UDC: 535.327: 666.225

1. Temperature Dependences of Optical Path Length in Inorganic Glasses

Akio Koike* and Naoki Sugimoto*

Temperature dependences of optical path length (dS/dT); calculated using the equation, $dS/dT = dn/dT + n\alpha$, where α is the coefficient of thermal expansion, n is the refractive index and dn/dT is the temperature coefficient of refractive index) in various oxide glasses were investigated. The dS/dT is generally difficult to be controlled by change of glass composition because dn/dT and α are interrelated. This experiment also showed that the values of dS/dT for most glasses ranged between 10 ppm/°C and 20 ppm/°C except for bismuthate glasses. Pure silica glass is well-known as a typical material with low dS/dT. However, fluorine-doped silica glass showed a lower dS/dT than that of pure silica glass. By fluorine-doping in silica glass, refractive index and dn/dT decreased but α stayed at the same level near room temperature. As a result, the dS/dT decreased with increasing fluorine concentration. On the other hand, a bismuthate glass showed the highest dS/dT in this study. Although most glasses having high α such as tellurite glass showed negative dn/dT, bismuthate glasses showed positive dn/dT in spite of high α . It was assumed that bismuthate glass showed high dn/dT due to high polarizability of Bi_2O_3 which is similar to PbO. These results indicate that dS/dT of glass can be designed by considering the electronic configuration of its components and the glass structure.

1. Introduction

Inorganic glasses are widely used for optical applications due to those excellent properties such as transparency, strength, thermal stability, and chemical durability. In some applications, precise controls of the optical properties in the glasses are strictly required. In wavelength division multiplexing (WDM) systems, for example, many kinds of optical components such as optical add/drop multiplexing (OADM) and optical cross connect (OXC) are used. These components can work without changing light to electricity. Therefore, optical properties of the optical component materials are quite important. Recently, the spacing between channels in dense WDM becomes narrower to meet capacity demands. For this reason, the accuracy for wavelength becomes more important⁽¹⁾. In the Fabry-Perot etalon, which is used for wavelength locker in laser module, for example, a resonant wavelength is determined by optical path length. Optical path length, L, is given by refractive index, n, and length of optical device (the thickness of etalon), l, by

$$L = n \cdot l \tag{1}$$

If *n* or *l* changes according to environmental condition, i.e. temperature fluctuation, the resonant wavelength varies due to the change of the optical path length. Temperature coefficient of the optical path length, ΔL , is given by

$$\Delta L = (n \cdot \alpha + dn / dT) \cdot l \cdot \Delta T \qquad [2]$$

where α is coefficient of linear thermal expansion. The dn/dT is temperature coefficient of refractive index and also called as thermo-optic coefficient. Thus, temperature coefficient of the optical path length per unit length (*S*=*L*/*l*), *dS*/*dT*, is defined by following equation:

 $dS / dT = n \cdot \alpha + dn / dT$ [3] In order to reduce the change of the optical path length, dS/dT is required to become small in practical temperature range in telecommunications (Telcordia's requirement in GR-63-CORE for operating temperature is from -5 to 50°C). In dense WDM systems, low temperature dependence material, i.e., athermal glass is strongly required^{(2) (3)}.

Prod'homme ⁽⁴⁾ considered dn/dT as resulting from two counteraction factors. One is the volume expansion coefficient, β , which is given by

$$\beta = \frac{1}{V} \frac{dV}{dT} - \frac{1}{\rho} \frac{d\rho}{dT}$$
[4]

where *V* is volume and ρ is density, and the second is the polarizability coefficient, ϕ which is given by

$$\phi = \frac{1}{P} \frac{dP}{dT}$$
[5]

where *P* is mean polarizability. The dn/dT is given by differentiating Lorentz-Lorenz equation:

$$dn \, / \, dT = \frac{(n^2 - 1)(n^2 + 2)}{6n} \cdot (\phi - \beta)$$
 [6]

The volume expansion coefficient, β , can be approximated to 3α , therefore, dn/dT is obtained by

$$dn \, / \, dT = \frac{(n^2 - 1)(n^2 + 2)}{6n} \cdot (\phi - 3\alpha)$$
 [7]

This equation means that dn/dT depends on α . Since dn/dT and α are interrelated, the dS/dT is generally difficult to be controlled by change of glass composition. In this study, temperature coefficient of refractive index (dn/dT), coefficient of thermal expansion (α), and temperature coefficient of the optical path length (dS/dT) in inorganic glasses were investigated.

2. Experimental

The oxide glasses which were examined in this study are listed in **Table 1**. Silica glasses were prepared using vapor-phase axial deposition (VAD) process. In the VAD process, the soot was prepared by flame hydrolysis deposition (FHD) of Si precursor, and Ti precursor was added in the case of Ti-doped silica glass. By sintering in He atmosphere, transparent silica glasses were obtained. For F-doped silica glass, the soot was exposed to fluorine-containing atmosphere at high temperature such as 1000°C before sintering. By changing the fluorine concentration in the atmosphere and/or heating temperature, F-doped silica glasses with

different concentration were prepared. The F concentration in the glasses was evaluated by using a fluorine ion selective method ⁽⁵⁾. In this study, Fdoped silica glasses with F concentrations from 0 to 16000 ppm by weight were prepared. The OH content in each sample, which was measured by FT-IR⁶⁶, was around 70 ppm by weight in pure silica glass and Ti-doped silica glass, and less than 10 ppm by weight in F-doped silica glasses. Other glasses were prepared by the conventional melting method. The glass samples were obtained by melting the well-mixed batch of appropriately weighted quantities of raw materials, which were the constituent oxides or compounds that convert to oxides during heating. Platinum crucible was used for melting glasses except for tellurite glasses, and gold crucible was used for melting tellurite glasses. Obtained glasses were visibly homogeneous and bubble free. Those glasses were annealed at the temperatures which were 10°C higher than those glass transition temperatures (T_g) for 1 hour, and then cooled at the rate of $1^{\circ}C/min$. Refractive index at 1550 nm, n_{1550} , was measured by a minimum deviation method ⁽⁷⁾. The accuracy of this measurement was $\pm 10^{-5}$. In order to obtain the temperature coefficient of the refractive index, dn_{1550}/dT , the refractive index was measured from -5 to 65°C. In this study, the dn_{1550}/dT was defined as the average temperature coefficient of refractive index from -5 to 65° C, calculated by the following equation:

$$\frac{dn_{1550}}{dT} = \frac{n_{1550 \text{ at } 65^{\circ}\text{C}} - n_{1550 \text{ at } -5^{\circ}\text{C}}}{65 - (-5)}$$
[8]

The linear thermal expansion was measured by laser interferometer from -150 to 200° C⁽⁸⁾ for silica glasses, and by double pushrod differential dilatometer from -70 to 200° C for other oxide glasses. The accuracy of measurement by laser interferometer was $\pm 0.01 \text{ ppm/°C}$. From the linear thermal expansion data, the average temperature coefficient of thermal expansion from -5 to 65° C were calculated as the $\alpha_{-5\sim65}$.

3. Results

The results are summarized in **Table 2**. The values of ϕ and dS/dT were calculated from measured n_{1550} and dn_{1550}/dT and α_{-5-65} . In this experiment, silica glasses showed low dS/dT, and especially, F-doped silica glasses showed the lowest dS/dT. In the F-doped silica glasses, the dS/dT decreased with F concentration. On the other hand, bismuthate glasses showed the highest dS/dT.

Glass	Glass composition		
Silica glass 1	Pure silica glass by VAD		
Silica glass 2	Ti-doped silica glass (Ti : 7 mole%) ⁽⁹⁾		
Silica glass 3	F-doped silica glass (F : 3000 ppm in weight)		
Silica glass 4	F-doped silica glass (F : 5000 ppm in weight)		
Silica glass 5	F-doped silica glass (F: 8000 ppm in weight)		
Silica glass 6	F-doped silica glass (F : 10000 ppm in weight)		
Silica glass 7	F-doped silica glass (F : 12000 ppm in weight)		
Silica glass 8	F-doped silica glass (F : 13500 ppm in weight)		
Silica glass 9	F-doped silica glass (F : 16000 ppm in weight)		
Silicate glass 1	Commercial window glass		
Silicate glass 2	Non-alkaline glass, SiO ₂ -Al ₂ O ₃ -B ₂ O ₃ -RO system*		
Silicate glass 3	50SiO ₂ -25Al ₂ O ₃ -5TiO ₂ -20R ₂ O ^{**}		
Titanium silicate glass 1	40SiO ₂ -25TiO ₂ -25R ₂ O-10RO*		
Titanium silicate glass 2	50SiO ₂ -25TiO ₂ -25R ₂ O ^{**}		
Calcium aluminate glass	58CaO-28Al ₂ O ₃ -7SiO ₂ -7MgO ^{(10), (11)}		
Tellurite glass 1	60TeO ₂ -20ZnO-20WO ₃		
Tellurite glass 2	75TeO₂-20ZnO-5Na₂O		
Bismuthate glass 1	Bi ₂ O ₃ rich glass (Bi ₂ O ₃ : 40 mole %)		
Bismuthate glass 2	Bi_2O_3 rich glass (Bi_2O_3 : 40 mole %)		
Bismuthate glass 3	Bi_2O_3 rich glass (Bi_2O_3 : 65 mole %)		

 Table 1
 Oxide Glass Compositions in This Study.

* RO means the sum of alkaline earth oxide components such as MgO, CaO, SrO and BaO

** R₂O means the sum of alkaline oxide components such as Li₂O, Na₂O and K₂O

Glass	<i>n</i> ₁₅₅₀	<i>dn</i> ₁₅₅₀∕ <i>dT</i> (ppm/℃)	α _₅₅ (ppm/°C)	¢ (ppm/℃)	<i>dS/dT</i> (ppm/℃)
Silica glass 1	1.4441	8.75	0.443	18.4	9.39
Silica glass 2	1.4651	9.74	0.061	18.2	9.83
Silica glass 3	1.4432	8.66	0.436	18.3	9.29
Silica glass 4	1.4430	8.54	0.427	18.0	9.15
Silica glass 5	1.4421	8.48	0.449	18.0	9.13
Silica glass 6	1.4397	8.40	0.425	17.9	9.01
Silica glass 7	1.4392	8.36	0.430	17.8	8.98
Silica glass 8	1.4385	8.30	0.425	17.7	8.91
Silica glass 9	1.4376	8.29	0.440	17.8	8.92
Silicate glass 1	1.5000	2.94	7.00	26.0	13.4
Silicate glass 2	1.4961	8.92	2.60	23.1	12.8
Silicate glass 3	1.5279	0.70	8.25	25.9	13.3
Titanium silicate glass 1	1.6908	-2.74	10.5	28.4	15.0
Titanium silicate glass 2	1.6580	-0.70	10.1	29.5	16.0
Calcium aluminate glass	1.6444	6.87	7.00	29.5	18.4
Tellurite glass 1	2.0547	-4.11	11.8	32.9	20.1
Tellurite glass 2	1.9947	-11.5	16.2	40.9	20.9
Bismuthate glass 1	1.9772	16.5	8.00	35.4	32.4
Bismuthate glass 2	2.0184	21.6	7.57	36.7	36.9
Bismuthate glass 3	2.2095	20.1	10.5	41.3	43.2

Table 2 Obtained Thermo-optic Data in Various Oxide Glasses.

Although tellurite glasses had high refractive indices as same as bismuthate glasses, tellurite glasses did not show high dS/dT. Figure 1 shows

relationship between dn/dT and $n\alpha$ in this experiment. In this figure, diagonal lines show $dn/dT + n\alpha$, i.e., dS/dT. Except for bismuthate glasses, most



Fig. 1 Relationship between dn/dT and $n\alpha$ in various oxide glasses.

glasses lied on the area between diagonal lines, dS/dT=10 ppm/°C and 20 ppm/°C. Since the tellurite glasses had high α , the dn/dT became negative. From the same reason, titanium silicate glass group showed negative dn/dT.

4. Discussion

Although dn/dT and $n\alpha$ changed widely with glass composition, dS/dT remained similar value except for bismuthate glasses. Since low α causes high dn/dT and negative dn/dT glass shows high α , dS/dT is difficult to be controlled. For example, Ti-doped silica glass, which is well-known as the zero expansion material ^{(9) (12)}, showed higher dn/dTthan pure silica glass. Consequently, dS/dT of Tidoped silica glass was slightly higher than that of pure silica glass. However, F-doped silica glasses showed lower dS/dT than pure silica glass, even though α was almost same as that of pure silica glass. The electronic polarizability of F⁻ in glass is smaller than that of O²⁻. Accordingly, the replacement from $O^{2^{-}}$ to F^{-} causes increase in thermal expansion and decrease in refractive index (13). Properties of fluoride glasses were investigated by Izumitani et al.⁽¹⁴⁾ in detail. The relationship between dn/dT and $n\alpha$ in fluoride glasses are shown in **Fig. 2**. Since fluoride glass has high α and negative dn/dT, resulting dS/dT remains typical value. The measured refractive index, n_{1550} , and



Fig. 2 Relationship between *dn/dT* and *nα* in fluoride glasses ⁽¹⁴⁾ and lead glasses ⁽²¹⁾. Data of fluoride glasses (●) were measured by the light of 633 nm in wavelength. Data of lead glasses (■, ▲, ▼) were measured by the light of 589 nm in wavelength. Numbers added to the data of lead glasses mean mole fraction of lead component. For comparison, data obtained in this experiment (○) are also shown.



Fig. 3 Refractive indices (n_{1550}) of various concentrations of F-doped silica glasses at 25°C.

 dn_{1550}/dT in F-doped silica glasses are shown in **Fig. 3** and **Fig. 4**. The n_{1550} , and dn_{1550}/dT decreased as F concentration increased, which was consistent with the theory for fluoride glasses and also agreed to previous studies about F-doped silica glass⁽¹⁵⁾ (¹⁶⁾. Variation of α with temperature from -150 to 200°C for various F-doped silica glasses is shown in **Fig. 5**. At the low temperature region such as



Fig. 4 Temperature coefficients of refractive index (dn_{1550}/dT) of various concentrations of F-doped silica glasses.



Fig. 5 Temperature dependence of α in various concentrations of F-doped silica glasses.

-150°C, the coefficient of thermal expansion increased as F concentration increased. On the contrary, α decreased as F concentration increased at the high temperature region such as 200°C. Around near room temperature, for example at 20°C, α showed no dependence on F concentration. In practical temperature range from -5°C to 65°C, the coefficient of average thermal expansion, $\alpha_{-5\sim65}$, was also constant as shown in Fig. 6. The obtained dS/dTs in F-doped silica glasses are summarized in **Fig. 7.** As a result, dS/dT became smaller as F concentration increased. As mentioned above, α and dn/dT is interrelated. However, in the case of Fdoped silica glass, α was almost constant but refractive index decreased with F-doping. It seems to be related to anomaly of thermal expansion behavior in silica glass⁽¹⁷⁾.

On the other hand, bismuthate glass showed anomalistically high dS/dT. This can be attributed



Fig. 6 Coefficient of average thermal expansion from -5° to 65° of various concentrations of F-doped silica glasses.



Fig. 7 Temperature coefficients of optical path length (*dS/dT*) of various concentrations of F-doped silica glasses.

to high dn/dT in spite of relatively high α . In order to consider the high dS/dT of the bismuthate glasses, theory in lead glass can be applicable, since there are similarities between bismuth ion and lead ion in atomic weight (Pb: 207.2, Bi: 208.98), ionic radius (Pb²⁺: 1.26 Å, Bi³⁺: 1.20 Å) and electronic configuration (Pb: 6s²6p², Bi: 6s²6p³)⁽¹⁸⁾. In fact, most properties of bismuthate glasses are similar as those of lead glasses. In lead-borate, lead-silicate and lead-borosilicate glasses with low content of PbO, Pb^{2+} ion acts as a modifier by forming $[PbO_6]$ group. However, with high content of PbO, Pb²⁺ ion behaves as a glass former by forming asymmetric [PbO₄] tetrahedral unit. Leventhal et al.⁽¹⁹⁾ concluded from their NMR analysis that glass structure in SiO₂-PbO system changes over 45 mole% in PbO. Correspondingly, in the glasses with high content of Bi₂O₃, Bi³⁺ ion acts as a glass former by forming asymmetric [BiO₆] octahedral unit ^{(18) (20)}. Factors for calculation of dn/dT of each glass component were

obtained by Komorita et al.⁽²¹⁾. In their results, the factor of PbO was positive and increased with PbO content. On the other hand, factor for calculation of α of PbO is also positive ⁽²²⁾. These results mean that lead oxide glass shows both high α and high dn/dT. The relationship between dn/dT and $n\alpha$ in lead glasses are shown in **Fig. 2**. The lead glasses with high concentration of PbO also showed high dS/dT.

There is a dependence of the glass composition for stress-optical coefficient. The PbO-SiO₂ glass of high PbO content shows zero stress-optical coefficient and higher PbO causes negative value⁽²³⁾. When uniaxial tensile stress is applied to normal glass, oxygen anions are deformed in the direction to the tensile stress and cause different refractive indices between parallel and perpendicular, i.e., birefringence. If easily polarizable cations such as Pb²⁺ exist, these cations also deform and cause decrease of birefringence. Although temperature dependence of poralizabitity includes effect of lattice vibration as well as change of interatomic distance, thermal expansion is similar to isotropic tensile stress from the point of view of spatial configuration. Accordingly, in the case of glass containing high amount of high poralizability component, high thermal expansion does not cause low or negative temperature coefficient of refractive index, dn/dT. Tellurite glass, where TeO₂ has low electronic polarizability (oxide poralizability of TeO₂: 2.44×10^{-24} cm³, oxide poralizability of PbO: 3.45×10^{-24} cm^{3 (24)}), shows normal behavior, that is, negative dn/dTwith high α . However, bismuthate glass as well as lead glass shows both high α and high dn/dT due to high polarizability of Bi₂O₃ or PbO.

5. Conclusion

Temperature dependence of refractive index, dn/dT, and thermal expansion coefficient, α , and resulting temperature dependence of optical path length, dS/dT, in various glasses were investigated. Generally dS/dT is difficult to be controlled by changing the glass composition due to interrelated relationship between dn/dT and α . In fact, the dS/dTs of most glasses including fluoride glasses ranged between 10 ppm/°C and 20 ppm/°C except for bismuthate glasses and lead glasses. F-doped silica glass showed the lowest dS/dT in this study. Since the electronic polarizability of F⁻ is smaller than that of O^{2-} , refractive index and dn/dTdecrease as F concentration increase. However, α near room temperature did not change with F-doping. As a result, the dS/dT decreased with increasing F concentration. On the other hand, bismuthate glass showed the highest dS/dT. This seems to be attributed to high dn/dT in spite of relatively high α . Generally high amount of high poralizability component such as PbO causes small or negative stress-optical coefficient. Similarly, anomalous relationship between dn/dT and α seems to appear in glasses containing high amount of high poralizability component. Therefore, bismuthate glasses as well as lead glasses show both high α and high dn/dT due to high polarizability of Bi₂O₃ or PbO. These results suggest that temperature coefficient of optical path length and refractive index can be designed by considering the electronic configuration of its components and the glass structure.

旭硝子研究報告 56 (2006)

-References-

- Y. Kokubun, N. Funato and M. Takizawa, *IEEE Photon. Technol. Lett.*, Vol. 5, No. 11, 1297 (1993).
- (2) K. Tanaka, The 12th Meeting on Glass for Photonics, Japan (2001).
- (3) T. Nagakane, N. Kitamura, J. Nishii, and K. Hirao, New Glass, Vol. 19, No. 1, 60 (2004).
- (4) L. Prod'homme., Phys. Chem. Glasses, Vol. 1, No. 4, 119 (1960).
- M. Noshiro and Y. Jitsugiri., Nippon Kagaku Kaishi, Vol. 2, 350 (1972).
- (6) J. P. Williams, Y. Su, W. R. Strzegowski, B. L. Butker, H. L. Hoover, and V. O. Altemose, *Am. Ceram. Soc. Bull.*, Vol. 55, No. 5, 524 (1976).
- (7) M. Born and E. Wolf, Principles of Optics, Pergamon, Oxford, UK (1980).
- (8) R. Kato, T. Azumi, S. Sekino and A. Maesono, *Thermochimica Acta*, Vol. 134, 383 (1988).
- (9) P. C. Schultz and H. T. Smyth, in: R. W. Douglas and B. Ellis, Amorphous Materials, Willey, New York, p. 453 (1972).
- (10) K. H Sun, Glass Ind., Vol. 27, No. 11, 552 (1946).
- (11) K. H Sun, Glass Ind., Vol. 30, No. 4, 199 (1949).
- (12) P. C. Schultz, J. Am. Ceram. Soc., Vol. 59, 214 (1976).
- (13) D. R. Uhlmann and N. J. Kreidl, Optical Properties of Glass, Am. Ceram. Soc., Westerville (1991).
- (14) T. Izumitani, T. Yamashita, M. Kukida, K. Miura and H. Tashima, in: R. M. Almeida and M. Nijhoff, Halide glasses for infrared fiberoptics, Dordrecht, Boston, p. 187 (1987).
- (15) S. Shiraishi, K. Fujiwara, and S. Kurosaki., US Patent, 4082420 (1979).
- (16) T. Enomoto, M. Takagi, S. Ishikawa, and N. Kitamura., The 12th Fall Meeting of the Ceramics Society of Japan (1999).
- (17) R. Bruckner, J. Non-Cryst. Solids, Vol. 5, 123 (1970).
- (18) G. E. Rachkovskaya and C. B. Zakharevich, *Glass and Ceramics*, Vol. 61, 9 (2004).
- (19) M. Leventhal and P. J. Bray, *Phys. Chem. Glasses*, Vol. 6, No. 4, 113 (1965).
- (20) H. B. George, C. Vira, C. Stehle, J. Meyer, S. Evers, D. Hogan, S. Feller and M. Affatigato, *Phys. Chem. Glasses*, Vol. 40, No. 6, 326 (1999).
- (21) F. Komorita, B. Sato and M. Motai, J. Mater. Sci. Soc. Japan, Vol. 15, 163 (1978).
- (22) H. Scholze, Glass, Springer-Verlag, New York, p. 190 (1990).
- (23) M. Tashiro, J. Soc. Glass Technol., Vol. 40, 353 (1956).
- (24) V. Dimitrov and S. Sakka, J. Appl. Phys., Vol. 79, No. 3, 1736 (1996).