*Journal of the European Ceramic Society* **19** (1999) 637–639
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00234-9 0955-2219/99/$—see front matter

# Visible Rays Cutoff and Infrared Transmission Properties of $TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ Glass Systems

Keiji Kobayashi* and Hideyuki Sasaki

Toshiba Research and Development Center, 1-Komukai, Toshibacho, Kawasaki, Japan

(Received 1 July 1998; accepted 30 August 1998)

***Abstract***

*Visible rays cutoff infrared transmitting glasses in $TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ glass systems were investigated. Glasses without $OH^-$ absorption band transmitting wavelength regions from 2·0 to 5·0 nm were obtained. The addition of fluoride to these glasses and the treatment of dry-air-bubbling during melting decreased markedly absorption coefficient and reflectivity of $OH^-$ bands. Reflectivity of $OH^-$ bands increased with increasing absorption coefficient. Values of glass transition points from 520 to 540°C and flow points from 560 to 580°C were obtained. © 1999 Elsevier Science Limited. All rights reserved*

*Keywords*: optical properties, glass, spectroscopy, tellurite glasses, thermal expansion.

## 1 Introduction

Tellurite glasses have been developed for high refractive index, high dielectric constant[1,2] and good infrared transmitting properties for use in various kinds of electronic glasses. However, although the problem to remove $OH^-$ radicals in tellurite glasses has been important in infrared transmitting glasses, they have hardly been accomplished. It is an interesting fact that they have much residual water and $OH^-$ radicals, which are caused by water in raw materials and atmospheric moisture during melting. Experiments carried out by Grove *et al.*[3,4] showed that $OH^-$ absorption bands decreased by the use of dry-air-bubbling through molten glass during melting and vacuum melting. They are effective methods for the removal of water or the expellation of $OH^-$ ions from glasses.[5] The introduction of fluoride ions into raw materials is advantageous as a means of decreasing the infrared absorption bands in the region of water peaks.[6] The hydroxyl ion and the fluoride ion are isoelectronic and are also similar in ionic size and therefore, hydroxyl ions can be easily replaced by fluoride ions during melting.[7]

Harrison[8] was the first worker to measure systematically $OH^-$ absorption bands of various oxide glasses. He found the $OH^-$ absorption bands at 2·70 $\mu$ in fused silica, at 2·85 $\mu$ in boric oxide, at 2·95 $\mu$ in sodium tetraborate and at 3·2 $\mu$ in fused metaphosphoric acid. Scholze[9] also observed $OH^-$ absorption bands around 2·75 $\mu$ in silica glass. They are absorption bands of fundamental vibration due to $OH^-$ absorption and another overtone frequencies may be observed by the use of infrared absorption spectroscopy. The author investigated the visible rays cut-off and infrared transmitting properties of $TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ glass systems and the removal of $OH^-$ absorption bands in the infrared region.

## 2 Experimental

$TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ and $TeO_2$–$GeO_2$–PbO–$V_2O_5$ glasses were prepared for use in the experiment. Batches comprising 1 kg of reagent grade chemicals were melted at 1000°C for 3 h in an ultra-high-purity Au–Pd crucible with an electric furnace in an oxidizing atmosphere. Dry air passed through silica gels was blown for 0·5 h through liquid glass during melting in an oxidizing atmosphere. This is the dry-air-bubbling technique.[10] After homogeneous melting, the glass was poured onto a stainless steel plate and annealed. Infrared transmission spectra were measured using a Digi-Labo spectrophotometer with 10×20×1 mm and 10×20×2 mm plates. Thermal expansion curves

*To whom correspondence should be addressed

were measured using a Rigaku-TMA Thermomechanical testmeter with rods 3 mm in diameter and 30 mm long. Glass transition points and flow points were obtained from thermal expansion curves, using a method previously described.[11]

## 3 Results and Discussion

Transmittance T is given as follows:[12]

$$\mathrm{T} = \frac{(1-R)^2 \exp(-\beta t)}{1 - R^2 \exp(-2\beta t)} \tag{1}$$

where $R$ is the reflectivity, $\beta$ is the absorption coefficient and $t$ is the thickness.

When $\frac{R^2}{\exp(2\beta t)} \ll 1$ eqn (1) is written as follows:

$$T = (1-R)^2 \exp(-\beta t) \tag{2}$$

When $T_1$ is the transmittance of a specimen 1 mm thick and $T_2$ is the transmittance of a specimen 2 mm thick, $T_1$ and $T_2$ are respectively written as follows:

$$T_1 = (1-R)^2 \exp(-0{\cdot}1\beta) \tag{3}$$

$$T_2 = (1-R)^2 \exp(-0{\cdot}2\beta) \tag{4}$$

From eqns (3) and (4), $\beta$ is obtained as follows:

$$\beta = 23{\cdot}03 \log(T_1/T_2) \tag{5}$$

The value of $R$ is computed from eqn (1) by the use of values $T$ and $\beta$. Values of $\beta$ are computed from eqn (5), using the transmittance of glasses with two different thicknesses.

Glass composition, $R, T$ and $\beta$ are listed in Table 1. Infrared transmission spectra of $TeO_2$–$GeO_2$–$PbF_2$–$V_2O_5$ and $TeO_2$–$GeO_2$–$PbO$–$V_2O_5$ glass systems are given in Fig. 1. These absorption bands around 3500 cm$^{-1}$ are due to the fundamental vibration of $OH^-$ absorption bands, but the over-tone frequency of $OH^-$ band is not observed in these glasses. As shown in Table 1, $PbF_2$-containing glass showed improvement in absorption coefficient of $OH^-$ band. Particularly, the glass treated by dry-air-bubbling showed much improvement in absorption coefficient. Fluoride-containing and bubbled glasses showed the best improvement in $OH^-$ bands in comparison with the glass without fluoride and dry-air-bubbling treatment. Pyrohydrolysis reaction[11,13] to remove water in glasses is represented as follows:

$$PbF_2 + 2H_2O \rightarrow PbO + 2HF\uparrow \tag{6}$$

The values of $R$ also increased with increasing values of $\beta$ and they are not negligible, since they have a tendency that $R$ becomes substantially larger, when $\beta$ increases. These equations for obtaining the values of $\beta$ and $R$ from infrared spectra of glasses with different two thicknesses were derived. The method for calculation of absorption coefficient and reflectivity is not only for use in calculations for infrared region, but is also in those for ultraviolet and visible wavelength regions.

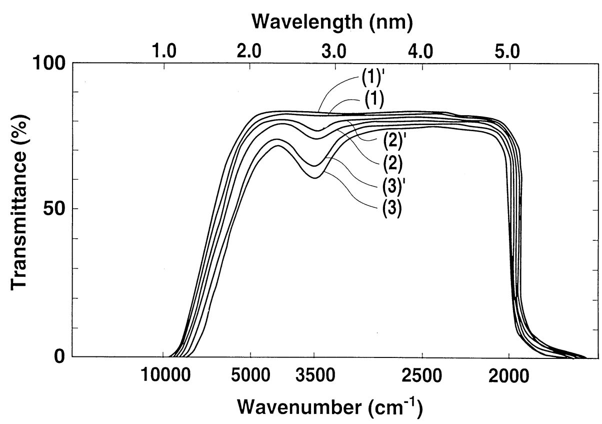


**Fig. 1.** Infrared transmission spectra of tellurite glasses.

**Table 1.** List of glass compositions and values of $T$, $R$ and $\beta$ calculated from infrared transmission spectra of glasses with different two thicknesses

| *Glass no.* | *Treatment* | *$TeO_2$ (mol%)* | *$GeO_2$ (mol%)* | *$V_2O_5$ (mol%)* | *PbO (mol%)* | *$PbF_2$ (mol%)* | T*(%)* | R | β *(cm$^{-1}$)* |
|---|---|---|---|---|---|---|---|---|---|
| (1) | Bubbling | 70 | 24 | 1 | — | 5 | 83 | 0·07 | 0·20 |
| (1)′ | Bubbling | 70 | 24 | 1 | — | 5 | 85 | 0·07 | 0·20 |
| (2) | — | 70 | 24 | 1 | — | 5 | 75 | 0·10 | 0·39 |
| (2)′ | — | 70 | 24 | 1 | — | 5 | 78 | 0·10 | 0·39 |
| (3) | — | 70 | 24 | 1 | 5 | — | 62 | 0·17 | 0·58 |
| (3)′ | — | 70 | 24 | 1 | 5 | — | 66 | 0·17 | 0·58 |

(1) $TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ glass with dry-air-bubbling, 2 mm thick;
(1)′ $TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ glass with dry-air-bubbling, 1 mm thick;
(2) $TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ glass 2 mm thick;
(2)′ $TeO_2$–$GeO_2$–$V_2O_5$–$PbF_2$ glass, 1 mm thick;
(3) $TeO_2$–$GeO_2$–$V_2O_5$–PbO glass, 2 mm thick;
(3)′ $TeO_2$–$GeO_2$–$V_2O_5$–PbO glass, 1 mm thick.

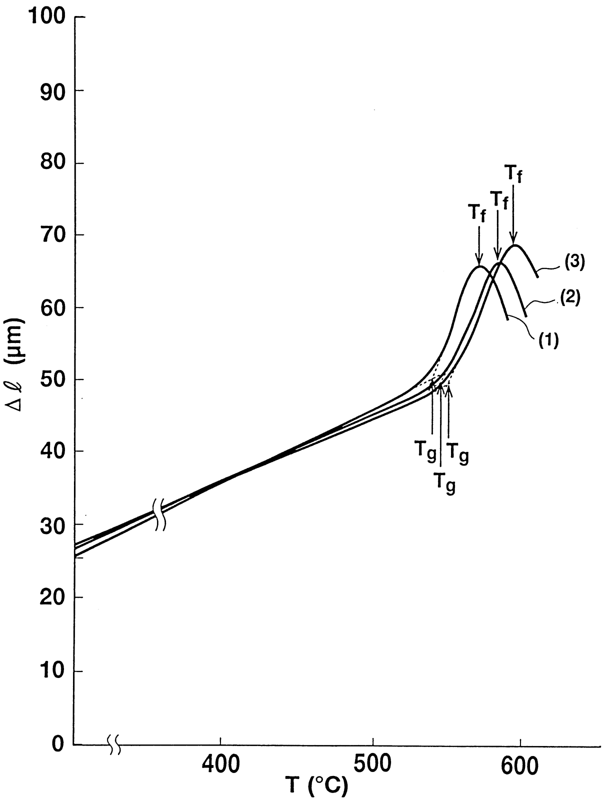


**Fig. 2.** Thermal expansion curves of tellurite glasses: 1. glass no. (1); 2. glass no. (2); 3. glass no. (3).

## 4 Conclusion

Visible rays cutoff infrared transmitting glass without $OH^-$ absorption bands which transmits wavelength regions from 2·0 to 5·0 nm was obtained. Thermal expansion curves of these glasses have been presented. Glass transition points $T_g$ from 520 to 540 °C and flow points $T_f$ from 560 to 580 °C of these glasses have been obtained.

## References

1. Kobayashi, K. and Yokota, R., *Yogyo-Kyokaishi (J. Ceram. Assoc. Japan)*, 1964, **72**, 116.
2. Stanworth, J. E., *Nature*, 1952, **169**, 581.
3. Grove F. J., Symposium sur I Affinage du Verre, Paris, 1995, **6**, 102.
4. Kobayashi, K., *Journal of the European Ceramic Society*, 1997, **17**, 49.
5. Kobayashi, K., *J. Mater. Chem.*, 1997, **7**, 127.
6. Adams, R. V., *Phys. Chem. Glasses*, 1961, **50**, 2.
7. Kobayashi, K., *J. Phys. Chem. Solids*, 1998, in press.
8. Harrison, A. J., *J. Amer. Ceram. Soc.*, 1947, **30**, 362.
9. Scholze, H., *Glastech. Ber.*, 1959, **32**, 81.
10. Kobayashi, K., *J. Electrochem. Soc.*, 1984, **131**, 2190.
11. Kobayashi, K., *J. Solid State Chem.*, 1995, **120**, 54.
12. Zhenhua, L. and Frischat, G. H., *J. Noncryst. Solids*, 1993, **163**, 169.
13. Kobayashi, K., *J. Solid State Chem.*, 1997, **130**, 330.