Determination of Refractive Indices and Linear Coefficients of Thermal Expansion of Silicate Glasses Containing Titanium Oxides

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A growing attention has been paid to development of ‘athermal glass’, which is a material showing no temperature dependence in its optical path length and is expected to be used in optical devices for the optical fibre transmission system. The athermal characteristic is usually evaluated using the dependence of optical path length (S) on temperature (T) expressed by the following equation:

\[
\frac{1}{l} \frac{dS}{dT} = n\alpha + \frac{dn}{dT}
\]

where \( l \), \( n \) and \( \alpha \) are the geometrical length, refractive index and linear coefficient of thermal expansion of a sample, respectively. In the present work, the refractive index and liner coefficient of thermal expansion have been determined for silicate glasses containing titanium oxides in the temperature range from room temperature to about 673 K, respectively, using ellipsometry and the apparatus with image analysis equipment. The values of \( n\alpha \) and temperature coefficient of \( n \) ranged from \( 1.289 \times 10^{-5} \) to \( 3.345 \times 10^{-5} \) K\(^{-1}\) and from \( 0.270 \times 10^{-5} \) to \( 1.467 \times 10^{-5} \) K\(^{-1}\), respectively, depending on the glass composition. As a consequence, it has been found that additions of titanium oxides do not have good effects on the athermal characteristic. However, only \( 80\text{SiO}_2-5\text{TiO}_2-15\text{Na}_2\text{O} \) (on a mole basis) glass has shown almost the same degree of athermal characteristic as \( \text{SiO}_2 \) glass, and it is suggested that \( 80\text{SiO}_2-5\text{TiO}_2-15\text{Na}_2\text{O} \) glass has more advantages in practice due to its lower melting temperature than \( \text{SiO}_2 \).

KEY WORDS: refractive index; linear coefficient of thermal; athermal glass; optical property; glass technology.

1. Introduction

The widespread use of the Internet has enabled us to communicate an enormous amount of information very quickly; as a result, the volume of information transmitted has been increased year by year. Further progress of communication technology strongly requires establishment of the wavelength division multiplexing (WDM) technique because this technique can transmit massive information by only one optical fibre using many optical signals with different wavelengths. This technique, in turn, requires development of arrayed waveguide grating (AWG) devices for merging and dividing various optical signals as a key technology. Thus, the AWG device as well as the WDM technique plays a very important role in digital broadcasting and broadband network developed from now.

The optical characteristics of AWG devices can be influenced by the variation in the optical path length with temperature change. Amorphous silica is currently used as this material; however, the temperature of the device must be maintained strictly constant using an electric heater to guarantee the device performance. To expand applications of AWG devices, it is necessary to remove the heater from the device, which requires development of materials having no temperature dependence of the optical path length—such a material is termed athermal glass. The athermal characteristic of glass is usually evaluated using the dependence of optical path length (S) on temperature (T) expressed by the following equation:

\[
\frac{1}{l} \frac{dS}{dT} = n\alpha + \frac{dn}{dT}
\]
signing chemical compositions. In practice, these materials can offer lower prices than amorphous silica since the production is much easier due to lower melting temperatures. The systems studied so far include Li₂O–Al₂O₃–SiO₂(–B₂O₃), CaO–Na₂O–SiO₂, F–SiO₂, Bi₂O₃–SiO₂, CaO–Na₂O–SiO₂, CaO–K₂O–SiO₂, and CaO–K₂O–SiO₂. However, the temperature dependencies of optical path lengths of these systems are stronger than that of SiO₂ glass, except for F-doped SiO₂, in the temperature range from 268 to 338 K investigated. The important finding is that additions of alkali and alkaline earth metal oxides are generally prone to increase \( n \), to decrease \( dn/dT \) and to increase \( dS/dT \) totally.

On the other hand, Sanghera et al. have measured values of refractive index and linear coefficient of thermal expansion for SiO₂–TiO₂ glasses and reported that the linear coefficient of thermal expansion decreases with increasing TiO₂ concentration, which suggests that addition of TiO₂ to SiO₂ has a possibility of decreasing the term \( n_a \). However, they have neither investigated the temperature dependence of refractive indices of the glasses nor mentioned their optical path lengths.

Against the above background, the present work focuses on SiO₂–TiO₂ glasses as new candidates for athermal glass. However, the phase diagram for the SiO₂–TiO₂ system says that the melting temperature is higher than 1 823 K at any composition, while industrial processes prefer glasses having lower melting temperatures. To lower the melting temperature, Na₂O and B₂O₃ additions are also attempted according to practical glass melting processes. Consequently, the present work aims:

- to measure refractive indices and linear coefficients of thermal expansion for SiO₂–TiO₂–Na₂O(–B₂O₃) glasses with systematic variations in chemical compositions and temperature
- to explain the compositional and temperature dependencies of these physical properties
- to discuss the possibility of obtaining athermal glass.

2. Experimental

2.1. Sample Preparation

Table 1 gives the nominal chemical compositions of glass samples on a mole basis. The samples were prepared from reagent grade powders of TiO₂, Na₂CO₃, B₂O₃ and SiO₂. These powders were dried in air at a temperature of 423 K, weighed to the desired compositions and mixed in an alumina mortar for 2 ks. These mixtures were melted in platinum crucibles (30 mm diameter and 35 mm depth) at 1 723 K in air for 1.8 ks. After melting and degassing, glassy samples were prepared by quenching the melts (samples for refractive index measurements were cooled by sandwiching with two brass plates, and samples for measurements of linear coefficient of thermal expansion were cast into brass moulds), and then were placed in a muffle furnace at 623 K for 8 h in air to remove residual strain, followed by machining and polishing to obtain mirror finished surfaces for the subsequent measurements. Samples for refractive index and thermal expansion measurements were machined, respectively, into the shape of a disc (30 mm diameter and 2 mm thickness) and into the shape of a trapezoidal prism. The chemical compositions of the samples were analysed using an X-ray fluorescence spectrometer (XRF), and there were no considerable changes from the nominal compositions.

2.2. Measurements

2.2.1. Linear Coefficient of Thermal Expansion

The linear coefficient of thermal expansion is defined as follows:

\[
\alpha = \left(1/l_0\right) \cdot (dl/dT) \quad \text{.........(2)}
\]

where \( l_0 \) is the sample length at 298 K. In the present work, the value of \( \alpha \) was determined by using the apparatus with image analysis equipment as shown in Fig. 1. The apparatus consisted of a furnace with a mullite tube, a He–Ne laser source and a CCD camera. The furnace tube (1 m length and 5 cm inner diameter) had two metal stoppers at both ends, and the stoppers had a gas inlet and outlet as well as optical windows. Furthermore, the stoppers and the furnace tube ends were water-cooled. In addition, two micrometer-levelers were attached to both ends of the tube. A He–Ne laser source with a beam expander was placed at
one side of the furnace to project the sample shape through an optical filter to control the brightness, and a CCD camera (10M pixels) was placed at the other side. The whole system was set on an aluminium rail system to make optical alignment easier. The furnace had a uniform temperature zone large enough to accommodate the sample. Temperature of the sample was measured using an R type thermocouple positioned just outside the furnace tube; prior to the measurement, calibration was made between this thermocouple temperature and the sample temperature.

In the measurement, a sample was placed on a BN substrate on the sample stage made of ceramic brick in the furnace and was kept strictly horizontal by adjusting the levellers. Subsequently, the sample was heated in a flow of He up to a measurement temperature and illuminated by the laser. The sample image was recorded with the CCD camera (Fig. 2), and the image data were transferred onto a PC for image processing. The number of pixels covering the sample width was counted, where necessary, pixels at the sample edge were edited so that the contour of the sample became smoother. The linear coefficient of thermal expansion was derived from the elongation, i.e., the change in the sample width, with temperature increase. Measurements were made in the temperature range between room temperature and 673 K. Several runs were carried out at each temperature to confirm the reproducibility of the elongation measurements.

2.2.2. Refractive Index

Refractive indices of glass samples were measured using a rotating-analyser type ellipsometer combined with an electric furnace having six MoSi$_2$ heating elements, as shown in Fig. 3. This ellipsometer had a 2 mW He–Ne laser (632.8 nm wavelength and 1 mm beam diameter) as the probe light, whose angles of incidence and reflectance were adjusted to 59.9° with respect to the sample surface. To reduce radiation effects from the sample and the heating elements, two diaphragms (5.0 mm and 2.0 mm diameter) were placed in the optical path and, furthermore, an interference filter for 632.8 nm was attached to the detector. The reflected probe light was linearly polarised with the polariser and difference filter for 632.8 nm was attached to the detector. The sample stage of alumina in the furnace so that the reflected light entered the analyser. Measurements were started at room temperature and made at intervals of about 50 K during the heating cycle up to 573 K in air. The sample temperature was measured with a K-type thermocouple positioned near the sample. The total pressure in the furnace was reduced to 0.5 atm to avoid the fluctuation of the probe light due to air convection. About 20 runs were carried out at each temperature to confirm the reproducibility of the measurements.

3. Results

3.1. Data for Linear Coefficient of Thermal Expansion

To confirm the accuracy of the present method, preliminary measurements of elongation were made on SiO$_2$, 80SiO$_2$–20Na$_2$O and 70SiO$_2$–30Na$_2$O glasses in the temperature range from room temperature to 673 K, and then the linear coefficients of thermal expansion were derived from Eq. (2) using linear regression. Figure 4 shows the linear coefficients of thermal expansion for SiO$_2$–Na$_2$O glasses along with reported values. The present data lie roughly in the middle of the reported values; thus, the present method is considered to be suitable for measurement of linear coefficients of thermal expansion for silicate glasses.

Figure 5 shows the length in pixel for a 60SiO$_2$–25TiO$_2$–15Na$_2$O glass as a function of temperature as an example from the SiO$_2$–TiO$_2$–Na$_2$O system, where the uncertainty range represents the maximum and minimum data at each temperature. Table 2 gives the linear coefficients of thermal expansion for all the glasses investigated along with their standard deviations. Figure 6 shows the linear coefficients of thermal expansion for the SiO$_2$–TiO$_2$–Na$_2$O ternary system, where the compositions of the SiO$_2$–TiO$_2$–Na$_2$O–B$_2$O$_3$ glasses are plotted by neglecting the presence of B$_2$O$_3$ due to its low concentrations. The linear coefficients of thermal expansion tend to increase with increasing TiO$_2$ concentration. This tendency conflicts with the reported tendency that TiO$_2$ additions to SiO$_2$ glass reduce the linear coefficient of thermal expansion, finally to a negative value. This discrepancy is considered in Discussion. Figure 5 also shows the length for a 50SiO$_2$–20TiO$_2$–25Na$_2$O–5B$_2$O$_3$ glass as a function of temperature. This linear coefficient of
Thermal expansion is largest in all the samples investigated in the present work, probably due to the lowest concentration of SiO$_2$ rather than due to the effect of B$_2$O$_3$ additions.

3.2. Data for Refractive Index

To confirm the accuracy of the present method, preliminary measurements of refractive index were made on synthesized fused silica (50 mm diameter and 5 mm thickness) in the temperature range from room temperature to 600 K. Values of refractive index and its temperature coefficient ($\frac{dn}{dT}$) obtained are 1.458–1.462 (room temperature—590 K) and (1.442 ± 0.028) $\times$ 10$^{-5}$K$^{-1}$, respectively, which are in very good agreement with reported values. In addition, the standard deviation ($\sigma$) of the refractive indices is within ±1.2 $\times$ 10$^{-4}$. Thus, the present method is considered to be reliable enough for measurements of refractive indices of silicate glasses.

Figure 7 shows the refractive indices of SiO$_2$–TiO$_2$–Na$_2$O glasses as functions of temperature.
Figure 8 shows the refractive indices of 50SiO$_2$–20TiO$_2$–25Na$_2$O–5B$_2$O$_3$, 60SiO$_2$–24TiO$_2$–11Na$_2$O–5B$_2$O$_3$ and 60SiO$_2$–20TiO$_2$–15Na$_2$O–5B$_2$O$_3$ glasses as functions of TiO$_2$ concentration. The refractive indices tend to increase with increasing TiO$_2$ concentration, which tendency is similar to that observed for SiO$_2$–TiO$_2$–Na$_2$O glasses. The values of $n$ and $dn/dT$ are used to evaluate the athermal characteristic of these glasses in Discussion.

4. Discussion

4.1. Compositional Dependence of Linear Coefficient of Thermal Expansion

Figure 9 shows the linear coefficients of thermal expansion of (85–$x$)SiO$_2$–15TiO$_2$–$x$Na$_2$O and (90–$x$)SiO$_2$–10TiO$_2$–$x$Na$_2$O glasses as functions of Na$_2$O concentration.

Figure 10 shows the linear coefficients of thermal expansion of (85–$y$)SiO$_2$–$y$TiO$_2$–15Na$_2$O, (80–$y$)SiO$_2$–$y$TiO$_2$–20Na$_2$O and (90–$y$)SiO$_2$–$y$TiO$_2$–10Na$_2$O glasses as functions of TiO$_2$ concentration.

Figure 11 shows the refractive indices of SiO$_2$–TiO$_2$–Na$_2$O system: solid circles represent the pseudo ternary compositions of SiO$_2$–TiO$_2$–Na$_2$O–B$_2$O$_3$ glasses by neglecting the presence of B$_2$O$_3$.

Figure 12 shows the refractive indices of (85–$x$)SiO$_2$–15TiO$_2$–$x$Na$_2$O, (90–$x$)SiO$_2$–10TiO$_2$–$x$Na$_2$O and (100–$x$)SiO$_2$–$x$Na$_2$O glasses as functions of Na$_2$O concentration.

Figure 8 shows the refractive indices of 50SiO$_2$–20TiO$_2$–25Na$_2$O–5B$_2$O$_3$, 60SiO$_2$–24TiO$_2$–11Na$_2$O–5B$_2$O$_3$ and 60SiO$_2$–20TiO$_2$–15Na$_2$O–5B$_2$O$_3$ glasses. The refractive indices tend to increase with increasing TiO$_2$ concentration, which tendency is similar to that observed for SiO$_2$–TiO$_2$–Na$_2$O glasses. The values of $n$ and $dn/dT$ are used to evaluate the athermal characteristic of these glasses in Discussion.

Decreases with increasing TiO$_2$ concentration. Now consider bond distances between Si$^{4+}$ and O$^{2-}$ and between Ti$^{4+}$ and O$^{2-}$. The former distance is smaller than the latter distance according to ionic radii: 0.26 Å for Si$^{4+}$, 0.42 Å for Ti$^{4+}$ in tetrahedral symmetry, 0.605 Å for Ti$^{4+}$ in octahedral symmetry and 1.35 Å for O$^{2-}$. Thus, the bond between Si$^{4+}$ and O$^{2-}$ is more covalent and stronger; as a result, the addition of TiO$_2$ is likely to increase the linear coefficient of thermal expansion. According to this consideration, the report by Sanghera et al. seems strange. From the perspective of linear coefficient of thermal expansion, additions of smaller amounts of Na$_2$O and TiO$_2$ are better for decreasing the value of $(1/l)\cdot(dS/dT)$ on the basis of the present data.

4.2. Compositional Dependence of Refractive Indices

Figure 11 shows the refractive indices for the SiO$_2$–TiO$_2$–Na$_2$O ternary system, where the compositions of the SiO$_2$–TiO$_2$–Na$_2$O–B$_2$O$_3$ glasses are plotted by neglecting the presence of B$_2$O$_3$. In all the glasses, the refractive indices increase with increasing Na$_2$O concentration. To examine the effect of Na$_2$O additions on the refractive indices, consider the
Lorentz–Lorenz equation expressed by Eq. (3).

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \alpha_m D \tag{3}
\]

where \(\alpha_m\) is the molar electronic polarisability of the glass [Å\(^3\)] and \(D\) is the number density of constituent ions of the glass [Å\(^3\)]. For \(n > 1\), the left side of Eq. (3) increases monotonically with an increase in \(n\); and thus the value of \(n\) would also be controlled by the product of \(\alpha_m\) and \(D\). Values of \(D\) for SiO\(_2\) and 80SiO\(_2\)-20Na\(_2\)O can be estimated as 2.21\(\times\)10\(^{-2}\)Å\(^3\) and 2.37\(\times\)10\(^{-2}\)Å\(^3\), respectively, based upon the reported data for density.\(^{17}\) This increase in \(D\) is responsible for the increase in \(n\) with additions of NaO.

On the other hand, the molar electronic polarisability is the sum of the electronic polarisabilities of constituent ions of the glass, and \(\alpha_m\) can be expressed by the following equation.

\[
\alpha_m = N_0\alpha_0 + N_1\alpha_1 \tag{4}
\]

where \(N_0\) and \(N_1\) are, respectively, the numbers of oxide ion and each cation in the composition formula of the glass, and \(\alpha_0\) and \(\alpha_1\) are the electronic polarisabilities of oxide ion and each cation, respectively. The value of \(\alpha_1\) is greater than those of \(\alpha_0\) and dominates \(\alpha_m\); for example, the values of \(\alpha_0\)\(^{19}\) are 1.467 Å\(^3\), 1.74 Å\(^3\), 1.90 Å\(^3\) and 2.08 Å\(^3\) for SiO\(_2\), Li\(_2\)O, Na\(_2\)O and K\(_2\)O, while the values of \(\alpha_1\)\(^{19}\) are 0.0165 Å\(^3\), 0.029 Å\(^3\), 0.179 Å\(^3\) and 0.83 Å\(^3\) for SiO\(_2\), Li\(_2\)O, Na\(_2\)O and K\(_2\)O, respectively. The value of \(\alpha_0\) is also assumed to be more changeable than those of \(\alpha_1\) by glass composition because outermost electrons in oxide ion are less attracted by the nuclei. Thus, the change in \(\alpha_0\) would dominate the change in \(\alpha_m\) as well. Thus, additions of NaO provide non-bridging oxygen ions, leading to the increase in \(\alpha_m\) and \(n\). It is uncertain that additions of TiO\(_2\) provide non-bridging oxygen ions but can introduce oxide ions two times more than those of NaO, which would cause to increase \(\alpha_m\) and \(n\). In addition, in the present SiO\(_2\)-TiO\(_2\)-NaO samples, the coordination number of Ti\(^{3+}\) may change from 4 to 6 since Sandstrom et al.\(^{21}\) have reported that the coordination number of Ti\(^{4+}\) changes from 4 to 6 at 7.32 mol% TiO\(_2\) in the SiO\(_2\)-TiO\(_2\) system. Ti\(^{3+}\) in octahedral symmetry would have a greater effect of increasing \(n\) because the value of \(D\) is greater owing to the crystallographic structure and the bond distance of Ti-O.\(^{21}\) From the perspective of refractive index, additions of smaller amounts of NaO and TiO\(_2\) are better for decreasing the value of \(\left\langle\frac{1}{n}\right\rangle\cdot\left\langle\frac{d\bar{n}}{dT}\right\rangle\) of TiO\(_2\) has a greater effect. To examine this effect, consider SiO\(_2\), 95SiO\(_2\)-5NaO and 95SiO\(_2\)-5TiO\(_2\) glasses. The values of \(D\) can be estimated as 2.21\(\times\)10\(^{-2}\)Å\(^3\) for SiO\(_2\), 2.24\(\times\)10\(^{-2}\)Å\(^3\) for 95SiO\(_2\)-5NaO and 2.20\(\times\)10\(^{-2}\)Å\(^3\) for 95SiO\(_2\)-5TiO\(_2\) based upon the reported data for density.\(^{17,20}\) and are almost the same. Thus, the value of \(D\) is not responsible for the effect by TiO\(_2\) on the basis of Eq. (3), which would be explained by the value of \(\alpha_m\). As mentioned earlier, additions of NaO provide non-bridging oxygen ions, leading to the increase in \(\alpha_m\) and \(n\). It is certain that additions of TiO\(_2\) provide non-bridging oxygen ions but can introduce oxide ions two times more than those of NaO, which would cause to increase \(\alpha_m\) and \(n\). In addition, in the present SiO\(_2\)-TiO\(_2\)-NaO samples, the coordination number of Ti\(^{3+}\) may change from 4 to 6 since Sandstrom et al.\(^{21}\) have reported that the coordination number of Ti\(^{4+}\) changes from 4 to 6 at 7.32 mol% TiO\(_2\) in the SiO\(_2\)-TiO\(_2\) system. Ti\(^{3+}\) in octahedral symmetry would have a greater effect of increasing \(n\) because the value of \(D\) is greater owing to the crystallographic structure and the bond distance of Ti-O.\(^{21}\)

### 4.3. Temperature Dependence of Refractive Indices

Figure 14 shows the temperature coefficients of refractive indices of (75-x)SiO\(_2\)-20TiO\(_2\)-xNaO-5B\(_2\)O\(_3\), (85-x)SiO\(_2\)-15TiO\(_2\)-xNaO and (90-x)SiO\(_2\)-10TiO\(_2\)-xNaO glasses as functions of NaO concentration. This figure indicates that the values of \(d\bar{n}/dT\) decrease with increasing NaO concentration and that the effect of decreasing is smaller in the system containing B\(_2\)O\(_3\). Figure 15 shows the temperature coefficients of refractive indices.
of (80–y)SiO$_2$–yTiO$_2$–20Na$_2$O, (85–y)SiO$_2$–yTiO$_2$–15Na$_2$O and (90–y)SiO$_2$–yTiO$_2$–10Na$_2$O glasses as functions of the TiO$_2$ concentration and indicates that the values of $dn/dT$ increase with increasing TiO$_2$ concentration. The difference in these compositional dependences is discussed on the basis of Eq. (3). In principle, the value of $dn/dT$ is dominated by $d\alpha_x/dT$ and $dD/dT$. The value of $dD/dT$ is relevant to thermal expansion and decreases as the linear coefficient of thermal expansion ($\alpha$) becomes greater. As shown in Figs. 9 and 10, the values of $\alpha$ for all the samples range approximately between 1 and 2$\times 10^{-5}$ K$^{-1}$ and have the positive dependencies on $x$ and $y$. Accordingly, thermal expansion can explain the dependence of $dn/dT$ on the Na$_2$O concentration but not on the TiO$_2$ concentration. The dependence of $dn/dT$ on the TiO$_2$ concentration would arise from the value of $d\alpha_x/dT$. TiO$_2$ is a more covalent substance than Na$_2$O, and the bond distance between Ti$^{4+}$ and $O^{2-}$ is shorter than that between Na$^+$ and $O^{2-}$ according to ion radii of 0.26 Å, 0.42 Å, 0.605 Å and 1.35 Å for Si$^{4+}$, Ti$^{4+}$ (4 coordinate), Ti$^{4+}$ (6 coordinate) and O$^{2-}$. From the perspective of pair potential, the electronic polarisability of oxide ion in TiO$_2$ could be more sensitive to thermal expansion; as a result, additions of TiO$_2$ could provide greater values of $d\alpha_x/dT$. It is still uncertain why additions of Na$_2$O and TiO$_2$ cause the different effects on $dn/dT$ but additions of Na$_2$O are suitable for decreasing the value of (1/y)$(dS/dT)$.

4.4. Effect of TiO$_2$ Additions on Athermal Characteristic

Figure 16 shows the values of (1/l)×($dS/dT$) derived from Eq. (1) using the data obtained in the present work, plotted in the $na$–$dn/dT$ diagram. All the samples show greater values of (1/l)×($dS/dT$) than SiO$_2$, which is contrary to the initial expectation that additions of TiO$_2$ to SiO$_2$ decrease the value of $na$ and resultantly decrease the value of (1/l)×($dS/dT$). However, the 80SiO$_2$–5TiO$_2$–15Na$_2$O glass shows almost the same value as SiO$_2$. Generally, multi-component silicate systems have lower melting temperatures, which facilitates the melting process, in that heating energy can be saved and that melts can be more free from chemical contamination due to containers. In addition, introduction of more chemically stable oxides than TiO$_2$ tends to strengthen the mechanical properties of silicate glass. In these respects, the 80SiO$_2$–5TiO$_2$–15Na$_2$O glass can be an alternative to SiO$_2$, and more decrease in Na$_2$O and TiO$_2$ concentrations might give glasses with better athermal characteristic from the discussion in Sec. 4.1 and Sec. 4.2.

5. Conclusions

For the development of athermal glass, the linear coefficients of thermal expansion and refractive indices have been measured for SiO$_2$–TiO$_2$–Na$_2$O and SiO$_2$–TiO$_2$–Na$_2$O–B$_2$O$_3$ glasses with variations in chemical compositions and temperature. The findings are summarised as follows:

1. Additions of either Na$_2$O or TiO$_2$ to SiO$_2$ increase both linear coefficients of thermal expansion and refractive indices of the glasses.

2. The temperature coefficient of refractive index $dn/dT$ is increased by additions of TiO$_2$ but decreased by additions of Na$_2$O.

3. Almost all the samples have greater values of (1/l)×($dS/dT$) than SiO$_2$ glass; however, only 80SiO$_2$–5TiO$_2$–15Na$_2$O glass shows almost the same value as SiO$_2$. This finding suggests a possibility of manufacturing a glass with the same athermal characteristic as SiO$_2$ at lower temperature.

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Fig. 16. Values of (1/l)×($dS/dT$) for SiO$_2$–TiO$_2$–Na$_2$O–B$_2$O$_3$, SiO$_2$–TiO$_2$–Na$_2$O and SiO$_2$ glasses.