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Microscopic model of photoinduced and pressure-induced UV spectral changes in germanosilicate glass

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We carry out quantum-chemical calculations on clusters of atoms modeling the local structure of the divalent Ge defect in germanosilicate glass. It is found that the divalent Ge defect can interact with a nearby bridging oxygen atom, leading to denser defect configurations. The excitation energy of the resulting diamagnetic defect center is calculated to be ∼5.5–∼5.8 eV, explaining a growth of the compaction-derived metastable absorption band in germanosilicate glass in the range 5.5–6.0 eV.

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Much effort has gone into the study of the mechanism and relative contributions to the photorefractive effect in glass waveguides. This effect is closely related to the photosensitivity of pure and doped silica glass, which is the material of choice for most optical fibers in use today. In particular, the photosensitive phenomenon of germanosilicate glass has been recognized as having tremendous practical importance, since this allows us to produce fiber Bragg gratings in optical fibers with a number of applications, including wavelength multiplexers, sensors, fiber mirrors, and dispersion control devices.[1] It has been demonstrated that a significant refractive index change occurs when a germanium-doped fiber is exposed to ultraviolet (UV) light close to 5 eV. Since this energy coincides with the absorption peak of germanium oxygen-deficient centers (GODCs), it is generally believed that photosensitive GODCs play a major role in the mechanisms of UV-induced refractive index changes in germanosilicate optical fibers.[2,3] Indeed, the defect band at ∼5 eV is bleached by UV radiation, and, accordingly, several broad Gaussian components emerge in the region of 4–8 eV.[4,5] The most pronounced components are centered at ∼4.4, ∼5.8, and ∼6.5 eV.[6,7] Thus one probable model of the photoinduced refractive index change is the so-called color-center model; that is, these photoinduced color centers produced especially in the deep UV (>∼6 eV) region yield positive refractive-index changes on the longer-wavelength side of the absorption band through the Kramers-Krönig mechanism.[6] However, this color-center model does not completely explain all the accumulated experimental findings concerning the relevant photorefractive effect.[1] Other researchers have hence proposed an alternative model which is based on glass densification induced by photostructural changes of the GODCs,[8] and direct observation of photoinduced compaction was obtained recently.[9,10]

It should also be noted that when germanosilicate glass is densified by the high-hydrostatic-pressure treatment, the absorption spectrum of the initial sample also changes.[11] Dianov *et al.*[11] showed that after hydrostatic densification the broad absorption bands centered at ∼5.8 and ∼7.3 eV grow significantly at the expense of the original defect band at ∼5 eV. Thus the photoinduced and pressure-induced spectral changes are very similar, except that the 4.4-eV band does not grow in the spectra of hydrostatically pressurized germanosilicate glass. It is hence quite probable that there is a close connection between UV and hydrostatically induced compaction.[1] Dianov *et al.*[11] also reported that no paramagnetic defects are created during the hydrostatic densification process, indicating that all the pressure-induced absorption bands are associated with diamagnetic defect centers.

The photoinduced absorption bands at ∼4.4, ∼5.8, and ∼6.5 eV mentioned earlier have been attributed to different types of paramagnetic centers called Ge(1), Ge(2), and Ge(E'), respectively.[12–14] The Ge(E') center consists of a threefold-coordinated Ge with an unpaired electron, and the Ge(1) center is attributed to an electron trapped at a Ge tetrahedron.[15] However, the origin of Ge(2) giving rise to the ∼5.8-eV band is still a matter of controversy, and it is not yet clear whether Ge(2) is an electron center or a hole center.[7,12] Recently, from the measurements of the magnetic circular dichroism absorption (MCDA) and optically detected magnetic resonance (ODMR) spectra of an x-ray-irradiated germanosilicate glass, the authors of Ref. 16 demonstrated that contrary to the standard model mentioned above, Ge(2) is diamagnetic in nature. Thus, as for the origin of the ∼5.8-eV band, the results of the MCDA and ODMR measurements are consistent with those obtained from the hydrostatically densified sample; that is, the photoinduced and pressure-induced absorption at ∼5.8 eV results from a certain diamagnetic center, although its structural origin is still unidentified. In this work, we therefore concentrate our interest on the origin of the ∼5.8-eV band, and present a possible structural model responsible for this pressure-induced and photoinduced absorption band on the basis of quantum-chemical calculations using clusters of atoms that model the local structure of germanosilicate glass.

Considering that the ∼5.8-eV band grows at the expense of the 5-eV band, here we assume that a divalent Ge defect, which is believed to be one possible origin of the 5-eV band,[5,17] is structurally transformed into another diamagnetic defect center to yield a ∼5.8-eV band under compression or UV irradiation. As far as the photoinduced process is concerned, it has indeed been suggested that the structure around the divalent Ge defect relaxes to prevent recombination and to yield a permanent structural arrangements, leading to local densification.[18] In previous papers,[19,20] we showed that the divalent Ge defect tends to interact with a nearby bridging oxygen atom to form a compacted structural unit having a threefold-coordinated Ge atom and fivefold-coordinated Ge

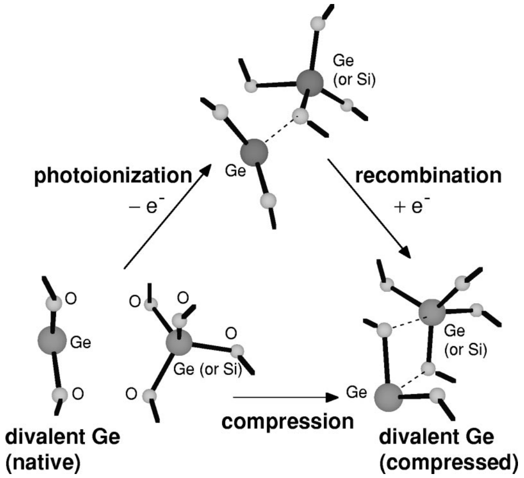

FIG. 1. A possible photoinduced and pressure-induced compression mechanism associated with the divalent Ge defect in germanosilicate glass. The native and compressed forms of the divalent Ge defect will contribute to the ~5.0- and ~5.8-eV photoabsorption bands, respectively.

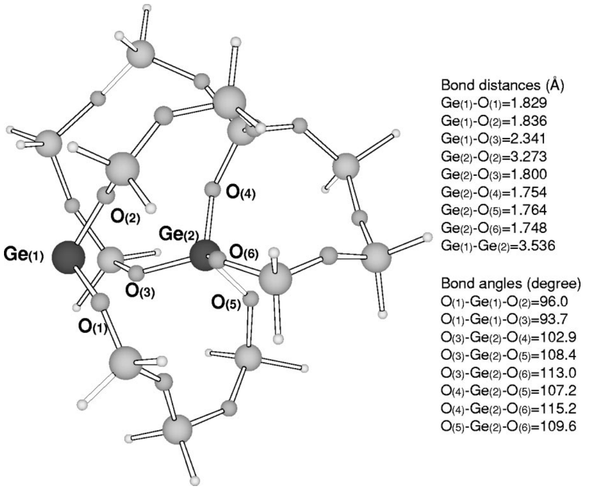

FIG. 2. The $Ge_2Si_{12}O_{16}H_{22}$ cluster (model 1) modeling the local structure of the native divalent Ge defect in germanosilicate glass. The geometry optimization was performed at the B3LYP/6-31$G(d)$ level without imposing any structural constraints.

atoms. We have also demonstrated that this structural unit yields a higher excitation energy than the native divalent Ge defect by ~0.2 eV.[19] This result suggests that the proposed threefold- and fivefold-coordinated Ge units, which are likely to be formed as a result of the mechanical compaction and/or photoionization of the native divalent Ge and the subsequent recombination process (see also Fig. 1), are responsible for the pressure-induced and photoinduced absorption over ~5 eV. The formation of such "overcoordinated" Ge atoms can be interpreted in terms of an electron-trapping nature of Ge atoms. It has been demonstrated that a fourfold-coordinated Ge atom is able to capture an electron from neighboring oxygen atoms to change its coordination number within the glass network. For example, when an alkali oxide is added to germanate glasses, one sees a change in germanium coordination from GeO_4 to GeO_5 and/or GeO_6, leading to densification at ambient pressure.[21–23] Such an electron capture process followed by the formation of the overcoordinated Ge atom does not occur in pure silica unless the system is subject to high pressures over ~30 GPa.[24] It is hence likely that the proposed mechanism of the photoinduced densification associated the divalent Ge and its neighboring GeO_4 tetrahedral unit[19,20] is peculiar to Ge-doped silica; that is, the mechanism cannot be applied to pure silica.

In our previous papers,[19,20] however, we used rather small clusters to model the divalent Ge and its related defect centers. The clusters employed previously comprised two Ge atoms and three Si atoms, neglecting surrounding environments around the defect of interest. Thus larger clusters would be more favorable to show that the above defect interconversion and the resultant change in excitation energies indeed occur. In the present work, we hence employ clusters of atoms consisting of two Ge atoms and 12 Si atoms to model the native and compressed forms of the divalent Ge defect. Figure 2 shows a cluster, termed model 1, to model a native divalent Ge defect. In model 1, the defect site is embedded in the germanosilicate network in order to include, although not perfectly, an effect of condensed environments in the actual glassy system. The dangling bonds of the "surface" silicon atoms of the clusters were saturated by H atoms, and the geometry optimization was performed at the density functional theory (DFT) levels with the 6-31$G(d)$ basis set.[25] For the DFT calculations, we used the B3LYP exchange-correlation functional consisting of the Lee-Yang-Parr correlation functional[26] in conjunction with a hybrid exchange functional proposed by Becke.[27] We did not impose any structural constraints during the optimization; that is, all the atoms in the clusters are allowed to relax to obtain the optimized configuration. In Fig. 2, we show the resultant optimized geometry of model 1 along with principal structural parameters.

We then assumed that the native divalent Ge defect in model 1 can interact with a nearby bridging oxygen atom under compression and ionization processes. Thus we intentionally changed the position of the divalent Ge atom [Ge(1)] in model 1 in such a way that Ge(1) can interact with one of the bridging oxygen atoms [O(3)] in the model cluster. Using such a modified configuration as an initial geometry, we performed a full geometry optimization at the B3LYP/6-31$G(d)$ level in its neutral charge state; that is, the resulting defect center in the cluster is diamagnetic in nature. The obtained equilibrium geometry of the cluster, termed model 2, is shown in Fig. 3(a). *Ab initio* quantum-chemical calculations in this work were performed using the GAUSSIAN 98 program[28] on a supercomputer CRAY T94/4128.

We see from Figs. 2 and 3(a) that the atomic reorganizations from model 1 to model 2 allow the interaction between the divalent Ge and its surrounding atoms, forming a complex defect configuration. The defect center in model 2 is basically the same as that reported in our previous paper employing a smaller cluster.[19] We should also note that the Ge(1)-O(3) and Ge(2)-O(2) bond distances become shorter by 0.33 and 1.25 Å, respectively, as we go from model 1 to model 2. That is, it is quite likely that the "open" structure around the divalent Ge defect in model 1 is compacted as a

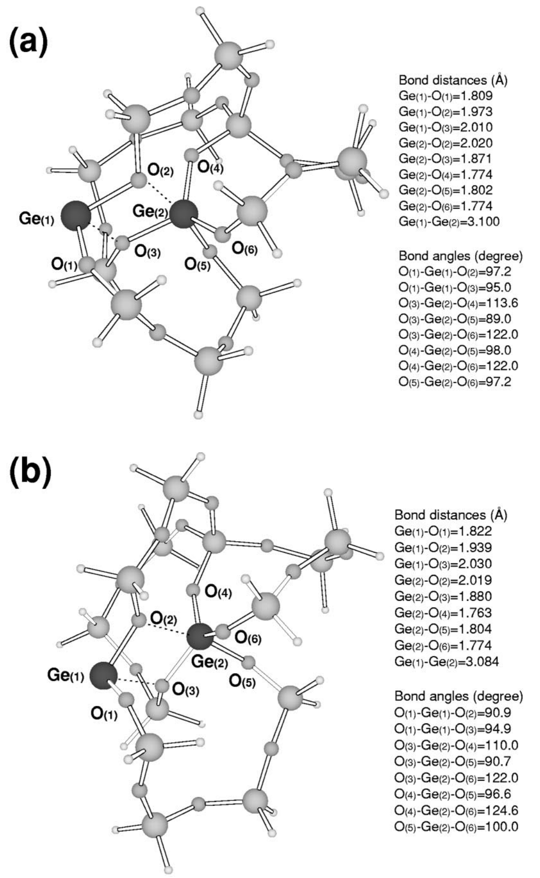

FIG. 3. The $Ge_2Si_{12}O_{16}H_{22}$ (model 2) (a) and $Ge_2Si_{13}O_{17}H_{24}$ (model 3) (b) clusters modeling the local structure of the compressed form of the divalent Ge defect in germanosilicate glass. The geometries of the clusters were optimized at the B3LYP/6-31$G(d)$ level. Before the optimization procedure of the $Ge_2Si_{12}O_{16}H_{22}$ cluster, we intentionally changed the position of Ge(1) in model 1 in such a way that it can interact with O(3). Using this geometry as an initial configuration, we then carried out the geometry optimization without imposing any structural constraints.

result of the present atomic reconfigurations. We have found that the total energy of model 2 is almost identical to that of model 1; the former cluster is even slightly lower in total energy than the latter by 0.28 eV. We therefore consider that the defect conversion from model 1 to model 2 is not an artifact of the calculations using small clusters, but is likely to occur in actual systems under compression and/or photoionization processes.

We then turn to excitation energies of models 1 and 2. The first excitation energy of the respective clusters was calculated by using time-dependent density-functional response theory (TD DFRT).[29] It was recently shown in a number of papers[30–35] that the TD DFRT gives excitation energies that are comparable to those obtained from the more costly correlated *ab initio* method such as the configuration interaction (CI) method, and are hence in good agreement with experiment. The TD DFRT excitation energies were calculated at the B3LYP level using the 6-31$G(d)$ basis set augmented by a set of diffuse *s* and *p* functions on Si, Ge, and O atoms, namely, the 6-31+$G(d)$ basis set.[28]

The S_0-S_1 transition of model 1 was calculated to be 4.89 eV, which is in reasonable agreement with previous *ab initio* calculations based on the CI method (5.05 eV).[36] On the other hand, the S_0-S_1 transition of model 2 was computed at 5.78 eV, which is substantially higher than the corresponding transition energy calculated for model 1. To corroborate this tendency, the excitation energy of such a compacted defect as seen in model 2 was calculated using a different cluster having two Ge atoms and 13 Si atoms [model 3; see Fig. 3(b)]. The S_0-S_1 transition of model 3 was calculated to be 5.52 eV at the B3LYP/6-31+$G(d)$ level. Although the excitation energies of models 2 and 3 are not identical to each other, the present results as well as previous calculations[19] give the same tendency that the compacted divalent Ge defect yields a higher excitation energy than the native one. It is also interesting to note that the S_0-S_1 transition energies calculated for models 2 and 3 are comparable to the photoinduced and pressure-induced absorption band at ~5.8 eV. Taking the facts mentioned above into account, we suggest that the higher-energy component of the ~5-eV photoabsorption band, namely, the photoabsorption band centered at ~5.8 eV, results from the compressed form of the divalent Ge defect.[37]

In conclusion, we have shown that the native divalent Ge defect yielding the ~5-eV band in germanosilicate glass (model 1) can be converted into the other diamagnetic defect having a threefold-coordinated Ge atom (models 2 and 3). This conversion is expected to occur under photoionization as well as compression (see Fig. 1). Judging from the calculated excitation energies, we suggest that the defect center in model 2 or model 3 is responsible for the observed photoabsorption band in the range of ~5.5–~6 eV. As for the photoinduced process, other defect centers that are associated with free charge carriers and radicals having unpaired electrons will be also created.[1] However we believe that the present defect conversion mechanism is capable of explaining one fundamental facet of the photoinduced structural modifications and concomitant UV spectral changes in germanosilicate glass.

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[37] In the photoabsorption spectra of as-prepared germanosilicate glasses, one also observes a broad high-energy Gaussian component (~5.4 eV) along with the main ~5.1-eV band in the energy range from 5 to 6 eV (Refs. 7 and 11). It is hence likely that the compressed form of the divalent Ge defect as well as the native divalent Ge defect already exists in as-prepared germanosilicate glass.