

A Model for Triboluminescence from Fracture Surfaces of Silica Glass*

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Mechanisms of triboluminescence of silica glass are discussed from a theoretical viewpoint on the basis of several experimental reports on triboluminescent spectra of a variety of silica glasses. Until now, two different mechanisms have been proposed for triboluminescence of silica glass. Triboluminescent spectra with a single peak were regarded as the emission from a black-body radiator, but spectra with two peaks were interpreted as the emission from defect centers. We here propose a model for explaining the two types of triboluminescent spectra reported in silica glass. In our model, triboluminescence of silica glass is due to the emission from defect centers near fracture surfaces. Radiative relaxation of electronic states on these defects would explain the two types of triboluminescent spectra reported in silica glass. Triboluminescent spectra of silica glass depend on fracture methods which influence disorder in atomic configuration near fracture surfaces. [DOI: 10.1380/ejsnt.2015.159]

Keywords: Surface electronic phenomena; Glass surfaces; Surface defects; Semi-empirical models and model calculations; Triboluminescence; Fracture surfaces; Silica glass

I. INTRODUCTION

Triboluminescence is light emission caused by fracture of a material. It can be observed when a material is crushed, scratched, or rubbed. Although triboluminescence has long been known, its mechanism has not yet been made clear because the structure and electronic states near fracture surfaces are almost unknown. Different mechanisms, such as gas-discharge luminescence, thermal radiation and emission from defects, have been proposed for different materials [1].

Some information on fracture surfaces has been obtained from observations of fractoemission, that is, the emission of electrons, atoms, molecules and photons from fracture surfaces. The measurements of fractoemission for a variety of materials [2-6] have shown that fracture surfaces are in highly-excited states and involve complex nonequilibrium processes. The emission of high-energy electrons of a few hundred eV was observed after fracture of several materials [2]. The experiment of peeling adhesive tape has shown that electromagnetic radiations extending even to X-ray energies are observed from peeled surfaces of the tape [7].

In the first place, the mechanism of energy-excitation by fracture has not yet been understood. Very little is known about excited states of atoms and electrons near fracture surfaces. Because triboluminescence is one of the energy-relaxation processes which occur after energy-excitation processes near fracture surfaces, we have to grope in the dark in the study of the mechanism of triboluminescence on the basis of limited experimental information.

We here consider triboluminescence of silica glass, for which triboluminescent spectra have been reported by several researchers [8-12]. After briefly reviewing the characteristics of reported triboluminescent spectra of silica glasses and proposed mechanisms, we will propose a

model for triboluminescence of silica glass which would explain the reported spectra. Experimental and theoretical subjects for the future will also be given.

II. PRESENT SITUATION

Triboluminescent spectra of silica glass have been measured by several researchers who fractured glasses using different methods. Two models for explaining the observed spectra have been proposed: the thermal radiation model and the defect model. We here review the characteristics of the reported spectra, the two models, and some related subjects.

Chapman and Walton [8] measured triboluminescent spectra of a variety of glasses while specimens were cut with a rotating diamond-impregnated saw blade in air. The spectra were broad bands in the visible region between 400 and 800 nm and have a maximum around 600 nm. They regarded the broad spectra as black-body radiation emitted from crack tips. Emission temperatures estimated by comparing the measured spectra with black-body spectra were between 1800 and 2700 K for different glasses. The high temperature region was considered to be caused by the release of plastic deformation energy at the tips of growing cracks.

Recently, Pallares *et al.* [9] performed triboluminescence experiments on two kinds of silicate glasses. They cleaved specimens with precracks by compression in a bath of dodecane oil. The broad spectra measured between 400 and 1000 nm had a maximum around 700 nm. They interpreted the spectra as black-body radiation from plastic zones at crack tips, as Chapman and Walton [8] did. A crack velocity-dependent temperature rise was considered to occur in the zones. The estimated crack velocity was 1300 m/s and the estimated temperatures of the zones were 4000 to 5000 K.

Zink *et al.* [10] measured triboluminescent spectra by cutting three kinds of silica core optical fibers. The spectra contained two prominent peaks between 300 and 700 nm, one at 430 nm and the other at 630 nm. The relative intensities of the two peaks varied with fiber type. They ascribed the two peaks in the spectra to two different de-

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fect centers. The band around 430 nm was assigned to the emission from the E' center and the nonbridging oxygen hole center on the basis of photoluminescence bands in bulk silica glass, and the band around 630 nm was regarded as the emission from defect centers created by fracture.

Kawaguchi [11, 12] investigated time-resolved triboluminescent spectra of silica glass by three-point bending fracture in vacuum and nitrogen atmosphere. The time-integrated spectrum between 400 and 750 nm had two peaks, one at 450 nm and the other at 650 nm, being similar to the spectra observed by Zink *et al.* [10]. The 650-nm band first rose within 500 ns after fracture and decayed at around 100 μ s. The 450-nm band rose at about 50 μ s and decayed in the order of 10 ms. They attributed the two emission bands in the spectrum to surface defect centers. The 650-nm band was assigned to the emission from the nonbridging oxygen hole center and the 450-nm band to the emission from the oxygen deficiency center on the basis of assignments in photoluminescent spectra of bulk silica glass.

The triboluminescent spectra reported to date have shown that light emissions are observed between 300 and 1000 nm. However, two types of spectra have been observed, namely the spectra with a single and two peaks. A basic subject is whether triboluminescence of silica glass is due to the thermal radiation or the emission from defects. Both the two models have some problems.

In the thermal radiation model, light is emitted from the front of a propagating crack. However, there has been no experimental evidence of emission from the front of a crack. Triboluminescence may occur on fracture surfaces excited by bond breakings. Although the observed broad spectra with a single peak roughly resemble black-body spectra, the curves of the spectra are not the same. Chapman and Walton [8] compared the measured spectra with black-body spectra in the ranges from 460 to 550 nm and from 550 to 700 nm. Pallares *et al.* [9] fitted the measured spectra to black-body spectra in the domain of 400-700 nm or 400-600 nm. The estimated temperatures of 4000-5000 K seem to be too high as compared to the melting point of 1900 K and the boiling point of 2500 K of quartz.

In the defect model, light is emitted from defects near fracture surfaces. However, there is little experimental information on what defects are created near fracture surfaces. Helpful information comes from photoluminescent spectra of bulk silica glass. Zink *et al.* [10] and Kawaguchi [11, 12] assigned the two bands in the observed spectra on the basis of assignments of defects in photoluminescence of bulk silica glass. If triboluminescence of silica glass is due to two kinds of defects created by fracture, the spectra with a single peak, as well as that with two peaks, should be explained in terms of defects near fracture surfaces.

III. MODEL SPECTRA

We here propose a model for explaining the two types of triboluminescent spectra reported in silica glass: the spectra with a single peak and two peaks. We take the position that defect centers created near fracture surfaces would cause light emission because the spectra with two peaks cannot easily be explained by the thermal radiation

TABLE I. The peak energy (wave length) and the full width at half maximum (FWHM) of photoluminescence bands in bulk silica glass, that are related to NBOHC and ODC [13, 14].

	Peak energy (Wave length)	FWHM
NBOHC	1.9 eV (650 nm)	0.1 - 0.2 eV
ODC	2.7 eV (450 nm)	0.1 - 0.5 eV

model.

Since there is little experimental information on defects created by fracture, we make use of information on defects in bulk silica glass which are created by electron-beam, X-ray, or γ -ray irradiation. These irradiations generate a variety of defects [13, 14]. Silica glass is composed of the network of $\equiv\text{Si}-\text{O}-\text{Si}\equiv$; one oxygen atom bridges two silicon atoms. Our scenario for triboluminescence of silica glass is the following sequence of events. Fracture will mostly generate two kinds of defects, $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ and $\equiv\text{Si}-\text{O}-\text{Si}\equiv$, near fracture surfaces. The former is created by breaking one Si-O bond, and the latter by breaking two Si-O bonds of oxygen. An oxygen atom in the latter is released thereafter. Then the two kinds of defects result in $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ and $\equiv\text{Si}-\text{Si}\equiv$. The bonding electrons of the broken bonds will be excited to localized excited-states on the defects or extended states on fracture surfaces. Highly-excited bonding electrons may be emitted, as fractoemission, from fracture surfaces.

Surface relaxation will result in $\equiv\text{Si}\cdot + \cdots \text{O}-\text{Si}\equiv$ and $\equiv\text{Si}\cdots\text{Si}\equiv$, where the mark $\cdots$ denotes that electrons excited by bond breaking have been captured into excited states localized on the defects. The defect center $\cdots\text{O}-\text{Si}\equiv$ is called the non-bridging oxygen hole center (NBOHC), $\equiv\text{Si}\cdots\text{Si}\equiv$ the oxygen deficiency center (ODC) and $\equiv\text{Si}\cdot$ the E' center in the context of defect centers in bulk silica glass. Then we would suppose that triboluminescence will be caused by radiative transitions from an excited state to the ground state on NBOHC and ODC. Since photoluminescence bands associated with the E' center have not been observed in bulk silica glass [13], the E' center is not considered to be associated with triboluminescence. Finally, after the radiative transitions, NBOHC and ODC would result in $\cdot\text{O}-\text{Si}\equiv$ and $\equiv\text{Si}-\text{Si}\equiv$.

The characteristics of NBOHC and ODC have been investigated in the context of photoluminescence of silica glass [13-19]. Table I shows the peak energy (wave length) and the full width at half maximum (FWHM) of photoluminescence bands in bulk silica glass, which are related to NBOHC and ODC. The electronic states associated with radiative transition have been investigated by several researchers. The ground state on ODC has paired spins. The *ab initio* molecular-orbital calculations by Tohmon *et al.* [20] showed that 2.7-eV luminescence in bulk silica glass is due to the transition from a triplet excited state to the singlet ground state of a neutral ODC. The ground state on NBOHC has an unpaired spin that can be detected by electron spin resonance. The electronic states associated with radiative transition are those of a dangling bond of an oxygen atom in $\cdot\text{O}-\text{Si}\equiv$ [21-23].

We consider triboluminescent spectra by calculating the emission intensity owing to NBOHC and ODC. We use the values in Table I as the values of the peak energies of

emission bands. The FWHM of each band is influenced by two causes: homogeneous broadening that is related to electron-phonon interaction and inhomogeneous broadening that is due to structural disorder around a defect. The FWHM associated with NBOHC and ODC in Table I has been estimated from photoluminescent bands in bulk silica glasses at room temperature. Triboluminescence is usually measured at room temperature, but fracture surfaces are in excited states corresponding to higher temperatures than room temperature. Also defects created near fracture surfaces may have larger disorder in atomic configuration than defects in bulk. Therefore we may assume that FWHM of triboluminescent bands is larger than that of photoluminescent bands in bulk silica glasses. Thus we here vary the values for FWHM of NBOHC and ODC created near fracture surfaces between 0.1 and 0.5 eV.

We here assume that the emission energy E is given by the normal distribution. The emission intensity is then

$$I(E) = I_0 \frac{1}{D\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{E-E_0}{D}\right)^2}, \quad (1)$$

$$\int_0^\infty I(E) dE = I_0,$$

where the mean value E_0 corresponds to the peak energy and the standard deviation D to FWHM. The integrated intensity I_0 is proportional to the defect density. The emission intensity for wave length is given by

$$J(\lambda) = I_0 \frac{1}{D\sqrt{2\pi}} \frac{hc}{\lambda^2} e^{-\frac{1}{2}\left(\frac{hc}{D}\right)^2 \left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)^2}, \quad (2)$$

where $\lambda_0 = hc/E_0$, h is Planck's constant and c is the speed of light. Since the ratio of the integrated intensities of NBOHC and ODC is equal to the ratio of defect densities n of the two defects, we define the ratio n_r as

$$n_r \equiv \frac{I_0^{\text{ODC}}}{I_0^{\text{NBOHC}}} = \frac{n^{\text{ODC}}}{n^{\text{NBOHC}}}. \quad (3)$$

Then the total emission intensity is given by

$$J(\lambda) = J_N(\lambda) + J_O(\lambda), \quad (4)$$

$$J_N(\lambda) = I_N \frac{1}{D_N\sqrt{2\pi}} \frac{hc}{\lambda^2} e^{-\frac{1}{2}\left(\frac{hc}{D_N}\right)^2 \left(\frac{1}{\lambda} - \frac{1}{\lambda_N}\right)^2}, \quad (5)$$

$$J_O(\lambda) = n_r I_N \frac{1}{D_O\sqrt{2\pi}} \frac{hc}{\lambda^2} e^{-\frac{1}{2}\left(\frac{hc}{D_O}\right)^2 \left(\frac{1}{\lambda} - \frac{1}{\lambda_O}\right)^2}, \quad (6)$$

where we have used abbreviated notations, N and O, for NBOHC and ODC.

The parameters for calculating the total emission intensity are E_N , E_O , D_N , D_O and n_r . A reasonable value for n_r is 0.5 because the energy for breaking two Si-O bonds for ODC is roughly twice of that for breaking one Si-O bond for NBOHC. When we set that $E_N = 1.9$ eV and $E_O = 2.7$ eV, we can calculate the total emission intensity with two parameters, D_N and D_O . These parameters are varied between 0.1 and 0.5 eV.

We here show three typical results of triboluminescent spectra given by the total emission intensity of eq. (4).

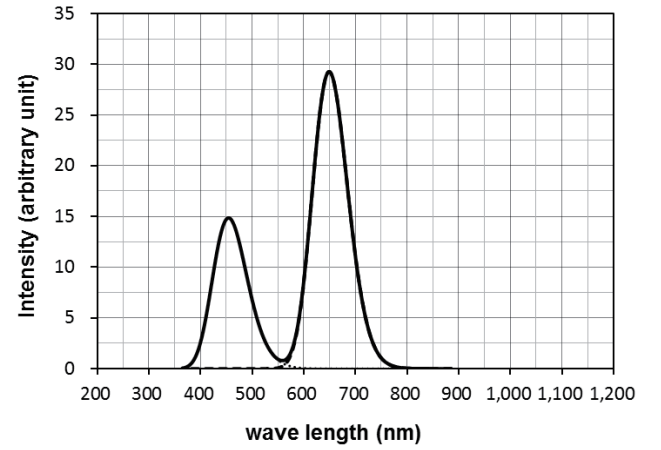


FIG. 1. The calculated triboluminescent spectrum showing two separate bands: the spectrum for $n_r = 0.5$, $D_N = 0.1$ eV and $D_O = 0.2$ eV. The dashed and dotted curves are the bands of NBOHC and ODC, respectively.

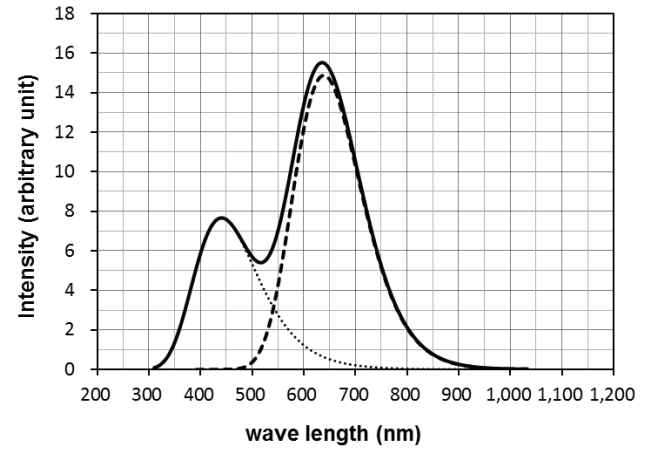


FIG. 2. The calculated triboluminescent spectrum showing two overlapping bands: the spectrum for $n_r = 0.5$, $D_N = 0.2$ eV and $D_O = 0.4$ eV. The dashed and dotted curves are the bands of NBOHC and ODC, respectively.

Figure 1 shows the spectrum for $n_r = 0.5$, $D_N = 0.1$ eV and $D_O = 0.2$ eV. In this case, two bands of NBOHC and ODC are separated with slight overlap. Figure 2 shows the spectrum for $n_r = 0.5$, $D_N = 0.2$ eV and $D_O = 0.4$ eV. In this case, the two bands overlap, but still showing two peaks. Figure 3 shows the spectrum for $n_r = 0.5$, $D_N = 0.4$ eV and $D_O = 0.4$ eV. In this case, the two bands overlap largely and the spectrum shows one peak. Thus, we can obtain both the two types of triboluminescent spectra of silica glass, the two-peak and one-peak spectra, in the reasonable range of band width for triboluminescent bands in silica glass.

IV. DISCUSSION

Our model spectra have been calculated on the assumption that defects created near fracture surfaces are the same as defects assigned in photoluminescence in bulk silica glass and that there is large disorder in atomic con-

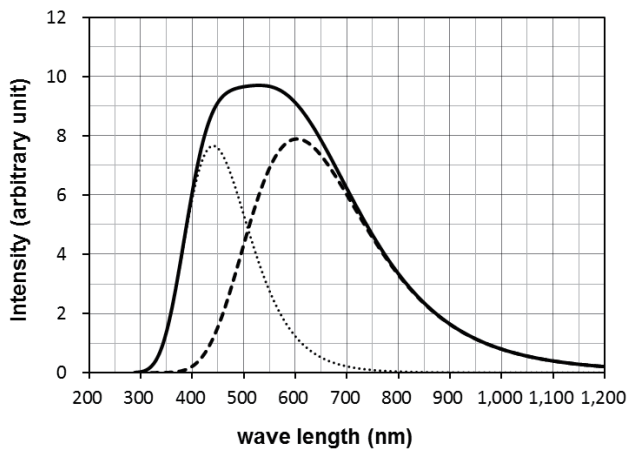


FIG. 3. The calculated triboluminescent spectrum showing a broad band: the spectrum for $n_r = 0.5$, $D_N = 0.4$ eV and $D_O = 0.4$ eV. The dashed and dotted curves are the bands of NBOHC and ODC, respectively.

figuration around defects near fracture surfaces. We here discuss the relation between fracture methods and atomic configuration around defects created near fracture surfaces. Although one cannot control excitation processes near fracture surfaces, we will be able to speculate about the degree of excitation near fracture surfaces, which depends on fracture methods.

If we cut specimens using a method such as a rotating saw blade, then created fracture surfaces will be highly excited. Many electrons, ions and atoms will be emitted from the excited fracture surfaces, and the emitted particles will bombard the fracture surfaces. As a result, fracture surfaces generated by such a relatively-violent fracture method will have large disorder in atomic configuration. Thus there may be large structural disorder around ODC and NBOHC near fracture surfaces. This results in wide triboluminescent bands of these defects. This case corresponds to broad spectra as Chapman and Walton [8] observed. In the method used by Pallares *et al.* [9], that is, the cleavage of specimens with precracks by compression, opened fracture surfaces are face to face. Then electrons, ions and atoms emitted from a fracture surface will hit the opposite surface. This case also results in wide triboluminescent bands of the two kinds of defects. Thus, relatively-violent fracture methods, in which particles emitted from a fracture surface bombard the opposite

surface, would result in broad triboluminescent spectra owing to band overlap of ODC and NBOHC, as shown in Fig. 3.

On the other hand, the method used by Kawaguchi [11, 12] is the three-point bending fracture. In this method created fracture surfaces tend to separate without facing each other. Therefore, electrons, ions and atoms emitted from fracture surfaces will not bombard the fracture surfaces severely. This results in relatively small structural disorder around ODC and NBOHC near fracture surfaces, thus narrow bands of triboluminescence of the two kinds of defects. This leads to a spectrum with two separate bands, as shown in Fig. 1 and observed by Kawaguchi [11, 12]. Three triboluminescent spectra of silica core optical fibers observed by Zink *et al.* [10] showed different degrees of overlap of two bands among three kinds of fibers. However, we here cannot discuss the difference in spectrum among the three kinds of fibers because the difference in quality of these fibers is not made clear.

The triboluminescent spectra owing to ODC and NBOHC depend on the density ratio of the two defects in eq. (3). We have set $n_r = 0.5$ for calculating spectra as shown in Figs. 1-3. Until now there is little experimental information on this ratio. It is expected in the future that we can have experimental information on the densities of defects near fracture surfaces using different fracture methods. The measurement of time-resolved triboluminescent spectra of silica glass by relatively-violent fracture methods is needed to confirm that broad spectra with a single peak are composed of at least two bands owing to different defects. Detailed theoretical study of electronic states and energy levels on ODC and NBOHC near fracture surfaces is also needed for understanding the mechanism of triboluminescence in silica glass.

In summary, we have discussed two types of triboluminescent spectra of silica glass and two models proposed to date. From model calculations based on the defect model, we have shown that the two types of spectra can be understood in terms of emission bands owing to two kinds of defects created near fracture surfaces.

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