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Full Length Article

Photon emission induced by brittle fracture of borosilicate glasses

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ABSTRACT

Photon emission (PE) at wavelength ranges of 430–490 nm (B-PE), 500–600 nm (G-PE) and 610–680 nm (R-PE) caused by brittle fracture was simultaneously measured in the nanosecond-to-microsecond and millisecond time domains for two types of borosilicate glasses: Pyrex-type Tempax glass and BK7 glass. The results were compared to those for silica and soda lime glasses. The time dependence of the PE of Tempax glass was similar to that of silica glass, while the PE intensity was lower. Because Tempax glass contains both silica-rich and borate-rich amorphous phases, the PE must be mainly produced by the fracture of the silica-rich phase. Moreover, the proportion of B-PE of Tempax glass was higher than that of silica glass. This suggests that the measured B-PE might also include very weak PE caused by the fracture of the borate-rich phase. The PE time dependence of BK7 glass was similar to that of soda lime glass, which was different from the case for Tempax glass. The PE intensity of BK7 glass was slightly higher than that of soda lime glass, but much lower than that of Tempax glass. The result indicates that non-bridging oxygen in the glasses affects crack propagation behavior and reduces the PE.

1. Introduction

Atomic-scale study of the brittle fracture of glasses is believed to be an effective approach to improve the durability of glasses [1]. However, it is difficult to use existing atom-resolved analysis methods such as atomic force microscopy and transmission electron microscopy to study brittle fracture of glasses because the time constant of observation is much slower than the rate of crack propagation. Fractoemission, which is the emission of particles such as photons, electrons, ions and neutral particles upon brittle fracture of solids, is a promising tool for atomic-scale study of brittle fracture [2]. We have studied photon emission (PE) induced by the fracture of various brittle materials including silica and soda lime glasses [3–11]. The PE characteristics of silica glass reported in our previous studies are summarized as follows:

(i) Blue PE (B-PE; 430–490 nm) with an exponential decay time of several milliseconds and red PE (R-PE; 610–680 nm) with an exponential decay time of several microseconds are observed. B-PE and R-PE are caused by relaxation of oxygen deficient centers and non-bridging oxygen hole centers (NBOHCs), respectively [5,7,10,11].

(ii) Green PE (G-PE; 500–600 nm) that might be related to interstitial oxygen ions is observed [11].

(iii) B-PE with a decay time of several hundred nanoseconds is a component of the measured B-PE. This component is associated with the radiative relaxation of self-trapped excitons [11].

Meanwhile, the PE intensity of soda lime glass is much weaker than that of silica glass [11]. We believe that this is caused by the alkali ions behaving as network modifiers. Other researchers have also reported similar PE properties for these glasses [12–15]. However, the PE of other practical glasses has not been investigated. Study of the PE of other glasses will lead to our further understanding of the PE process and also of atomic-scale brittle fracture.

Borosilicate glass is one of the glasses that have many practical uses. The structure of borosilicate glass depends on the content of boron trioxide (B_2O_3) and the role of alkali ions in borosilicate glass is different from that in soda lime glass [16–20]. In this study, the PE induced by the brittle fracture of borosilicate glasses, Pyrex-type and BK7 glasses, was measured. The PE characteristics of the borosilicate glasses were compared with those of silica and soda lime glasses to discuss the effect of the B_2O_3 phase on the PE.

2. Experimental procedure

The borosilicate glass samples were a Pyrex-type glass (Tempax FLOAT, SCHOTT Nippon K. K., Tokyo, Japan) and BK7 glass [21] (SBK7, Sumita Optical Glass, Inc., Saitama, Japan). Typical chemical

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compositions of these glasses are summarized in Table 1. Synthetic silica glass (ES grade, Tosoh Quartz Co., Tokyo, Japan) and soda lime glass [22] (Float glass, Asahi Glass Co., Ltd., Tokyo, Japan) were used as reference samples. A plate of each sample was cut into a three-point bending specimen with thickness of 3 mm, width of 2 mm and length of 25 mm. Fig. 1 depicts schematic diagrams of the experimental apparatus. The specimen was fractured by three-point bending under a high vacuum of 10^{-4} Pa at room temperature. A pusher was moved at a constant speed of 0.1 mm/s. The vacuum chamber had three observation windows each with a diameter of 23 mm that were equipped with optical bandpass filters to allow simultaneous measurement of three PE bands. In this study, the following emission bands were observed: 430–490 nm (B-PE band), 500–600 nm (G-PE band) and 610–680 nm (R-PE band). These spectral windows were identical to those in our previous study on silica and soda lime glasses [11]. The photons passing through these spectral windows were detected with photomultiplier tubes (PMTs) of type R329, R2256 and R1221 (Hamamatsu Photonics K. K., Hamamatsu, Japan) for B-PE, G-PE and R-PE, respectively, using a photon counting technique. In the measurement of the B-PE of Tempax and silica glasses, an aperture with a diameter of 10 mm was placed between the bandpass filter and PMT to avoid saturation of the PMT. The observation window area was reduced by the aperture to 19% of the original area. Both nanosecond and millisecond time-resolved measurements were obtained in this study because fast and slow decay components were found in the B-PE and G-PE of silica glass with decay time constants of less than a microsecond and several milliseconds, respectively [10,11].

Table 1
Typical chemical compositions (in molar ratio (%)) of the glasses used in this study.

	SiO_2	B_2O_3	K_2O/Na_2O	BaO	CaO	Al_2O_3	MgO
Tempax glass	81	13	4			2	
BK7 glass [21]	75	9	14	1			
Silica glass	99.9						
Soda lime glass [22]	72		12		9	1	6

The method used to obtain nanosecond time-resolved measurements has been described in detail elsewhere [10,11], but we briefly outline it here. A small triangle notch was cut at the edge in the middle of the bottom surface of the specimen. An Au thin film was coated on the top of the sample, and an Au thin film with a striped pattern was formed on the bottom surface by using DC sputtering. The specimen is shown in Fig. 2. Fast crack propagation during brittle fracture can be detected by monitoring the change of resistance of these Au thin films. The Au stripes were electrically connected in parallel, and then connected to a resistor (100 Ω) in series. A DC voltage was applied to the whole electrical circuit during fracture. Monitoring the voltage across the resistor (V_{det}) allowed us to detect the change of resistance of the Au thin films and thus measure fast crack propagation. V_{det} and the PMT outputs were simultaneously measured with a digital oscilloscope (DL7440, Yokogawa Electric Corporation, Tokyo, Japan) with a

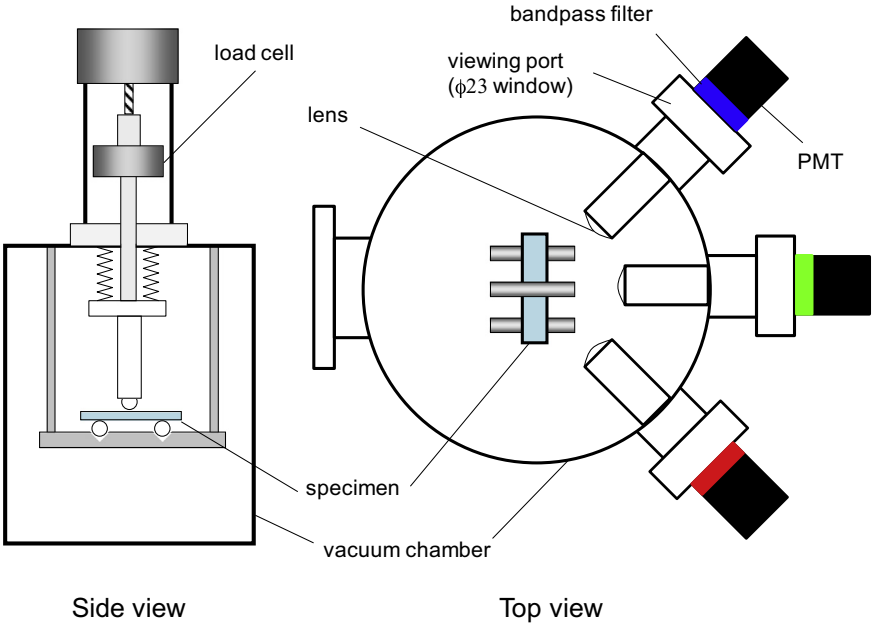

Fig. 1. Schematic diagrams of the experimental apparatus used to measure PE by brittle fracture.

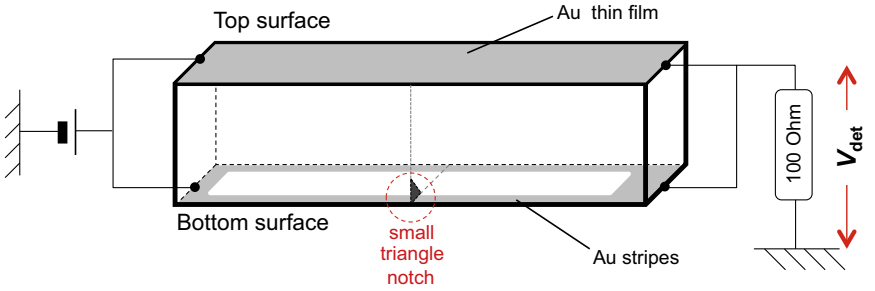

Fig. 2. Specimen used for nanosecond time-resolved measurement of PE and the electrical circuit used to detect fast crack propagation.