

Structure and Formation Mechanism of Ge Related Paramagnetic Centers in Ge-Doped Silica Glass

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We have performed ab initio quantum chemical calculations on clusters of atoms modeling a divalent Ge defect in Ge-doped SiO₂ glasses. It has been found that the divalent Ge defect interacts with a nearby GeO₄ tetrahedron, forming complex structural units that are responsible for the observed photoabsorption band at ~ 5eV. We have shown that these structural units can be transformed into two equivalent Ge E' centers by way of the positively charged defect center.

Keywords : Silica Glass / Paramagnetic defect centers/ Photostructural changes / Quantum chemical calculations

Photosensitivity and photoinduced holographic Bragg gratings were discovered in Ge-doped SiO₂ glasses about 20 years ago [1]. Presently photoinduced Bragg fiber- and planar waveguide gratings in the glasses are widely used in telecommunication technology for wavelength-divided multiplexing, signal shaping, fiber lasers and amplifiers, etc [2]. In contrast to these spectacular advances in practical applications, however, the fundamental understanding of the respective photoinduced processes in glass is very incomplete. In Ge-doped SiO₂ glasses, there exists an intense photoabsorption band at 5 eV, which is believed to be related to oxygen deficiency. Although the defect center associated with the 5-eV band most likely plays an important role in the photorefractive index change induced by ultraviolet (uv) irradiation, the details of the processes and mechanisms involved have remained obscure.

In this paper, we, therefore, investigate the formation mechanism of Ge E' centers from the divalent Ge defect in Ge-doped SiO₂ glasses by using ab initio cluster model calculations at the Hartree-Fock (HF) level. It has been demonstrated that ab initio quantum-chemical cluster approaches are useful to investigate the structure and vibrational properties of glassy systems [3]. In particular, since the defect states in glasses are in general quite localized, their structure and energy states will be reasonably modeled by the cluster calculations. Appropriate cluster models hence allow us to investigate the geometries and electronic structures of the defect centers in glasses, and the calculated results will shed new light on the unsolved problem concerning the formation mechanism of Ge E' centers associated with the photo-bleaching of the 5.16-eV band and other photoinduced phenomena of interest in Ge-doped SiO₂ glasses.

SOLID STATE CHEMISTRY — Amorphous Materials —

Scope of Research

Inorganic amorphous materials with various functions are the targets of research in this laboratory. (1) To obtain a clear view of glass materials and the bases for designing functional glasses, we investigate the structure of glasses using X-ray and neutron diffraction analysis, high resolution MAS-NMR, and ab initio MO calculation. (2) To develop materials with high optical nonlinearity, we search heavy metal oxide-based glasses and transition metal oxide thin films, and evaluate the nonlinear optical properties by Z-scan methods. (3) Photosensitivity of glasses for optical fibers and waveguides is investigated to design efficient fiber gratings and optical nonlinear materials. (4) Using sol-gel method, synthesis and microstructure control are carried out on various functional oxide thin films.



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In this work, we used a cluster of atoms modeling a divalent Ge atom in silica glass (model 1, see Fig. 1a). The geometry of the ground-state singlet (S_0) structure of the cluster was fully optimized at the HF level of theory with the polarized 6-311G(d) basis set by using analytical gradient methods. All ab initio MO calculations were carried out using the GAUSSIAN 94 computer program [4] on a supercomputer CRAY T94/4128. In order to obtain excitation energies for model 1, we employed time-dependent density-functional response theory (TD-DFRT). The TD-DFRT excitation energies were calculated for the HF/6-311G(d) geometries at the Becke's 1993 hybrid exchange functional with the Lee-Yang-Parr correlation energy functional (B3LYP) level with the 6-311G(d) basis set augmented by two sets of diffuse s and p functions on Ge1. The first transition energy was calculated to be 5.29 eV, which is in reasonable agreement with the observed transition at 5.16 eV.

The high-power density irradiation such as an excimer laser results in the photo-bleaching of the 5.16-eV band. Because of the high-power density of the laser pulses, electrons in the valence orbital will be excited to the conduction band via two photon processes, and, accordingly, a positively charged defect center is expected to be formed. It is hence interesting to reoptimize the geometry of model 1 by assuming a total charge of +1 for the cluster. We did not impose any structural constraint in optimizing the geometry of this positively charged cluster, which will be referred to as model 2 (see Fig. 1b). The Ge1–O1 (1.710 Å) and Ge1–O2 (1.725 Å) bond distances in model 2 are considerably shorter than the corresponding bond distances in model 1, and there exists no substantial interaction between O2 and Ge2 in model 2. It should also be noted that the Ge1–O3 bond distance in model 2 (1.903 Å) is shorter than that in model 1 (3.038 Å), indicating that the interaction between Ge1 and O3 becomes stronger as a result of the ionization process. The atomic spin density on Ge1 in model 2 is ~0.9, and its atomic charge is larger than that in models 1a and 1b by ~0.5. Thus, the center Ge1 atom in model 2 can be regarded as a positively charged defect center, and the shorter Ge1–O3 bond mentioned above can be interpreted in terms of the stronger Coulomb interaction between Ge1 and O3 as compared with that in model 1.

What happens when this positively charged cluster is neutralized? In order to simulate such a process, we then optimized the geometry of model 2 by assuming a triplet state at the restricted open HF level. The optimized geometry of the triplet state, which we call model 3, is illustrated in Fig. 1c. It is quite interesting to note that the resultant geometry of model 3 is completely different from that of the previous clusters. We see from Fig. 3 that the distance between Ge2 and O3 tends to become wide apart, resulting in two almost equivalent GeO_3 units. The atomic spin densities for Ge1 and Ge2 in model 3 are calculated to be 0.897 and 0.882, respectively, indicating that these two GeO_3 units are unambiguously Ge E' centers.

In conclusion, the present calculations have shown that

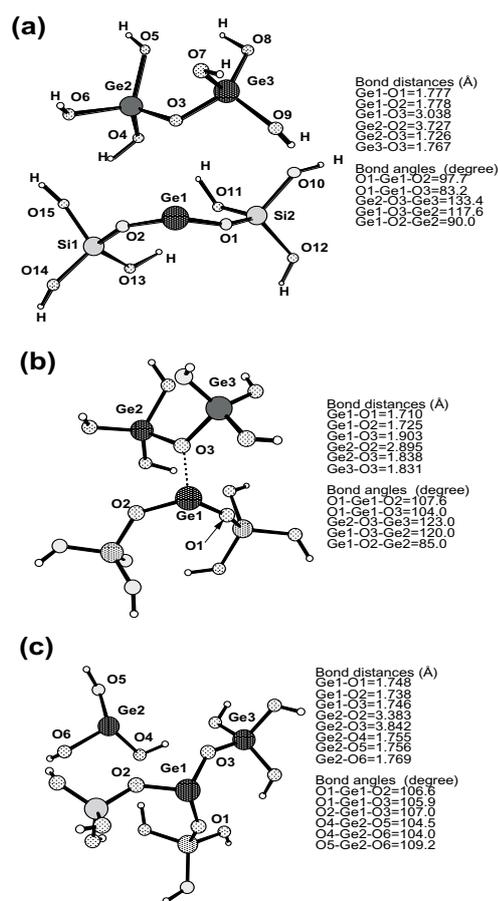


Figure 1. Equilibrium geometries for (a) a ground state singlet $\text{Ge}_3\text{Si}_2\text{O}_{15}\text{H}_{12}$, (b) a doublet ($\text{Ge}_3\text{Si}_2\text{O}_{15}\text{H}_{12}$)⁺, and (c) a triplet $\text{Ge}_3\text{Si}_2\text{O}_{15}\text{H}_{12}$ optimized at the HF/6-311G(d) level. Principal bond distances and angles are also shown.

the divalent Ge defect and its adjacent GeO_4 unit interact with each other, forming the combined structural units shown in Fig 1. We have further demonstrated that these structural units can be transformed into two equivalent GeO_3 units having an unpaired electron, namely, Ge E' centers, via positively charged defect centers. We consider that the structural conversion mechanism proposed in this study plays a vital role in the refractive index changes of Ge-doped SiO_2 glasses induced by high-power uv irradiation. More detailed results will be given in a forthcoming paper [5].

References

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