Color Centers in Sulfur-Doped Silica Glasses: Spectroscopic Manifestations of an SO₂ Interstitial Molecule

V. I. Gerasimova, A. O. Rybaltovskii, P. V. Chernov[†], and D. A. Spasskii

Skobeltsyn Research Institute of Nuclear Physics, Moscow State University, Vorob'evy gory, Moscow, 119992 Russia

Received January 23, 2002

Abstract—The photoluminescence spectra of sulfur-doped silica glass upon excitation into the absorption band at 203 nm and a temperature of 10 K are investigated. It is revealed that the photoluminescence band with a maximum at about 420 nm and the photoluminescence excitation band have a resolved vibrational structure. A model is proposed according to which the bands of absorption at 203 nm and luminescence at 420 nm are

assigned to SO₂ interstitial molecules that are weakly bound to the glass network (the transitions $\tilde{X}^1 A_1 \longrightarrow \tilde{C}^1 B_2$ and $\tilde{a}^3 B_1 \longrightarrow \tilde{X}^1 A_1$, respectively).

INTRODUCTION

Earlier [1-3], we carried out a series of spectroscopic investigations of color centers in sulfur-doped silica glasses. Our interest in these glasses was motivated both by the quest for new possible impurities, which would provide a means of controlling the optical properties of glasses, and by the prospects of producing photosensitive glasses for use in photorefractive devices of fiber optics. Optical fibers based on glasses with a high photosensitivity are widely used in laser writing of space refractive-index gratings. One of the most efficient methods of controlling the photosensitivity of glasses, in our opinion, is the introduction of dopants. In this respect, the search for new doping impurities is of considerable importance. In our recent work [4], we reported on the fabrication of a sulfurdoped silica glass optical fiber with small optical losses, in which we succeeded in writing the Bragg grating of the refraction index $\Delta n = 7.8 \times 10^{-4}$.

Furthermore, it turned out that, among color centers in glasses, the color centers induced in sulfur-doped silica glasses stand out for their unique spectroscopic properties. In particular, almost all the bands of absorption and luminescence attributed to these centers are characterized by an anomalously small inhomogeneous broadening and, hence, exhibit a well-resolved vibrational structure [1–3]. The latter circumstance made it possible to establish reliably their nature. We assigned the absorption band at 280 nm and the photoluminescence band at 385 nm to an S_2 interstitial molecule (the

transitions $X^3 \sum_{g}^{-} \longrightarrow B^3 \sum_{u}^{-}$ [1], whereas the absorp-

tion bands at 237 and 400 nm were attributed to an S_2^+ interstitial molecular ion (the transitions $X^2\Pi_{g,r} \longrightarrow B^2 \sum_{g}^{-}$ and $X^2\Pi_{g,r} \longrightarrow A^2\Pi_{u}$, respectively) [2]. In both cases, the molecules occupy pores in the glass network and are weakly bound to it: the interaction of molecules with the glass network is reduced to their collisions with pore walls [3].

Among the dominant absorption bands of sulfurdoped silica glasses, the band at 203 nm remains unidentified. Our attempts to resolve the vibrational structure of this band at room temperature have failed. The aim of the present work was to investigate this band thoroughly and to elucidate the nature of the relevant color center.

SAMPLES AND EXPERIMENTAL TECHNIQUE

The experiments were carried out with the same preforms for drawing of optical fibers with a sulfur-doped core as was used in [1]. The preforms were synthesized at 1200°C by the plasma chemical technique described earlier in [5] and were then treated in a dry oxygen atmosphere. The experimental samples were prepared in the form of 1-mm-thick disks cut out normally to the preform axis. The sulfur-doped region had the form of a pink ring with diameters of 3.5 and 2 mm. The sulfur content in this region was approximately equal to 0.05 wt %, which corresponds to 2×10^{19} atoms/cm³.

The optical absorption spectra were recorded according to the procedure described in [1]. However, in our case, the diaphragm (d = 1 mm) limiting the probe optical beam was positioned not in the region of the pink ring but at the center of the sample, where the

[†] Deceased.

intensity of the absorption band at 203 nm reaches a maximum [4].

The luminescence and luminescence excitation spectra were recorded on a SUPERLUMI setup in a synchrotron radiation channel of a DORIS III positron accelerator in a DESY synchrotron (II Institute of Experimental Physics, Hamburg University, Germany). The measurements were performed under ultrahigh vacuum $(10^{-9}-10^{-10}$ Torr) at a temperature of 10 K. The luminescence excitation spectra were recorded in the range 190–350 nm with a spectral resolution of 0.4 nm and were corrected for the channel spectral radiance, which was determined from the signal of a phosphor (sodium salicylate) with a constant quantum yield of luminescence. The photoluminescence spectra were measured in the range 350–550 nm with a spectral resolution of 2 nm.

RESULTS

The absorption spectrum of the initial sulfur-doped silica glass, which was measured in the central part of the sample, is displayed in Fig. 1 (curve 1). As can be seen from Fig. 1, the width of the absorption band at 203 nm is equal to 27 nm (0.8 eV) and, at room temperature, this band has no resolved vibrational structure. In an attempt to resolve this structure, we carried out spectral measurements at liquid-helium temperature.

The photoluminescence spectrum of the central part of the initial sample, which was recorded at a temperature of 10 K upon excitation into the absorption band at 203 nm (Fig. 2, curve 1), exhibits a photoluminescence band with the maximum at about 420 nm. This band is characterized by a large Stokes shift with respect to the excitation wavelength and a clearly pronounced vibrational structure. In order to determine the locations of the maximum number of vibrational components of the photoluminescence band, we used the same procedure of mathematical treatment as was applied in [1]. The experimental spectrum was smoothed according to the Savitzky–Golay algorithm, and the smoothed spectrum was subtracted from the experimental spectrum. The spectrum of oscillations of the photoluminescence band (Fig. 2, curve 3) contains a series of 10 vibrational components with gradually varying intensities and a mean step of 550 cm⁻¹.

The photoluminescence excitation spectrum with the maximum at about 420 nm, which was recorded at 10 K, is shown in Fig. 3 (curve 1). In this case, the photoluminescence excitation band coincides in location and width with the absorption band at 203 nm but has a clearly defined vibrational structure. With the use of the same mathematical procedure [1], we obtained the spectrum of oscillations of the photoluminescence excitation band. This spectrum contains 24 well-distinguishable vibrational components with an irregular step and a nonuniform intensity distribution (Fig. 3, curve 3).



Fig. 1. Absorption spectra of (1) sulfur-doped silica glass (T = 300 K) and (2) gaseous SO₂ [8, 9].



Fig. 2. Luminescence spectrum of sulfur-doped silica glass ($\lambda_{\text{exc}} = 203 \text{ nm}, T = 10 \text{ K}$): (1) experimental spectrum, (3) oscillations of the experimental spectrum, and (2) phosphorescence spectrum of the SO₂ molecule (T = 20 K) in the matrix of solid krypton [10].

DISCUSSION

In our previous work [4], we already reported on the band at 203 nm in the absorption spectrum of sulfurdoped silica glass. It was found that the intensity of this band reaches a maximum in the region close to the central part of the studied samples (0.5 mm) rather than in the pink ring, as is the case with the bands attributed to the S₂ molecule and the S⁺₂ molecular ion [2, 4]. Since the color centers responsible for the band at 203 nm were observed in the oxygen-enriched region, we assumed that these centers are the SO molecules formed upon oxidation of S₂ molecules [4]. The model, which assigned the band at 203 nm to the transition



Fig. 3. Excitation spectrum of sulfur-doped silica glass $(\lambda_{\text{exc}} = 390 \text{ nm}, T = 10 \text{ K})$: (1) experimental spectrum, (3) oscillations of the experimental spectrum, and (2) absorption spectrum of gaseous SO₂ [8, 9].

 $X^3 \Sigma^- \longrightarrow B^3 \Sigma^-$ in the SO molecule, offered a satisfactory explanation of the location and width of this band until we obtained the experimental data on the photoluminescence.

The photoluminescence observations provided additional information, according to which the model of the SO molecule proved to be inapplicable for describing the properties of the absorption band at 203 nm. First, the excitation into the absorption band at 203 nm (the transition $X \rightarrow B$) should lead to the progression of photoluminescence lines in the vicinity of 320 nm (the transition $B \longrightarrow X$) with the vibrational frequency $\omega_e = 1149 \text{ cm}^{-1}$ [6, 7]. In our case, the photoluminescence is observed at about 420 nm with a mean step of 550 cm⁻¹ (Fig. 2, curve 1). Second, the photoluminescence excitation spectrum of the SO molecule (the transition $X \longrightarrow B$) should exhibit a progression of vibrational lines with $\omega_e = 630 \text{ cm}^{-1}$ and gradually varying intensities. The experimental spectrum shows a system of oscillation, which is characterized by an irregular step (on average, 350 cm⁻¹) and an irregular intensity distribution.

The irregular intensity distribution of vibrational components of the photoluminescence excitation band directly indicates that the color centers responsible for this band belong not to a diatomic molecule with a one vibrational frequency but to a polyatomic molecule whose vibrational spectrum is formed by a combination of three vibrational frequencies. It is this reason why we attempted to identify this color center with the SO₂ molecule. It turned out that all the specific features of the spectra of this color center coincide with those of the spectra obtained. First, the profile of the absorption band at 203 nm (Fig. 1, curve *I*) coincides in location and shape with the absorption band of gaseous sulfur dioxide (the transition $\tilde{X}^1 A_1 \longrightarrow \tilde{C}^1 B_2$) [8, 9], which is

shown in Fig. 1 (curve 2). Second, all the 24 oscillations of the photoluminescence excitation band, which we separated, coincide in location with the vibrational lines of the absorption band at 203 nm for gaseous SO_2 (see table and Fig. 3; curves 2, 3). Third, the location and intensity distribution of the observed progression of the photoluminescence lines agree well with those of the progression in the phosphorescence spectrum of the

SO₂ molecule (the transition $\tilde{a}^3 B_1 \longrightarrow \tilde{X}^1 A_1$) in the matrix of solid krypton (Fig. 2, curves 2, 3) [10]. The coincidence of locations of the vibrational components becomes almost complete in comparison with the thermoluminescence spectrum of the SO₂ molecule in the matrix of solid argon [11] (see table). The mean difference between the corresponding frequencies is approximately equal to 30 cm⁻¹ or 0.5 nm.

The $\tilde{C}^1 B_2$ level of the SO₂ molecule is predissocia-tive; therefore, upon excitation into the absorption band associated with the transition $X \longrightarrow C$, the fluorescence and dissociation are competitive processes [12]. In the case when the excitation occurs below the predissociation energy threshold of 5.7 eV (219 nm), the observation of the resonance fluorescence becomes possible. This photoluminescence was observed in [13] upon laser pumping into the long-wavelength region of the band attributed to the transition $X \longrightarrow C$ (219.8 nm and more). For shorter wavelength excitation ($\lambda < 219$ nm), as in our experiment ($\lambda = 203$ nm), the primary dissociation of the SO₂ molecule dominates: $SO_2 \xrightarrow{hv} SO + O$. The SO molecule and atomic oxygen formed can react either with each other or with the SO_2 molecules to form SO_3 and other compounds [12]. The inverse recombination SO + O \longrightarrow SO₂^{*} \longrightarrow $SO_2(\tilde{a}^3 B_1)$ is also possible, which leads to the formation of the SO_2 molecule in the metastable *a* state. Upon transition from this state, there appears a luminescence band at 420 nm, which is associated with the transition $\tilde{a}^{3}B_{1} \longrightarrow \tilde{X}^{1}A_{1}$. In our sample, the number of chemical reactions for the SO molecule and atomic oxygen, as in the case with S_2 molecules [3], is severely limited by the fact that, for the most part, the molecules are singly located in pores of the glass. The absence of photochemical dissociation of the SO₂ molecule in the glass is also confirmed by the fact that the intensity of the band at 203 nm remains almost unchanged under the action of an ArF laser ($\lambda = 193$ nm) [4].

The proposed model provides an explanation for the large Stokes shift of the photoluminescence band (420 nm) of the glass with respect to the photoluminescence excitation band (203 nm). This shift is associated with the energy losses through the dissociation of the SO_2 molecules with subsequent recombination into the metastable state.

Comparison of the locations (cm⁻¹) of lines in the progressions of absorption ($\tilde{X} \longrightarrow \tilde{C}$) and emission ($\tilde{a} \longrightarrow \tilde{X}$) of the SO₂ molecule

Absorption			Emission		
no.	gas [8, 9]	glass	vibrational numbers $(V_1^{"}, V_2^{"}, V_3^{"})$	Ar matrix [11]	glass
1		43573	(000)	25439	25523
2		43956	(010)	24913	24944
3	44267	44326	(100)	24301	24331
4	44623	44643	(110)	23770	23787
5	44944	44964	(120)(200)	23191	23218
6	45351	45351	(130)(210)	22660	22660
7	45725	45746	(140)(220)(300)	22114	22095
8	46104	46125	(150)(230)(310)	21561	21566
9	46447	46447		21017	21030
10	46794	46838		20492	20500
11	47237	47170			
12	47596	47551			
13	47962	47939			
14	48379	48286			
15	48733	48685			
16	49116	49020			
17	49505	49334			
18	49850	49727			
19	50125	50125			
20	50632	50479			
21	50942	50813			
22	51256	51335			
23	51652	51652			
24	51975	52029			

Within the above model, it is possible to estimate the concentration of SO₂ interstitial molecules in the studied glass from the ratio of the absorption coefficients for the gas and glass (Fig. 1). The estimation gives a value of 3×10^{18} cm⁻³. On this basis, the oscillator strength (f = 0.06) for the absorption band at 203 nm was estimated from the Smakula formula.

CONCLUSIONS

The photoluminescence of the sulfur-doped silica glass upon excitation into the absorption band at 203 nm was investigated. It was demonstrated that the photoluminescence band at 420 nm and the photoluminescence excitation band have a resolved vibrational structure at a temperature of 10 K. According to the proposed model, these bands were attributed to transitions of SO₂ interstitial molecules. This model accounts

GLASS PHYSICS AND CHEMISTRY Vol. 29 No. 3 2003

for all specific features of the observed spectra, including the large Stokes shift in the photoluminescence.

Moreover, we estimated the concentration of SO_2 molecules (3 × 10¹⁸ cm⁻³) in the studied glass and the oscillator strength for the absorption band at 203 nm (0.06).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 00-02-17400 and 00-15-96679.

REFERENCES

 Zavorotny, Yu.S., Lutsko, E.V., Rybaltovskii, A.A., Chernov, P.V., Sokolov, V.O., and Khrapko, R.R., Color Centers in Sulfur-Doped Silica Glass: Spectroscopic Manifestations of an Interstitial Molecule S₂, *Fiz. Khim.* *Stekla*, 2001, vol. 27, no. 4, pp. 495–502 [*Glass Phys. Chem.* (Engl. transl.), 2001, vol. 27, no. 4, pp. 331–336].

- 2. Gerasimova, V.I., Zavorotny, Yu.S., Rybaltovskii, A.O., Chernov, P.V., Sazhin, O.D., Khrapko, R.R., and Frolov, A.A., Color Centers in Sulfur-Doped Silica Glasses: Spectroscopic Manifestations of an S_2^+ Interstitial Molecular Ion, *Fiz. Khim. Stekla*, 2002, vol. 28, no. 1, pp. 8–16 [*Glass Phys. Chem.* (Engl. transl.), 2002, vol. 28, no. 1, pp. 5–10].
- Gerasimova, V.I., Rybaltovskii, A.O., Chernov, P.V., and Zimmerer, G., The Influence of Silica Glass Matrix on the Spectra of Interstitial Molecules S₂, *Fiz. Khim. Stekla*, 2002, vol. 28, no. 2, pp. 89–98 [*Glass Phys. Chem.* (Engl. transl.), 2002, vol. 28, no. 2, pp. 59–65].
- Gerasimosa, V.I., Rybaltovskii, A.O., Chernov, P.V., Mashinsky, V.M., Sazhin, O.D., Medvedkov, O.I., Rybaltovskii, A.A., and Khrapko, R.R., Sulfur-Doped Silica Glass Optical Fibers, *Kvantovaya Elektron*. (Moscow), 2003, vol. 33, no. 1, pp. 90–94.
- Dianov, E.M., Golant, K.M., Karpov, V.B., Khrapko, R.R., Kurkov, A.S., Mashinsky, V.M., and Protopopov, V.N., Fluorine-Doped Silica Optical Fibers Fabricated Using Plasma Chemical Technologies, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1994, vol. 2425, pp. 53–57.
- 6. Huber, K.-P. and Herzberg, G., *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules*, New York: Van Nostrand, 1979. Translated under the title *Konstanty dvukhatomnykh molekul*, Moscow: Mir, 1984, part 2.

- 7. Miller, H.C., Yamasaki, K., Smedley, J.E., and Leone, S.R., An Optically Pumped Ultraviolet Laser on SO $(B^3 \sum_{g}^{-} \longrightarrow X^3 \sum_{u}^{-})$, *Chem. Phys. Lett.*, 1991, vol. 181, nos. 2–3, pp. 250–254.
- Warneck, P., Marmo, F.F., and Sullivan, J.O., Ultraviolet Absorption of SO₂: Dissociation Energies of SO₂ and SO, *J. Chem. Phys.*, 1964, vol. 40, no. 4, pp. 1132–1136.
- Golomb, D., Watanabe, K., and Marmo, F.F., Absorption Coefficients of Sulfur Dioxide in the Vacuum Ultraviolet, J. Chem. Phys., 1962, vol. 36, no. 4, pp. 958–960.
- Phillips, L.F., Smith, J.J., and Meyer, B., The Ultraviolet Spectra of Matrix Isolated Disulfur Monoxide and Sulfur Dioxide, *J. Mol. Spectrosc.*, 1969, vol. 29, pp. 230– 243.
- Randolph Long, S. and Pimentel Georg, C., Chemiluminescent Reactions of Sulfur (³P₂) Atoms in Cryogenic Matrices S + O₂ → SO₂ (ã³ B₁), J. Chem. Phys., 1977,

vol. 66, no. 5, pp. 2219–2220.
12. Okabe, H., *Photochemistry of Small Molecules*, New York: Wiley, 1978.

Parson, B., Butler, L.J., Xie, D., and Guo, H., A Combined Experimental and Theoretical Study of Resonance Emission Spectra of SO₂ (*C*¹ *B*₂), *Chem. Phys. Lett.*, 2000, vol. 320, pp. 499–506.