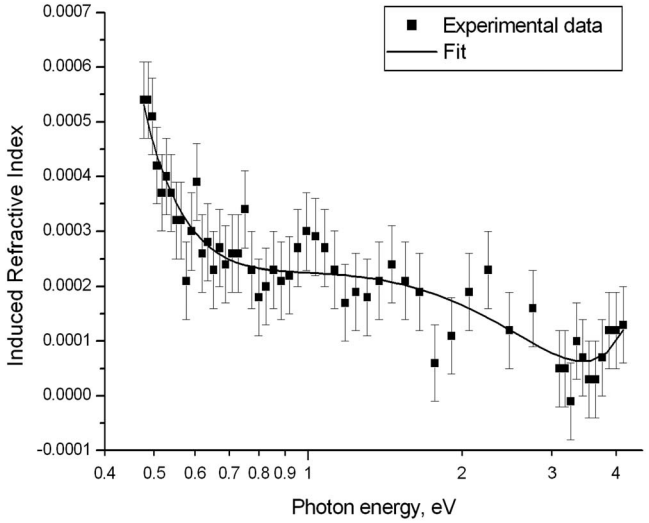

FIG. 2. Gamma radiation-induced refractive index spectrum in gemanosilicate glass.

II. SAMPLE PREPARATION AND IRRADIATION

The procedure consists in measuring the glass refractive index dispersion before and after irradiation. The refractive index spectrum was recorded with 10^{-4} accuracy in the wavelength range of 300–2500 nm (corresponding photon energies are 4.13–0.5 eV) using prism samples. The automated setup and the refractive index measuring technique used are described in detail in Ref. 14.

The glass prisms are cut off from two prepared fiber preforms doped either with Ge or N. The synthesis of the core glass preforms occurs on the inner surface of a silica substrate tube using the plasma chemical method described in detail in Ref. 15. We determined the germanium and nitrogen contents in the region of the core preform by measuring the refractive index profiles of the preforms (using a profile analyzer). In the present case, the Ge-doped glass contains 12 mol % GeO_2, while the N-doped glass has 1 at. % N.

The initial (before irradiation) dispersion curves for all the samples under investigation are summarized in Fig. 1. The prism fabrications and dispersion measurements were carried out in the Plasma Chemical Laboratory of FORC in Moscow.

The prism cuts from Ge-doped and N-doped silica were gamma irradiated using the Co^{60} irradiation facility of SCK-CEN, Belgium.[16] The prisms were irradiated simultaneously in the same irradiation conditions up to a dose of 7 MGy at a dose rate of 20 kGy/h and a temperature not exceeding 50 °C.

III. RESULT AND DISCUSSION

The dispersion curves in an optical transparency window of glasses can be fitted using the well-known Sellmeier dispersion relation,[17]

$$n^2(\lambda) = 1 + \sum_{i=1}^{3} \frac{a_i \lambda^2}{\lambda^2 - b_i^2}, \tag{1}$$

where a_i are the oscillator strengths and b_i the resonance wavelengths. We used a three-oscillator model, two oscillators being responsible for the electron component of the glass polarizability and one oscillator describing the vibration component.[14]

Figures 2 and 3 show the spectral dependencies of gamma induced refractive index change in germanosilicate and nitrosilicate glasses, respectively. The curves show the differences between the Sellmeier fits before and after gamma irradiation. The data and its associated error bars result from a statistical average obtained by repeating the measurement procedures. The prisms are carefully reinstalled in the dispersion measurement setup, and the obtained dispersion curve is subtracted by its corresponding

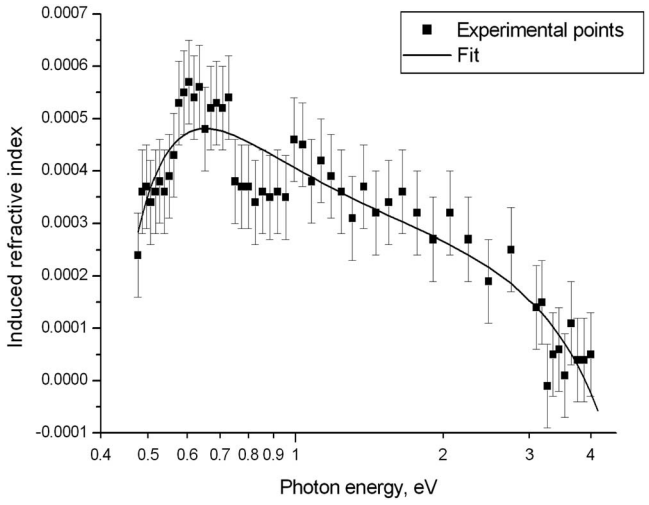

FIG. 3. Gamma radiation-induced refractive index spectrum in nitrosilicate glass.

value prior to irradiation. Great cares have been taken in order to precisely reproduce the initial position of the prisms during the installation.

We note the increase of the refractive index, up to 3×10^{-4} at 1 μm, in the irradiated doped samples. Such refractive index changes are in agreement, both in sign and in magnitude, with previous data obtained from the gamma irradiation of the fiber Bragg grating[18] or International Telecommunication Union couplers.[19] Both spectra feature a detectable increase of the induced refractive index when moving toward the infrared region of the spectrum under study. At the same time in the UV spectral region, the induced refractive index practically goes to zero in nitrosilicate glass and displays a tendency to re-increase at shorter wavelengths in germanosilicate one. This behavior is in qualitative agreement with the fact that the RIA in the N-doped silica fiber is by an order of magnitude lower than in Ge-doped silica fiber. According to the Kramers–Kronig relations, a lower (as an integral) induced absorption level in the nitrogen-doped fiber as compared to the germanosilicate glass in a high-frequency part of the spectrum denotes a lower refractive index change.

When comparing more carefully the variation of the dispersion curves of both glasses in the infrared region, we note the following important differences. In particular, the curve shows a monotonous increase in the case of the germanosilicate glass (Fig. 2), while it is nonmonotonous in the N-doped glass. This increase in the long-wavelength region means that the gamma irradiation significantly affects the optical absorption spectrum associated with the excitation of optical phonons in the 0.1 eV region corresponding to the Si–O bond vibration resonance.

The contribution to the refractive index dispersion of the low frequency relative to transparency window band ($\omega_l < \omega$) absorption spectrum component can be expressed according to Ref. 20 as

$$\delta n(\omega) = \frac{c}{\pi} \int_0^{\omega_l} \frac{\alpha(x)dx}{x^2 - \omega^2}, \tag{2}$$

where c is the speed of light and α the absorption coefficient. Note that the denominator in Eq. (2) is negative and thus the vibration component contribution in the frequency band under consideration leads to a refractive index decrease.

To calculate the integral, we approximate the shape of the absorption band by a Gaussian band centered at 0.125 eV which corresponds to Si–O bond vibration resonance. As previously discussed, the gamma radiation causes the change of the absorption band. This change is caused by gamma radiation-induced disordering of the glass network which can lead to both broadening and spectral shift of the fundamental infrared absorption band. The absorption band modification results in a change of the refractive index in the optical transparency window of the material.

Let us consider the simplest model, in which the only effect of the gamma radiation is spectral broadening of the absorption band. Figure 4 quantitatively depicts this effect by showing the relation between the induced refractive index spectrum calculated by relation (2) and its associated broadening of the optical absorption spectrum in the far infrared region. The initial (before irradiation) spectral width was set to a value of 0.04 eV (Fig. 4(a), solid curve). The spectrum variation resulting from gamma irradiation is defined as a uniform spectrum band broadening keeping the area under the spectral curve unchanged. The dashed and dotted curves in Fig. 4(a) correspond to the spectral widths of 0.0404 and 0.041 eV, respectively. The refractive index variations [Fig. 4(b)] are calculated from the sample spectra via relation (2) at ω_l=0.4 eV. Based on this model, we can see that a "randomization" in the vibration structure expressed by a 5% broadening of the phonon absorption band yields the contribution in the refractive index increase which is of the order of magnitude close to the experimentally observed values in the infrared region. One can also note a fast decrease of the vibration component contribution when shifting to the high-frequency region. This trend decrease should be better estimated by measuring the absorption spectra of film specimens.

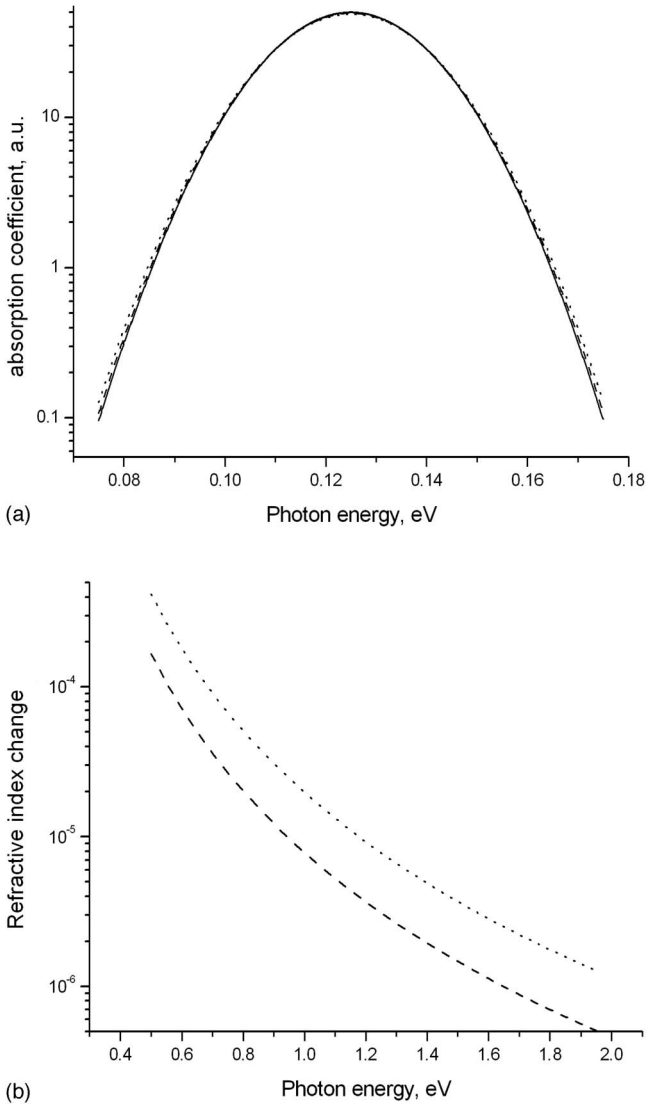

FIG. 4. Model of the absorption spectrum broadening resulting from gamma irradiation (a) and corresponding to this broadening induced refractive index spectra (b).

IV. CONCLUSION

We found experimental evidences that the refractive index of Ge- and N-doped silica increases under the gamma irradiation to the dose of 7 MGy by a value greater than 10^{-4} in the optical transparency window. This increase tends to be greater in the infrared part of the spectrum, which distinguishes the effect of gamma irradiation from the one of the excimer laser irradiation. The effect of the latter in the similar samples displays an opposite behavior of the induced refractive index spectrum.[12] It is clear that UV radiation with energy of the order of magnitude of the band gap is efficiently absorbed in silica material modifying primarily the electronic structure without significantly altering the atomic structure. By contrast, high energy photons are by far less efficiently absorbed but, however, have sufficient energy to break chemical bonds impacting directly the atomic network.

The revealed spectral feature is believed to originate from a randomization of the radiation—induced atomic vibration structure in the doped glasses accompanied by an absorption band change in the neighborhood of 0.125 eV photon energy. This band corresponds to the shortest-wavelength vibration resonance of the glass network.

The simplest hypothesis by which the optical vibration band of the glass network undergoes a broadening due to the action of energetic radiation represents an attempt to explain the general trend of the continuous increase of the RIA beyond the 1.6 μm in irradiated pure silica glass optical fibers.[21]

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