

Thermal Expansion Calculation of Silicate Glasses at 210°C, Based on the Systematic Analysis of Global Databases

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Abstract: Thermal expansion data for more than 5500 compositions of silicate glasses were analyzed statistically. These data were gathered from the scientific literature, summarized in SciGlass[®] 6.5. The analysis resulted in a data reduction from 5500 glasses to a core of 900, where the majority of the published values is located within commercial glass composition ranges and obtained over the temperature range 20 to 500°C. A multiple regression model for the linear thermal expansivity at 210°C, including error formula and detailed application limits, was developed based on those 900 core data from over 100 publications. The accuracy of the model predictions is improved about twice compared to previous work because systematic errors from certain laboratories were investigated and corrected. The standard model error was 0.37 ppm/K, with $R^2 = 0.985$. The 95% confidence interval of predictions for glass in mass production largely depends on the glass composition of interest and the composition uncertainty. The model is valid for commercial silicate glasses containing Na₂O, CaO, Al₂O₃, K₂O, MgO, B₂O₃, Li₂O, BaO, ZrO₂, TiO₂, ZnO, PbO, SrO, Fe₂O₃, CeO₂, fining agents, and coloring and de-coloring components. In addition, a special model for ultra-low expansion glasses in the system SiO₂-TiO₂ is presented.

1. Introduction

The thermal expansion of glasses below the glass transition range is important for glass-to-metal bonding in the lighting industry, it plays a vital role for optimizing the time-temperature cooling schedule of glassware, and it enables the development of glass sealing materials as well as the design of specialty glass products that are exposed to varying temperatures.

Numerous thermal expansion models exist in the scientific literature [1-15], summarized in a monograph by Scholze [16] and the SciGlass[®] database [17], which enable the calculation of the thermal expansion of glass below the transition range from the chemical composition. However, the accuracy of the predictions is not yet satisfactory, mainly because of the limited number of model source data employed. For example, the standard deviation, σ , of the model residuals may be listed with the residuals being the differences between experimentally observed and calculated data. The σ values in ppm/K after deletion of outliers given by Priven and Mazurin [18] are 0.59 (Appen [2]), 0.67 (Gan Fu-Si [3]), 0.89 (Novopashin and Seregin [5]), 0.60 (Shchavalev [6]), 0.62 (Takahashi [7]). The contemporary structural-chemical model by Priven has a standard deviation of the model residuals of 0.86 ppm/K [1]. Selected models are listed in Table I.

It is the objective of this work to substantially increase the model accuracy through statistical analysis of the SciGlass[®] database.

Table I: Thermal expansion models by various authors (For calculation all weight fractions are multiplied by the coefficients below, and the products are summed to obtain α in ppm/K.)

Oxide	Coefficients based on weight fraction of oxide (Appen based on mol fraction)				
	Winkelmann and Schott [9]	Appen [2]	Lederova et al. [15]	English and Turner [10]	Hall [11]
SiO ₂	2.67	0.5...3.8 ^a	0 ^b	0.50	0.5...4.5 ^c
B ₂ O ₃	0.33	-5.0...0.0 ^d	/	-6.53	2.0
P ₂ O ₅	6.67	14.0	/	/	/
Al ₂ O ₃	16.67	-3.0	1.685	1.40	5.0
Li ₂ O	6.67	27	/	/	/
Na ₂ O	33.33	39.5 (41) ^e	32.172	41.60	38.0
K ₂ O	28.33	46.5 (49) ^e	38.068	39.00	30.0
MgO	0.33	6.0	3.059	4.50	2.0
CaO	16.67	13	11.680	16.30	15.0
SrO	/	16	/	/	/
BaO	10.00	20	5.375	14.00	12.0
Fe ₂ O ₃	13.33	5.5 ^f	/	/	/
ZnO	6.00	5.0	/	7.00	10.0
PbO	13.00	13...19 ^g	/	10.60	7.5
TiO ₂	13.67	-1.5...3.0 ^h	/	/	/
As ₂ O ₃	6.67	/	/	/	/
ZrO ₂	/	-6.0	/	/	/
Sb ₂ O ₅	12.00	7.5	/	/	/
SnO ₂	6.67	-4.5	/	/	/
Cr ₂ O ₃	17.00	/	/	/	/
MnO	7.33	10.5 ^f	/	/	/
NiO	/	5.0	/	/	/
CoO	14.67	5.0	/	/	/
Applicable temperature range in °C					
/	20-100	20-400	20-300	25-90	25-T _g

^a Coefficient for SiO₂ = 10.5 – 0.1·[SiO₂] for [SiO₂] ≥ 67 mol%; otherwise 3.8 (expressions in brackets represent mol%)

^b SiO₂ is excluded from the calculation in the model by Lederova et al. Instead, a constant of 2.976 ppm/K is added.

^c Coefficient for SiO₂ derived from figure = 4.4071 + 0.04381·[SiO₂] – 0.0008333·[SiO₂]²; [SiO₂] ≥ 40 wt%

^d For glasses containing B₂O₃ the proportion F must be formed first, whereby the expressions in brackets represent mol%:

$$F = \{([Na_2O]+[K_2O]+[BaO])+0.7([CaO]+[SrO]+[CdO]+[PbO])+0.3([Li_2O]+[MgO]+[ZnO])-[Al_2O_3]\}/[B_2O_3]$$

One then obtains: Coefficient for B₂O₃ = -1.25F for F ≤ 4; otherwise -5.0.

^e Values in parentheses are valid for binary glasses SiO₂-R₂O. The coefficient for K₂O of 46.5 applies only to those glasses that contain more than 1 mol% Na₂O; otherwise, it is 42.0.

^f The coefficients for Fe₂O₃ and MnO are valid for the normally occurring oxidation states.

^g Coefficient for PbO = 13.0 for glasses with $\Sigma[R_2O] < 3$ mol%, otherwise coefficient for PbO = 11.5 + 0.5· $\Sigma[R_2O]$

^h Coefficient for TiO₂ = 10.5 – 0.15·[SiO₂] for 80 ≥ [SiO₂] ≥ 50

Accurate model predictions are only possible based on accurate experimental data. In the following paragraphs, basic measurement principles will be described with the intention to

increase experimental accuracy. The thermal expansion is ascribed to the asymmetry of the amplitude of thermal vibrations in the glass [19]. In turn, the asymmetric vibrations can be related to (a) the chemical bonding and composition, and (b) the temperature and fictive temperature (thermal history). The presence of more loosely bonded chemical units [20], an increased temperature [21, 22], and a fast cooling rate [21, 23] increase the thermal expansion. On the other hand, a more coherent network, a decreased temperature, and annealing lead to low-expansion glasses.

Most investigators publish thermal expansion values in connection with the chemical composition of the investigated glasses and the temperature range for the expansion measurement. Generally, the thermal history is assumed to have an insignificant influence as long as well annealed samples are used. However, J. P. Joule was the first to report volume changes of glass caused by expansion effects over 45 years, later connected to the "zero point depression" in precision thermometers [24, 25]. This effect is related to long-term arrangements of mobile alkali ions in glasses that are not sufficiently annealed, and it decreases the thermal expansion. O. Schott found up to 5% expansion differences between fine annealed and chilled bulk glass [26]. Hence, in this work, only annealed glasses were considered, and the thermal history was neglected.

In addition, it needs to be mentioned that glasses in specific composition ranges tend to phase-separation [27] and crystallization [28]. Because those effects can result in sudden composition-expansivity changes, only homogeneous glasses were included in this study. The findings of Stozharov and Bogatyreva [29] about expansion "jumps" in glasses were regarded as incorrect for homogeneous and well annealed glasses or categorized as a crystallization effect.

In this study, the following nomenclature will be used:

$$\text{Coefficient of linear thermal expansion, CTE} = \frac{\Delta L}{L_0 \cdot \Delta T} \quad (1)$$

$$\text{Expansivity, } \alpha = \frac{dL}{L_0 \cdot dT} \quad (2)$$

where L_0 is the initial length of the sample at room temperature, ΔL is the change of the length of the sample caused by the temperature change ΔT (for expansion, $\Delta L = \text{positive}$), and dL is the infinitesimal change of the length of the sample resulting from the infinitesimal temperature change dT ($dL = \Delta L$ for $\Delta T \rightarrow 0$).

The coefficient of linear thermal expansion (CTE) is the average slope of the $\Delta L/L_0 = f(T)$ curve within the interval ΔT , whereby α is the first derivative of the $\Delta L/L_0 = f(T)$ curve over T ; i.e., $\text{CTE} = \alpha$ for $\Delta T \rightarrow 0$ [30]. In general, α increases with increasing temperature*, which means that the CTE increases with increasing ΔT and/or if ΔT is calculated at higher temperatures [30, 31]. Most glass expansion data in the literature are stated as the CTE, for $T = 20\text{-}300^\circ\text{C}$ or $100\text{-}300^\circ\text{C}$, as given in the source data references summarized in SciGlass[®] [17] and listed in Reference [32] and partially in Table V. As estimate, it can be assumed that $\text{CTE}(20\text{-}300^\circ\text{C}) = \alpha(160^\circ\text{C})$ and $\text{CTE}(100\text{-}300^\circ\text{C}) = \alpha(200^\circ\text{C})$.

The units of the CTE and expansivity are $\text{ppm/K} = 10^{-6} \text{ K}^{-1} = 10^{-6} / ^\circ\text{C} = 10 \times 10^{-7} \text{ K}^{-1}$.

* For very few glasses the expansivity decreases with increasing temperature, such as for pure silica glass [17].

Thermal expansion measurements on glass are usually performed in push-rod dilatometers (single push rod, or differential double push rod) [33, 34]. High precision experiments require the interferometric method [35-37].

It needs to be emphasized that it is certainly not possible to obtain high-quality expansion data during the first run from a push-rod dilatometer. Even though the first cooling curve shows somewhat better reproducibility than the first heating curve, often the error is still several micrometers in the first run caused by irregular settlement of the sample and push rods, stress relaxation, change of the morphology, and the dependence of the cooling rate below 300°C from an un-controlled room temperature and air ventilation. Therefore, it is advisable to heat and cool the sample several times below the transition range without touching the dilatometer or the sample [38]. In most cases, from the second or third cycle onwards, the heating curves above 100°C become reproducible with maximal resolution. Unfortunately, these caveats were neglected in many studies reported in the scientific literature, which makes some thermal expansion values less reliable and leads to increased apparent error in predicted values.

An additional data reliability problem is depicted in the Fig. 1 and Fig. 2. Fig. 1 shows an example $\Delta L/L_0$ expansion plot for an alkaline-free sealing glass composition, measured by the author using a differential (double push-rod) dilatometer. Traditionally, the dilatometric transition temperature $T_g(\text{dil})$ is determined from the $\Delta L/L_0$ curve as the point of intersection of the tangents below and above the slope change [38]; in Fig. 1 it is about 656°C. Fig. 2 displays the first derivative of the $\Delta L/L_0$ curve from Fig. 1, calculated from a polynomial fit of the 6th degree to the $\Delta L/L_0$ curve between 100 and 620°C and defined as the expansivity in Equation (2). A graphical differentiation of the curve in Fig. 1 leads to the same result.

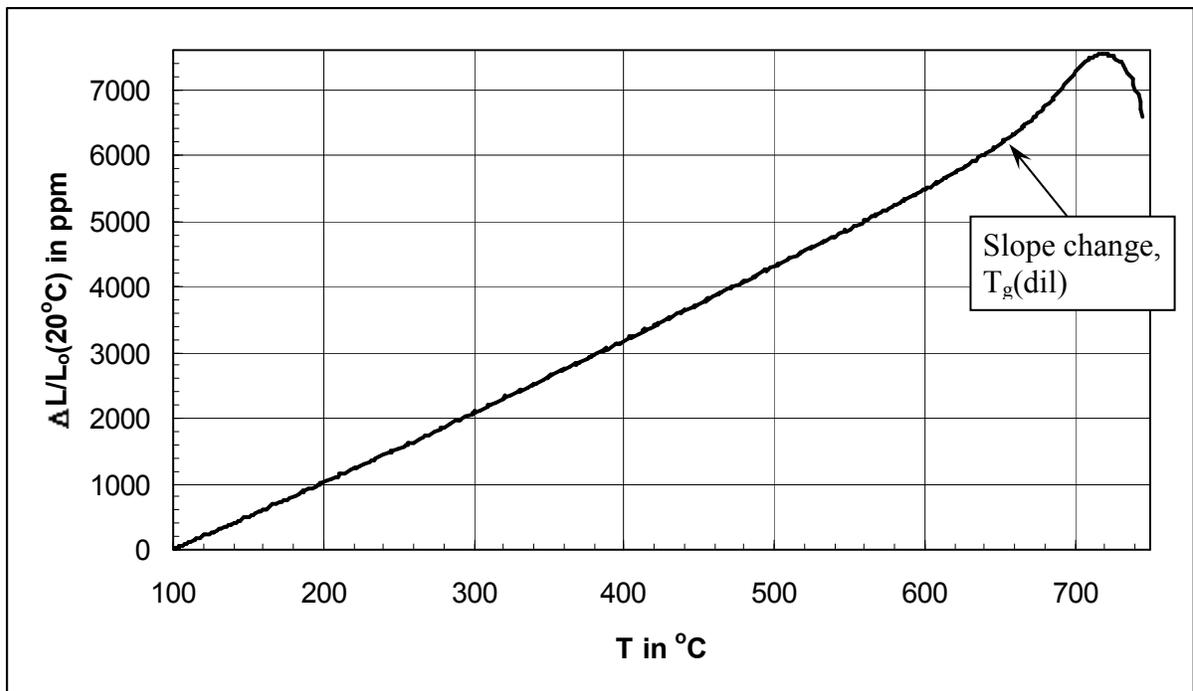


Fig. 1: Example $\Delta L/L_0$ curve (error of repeated successive runs: 9 ppm)

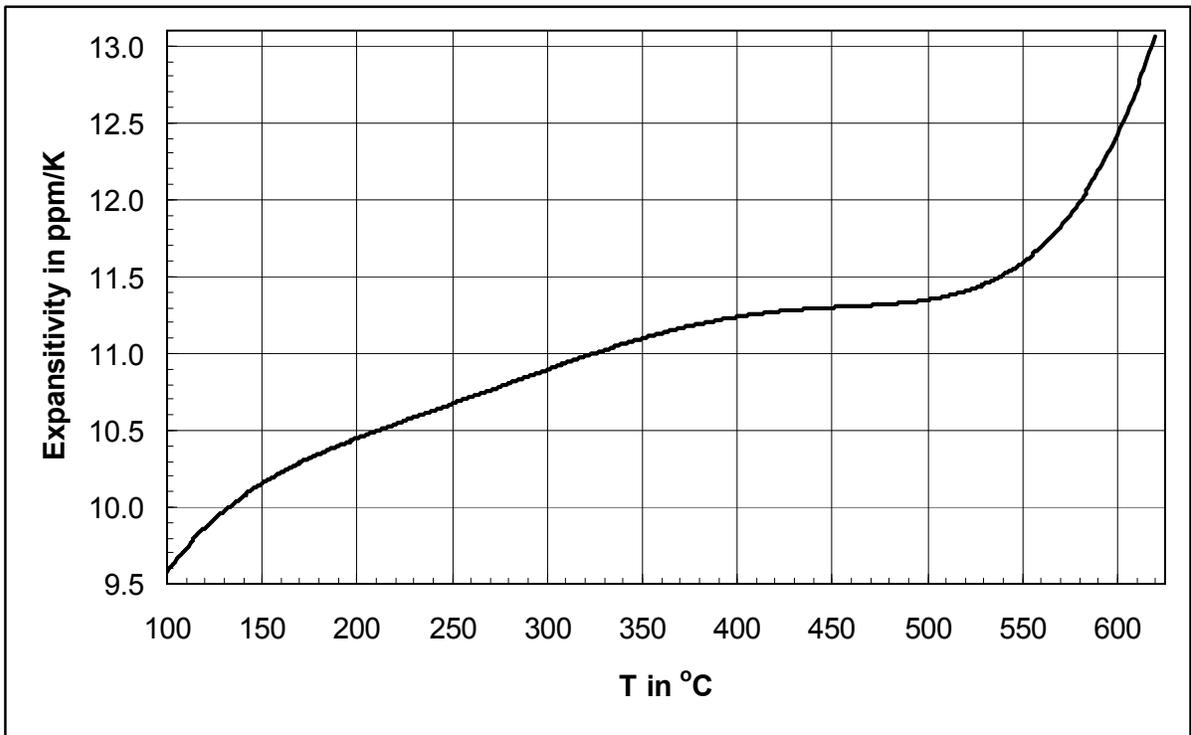


Fig. 2: Expansivity curve, example from Fig. 1 (error of repeated successive runs: 0.06 ppm/K)

Based on Fig. 2, it becomes obvious that the $\Delta L/L_0$ curve in Fig. 1 is not linear at any point, which causes CTE calculations to depend on the temperature range. In addition, the smooth slope change in Fig. 1 makes clear that $T_g(\text{dil})$ determinations by the tangent method do not result in an exact temperature, but in an approximation of the glass transition range. Also, it should be noted that the linear expansivity increases significantly even 150°C below the $T_g(\text{dil})$ of about 656°C. Therefore, CTE data valid up to $T_g(\text{dil})$ might be too high when these results are compared with the results from further authors. Other glasses show a similar expansion behavior, e.g., the borosilicate glass expansion standard reference material (SRM) 731 [31].

2. Statistical data analysis procedure

The basic principles of statistical data analysis for glasses were summarized and demonstrated previously by the author [39-41]. About 5500 thermal expansion data for silicate glasses from the SciGlass[®] 6.5 database [17] were employed. The 5500 data were reduced to about 900 when values beyond 160 to 260°C \pm 25°C and glasses outside commercial composition areas were eliminated. All references are summarized in detail in SciGlass[®] and on the authors website [32], while the important ones are also listed in Tables IV and V in the results section below. The concentrations were taken as given in mol%, or they were converted to mol% from the original numbers in wt%, wt-fraction, or mol-fraction. If available, the chemically analyzed glass compositions were used (e.g., [42]), but in most cases, the batched compositions were considered as given by the investigators. The CTE values were approximated to the corresponding α in intervals of 50°C [18] (160°C, 210°C,

260°C) with Equation (3), assuming that α can be considered as roughly constant within a temperature interval of 50°C well below the glass transition range.

$$\text{CTE}(\Delta T) = \alpha(T, \text{average}) \quad (3)$$

Example: $\text{CTE}(20\text{-}300^\circ\text{C}) = \alpha(160^\circ\text{C})$.

A slack-variable model with variable intercept was used, including multiplicative interactions and excluding silica (Equation (4)) [39, 41]. The independent variables were the concentrations in mol% (single-component variables C_j) and the multiplicative interactions (interaction variables $C_j \cdot C_k$); the dependent variable was α in ppm/K at 210°C.

$$\alpha(210^\circ\text{C}) = \beta_0 + \sum_{j=1}^n \left(\beta_j C_j + \beta_{j2} C_j^2 + \sum_{k=j+1}^n \beta_{jk} C_j C_k \right) \quad (4)$$

The β -values in the model represented by Equation (4) are the coefficients, with β_0 being the intercept, β_j being the single-component coefficients and the coefficients of squared influences, and β_{jk} being the two-component interaction coefficients [39, 41]. The variable n in Equation (4) is the total number of glass components (excluding silica); j and k are individual numbers of the glass components, and the C values are the concentrations in mol%. Expansivity data at 160°C and 260°C were included in the source database, considering a categorical offset [39, 41], compared to expansivity values at 210°C.

Linear correlations [39, 41] between variables were evaluated, and strongly correlated terms were excluded from further calculations. Reference [32] provides the correlation matrices of the significant variables. In the source database, all series published by specific laboratories were assigned categorical offset variables. The fitting method was ordinary least-square, and variable significance was determined through t-tests via mixed forward selection / backward elimination [39, 41]. Outlying datapoints were detected through standardized and externally studentized residuals [39, 41], and they were successively excluded from the calculations. Reference [32] lists the final information matrix [39, 41].

Goodness-of-fit indicators R^2 , $R^2(\text{adjusted})$, and $R^2(\text{predicted})$ were used, as well as the model standard error (Table III) and a comparison of the model standard error with the experimental error [39, 41]. In addition, a model validation procedure through data-splitting was performed. For this end, all expansivity values in the source database were sorted according to their value, and every fifth data-point was selected to form a validation database comprising 20% of all data. The remaining 80% of the data were used to establish a validation model for prediction expansivities of the 20% of the data not in the model. The residuals of the predicted 20% of the data resulted in $R^2(\text{validation})$ [39, 41].

The author's software [32] lists all model application limits. Predictions are possible through the coefficients in Table II using Equation (4), considering all application limits, or through corresponding software [32]. A property-calculation example is explained below. The standard confidence intervals of the mean model prediction and the confidence interval for glass in mass production can be derived through the mentioned software [32] following procedures given by Fluegel in a tutorial [41]. The influence of the glass composition uncertainty on the prediction confidence interval may be quantified [32, 41].

In this work, in addition to establishing a global glass expansivity model at 210°C based on about 900 experimental data from the literature, a local additivity model [39, 41] was developed for ultra-low expansion glasses.

3. Statistical data analysis results

Table II lists all significant coefficients and corresponding t-values of the global glass expansivity model at 210°C, while the coefficients are not mentioned that have an insignificant influence on the CTE as evaluated via t-test mentioned above. More than significant numbers are given in Table II to mitigate the error propagation during model application. A coefficient divided by its t-value equals the coefficient standard error. In Table III, goodness-of-fit and other related indicators [41] are displayed, and Table IV shows the data-series where the model resulted in systematic offsets as well as offsets of expansivity values reported at 160°C and 260°C. Reference [32] lists the application limits of the calculation in this study. Table V provides the properties of a large data series with 15 or more datapoints.

Table II: Coefficients and t-values of global thermal expansivity model at 210°C

Variable	Coefficient	t-value
Intercept	1.7672	/
Na ₂ O	0.4545	55.07
(Na ₂ O) ²	-0.001198	-5.62
CaO	0.1682	30.65
Al ₂ O ₃	-0.0641	-3.30
(Al ₂ O ₃) ²	0.006473	2.81
K ₂ O	0.5320	47.81
(K ₂ O) ²	-0.001710	-3.37
MgO	0.0499	6.85
B ₂ O ₃	0.0465	5.21
Li ₂ O	0.1896	15.32
(Li ₂ O) ²	0.003242	7.10
SrO	0.1717	21.63
BaO	0.3077	24.37
ZrO ₂	-0.0591	-5.23
TiO ₂	-0.0138	-3.88
ZnO	0.0102	1.96
PbO	0.1345	32.76
F	0.1305	3.93
Na ₂ O*CaO	-0.002579	-5.88
Na ₂ O*B ₂ O ₃	-0.005640	-9.91
Na ₂ O*Li ₂ O	0.018869	4.65
CaO*MgO	0.002627	4.29
CaO*B ₂ O ₃	-0.002682	-3.97
CaO*BaO	-0.011958	-5.02
K ₂ O*B ₂ O ₃	-0.012682	-5.97

Table III: Further statistical indicators of global expansivity model

Model standard error	0.3681
Standard deviation of residuals	0.3609
R²	0.9854
R ² (adjusted)	0.9848
R ² (predicted)	0.9840
R ² (validation)*	0.9850
Number of data total in model	905
Number of data, $\alpha(160^{\circ}\text{C})$	402
Number of data, $\alpha(210^{\circ}\text{C})$	298
Number of data, $\alpha(260^{\circ}\text{C})$	205
Degree of freedom	869
Observed CTE minimum	1.4700
Observed CTE average	8.3535
Observed CTE maximum	16.7000
Observed CTE standard deviation	2.9906

* A model was developed based on 80% of all data. This model was used to predict the remaining 20% of the data that resulted in R²(validation) reported above.

Table IV: Systematic offsets of global expansivity model

Variable	Coefficient	t-value
Shelby et al., 1976, 2000; Wright and Shelby, 2000 [43]	-0.477	-5.40
Karkhanavala et al., 1952 [44]	-0.649	-7.15
Bezborodov et al., 1957, 1959 [45]	0.714	5.08
Bonetti et al., 1971, 1975 [46]	0.434	4.80
Hurt et al., 1967, 1970 [47]	0.881	6.62
LaCourse et al, 1978 [48]	0.486	4.42
Deeg, 1958 [49]	-0.549	-5.44
Nakashima et al., 1999, 2001; Maeda et al., 1999, 2001 [50]	-0.233	-3.46
$\alpha(160^{\circ}\text{C})$	-0.503	-12.15
$\alpha(260^{\circ}\text{C})$	0.419	8.79

Table V: Properties of data-series with 15 or more data-points, global expansivity model (Δ - residual, σ - standard deviation, avg. - average)

Data source	# of data	Original T specification in °C	α category in °C	Δ avg. in ppm/K	σ of residuals in ppm/K	Glass type / system
Shelby, 2005 [42]	25	100-400	260	0.141	0.335	Soda-lime, container
Shelby, 2005 [42]	23	100-400	260	0.153	0.344	Soda-lime, float
Shelby, 2005 [42]	24	100-400	260	0.386	0.386	Low expansion borosilicate
Shelby, 2005 [42]	18	100-400	260	-0.201	0.438	Fiber wool
Shelby, 2005 [42]	21	100-400	260	0.212	0.383	TV panel
Shelby, 2005 [42]	24	100-400	260	-0.139	0.410	Textile fiber E-glass
Shelby et al., 1976, 2000; Wright and Shelby, 2000 [43]	26	200-300, 100-400	260	/	0.436	Alkali silicates
Baak et al., 1977 [51]	38	0-300	160	-0.136	0.159	SiO ₂ , Al ₂ O ₃ , Na ₂ O, K ₂ O, MgO, CaO, SrO, BaO, ZrO ₂
Corning Glass, 1969, 1974, 1978 [52]	19	0-300	160	0.039	0.234	SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , Na ₂ O, K ₂ O, MgO, CaO, SrO, BaO
Boyd et al., 1974, 1980 [53]	37	0-300	160	-0.103	0.363	SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , Li ₂ O, Na ₂ O, K ₂ O, MgO, CaO, SrO, BaO, ZrO ₂ , TiO ₂ , PbO
Turner et al., 1930, 1932; English et al., 1927 [54]	15	130-250	210	-0.171	0.409	SiO ₂ , Na ₂ O, Al ₂ O ₃ , BaO
Schmid et al., 1934 [55]	29	25-400	210	0.174	0.258	SiO ₂ , Na ₂ O, CaO
Akimov et al., 1960, 1989, 1991 [56]	53	20-300	160	0.023	0.257	SiO ₂ , B ₂ O ₃ , Na ₂ O
Peters et al., 1920 [57]	15	22-470	260	-0.046	0.409	SiO ₂ , B ₂ O ₃ , Na ₂ O, K ₂ O, MgO, CaO, BaO, ZnO, PbO
Mironova, 1959 [58]	30	20-400	260	0.023	0.313	SiO ₂ , Na ₂ O, TiO ₂
Karkhanavala et al., 1952 [44]	20	100-300	210	/	0.514	SiO ₂ , Na ₂ O, K ₂ O, MgO, CaO, SrO, BaO, PbO, ZnO
Bonetti et al., 1971, 1975 [46]	20	0-300	160	/	0.387	SiO ₂ , B ₂ O ₃ , Na ₂ O, K ₂ O, MgO, CaO, BaO
Dzhavuktsyan et al., 1971 [59]	30	100-300	210	0.135	0.391	SiO ₂ , Na ₂ O, K ₂ O, ZnO
Vargin et al., 1964, 1968, 1971, 1972 [60]	18	20-300, 20-420	160, 210	0.093	0.400	SiO ₂ , Li ₂ O, Al ₂ O ₃ , ZrO ₂
Tille et al., 1978 [61]	17	20-500	260	-0.034	0.311	SiO ₂ , Na ₂ O, CaO

Data source	# of data	Original T specification in °C	α category in °C	Δ avg. in ppm/K	σ of residuals in ppm/K	Glass type / system
Ambartsumyan, 1980 [62]	25	20-300	160	-0.094	0.327	SiO ₂ , Al ₂ O ₃ , Li ₂ O, Na ₂ O, K ₂ O
Tunker et al., 1982 [63]	19	20-300	160	-0.006	0.135	SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , Na ₂ O, MgO, CaO, BaO, ZnO
Deeg, 1958 [49]	15	20-300	160	/	0.340	SiO ₂ , Na ₂ O, K ₂ O, CaO, TiO ₂ , PbO
Nakashima et al., 1999, 2001; Maeda et al., 1999, 2001 [50]	61	50-350	210	/	0.281	SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , Na ₂ O, K ₂ O, MgO, CaO, BaO, ZrO ₂
Machishita et a., 1999 [64]	21	20-300	160	0.045	0.199	SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , Li ₂ O, Na ₂ O, K ₂ O, MgO, CaO, SrO, BaO, ZrO ₂

A model for ultra-low expansion glasses is given in Table VI, derived from all 29 available source data in SciGlass[®] for the System SiO₂-TiO₂ with 1.80-11.82 mol% TiO₂ [53, 65-69].

Table VI: Local model for ultra-low expansion glasses

Variable	Coefficient	t-value
Intercept	0.4088	/
TiO ₂	-0.0815	-8.68
Model standard error		0.1088
R ²		0.7436

For the purpose of error comparison with the values in Table III, small traditional additivity models were developed for various commercial glasses based on data by Shelby [42]. The standard model errors in ppm/K were 0.3307 for 48 soda-lime container and float glasses, 0.2862 for 23 low-expansion borosilicate glasses, 0.4891 for 25 fiber wool glasses, 0.7483 for 25 TV panel glasses, and 0.3041 for 25 textile fiber E-glasses.

For demonstrating model application the thermal expansivity at 210°C of a traditional TV panel glass will be estimated, examined by Shelby [42]. The chemical composition of the TV panel glass in mol% is 71.93 SiO₂, 8.66 Na₂O, 0.06 CaO, 1.42 Al₂O₃, 5.63 K₂O, 0.02 Li₂O, 6.23 SrO, 4.23 BaO, 0.79 ZrO₂, 0.38 TiO₂, 0.44 ZnO, 0.11 CeO₂, 0.07 Sb₂O₃, 0.02 Fe₂O₃, which is within the model application limits in Reference [32]. The thermal expansivity in ppm/K at 210°C can be calculated by multiplying the concentrations in mol% with the corresponding coefficients in Table II, and adding the obtained products, including the model intercept:

$$\begin{aligned}
\alpha(210^\circ\text{C}) &= 1.7672 + 8.66 \times 0.4545 - (8.66)^2 \times 0.001198 + 0.06 \times 0.1682 - 1.42 \times 0.0641 \\
&+ (1.42)^2 \times 0.006473 + 5.63 \times 0.5320 - (5.63)^2 \times 0.001710 + 0.02 \times 0.1896 \\
&+ (0.02)^2 \times 0.003242 + 6.23 \times 0.1717 + 4.23 \times 0.3077 - 0.79 \times 0.0591 - 0.38 \times 0.0138 \\
&+ 0.44 \times 0.0102 - 8.66 \times 0.06 \times 0.002579 + 8.66 \times 0.02 \times 0.018869 - 0.06 \times 4.23 \times 0.011958 \\
&= \mathbf{10.81 \text{ ppm/K}} = 108.1 \times 10^{-7} \text{ }^\circ\text{C}^{-1} = 108.1 \times 10^{-7} \text{ K}^{-1}
\end{aligned}$$

The average thermal expansion coefficient measured by Shelby [42] for 100-400°C is 11.20 ppm/K; i.e., the residual is 0.39 ppm/K. At this point it needs to be considered that Shelby performed his measurement for 100-400°C with the average at 250°C. Therefore, in the present work Shelby's data were categorized as the expansivity at 260±25°C. In table IV it can be seen that expansivity data at 260°C are on average 0.419 ppm/K higher than at 210°C. Consequently the model prediction at 210°C matches the experimental result very well for this TV panel glass. The 95% confidence interval for glass in mass production is 0.49 ppm/K [32, 41], which may be higher or lower for other glasses depending on how close it is to the average source data composition of the model.

4. Discussion

4.1. Modeling approach

The multiple regression slack-variable modeling technique with polynomial functions appeared to describe the expansivity data well for all silicate glasses studied. It was not observed that all glasses within a specific composition area were outlier suspects; i.e., sharp composition-property trends as seen in Fig. 3 did not seem to exist that could not be described through polynomial functions. In addition, phase-separation and crystallization effects did not occur, or, if present to a minor extent, did not influence the thermal expansivity. It is possible, however, that future experimental findings about sharp composition-property trends within the model application limits [32] may require modifications of the model Equation (4).

4.2. Model accuracy

This study enables predictions of the expansivity of silicate glasses at 210°C with a standard error of 0.37 ppm/K of the global model, based on over 100 references [17, 32]. The degree of freedom [39-41] (869, Table III) is very close to the total number of the analyzed data (905), and the model does not contain data-points with high influence [39-41] as demonstrated by R^2 (predicted) and R^2 (validation) in Table III.

The similarity between R^2 and R^2 (adjusted) in Table III shows that the model is not over-fitted with too many variables. The experimental error considering 14 investigators was estimated to be about 0.38 ppm/K, based on a simple model for 52 among the source data in the binary system SiO₂-Na₂O. The standard error of the global model of 0.37 ppm/K is sufficiently close to the experimental error, which is an indicator that the model is not over- or under-fitted. The model appears to produce the same accuracy as experimental measurements.

Table V compares hundreds of experimental data with model predictions from this work. It is not surprising that the majority of the experimental data agree well with the model because the model is based directly on these data, without intermediate assumptions about the glass structure or property relations (between expansivity and ionic radius, ionic charge, electronegativity, etc.), such as in the models by Makishima et al. [70], Hormadaly [12], Priven [1], or Novopashin et al. [5]. The advantage of the empirical modeling approach is high accuracy.

There exist numerous thermal expansivity models of other authors [1-15]. The global model in this study cannot be compared directly with the mentioned models of other authors because it is based on a high number of source data and advanced statistical analysis. It is not possible to apply the models in Table I to the source data used in this study and achieve a low error. For example, if the relatively elaborate model by Appen in Table I is applied to the source data in this work (restricted to c(SiO₂) = 50-80 mol%), the standard deviation of the

model residuals is 0.71 ppm/K, compared to 0.36 ppm/K in Table III. The average difference between model predictions derived from the global model in Table II and the model by Appen is zero, confirming overall accuracy despite a different magnitude of scattering of both models. The error in this study is reduced about twice compared to previous publications summarized in the introduction above.

At present, thermodynamic thermal expansion modeling [70] still has a limited direct practical application. However, thermodynamic models are based on basic principles that could be beneficial for understanding glass property relations.

An experimental model validation would be superior to the data-splitting and R^2 (predicted) calculation procedures used in this work. At present, it is not possible to compare model predictions to findings of other investigators because the model includes all investigators. Future experimental investigations are required.

Unfortunately, a large series by the Owens-Illinois Company [71] could not be included in this work because the expansivity values were collected in the relatively low temperature range of 80 to 170°C. The expansivity data by Owens-Illinois Company are systematically lower than the model predictions in this work because of the different temperature range examined.

The borosilicate glass expansion Standard Reference Material (SRM) 731 [31] fits in the model with a residual of 0.26 ppm/K; i.e., the standardized value is 0.26 ppm/K higher than the model predicts. It needs to be considered that the composition of SRM 731 is not certified and it comes very close to the model application limits in this work [32], i.e., the composition is rather unusual.

The data-series [43-50] in Table IV do not compare well to findings of other investigators. The systematic offsets of those series are assumed to indicate measurement errors that had to be corrected mathematically in this work. The correlation matrix in Reference [32] indicates that the systematic offsets of the series in Table IV are not strongly correlated with other model variables, which means that the offsets cannot be explained by unique glass composition regions investigated in those series. However, weak correlations remain. Future experimental investigations can help to improve the accuracy of the systematic offsets.

It cannot be claimed that all composition-expansivity trends found in Table II or rejected as insignificant are of the same accuracy. However, within the model application limits [32] all composition-property trends fall within the prediction 95% confidence interval for glass in mass production [32].

A comparison of the model standard errors of small additivity models for commercial glasses based on data by Shelby [42] mentioned in the modeling results section above with the model standard error of the global model in Table III shows that some commercial expansivity datasets cannot be described appropriately through common additivity [39-41] models, especially the multi-component TV panel glasses. This behavior is believed to be caused by component interactions that are not included in traditional additivity models, but which are considered in the global model in Table II. Traditional additivity models do not offer an advantage over the global model in Table II.

Based on those findings it is claimed that the global expansivity model in Table II is accurate, including error calculations [32]. Expansivity values of other investigators at 210°C that fall into the application ranges of this work in Reference [32], and with a residual larger than 1.1 ppm/K, might be questionable.

4.3. Model application limits

The experimental data in Fig. 3 (see discussion below about the boron oxide anomaly) demonstrate the fact that outside the composition range studied for the global model [32], glasses containing low amounts of glass network modifiers may show sharp composition-property trends (Fig. 3, 15 mol% silica) that are difficult to describe with polynomial functions [39-41]. Therefore, it is advised to consider all component-combination limits in Reference [32].

4.4. Dataset quality

Datasets without systematic offsets (Table IV) and with a low standard deviation σ of the residuals (Table V) were regarded as of high quality (high precision), for example the series by Baak et al. [51] or Tunker et al. [63]. The incorporation of those datasets in this study decreases the error of the global model and makes high accuracy predictions possible. In contrast, series with a high σ of the residuals increase the error.

4.5. Influences of glass components and component interactions on the thermal expansion

All single-component coefficients in this study have the unit (ppm/K)/mol%, and they quantify the thermal expansivity variation at 210°C from the exchange of 1 mol% SiO₂ with 1 mol% of the considered component. For example, if 1 mol% BaO is introduced into a silicate glass in exchange for 1 mol% SiO₂, the expansivity at 210°C increases 0.3077 ppm/K.

Because the main component SiO₂ was excluded from the calculation following the slack-variable modeling approach [39-41], all coefficients, in fact, represent interactions with SiO₂.

It is advised not to search for advanced physical interpretations of the model coefficients because the models are of an empirical nature. For example, it is not recommended to derive atomic radii, chemical equilibrium constants, or properties of pure silica from the coefficients in this study. A more advanced modeling approach would be required for this purpose. The models in this work only allow conclusions about experimentally observed composition-property trends.

For an accurate interpretation of model coefficients, the correlation matrix given in Reference [32] must be considered. Unfortunately, none of the variables are absolutely statistically independent; i.e., all variables more or less interfere mutually. It is believed that in the near future, it will be hardly possible to de-correlate all variables completely because it would require a high number of well-planned and accurate measurements. Therefore, it is recommended to consider the model coefficients in this paper as preliminary findings until further experimental data become available. Nevertheless, as long as all concentration limits summarized in Reference [32] are followed, accurate predictions are possible.

Because of mutual correlations, it is suggested that model predictions be compared rather than coefficient values for evaluating the influences of various glass components on the thermal expansivity for a specific practical application.

The model intercept of 1.7672 ppm/K is supposed to represent the thermal expansivity of a glass comprising mainly SiO₂ and all components with insignificant influence on the expansivity, such as H₂O, Fe_xO_y, fining agents, etc. However, few experimental data exist for high-silica glasses, and the global model in this paper is not applicable in those composition areas.

General influences of the chemical glass composition on the thermal expansion can be concluded from Table II. It appears that glass network modifying oxides such as alkali oxides (Li₂O, Na₂O, K₂O) and alkali earth oxides (MgO, CaO, SrO, BaO) increase the thermal expansion of silicate glasses the most, if exchanged for silica. Among the glass network

modifying oxides, the heavy ions with low ionic charge and large radius (i.e., low ionic potential) have the most significant influence, e.g., K_2O , Na_2O , and BaO [12]. These oxides result in a relatively loose glass network with high thermal expansion, as mentioned in the introduction. On the other hand, intermediate glass oxides, such as Al_2O_3 , ZrO_2 , and TiO_2 , tighten the glass network and decrease the thermal expansion. Similarly, many component interactions tend to decrease the thermal expansion. In general, it seems that low-expansion glasses can be obtained by introducing additional components, mainly glass network formers and intermediate oxides, to a base glass composition, while high-expansion glasses are obtained with simplified glass compositions in which intermediate glass oxides are excluded, and glass network formers are minimized.

4.5.1. Silica, SiO_2

In the work reported here, the influence of silica on the thermal expansivity is the difference resulting from the influences of the remaining glass components. In general, silica decreases the expansivity significantly. Specific values can be derived from the model in Table II.

4.5.2. Boron oxide, B_2O_3

Boron oxide increases only slightly the thermal expansion of silicate glasses on its own if exchanged for silica. However, in interaction with traditional network modifying oxides like Na_2O or CaO , the expansivity decreases significantly. Therefore, many borosilicate glasses exhibit low expansion values.

The influence of the boron oxide anomaly on the thermal expansion of glasses is well known and widely studied [20, 72]. This effect causes the expansion of borate glasses to decrease initially as alkali oxides are introduced. With further addition of alkali, the expansion goes through a minimum and increases again after the alkali concentration exceeds a specific level. The effect is commonly explained by a change in the coordination number of boron from three to four upon alkali incorporation [20, 72, 73]. The boron oxide anomaly increases in the order $K_2O < Na_2O < Li_2O$ (strongest effect), according to data by Konijnendijk and Stevels [17, 20, 74]. If silica is introduced in borate glasses, the boron oxide anomaly decreases, but it generally does not go to zero. This effect is demonstrated in Fig. 3.

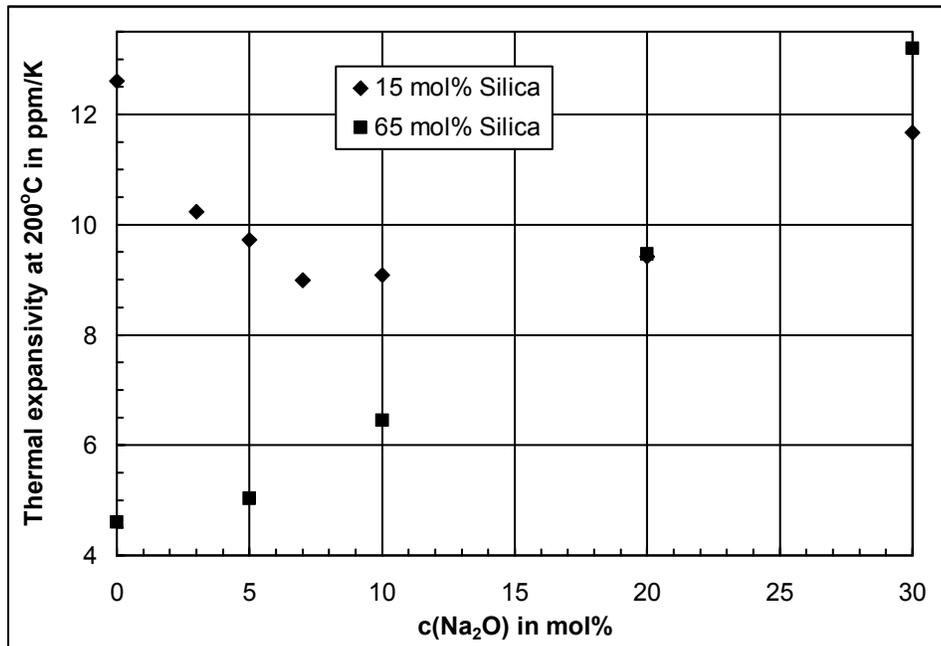


Fig. 3: Decrease of the boron oxide anomaly upon the introduction of SiO₂, data from Konijnendijk and Stevels [20, 74]

In the work reported here, 460 alkali borosilicate glasses in SciGlass[®] [17] were analyzed statistically concerning the boron oxide anomaly. The glasses contained up to 85 mol% boron oxide and as little as 5 mol% SiO₂. The coefficient for the Na₂O*B₂O₃ interaction was -0.0043, which compares well with the -0.0056 in this work. This is rather surprising, considering the different glass composition areas valid for the commercial glass global model in Table II and high-boron borosilicates. It appears that the Na₂O*B₂O₃ boron oxide anomaly itself is not much influenced by glass composition if all the remaining interactions are considered accordingly. It can be assumed that structural groups in glass do not change significantly with the glass composition [1]. The Na₂O*B₂O₃ coefficient is most significant among the interaction coefficients as seen on the t-values in Table II.

The K₂O*B₂O₃ interaction is not well represented in the global model, as evidenced through the application limits in Reference [32]. The K₂O*B₂O₃ interaction in Table II is stronger than expected from alkali borosilicate glasses in SciGlass[®] [17]. It is possible that this is an effect caused by not considering various K₂O interactions in the global model based on insufficient data and variable correlations. Therefore, it is advised for borosilicates containing K₂O to strictly follow the model application limits in Reference [32] and to consult the prediction confidence interval [39-41] derived from Reference [32].

Glasses containing appreciable amounts of Li₂O and B₂O₃ simultaneously were systematically excluded in the global model in this study because of the increased possibility of phase-separation [27].

Calcium oxide appears to cause a boron oxide anomaly compared to alkali oxides, which is reasonable based on the similar glass network modifying behavior of alkali oxides and alkali earth oxides. At the same time, it can not be completely ruled out that the CaO*B₂O₃ interaction is partly a result of phase-separation [27], especially in glasses containing high concentrations of CaO and B₂O₃. Specific model prediction confidence intervals always should be considered [32].

Fig. 4 displays expansivity values of borosilicate glasses that were calculated based on the global model in Table II. Low-expansion glasses can be obtained by reducing the concentration of Na₂O, or with lesser influence the concentration of CaO. All three components in the ternary diagram in Fig. 4 interact in such a way that the contours of constant expansivity appear nearly linear. As mentioned above, it must be considered that the simultaneous presence of B₂O₃ and CaO in glass tends to increase the phase-separation tendency [27]. The 4.34 mol% Al₂O₃ is believed to reduce the phase-separation tendency in the system shown in Fig. 4.

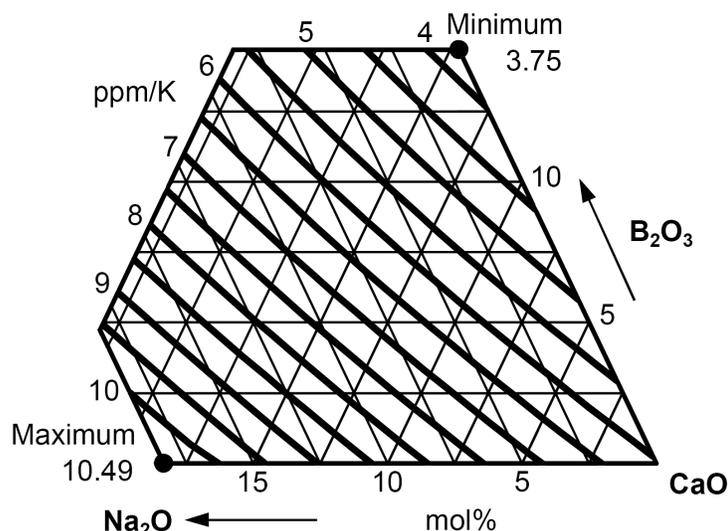


Fig. 4: Thermal expansivity predictions at 210°C in ppm/K in the system 67.94 SiO₂, 23.08 Na₂O+CaO+B₂O₃, 4.34 Al₂O₃, 3.91 MgO, 0.19 K₂O, 0.15 TiO₂, 0.23 F, 0.04 SO₃, 0.11 Fe₂O₃ (mol%); the fat lines show the expansivity contours; 95% confidence interval for glass in mass production = 0.41-0.68, depending on glass composition

4.5.3. Intermediate glass oxides (Al₂O₃, ZrO₂, TiO₂)

Most intermediate glass oxides decrease the thermal expansion of commercial glasses, which is consistent with a tightening of the glass forming network. Frequently, they are incorporated into low expanding borosilicate and other glasses (see also Table VI).

4.5.4. Alkali oxides (Na₂O, K₂O, Li₂O)

Alkali oxides increase the thermal expansion of silicate glasses in exchange for silica in the order Li₂O < Na₂O < K₂O (strongest effect), whereas in most commercial glasses sodium oxide is the component with the most significant influence. Alkali oxide interactions have various effects. Besides the boron oxide anomaly described above, the Na₂O*CaO interaction is very significant. It can be assumed that a combination of Na₂O and CaO polarizes bridging oxygen atoms effectively and tightens the glass network by increasing the strength of Si-O-Si bonds while residing in network interstices appropriate to their ionic sizes. To the authors' knowledge, no research has been published on this topic.

4.5.5. Alkaline earth oxides (MgO, CaO, SrO, BaO)

The alkaline earth oxides increase the thermal expansion in exchange for silica less than the alkali oxides. Barium oxide has the strongest influence, while MgO has only a small effect.

CaO interactions found in this work require further studies. The thermal expansion of soda-lime glasses is displayed in Fig. 5.

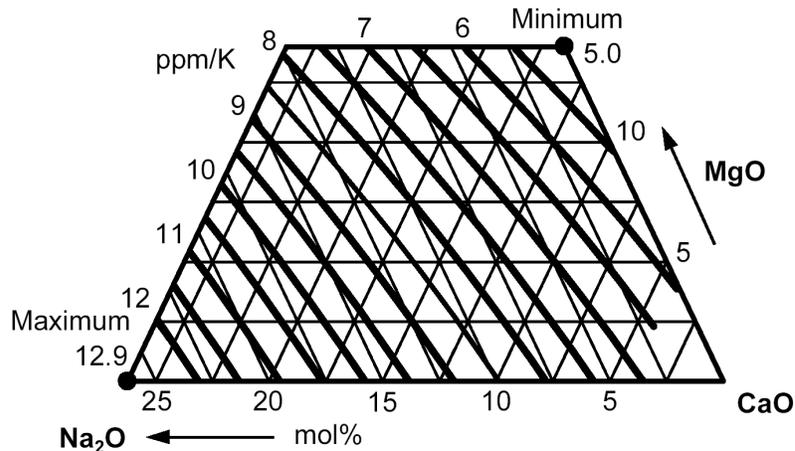


Fig. 5: Thermal expansivity predictions at 210°C in ppm/K in the system 73.13 SiO₂, 26.23 Na₂O+CaO+MgO, 0.42 Al₂O₃, 0.10 K₂O, 0.01 TiO₂, 0.08 SO₃, 0.03 Fe₂O₃ (mol%); the bold lines show the expansivity contours; 95% confidence interval for glass in mass production = 0.27-0.60 depending on glass composition

4.5.6. Lead oxide, zinc oxide (PbO, ZnO)

Lead and zinc oxide increase the thermal expansion similar to CaO and MgO, respectively. The expansivity trends in lead oxide containing glasses are displayed in Fig. 6. In the system 85 SiO₂+PbO, 15 K₂O (mol%), a relative large confidence interval of up to 0.73 ppm/K is found.

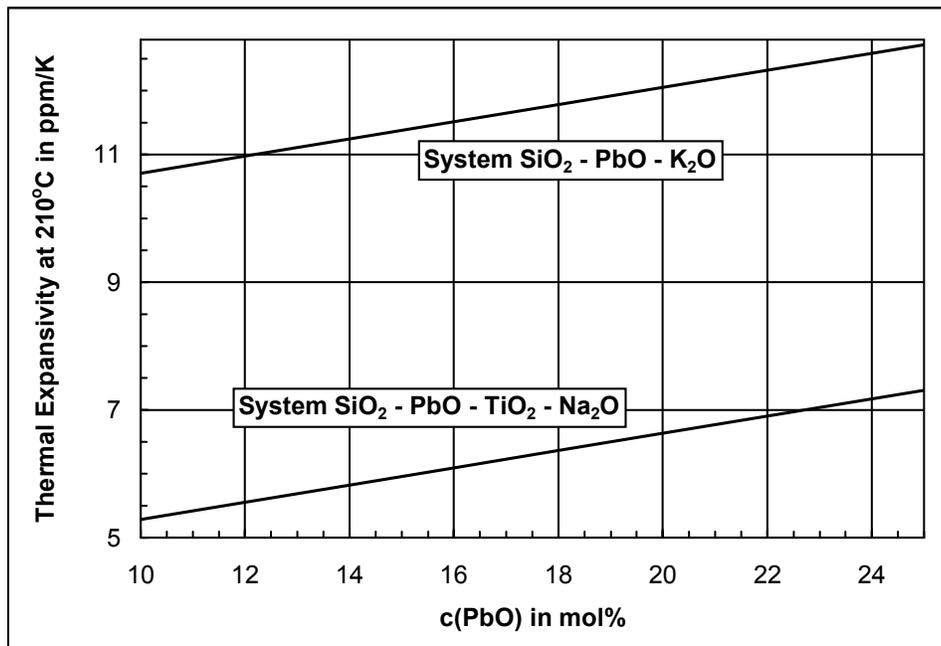


Fig. 6: Thermal expansivity predictions at 210°C in ppm/K in the systems 90 SiO₂+PbO, 5 Na₂O, 5 TiO₂ and 85 SiO₂+PbO, 15 K₂O (mol%); 95% confidence interval for glass in mass production = 0.37-0.73 depending on glass composition

4.5.7. Fluoride ions (F^-)

Fluoride ions increase the thermal expansion, most likely because they tend to break up the glass network by forming terminal Si-F bonds.

4.6. Temperature-specific offset corrections

The temperature-specific offset corrections for the expansivities at 160°C and 260°C in Table IV show that expansivity of silicate glasses increases about 0.46 ppm/K with increasing temperature in the studied composition and temperature range.

4.7. Recommendations for practical model application

The global model in Table II in this paper is suggested for thermal expansivity predictions of commercial silicate glasses at 210°C, following its application limits in Reference [32]. The expansivity of ultra-low expansion glasses can be calculated based on the model in Table VI.

It is advised to use the thermal expansivity software based on this study [32] because the application limits of the global model are evaluated automatically, and, at the same time, expansivity predictions and prediction confidence intervals are calculated. The software also considers the influence of uncertainties in glass composition in the error calculation.

5. Conclusions

Models based on multiple regression with polynomial functions were provided for estimating the thermal expansivity of silicate glasses at 210°C from their chemical composition with double the accuracy compared to previous publications. The accuracy of the model predictions is comparable to experimental measurements. The influences of specific glass components and component interactions could be quantified. Some important glass components are not included as yet. A number of interactions are correlated too strongly for analysis within the composition ranges covered. Notwithstanding these shortcomings, success has been demonstrated in estimating the thermal expansivity from the chemical composition.

Acknowledgements

I would like to thank Oleg V. Mazurin, St. Petersburg, Russia, for providing a large number of thermal expansion data from the SciGlass[®] information system and two unknown reviewers for their valuable input.

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