Bull. Inst. Chem. Res., Kyoto Univ., Vol. 63, No. 5–6, 1985

Photoconductivity of Bi_2O_3-Containing Glasses

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Received December 9, 1985

Photoconductivity was investigated for Bi_2O_3-rich glasses in the system Bi_2O_3-SiO_2-B_2O_3, a new family of photoconductive oxide glasses. All the examined glasses showed appreciable photoconductivities with the visible light. The photoconductivity was little affected by addition of CdO, In_2O_3 or PbO, but destroyed by addition of Fe_2O_3. It was considerably less than that of γ-$6Bi_2O_3 \cdot SiO_2$ crystal and a little less than that of a CdO-SiO_2-B_2O_3 glass. The light of 2.9 eV in photon energy, which corresponded to the absorption edge of the glass, was most effective in inducing photoconductivity. A time-dependent charge and discharge currents were observed in the dark at room temperature for a long time. Twice of the activation energy for the dark conduction, 2.4 eV, was appreciably less than the photon energy corresponding to the absorption edge. The dark current was little affected by oxygen pressure in the atmosphere on glass melting. Consequently, the dark current was attributed to ionic conduction, whereas the light current was attributed to electronic conduction of band-type.

KEY WORDS: Electronic conduction/ Photoconductivity/ Bi_2O_3-B_2O_3-SiO_2 glass/ Ionic conduction/

INTRODUCTION

It is well known that many glasses in chalcogenide systems show photoconductivity. In oxide systems, however, only glasses containing CdO or PbO are known to be photoconductive[1-3].

It can be expected that Bi_2O_3-containing oxide glasses are also photoconductive, in view of the fact that γ-$6Bi_2O_3 \cdot SiO_2$ crystal shows a remarkable photoconductivity[4].

In the present study, photoconductivity of Bi_2O_3-rich glasses in the system Bi_2O_3-SiO_2-B_2O_3 was investigated. These glasses have an advantage that they are free of toxic CdO.

EXPERIMENTAL

1. Glass preparation

Several workers[5-7] examined glass-forming tendencies of melts in the binary system Bi_2O_3-SiO_2, showing that $6Bi_2O_3 \cdot SiO_2$ melt does not form glass in an ordinary crucible-melting technique. No report has been published on the glass-formation in the ternary system Bi_2O_3-SiO_2-B_2O_3. Accordingly, glass-forming tendencies were examined in the present study.

About 20 g of batch mixtures prepared from reagent grade chemicals of Bi_2O_3,

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SiO_2 and B_2O_3 were melted in a 30 ml platinum crucible covered with a lid at 1200 °C for 30 min. The melts were poured onto a stainless steel plate and pressed into plates about 1 mm thick. The resultant substances were calssified into clear glass, opaque immiscible glass, partially devitrified glass, fully devitrified glass and imperfect melt by the visual observation and a powder x-ray diffracation analysis.

Out of the compositions which gave clear glasses, six compositions given in Table I were selected. Glass specimens for investigating their optical and electrical properties were newly prepared by the following method.

Batch mixtures prepared from chemicals with purity higher than 99.99 % were melted in Pt crucibles under an oxygen gas atmosphere at 1000°C for 30 min, using an electric furnace shown in Fig. 1. The oxygen gas was allowed to flow at a rate of 2 1/min. The melts were cast into a graphite mold 30 mm in diameter and 2 mm in depth, and then annealed by slowly cooling from 300°C.

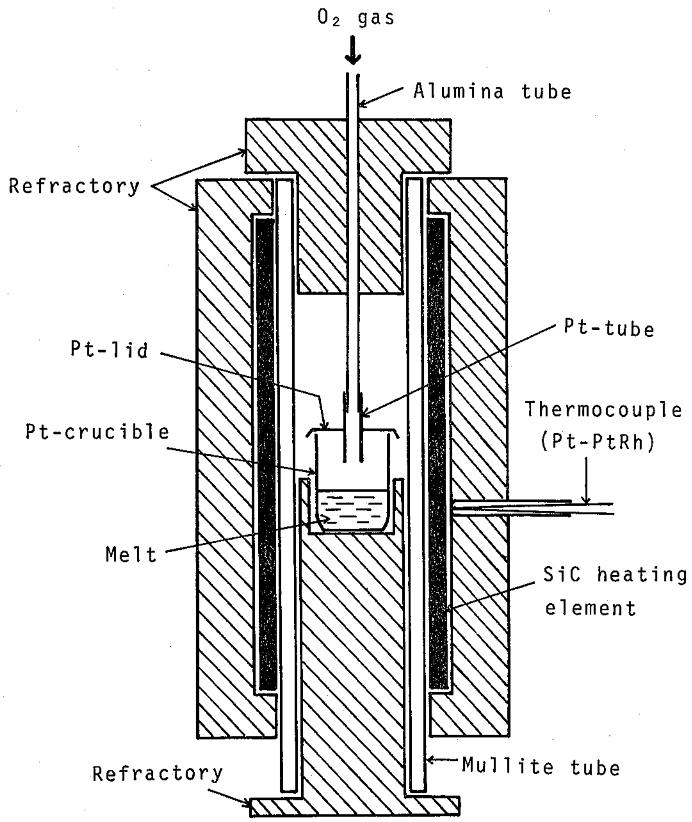


Fig. 1. Furnace for melting glass.

For camparison, glasses containing small amounts of the fourth components, nominal compositions of which are also given in Table I, were prepared by the same method.

Table I Nominal glass composition

Glass	Composition (mol %) Bi_2O_3	SiO_2	B_2O_3	
1	60.0	10.0	30.0	
2	68.6	11.4	20.0	
3	51.4	8.6	40.0	
4	60.0	20.0	20.0	
5	70.0	7.5	22.5	
6	50.0	12.5	37.5	
1–Cd	60.0	10.0	30.0	+3wt % CdO
1–In	60.0	10.0	30.0	+3wt % In_2O_3
1–Pb	60.0	10.0	30.0	+3wt % PbO
1–Fe	60.0	10.0	30.0	+3wt % Fe_2O_3

2. Measurement of optical and electrical properties

The glasses were abraded and polished to various thicknesses ranged from 0.5 to 1.4 mm.

Optical transmission spectra of the glasses of various thicknesses were measured with Hitachi 624 spectrophotometer.

Electrical properties of the glasses 0.5 to 0.7 mm thick were measured as follows. The glasses were rinsed with a distilled water and benzen. Gold electrodeds were vacuum-evaporated on both surfaces of the glasses with a guard ring annulus on one surface. The thickness of the electrode on the surface opposite to that with the guarded electrode was adjusted so that the electrode was electrically conductive and optically transparent. The optical transmission of the transparent electrodes evapo-

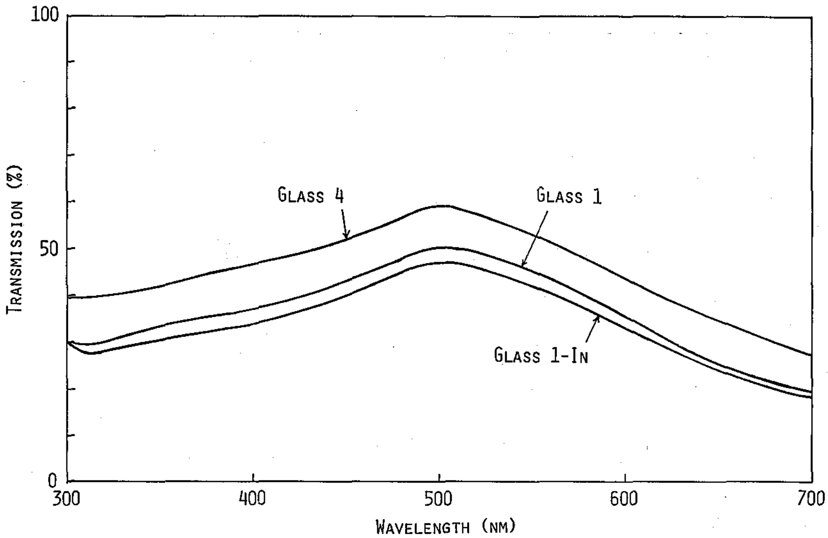


Fig. 2. Transmission spectra of transparent gold electrode evaporated on glass 1, 4 and 1–In.

rated on a few glasses are shown in Fig. 2. In these measurements, electrode-free glasses of the same composition and the same thickness were used as references. These glasses were set in a shielded light-tight box shown in Fig. 3 and left in the

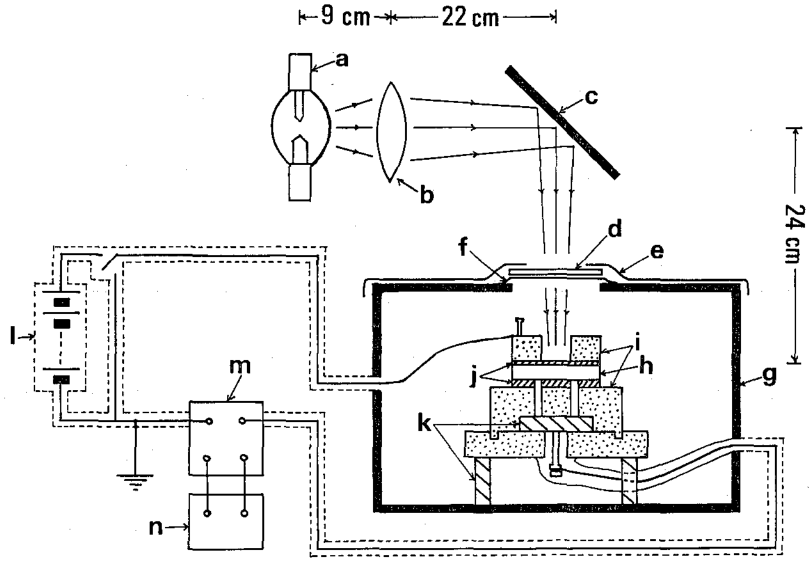


Fig. 3. Assembly for measuring photoconductivity.
a ; 500W super high pressure Hg-lamp, b ; silica glass lens (f=8 cm), c ; steel mirror, d ; heat-absorbing filter, e ; black cloth, f ; steel net, g ; steel box, h ; sample, i ; brass, j ; evaporated gold electrode, k ; teflon, l ; battery, m ; electrometer, n ; recorder.

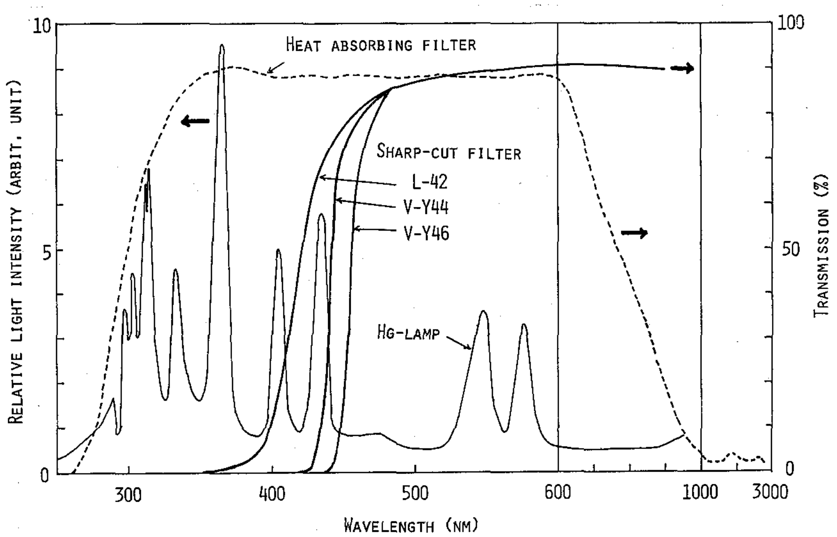


Fig. 4. Emission spectrum of 500 W super high pressur Hg-lamp, and transmission spectra of heat-absorbing filter and sharp-cut filters.

dark for 24 h before the measurement. The current through the glass was measured by Takadariken TR-8651 elecrometer. Generally, 90 d. c. voltage was applied to the glass. For the measurement of light current, a black cloth covering the sample box was removed and the glasses were illuminated with 500 W super-high-pressure mercury lamp through Hoya HA-50 heat-absorbing filter. In measuring spectral sensitivity, various sharp-cut filters (Toshiba Kase Kogyo, L-42, V-44 and V-Y46) were placed on the heat-aborbing filter. The emission spectrum of the mercury lamp and the transmission spectra of the filters are cited in Fig. 4 after their catalogues.

Electrical properties at high temperatures were measured using a shielded, light-tight sample box previously reported by the present authors[8], instead of that shown in Fig. 3.

RESULT AND DISCUSSION

1. Glass-forming tendency

Glass-forming tendencies of melts in the system Bi_2O_3-SiO_2-B_2O_3 are shown in Fig. 5. Clear glasses were obtained in the compositional region enclosed by a dotted line. Glasses of the compositions denoted with the numbers 1 to 6 were used for investigating their optical and electrical properties.

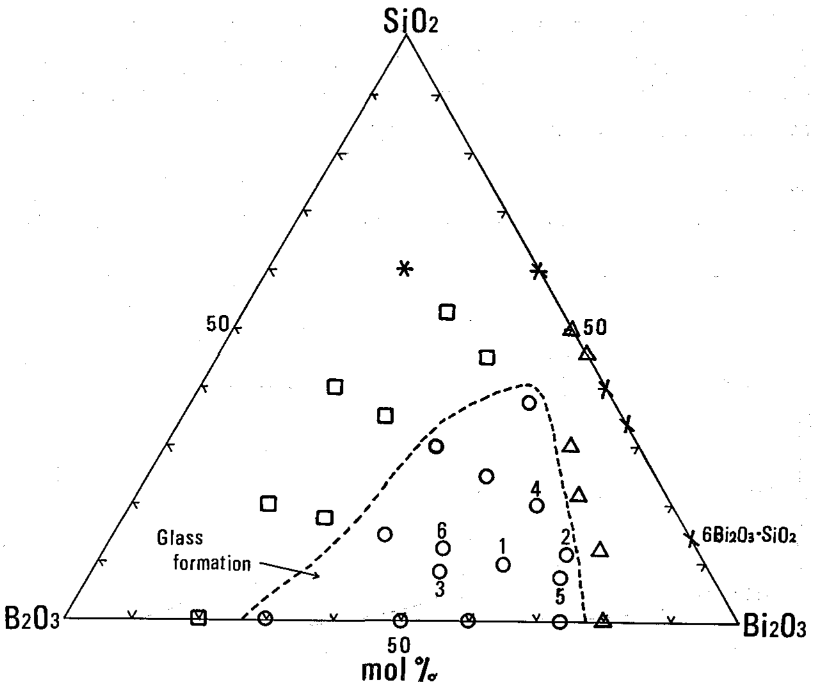
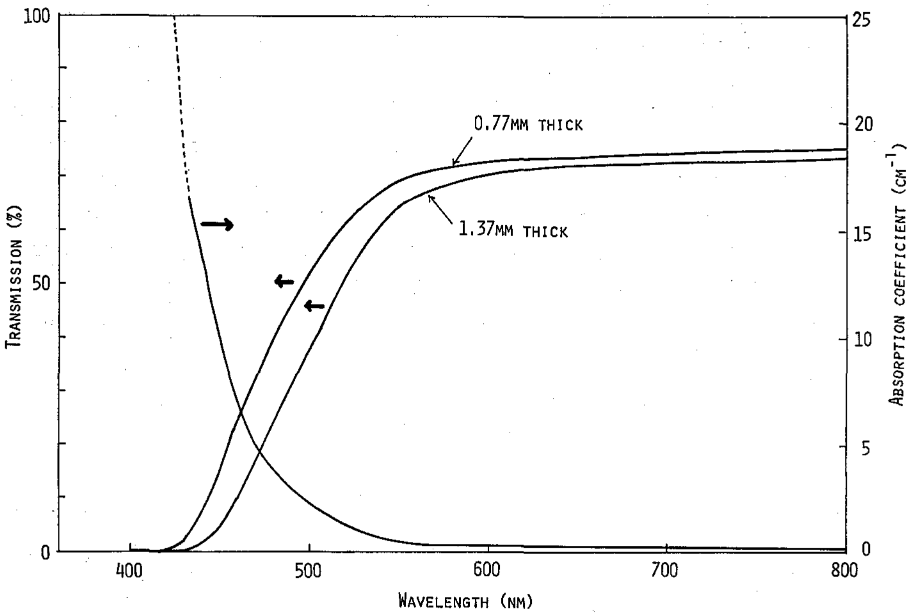


Fig. 5. Glass-forming tendency of Bi_2O_3-SiO_2-B_2-O_3 melts.
○; clear glass, □; opaque immiscible glass, △; partially devtrified glass, ×; fully devitrified glass, *; imperfect melt.



Figi 6. Transmissin and absorption coefficient spectra of glass 1.

2. Optical transmission

Transmission spectra of glass 1 are shown in Fig. 6 for the two different thicknesses. The absorption spectrum obtained from those spectra is also shown in Fig. 6. It can be seen from Fig. 6 that the absorption edge of glass 1 is located at about 420 nm in wavelengh, i. e. 3.0 eV in photon energy.

3. Photoconductivity

Figure 7 shows the time dependence of the electric current for glass 1. The

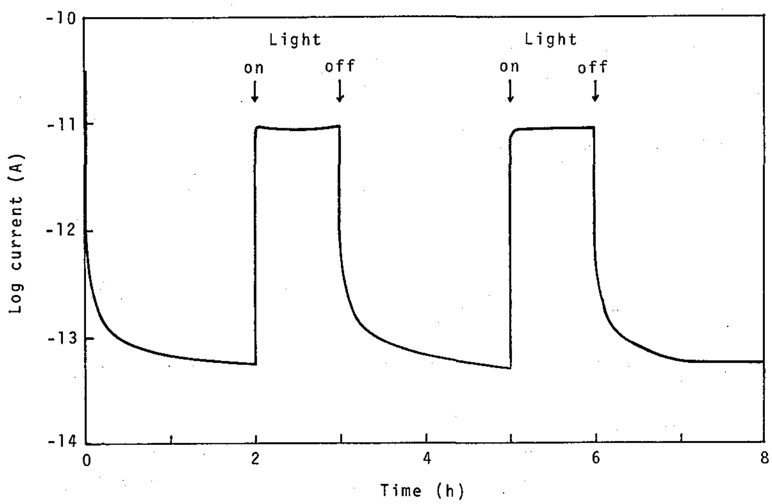


Fig. 7. Change in electric current of glass 1 with voltage application and light illumination.

glass was subjected to the 90 V d. c. voltage in the dark and then illuminate with the mercury light. The current gradually decreased with time after the voltage was applied in the dark, and instantaneously increased with the light illumination by larger than 100 times. The large current was maintained as long as the illumination was continued. It immediately decreased with a pause of the illumination to a certain value and then further gradually decreased with time. When the glass was reilluminated, the current again instantaneously increased to the same level as that for the previous illumination. These indicate that glass 1 shows photoconductivity.

Other glasses in Table I except for glass 1-Fe also showed a similar response to the light illumination. In the case of glass 1-Fe, the current was almost constant independent of time after the voltage was applied in the dark, and it gradually increased a litlle with the light illumination, as shown in Fig. 8.

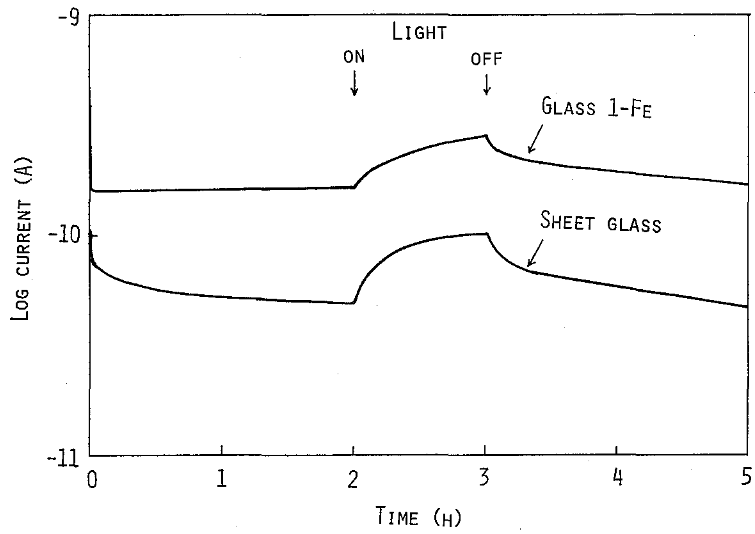


Fig. 8. Change in electric current of glass 1-Fe and sheet glass with voltage application and light illumination.

For comparing photoconductivity of the glasses, I_L/I_D was taken as a measure of their photoconductivities, where I_D is dark current measured at two hours after application of voltage, and I_L is the light current measured at one hour after the start of light illumination. The illumination was started after the I_D was measured. I_D, I_L and the ratio I_L/I_D for glasses of compositions given in Table I are listed in Table II. In Table II, those for $65CdO \cdot 15SiO_2 \cdot 20B_2O_3$ (in mol%) glass, a commercial sheet glass and a transparent polycrystalline γ-$6Bi_2O_3 \cdot SiO_2$ plate are also shown for comparison. The CdO-SiO_2-B_2O_3 glass is one of the photoconductive glasses reported by Strickler et al.[2]. It was prepared by sintering the batch mixture at 700°C and melting it at 1100°C under the oxygen gas atmosphere in the present study. The transparent polycrystalline γ-$6Bi_2O_3 \cdot SiO_2$ plate was prepared by a unidirectional solidification of melt, details of which were already reported elsewhere[9].

Table II Dark and light currents

Sample	Dark current I_D (A)	Light current I_L (A)	I_L/I_D
1	6.0×10^{-14}	8.8×10^{-12}	147
2	5.0×10^{-13}	1.0×10^{-11}	20
3	4.0×10^{-14}	4.3×10^{-12}	108
4	1.5×10^{-13}	5.6×10^{-12}	37
5	2.5×10^{-13}	1.2×10^{-11}	48
6	5.0×10^{-14}	3.4×10^{-12}	68
1-Cd	1.1×10^{-13}	1.2×10^{-11}	109
1-In	2.0×10^{-14}	4.5×10^{-12}	225
1-Pb	7.0×10^{-14}	1.1×10^{-11}	157
1-Fe	1.7×10^{-10}	2.9×10^{-10}	1.7
CdO-SiO_2-B_2O_3 glass	1.8×10^{-11}	1.5×10^{-7}	8.3×10^{3}
Sheet glass	4.9×10^{-12}	1.1×10^{-11}	2.2
γ-$6Bi_2O_3\cdot SiO_2$ crystal	2.0×10^{-14}	5.5×10^{-7}	2.8×10^{7}

Compositional dependence of the photoconductivity of the Bi_2O_3-SiO_2-B_2O_3 glasses is not clear from Table 2, except for the effect of the Fe_2O_3 addtion. The ratio I_L/I_D of the glass 1-Fe is as low as that of the sheet glass. The I_L/I_D ratios for these glasses being a little larger than unity might be attributed to occurrence of thermally activated current, since an increase in current with the illumination is gradual and small, as shown in Fig. 8. The increase in current as observed for the sheet glass can be caused by a rise in temperature of only 7°C. Actually, temperature rise by 4°C was detected by a thermocouple placed at the periphery of the illuminated area on the sheet glass, one hour after the light was cast on. Consequently, it can be said that the photoconductivity of the Bi_2O_3-SiO_2-B_2O_2 glass is destroyed by addition of the Fe_2O_3.

It also can be seen from Table II that the photoconductivities of the Bi_2O_2-SiO_2-B_2O_2 glasses are considerably less than that of the γ-$6Bi_2O_3\cdot SiO_2$ polycrystals and a little less than that of the CdO-SiO_2-B_2O_3 glass.

4. Nature of drak current

Dark currents of glass 1 which were measured under various voltages ranged from 90 to 520 V at 160°C are shown in Fig. 9. The Ohmic relation is held between the dark current and the applied voltage.

Conductivities of glass 1 measured at various temperatures in the dark are shown in Fig. 10. A linear relationship is found between log conductivity and the reciprocal temperature. Activation energy for conduction calculated from Fig. 10 was 1.2 eV. Twice of this energy, 2.4 eV, is considerably lower than that of the absorption edge of glass 1, 3.0 eV. Consequently, so-called band-type electronic conduction is denied for conduction in the dark of the Bi_2O_3-SiO_2-B_2O_3 glass. The value of the activation energy for the conduction described above is in the range of those reported for oxide

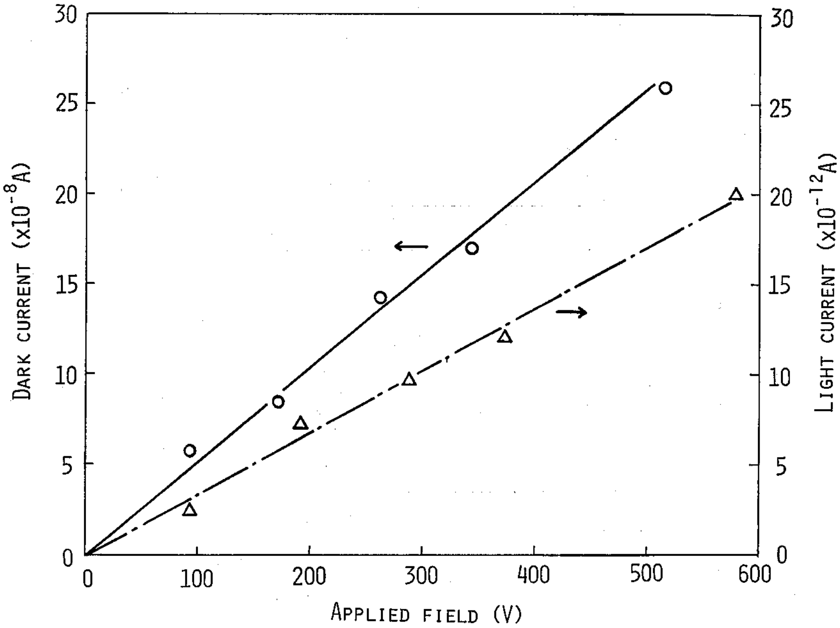


Fig. 9. Dark current of glass 1 at 160°C and its light current.

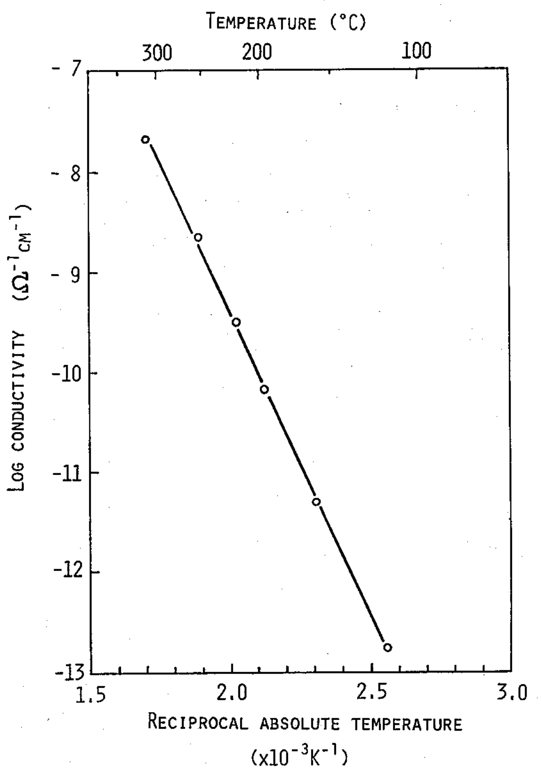


Fig. 10. Temperature dependence of dark conductivity of glass 1.

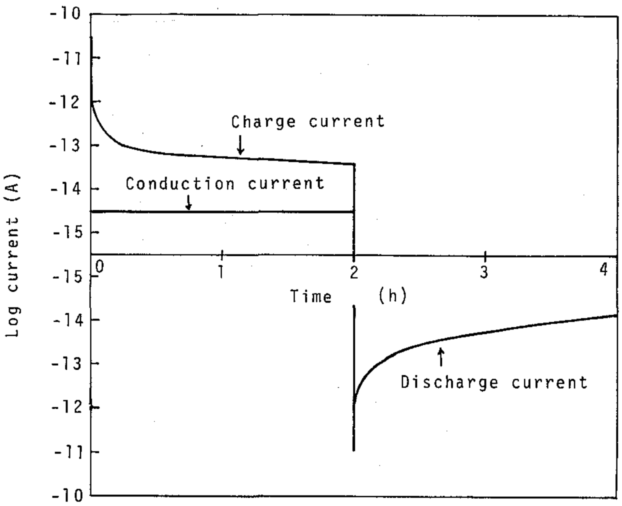


Fig. 11. Change in dark current of glass 1 with voltage application and shor-circuit.

glasses showing ionic conduction, i. e. 0. 5–1. 5 eV[10].

Figure 11 shows charge and discharge currents of glass 1 observed on application of 90 V d. c. voltage at room temperature for 2 h and on short-circuiting of the electrode thereafter. In Fig. 11, a conduction current at room temperature, which was estimated from conductivities at higher temperatures given in Fig. 10, is also shown. Figure 11 indicates that a time-dependent part of the charge current, i. e. charge current minus the constant steady conduction current, is observed for a very long time, and that it is almost identical to the discharge current. This means that the present glass shows dielectric relaxation with a very long relaxation time. Such phenomeon is typical for oxide glasses of ionic conduction[10]. Semiconducting oxide glasses of a so-called hopping-type electronic conduction may also show a dielectric relaxation. Their relaxation times are, however, not so long. Their activation energies for conduction are usually considerably lower than that of the present glass, i. e. 0. 3–0. 7 eV[10]. On the other hand, the dark conductivity of glass 1 was little affected by the atmosphere of glass melting, oxygen or dry nitrogen. Therefore, the hopping-type electronic conduction also denied for the conduction in the dark of the Bi_2O_3-SiO_2-B_2O_3 glass, and ionic conduction is considered to be most probable. Yamamomto et al[10] previously attribnuted the electrical conduction of Bi_2O_3-B_2O_3 glasses to Bi^{3+} ion migration on the basis of the experimental results of d. c. conductivity and dielectric relaxation.

5. Nature of light current

Light currents of glass 1, which were measured under various voltages ranged from 90 to 580 V at room temperature, are also shown in Fig. 9. It can be seen from Fig. 9 that Ohmic relation is also held between the light current and the applied voltage.

Table III Light currents of glass 1 for lights cut off by various filters

Filter	Light current I_L (A)	Relative I_L
HA-50	8.8×10^{-12}	1.00
HA-50+L-42	6.6×10^{-12}	0.75
HA-50+V-Y44	3.1×10^{-12}	0.35
HA-50+V-Y46	1.8×10^{-12}	0.20

Table III shows the light currents of glass 1 for the lights, some parts of which were cut off by various filters. It can be seen from Table III and Fig. 4 that the light current is little decreased even though the light shorter than 420 nm in wavelength is cut off, but appreciably decreases when the light shorter than 440 nm is cut off. This indicated that the light most effective for inducing the photoconductivity is that near 430 nm in wavelength, i.e. 2.9 eV in photon energy. This energy almost coincides with that of the absorption edge of glass 1, that is, 3.0 eV. Therefore, it can be concluded that conduction mechanism of the light current of the Bi_2O_3-SiO_2-B_2O_3 glass is electronic one of band-type.

ACKNOWLEDGMENT

The authors wish to thank Mr. Y. Kita, Laboratory of Dielectrics, Institute for Chemical Research, Kyoto University, for valuable suggestion for electrical measurements. Thanks are also due to Prof. M. Tashiro and S. Sakka, Institute for Chemical Research, Kyoto University, for helpful discussions.

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