

# Density and thermal expansion calculation of silicate glass melts from 1000°C to 1400°C

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*The relation between the chemical composition and the density of silicate glass melts at temperatures of 1000°C to 1400°C was analysed statistically. The analysis was founded on all 140 to 260 available values in the SciGlass information system for compositions containing more than 40 mol% silica, less than 40 mol% boron oxide, varying amounts of Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, MgO, CaO, PbO, and minor components. A model based on multiple regression was developed. The 95% confidence interval of the mean model prediction on the density was 0.5 to 3%, depending on the composition of interest. The prediction of density as a function of temperature made possible the estimation of the coefficient of thermal expansion in the molten state to within 20 to 40% error with a 95% level of confidence.*

## Introduction

The density and the thermal expansion of glass melts are important factors for glass furnace modelling. When combined with the knowledge of the viscosity–temperature curve, bubble content, temperature distribution, thermal conductivity, and other factors, it is possible to calculate the convective flow in a furnace tank. Furthermore, density and thermal expansion play important roles during glass fining and forming, e.g. during gob formation, glass fiberisation, and the float process. Despite its importance, the reported measurements of glass melt density and thermal expansion are few (compared to room temperature density and thermal expansion) because of experimental difficulties.

The SciGlass database and information system,<sup>(1)</sup> which summarises the findings from most glass related publications in material sciences over more than 100 years, contained at the time of this study 1698 chemical composition–density data of glass melts in the range of 800 to 1400°C. Most of the data, however, can not be used directly for technical application because of the unusual compositions studied, e.g. silica-free borates and high lead glasses, or glasses with high concentrations of transition metal oxides, phosphor pentoxide, cesium oxide, rubidium oxide, or bismuth oxide. The glass database Interglad<sup>(2)</sup> did not list any glass melt density or thermal expansion values at the time of the present study.

Therefore, in this work, an attempt was made to condense all information available in the SciGlass information system about the density of silicate glass melts containing more than 40 mol% silica, less than 40 mol% boron oxide, varying amounts of Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O, Na<sub>2</sub>O,

K<sub>2</sub>O, MgO, CaO, PbO, and minor components into a multiple regression model. Because of insufficient data, BaO and SrO-containing glass melts were not modelled. An adequately accurate model of density as a function of temperature enables one to calculate the coefficient of thermal expansion (CTE) of glass melts.

The density of glass melts has been determined using the following techniques:<sup>(3,4)</sup> (1) the Archimedes methods;<sup>(3–6)</sup> (2) the pycnometric technique;<sup>(7)</sup> (3) the pendant and sessile drop method;<sup>(3,8–12)</sup> (4) the maximum bubble pressure method (through bubble pressure variation);<sup>(13,14)</sup> (5) measurement of the thermal expansion at higher viscosity<sup>(15,16)</sup> combined with low temperature Archimedes method experiments; (6) flotation;<sup>(17)</sup> (7) and gamma ray absorption.<sup>(18,19)</sup> The reader may refer to the listed references for further information.

In this study the following nomenclature will be used:

$$\text{Coefficient of linear thermal expansion} \\ \text{CTE}_L = \Delta L / (L_o \Delta T) \quad (1)$$

$$\text{Coefficient of volume thermal expansion} \\ \text{CTE}_V = \Delta V / (V_o \Delta T) = -\Delta \rho / (\rho_T \Delta T) \quad (2)$$

$$\text{CTE}_V \approx 3 \text{CTE}_L \quad (3) \\ (\text{within relatively narrow temperature intervals})$$

where

$L_o, V_o, \rho_o$  Initial length/volume/density of the sample

$\rho_T$  Density of the sample after the temperature change  $\Delta T$ ,  $\rho_T = \rho_o + \Delta \rho$

$\Delta L, \Delta V, \Delta \rho$  Change of the length/volume/density of the sample due to the temperature change  $\Delta T$ ; for expansion  $\Delta L, \Delta V$  positive,  $\Delta \rho$  negative

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The CTE is the average slope of the  $\Delta L/L_0=f(T)$  or  $\Delta V/V_0=f(T)$  curve within the temperature interval  $\Delta T$ , whereby the linear expansivity  $\alpha$  or the volumetric expansivity  $\beta$  is the first derivative of the  $\Delta L/L_0=f(T)$  or  $\Delta V/V_0=f(T)$  curve over  $T$ .<sup>(20)</sup> The expansivity is also referred to in the literature as “instantaneous coefficient of thermal expansion” or “true expansivity” or “true coefficient of thermal expansion” where the CTE can be called “average coefficient of thermal expansion.” In general, the expansivity increases with increasing temperature, which means that the CTE increases as well with increasing  $\Delta T$  and/or if  $\Delta T$  is reported at higher temperatures. If the expansivity is relatively constant within a sufficiently narrow temperature interval, the coefficient of volume thermal expansion  $CTE_V$  is about three times the coefficient of linear thermal expansion  $CTE_L$ .

For glasses, it is mostly observed that the expansivity below the glass transition temperature  $T_g$  increases only slightly with increasing temperature. In the glass transition region up to the liquidus temperature, the expansivity often increases 3 to 5 times, compared to the expansivity of solid glass at room temperature.<sup>(16)</sup> The expansivity again becomes relatively constant well above the liquidus temperature.<sup>(16)</sup>

Within the temperature interval of 1000 to 1400°C studied in this work, it was assumed that the expansivity of glass melts can be approximately set to be a constant, i.e.  $\alpha=CTE_L$ .

The unit of the density used in this study is  $g/cm^3$ , while the expansivity and CTE are expressed in  $ppm/K=10 \times 10^{-7} K^{-1}$ . The reciprocal of density, i.e. the volume of 1 g of a substance, is called the specific volume (unit:  $cm^3/g$ ).

### Statistical data analysis<sup>(21–24)</sup>

Most of the statistical analysis techniques applied in this paper are explained by the author in detail in Refs 25, 26. The model equation was based on a slack variable model using a polynomial function of the second degree as seen in Equation (4).<sup>(25,26)</sup> The coefficients are  $b$ , with  $b_0$  being the *intercept*,  $b_i$  the single component coefficients and the coefficients of squared influences, and  $b_{ik}$  the coefficients of two-component interactions. The variable  $n$  in Equation (4) is the total number of the significant glass components, excluding silica;  $i$  and  $k$  are individual numbers of the significant glass components, and  $C_i$  and  $C_k$  are the component concentrations (excluding silica) in mol%.  $C_i$  and  $C_i^2$  are defined as *single component factors*, and the products  $C_i C_k$  are *interaction factors*:

$$\text{Density} = b_0 + \sum_{i=1}^n \left( b_i C_i + \sum_{k=i}^n b_{ik} C_i C_k \right) \quad (4)$$

The density in Equation (4) is the glass melt density in  $g/cm^3$  at 1000°C, 1200°C, and 1400°C, respectively.

In the commonly applied ordinary least squares (OLS) regression, also used in this study, the coefficients in Equation (4) are determined by mathematics programs through Equation (5) with  $\mathbf{Y}$  being the 1-column matrix of all experimental observations (glass melt densities), and  $\mathbf{B}$  the 1-column matrix containing the coefficients  $b$ . The  $\mathbf{X}$  in Equation (5) is the matrix including all significant factors, and  $\mathbf{X}^T$  is its transpose matrix. Table 6 in the modelling results section below provides an example of the factor matrix  $\mathbf{X}$ . The operation “ $^{-1}$ ” indicates matrix inversion, and the sign “ $\cdot$ ” stands for the scalar or “dot” product. Tables 3–5 in the modelling results section summarise all matrix products  $\mathbf{X}^T \cdot \mathbf{X}$  in this work, called information matrices

$$\mathbf{B} = (\mathbf{X}^T \cdot \mathbf{X})^{-1} \cdot \mathbf{X}^T \cdot \mathbf{Y} \quad (5)$$

It is important to evaluate factor correlations before regression analysis is performed. The linear *correlation matrix* is made up of the simple, or two-way, correlation coefficients. They are denoted by the letter  $r$  and have a range of  $-1 < r < +1$  (Pearson’s  $r$ ). The correlation coefficient for two factors (independent variables) is a measure of the linear relationship between the two factors. If  $r$  is close to 1, then a plot of the two factors against one another would look like a straight line with a positive slope. If  $r$  is close to negative  $-1$  then the plot of the two factors against one another would look like a straight line with a negative slope. If  $r$  is close to zero then a plot of the two factors would show no discernible linear trends.

For selecting the appropriate modelling approach, correlations between changes in the component concentrations and/or their interactions (concentration cross products) have to be considered if the data were not collected using a statistical design that is orthogonal for all of the factors of interest. If the absolute value of  $r$  is larger than approximately 0.5 to 0.6, the influences of the two considered factors are “partially correlated” (i.e. linked but not completely aliased) and may be difficult to separate. If the absolute value of  $r$  is larger than approximately 0.8 to 0.9, the influences are correlated so strongly that they may not be separated at all in most cases, and the factors should be combined, or one factor should be excluded. Equation (6) can be used to calculate  $r$ , with  $n$  being the number of experiments and  $x$  and  $z$  the variables that need to be tested for correlation:

$$r = \frac{\sum xz - (\sum x \sum z) / n}{\left[ \left( \sum x^2 - (\sum x)^2 / n \right) \left( \sum z^2 - (\sum z)^2 / n \right) \right]^{1/2}} \quad (6)$$

The *t-value* (also called *t-statistic*) is an indicator of the significance of a model factor (component concentration or concentration product). In other words, it is a measure of how much information a factor adds to the model. In general, a *t-value* with

absolute value greater than or equal to 2 is considered to be significant, with a statistical confidence level of approximately 95%. Most minor components are insignificant, i.e. their influence is less than the standard error (noise). The  $t$ -value is calculated from the quotient of the considered coefficient  $b$  and the standard error of the coefficient  $S_b$ . In general, the absolute  $t$ -value tends to increase with (1) increasing number of experiments, (2) decreasing standard error of the regression model (see below), (3) decreasing correlation between the levels of the different components, and (4) increasing variation of component levels (wider component concentration limits). The  $t$ -value for a specific coefficient  $t_b$  can be determined through Equation (7) with  $b$  being the coefficient,  $S$  being the model standard error from Equation (8), and  $S_b$  being the standard error of the coefficient  $b$ .  $C_{ij}$  in Equation (7) is the diagonal element of the inverse information matrix  $(\mathbf{X}^T \cdot \mathbf{X})^{-1}$  in Equation (5) corresponding to the coefficient  $b$ . An example for the calculation of the  $t$ -value is demonstrated in this paper in the section where the modelling results are reported. All  $C_{ij}$  in Table 8 in the modelling results section are underlined

$$t_b = b / (S \cdot C_{ij}^{1/2}) = b / S_b \quad (7)$$

The *model standard error* ( $S$ ) for regression analysis is given in Equation (8). It is the standard deviation of the residuals,  $\Delta$  ( $\Delta$  = observed value – calculated value), in terms of the regression degrees of freedom, which depends on the number of experiments ( $n$ ) and the number of factors in the model ( $p$ ) excluding the intercept  $b_0$ . Approximately 68% of all residuals fall within the limits of  $\pm S$ . The model standard error is a good estimate for the overall measurement repeatability, which comes close to accuracy if data from many sources are analysed appropriately:

$$S = \left( \frac{\sum \Delta^2}{n - p - 1} \right)^{1/2} \quad (8)$$

Regression analysis assumes the residuals are normally distributed. Thus, a datapoint may be regarded as an *outlier* if the residual is larger than three times the model standard error (=standardised residual larger than three), if the largest residual is higher than 1.5 times the next largest residual, or if the externally studentised residual<sup>(26,27)</sup> is higher than three.

The *standard deviation of the residuals*  $\sigma$  can be determined through Equation (8) with  $p=0$ .  $\sigma$  may be used for error comparison with other models that are not based on multiple regression.

The *standard prediction error of the mean* or “true” response (PE) for a specified glass composition of interest can be determined using Equation (9). The factor 1-column matrix is  $\mathbf{x}_0$ , which is derived from the glass composition of interest, with  $\mathbf{x}_0^T$  being its 1-row transpose. An example for  $\mathbf{x}_0^T$  can be found in

Table 7 in the modelling results section

$$PE = S(\mathbf{x}_0^T \cdot (\mathbf{X}^T \cdot \mathbf{X})^{-1} \cdot \mathbf{x}_0)^{1/2} \quad (9)$$

The standard *confidence interval* of the mean model prediction is obtained by multiplying the standard prediction error PE with the  $t$  distribution value  $t_{a,DF}$  ( $100 \times (1-a)$  = desired confidence,  $DF$  = *degree of freedom* =  $n - p - 1$ ). For a 95% confidence and  $DF > 15$ ,  $t_{a,DF}$  can be approximated as 2. The error and confidence interval of the mean model prediction in this study are a measure for the confidence of the predicted value to be reproducible through comparison with the average of *several* replicated measurements in *different* laboratories. The confidence interval of the mean model prediction can be estimated using a density and thermal expansion coefficient calculator based on this study.<sup>(28)</sup>

Naturally, the standard error for predicting a *single* future experiment (PS) is higher than the standard error for predicting the mean response (PE). The PS may be estimated through Equation (10). The comparison of PE and PS demonstrates the fact that single experiments are less valuable than measurement series for evaluating model accuracy, i.e. a single measurement has a higher error than the average from several measurements

$$PS = (S^2 + PE^2)^{1/2} \quad (10)$$

The model standard error  $S$  must be always larger than the standard deviation of repeated measurements, otherwise the model is “over-fitted” (i.e. unrealistically good fitted). The standard prediction error of the mean (PE) is lower than the standard deviation of repeated experiments.

The standard prediction confidence interval of the mean for *multiple* glass compositions or the *simultaneous confidence interval* of the mean (SCI, Equation (11)) reflects the certainty that all of several predicted values are within the specified range with the desired confidence (S-method<sup>(26,29)</sup>). SCI should be preferred over PE and PS in glass technology because it shows the confidence related to mass production

$$SCI = PE(pF_{a,p,DF})^{1/2} \quad (11)$$

The influence of the uncertainty of the chemical glass composition on the prediction confidence interval estimation is described elsewhere.<sup>(26)</sup>

For statistical *model validation*, the differences between *precision* (*repeatability*), *reproducibility*, and *accuracy* must be taken into account. The precision reflects the consistency and repeatability within a data-series of one experienced investigator, generally using one measurement technique. The reproducibility is a measure of how well other experienced investigators in other laboratories can reproduce the experiment. The accuracy shows the similarity to the “true” or “mean” value in case the absolute

truth is known. It is often assumed that experiments reproduced by several experienced and independent investigators are very close to being accurate, e.g. NIST or DGG glass property standards.

Consequently, for models based on one single investigator, a reproducibility and accuracy can *not* be established; only the precision may be evaluated. However, in high quality publications that contain experimental data the author is always using external values for calibration and/or comparison. Therefore, even for some models based on one single study accuracy can be estimated. For models based on several investigators, the reproducibility may be determined, which can be assumed to come close to accuracy if many investigators agree. Statistical model validation can be obtained by:

- (1) Splitting of the source data into one set for modelling and a second set for comparing predicted and experimental data,
- (2) Comparing the model predictions to experimental data from another investigator,
- (3) Comparative modelling of two data-series from different investigators where coefficients and residual trends are compared with and without the second series,
- (4) Comparative modelling of several data-series from various investigators including careful analysis of correlations, over/underfitting, systematic trends, and data leverage,<sup>(25,26)</sup>
- (5) Developing two independent models based on data-series from different investigators in similar composition regions, and comparing the model coefficients, and
- (6) Developing two independent models, including all possible component interactions based on data-series from different investigators in different composition regions (compositions in mol%) and comparing the model coefficients.

If the standard errors are comparable to the errors found during model evaluation, and correlations/trends are considered, it can be assumed that the model is accurate, i.e. it is "validated". Method (1) can be used for an internal validation of the model precision, and methods (2) to (6) allow conclusions concerning the total accuracy by comparison with other investigators. In this work method (4) was applied.

In general, a good multiple regression model has the following properties:

- All factors in the model are significant (absolute of  $t$ -values  $>2$ ), all excluded factors are insignificant (absolute of  $t$ -values  $<2$ ), i.e. no over/underfitting occurs.
- Accurate predictions can be made using the model. The standard error of the model  $S$  is not significantly (about 1.7 times) larger than the standard deviation of repeated experiments from

several investigators.

- The standard error of the model  $S$  is higher than the standard deviation of repeated experiments from several investigators, i.e. the model is not over-fitted.
- The coefficients make physical sense, according to the judgment of experts familiar with the modelled property.
- Follow-up experiments within the model application limits agree with the model predictions.

For further details of the regression procedure, please refer to Refs 25, 26.

### Application limits of polynomial equations, advanced regression techniques

In principle, regression analysis can be applied for handling properties of glass melts as long as a systematic relation exists between the experimental conditions and the resulting properties. However, even though regression analysis can be used in almost all cases, it could be used incorrectly. The most important issue is the possibility of sharp extrema in glass melt properties. Besides crystallisation and phase separation effects based on incomplete melting, sharp extrema may occur in glasses with a network former content higher than 85 to 90 mol%. For example, the Littleton softening point of 100% pure silica glass may be estimated as  $1666 \pm 50^\circ\text{C}$  from 54 datapoints in SciGlass.<sup>(1)</sup> If as little as 0.06 mol% sodium oxide is introduced, the Littleton softening point decreases dramatically to  $1280^\circ\text{C}$  according to Leko.<sup>(30)</sup> In addition to high silica glasses, sharp property extrema may also be expected for glasses with high concentrations of  $\text{B}_2\text{O}_3$  (based on modelling studies of the authors),  $\text{P}_2\text{O}_5$ , and  $\text{GeO}_2$ , or if extreme compositions on the limit of glass formation are studied (e.g. 50 mol%  $\text{Na}_2\text{O}$ +50 mol%  $\text{SiO}_2$ ).

Sharp property extrema also appear to exist in alkali aluminosilicate glass melts with high  $\text{Al}_2\text{O}_3$  concentrations,<sup>(31,32)</sup> especially if the molar ratio Al/Na is approximately 1 to 1.2.

If sharp property extrema occur, advanced regression techniques must be applied, i.e. Equation (4) must be modified substantially. One example is the modelling of glass liquidus temperatures through neural networks.<sup>(33)</sup> Alternatively, the thermodynamic understanding of glass melts can be incorporated in the regression equation directly. For example, in a binary model glass melt system A–B, the properties can be assumed to be determined through the species present in the glass melt, e.g. the equilibrium concentrations [A], [B], and the associate [AB] under ideal mixture conditions:

$$\text{property} = (\text{concentration} * \text{property}[\text{A}]) + (\text{concentration} * \text{property}[\text{B}]) + (\text{concentration} * \text{property}[\text{AB}])$$

An equilibrium constant  $K$  can be introduced that quantifies the reaction between A and B:  $K=[AB]/([A]*[B])$ . The equilibrium constant  $K$  is related to the Gibbs free energy of formation.<sup>(34)</sup> The equilibrium concentration of the associate [AB] in the glass melt can be determined through Equation (12), with A and B being the total analytical concentrations. The equilibrium concentrations of [A] and [B] are obtained through  $[A]=A-[AB]$  and  $[B]=B-[AB]$

$$[AB]=\frac{KA+KB+1-(K^2A^2-2K^2AB+2KA+K^2B^2+2KB+1)^{1/2}}{2K} \quad (12)$$

If developed correctly, an advanced formalism incorporated into multiple regression procedures could allow establishing detailed relations between experimentally observed glass melt properties, thermodynamic data of inorganic materials, and possibly properties of inorganic materials in general.

In this work, the mentioned advanced techniques were not applied for practical reasons. It was found that within the composition area studied, the polynomial Equation (4) leads to a sufficient accuracy. It can not be ruled out, however, that future experimental findings require modifications of the presented glass melt density models.

## Modelling procedure

The glass melt composition–density values reported in SciGlass 6.5 are as follows: among the total number of 1698 data, 365 correspond to a glass melt temperature of 800°C, 753 to a glass melt temperature of 1000°C, 666 to a temperature of 1200°C, and 761 to a temperature of 1400°C. At the lower temperatures, the composition of the glass melts often includes lead oxide PbO and boron oxide B<sub>2</sub>O<sub>3</sub>, but not a single lead glass melt datapoint is reported for 1400°C.

It was decided to limit this research to the list of the following components, because the few available data considering uncommon glass melt components could lead to incorrect interpretations. The considered components were as follows: more than 40 mol% SiO<sub>2</sub>, less than 40 mol% B<sub>2</sub>O<sub>3</sub>, varying amounts of Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, MgO, CaO, PbO, and minor components with concentrations below 0.5 mol%.

Table 1. Initial glass melt density modelling results

	Temperature in °C			
	800	1000	1200	1400
Total number of data in model, incl. outliers	63	143	231	293
Excluded outliers	0	7	20	29
Total number of data in model, incl. outliers	63	136	211	264
Number of significant factors (independent variables)	5	6	8	10
Standard error $S$ in g/cm <sup>3</sup>	0.0822	0.0538	0.0383	0.0204
Total number of investigators	7	14	25	26

This study also took five recent composition–density data by Clare *et al*<sup>(35)</sup> into account. The density model source data references except<sup>(35)</sup> are listed in detail in SciGlass 6.5<sup>(1)</sup> and on the author's website.<sup>(28)</sup> Models were developed at 800°C, 1000°C, 1200°C, and 1400°C following the procedure described in Refs 25, 26. Table 1 lists the initial modelling results.

From the standard errors and from the number of significant model factors, it appears that density data at low temperatures are subject to higher errors than density data at high temperatures. At 800°C, the model standard error  $S$  ( $\approx$ measurement reproducibility) is so large, that, in fact, hardly any reliable relation between the glass melt composition and its density can be established. At 800°C, all data appear more or less normally distributed (aside from some influence of PbO and K<sub>2</sub>O), i.e. anything is correct, no outliers occur. On the other hand, at 1400°C, many density measurement techniques appear to work very reliably. Erroneous values can be detected easily, based on the composition–density relation.

The model predictions were compared at all temperatures. Unfortunately, it seemed that for common soda–lime–silica glasses, the predicted density values at 800°C were lower than those at 1000°C. This unusual finding may be explained by the fact that the model at 800°C did not contain any experimental composition–density dataset of a soda–lime–silica glass; it mostly contained numerous compositions high in PbO, B<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O. Even for many lead glasses, the predicted density at 800°C was surprisingly close to that at 1000°C because of inconsistencies among investigators. For all individual datasets, the density decreased with increasing temperature.\* Because of its narrow application limits, the large standard error, and inconsistencies with models at higher temperatures, the model at 800°C was not taken into account in further studies.

Similar inconsistencies were detected at 1000°C as well, but to a lesser degree. It was possible to set the 1000°C model application limits accordingly,<sup>(28)</sup> so that inconsistent composition areas could be avoided.

It should be borne in mind that in this study, glass melt density models at high temperatures appeared more accurate than the ones at lower temperatures.

## Modelling results

Table 2 displays the model coefficients and further statistical indicators. The concentration limits and component combination limits that must be consid-

\* To the authors' knowledge, there exists only one publication, by Coenen,<sup>(6)</sup> where the glass melt density is reported to increase with increasing temperature (besides 100% silica glass). The experimental findings by Coenen are discussed below in the section about the influence of B<sub>2</sub>O<sub>3</sub> on the glass melt density.

Table 2. Density model coefficients based on the glass composition in mol%, model result in g/cm<sup>3</sup> at specified temperature; excluded insignificant factors not mentioned

Factors	Coefficients		
	1000°C	1200°C	1400°C
Intercept	2.27879	2.23531	2.20989
B <sub>2</sub> O <sub>3</sub>	-0.00199	-0.00409	-0.00424
Al <sub>2</sub> O <sub>3</sub>	-0.00334*	0.00156	0.00207
Li <sub>2</sub> O	0	-0.00254	-0.00163
(Li <sub>2</sub> O) <sup>2</sup>	0	0	-0.000035
Na <sub>2</sub> O	0	0	-0.00049
K <sub>2</sub> O	-0.00760*	-0.00163	-0.00194
MgO	0*	0.00678	0.00781
CaO	0.01241	0.01028	0.00971
(CaO) <sup>2</sup>	0	0	-0.000035
PbO	0.05882	0.05784	0
(PbO) <sup>2</sup>	0.000136	0.000139	0
Al <sub>2</sub> O <sub>3</sub> *Na <sub>2</sub> O	0	0	0.000167
95% Confidence interval of the mean**			0.007-0.04
Standard error S	0.0538	0.0383	0.0204
R <sup>2</sup>	0.9986	0.9990	0.9838

\*The low coefficients for K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and MgO at 1000°C are questionable. They are based on very few experimental data.

\*\*Confidence intervals of the mean model prediction can be determined using an Excel-based calculation program.<sup>(28)</sup>

ered for model application can be evaluated using the Excel-based calculation program connected to this publication.<sup>(28)</sup> Tables 3–5 provide the information matrices  $X^T \cdot X$  for determining errors and confidence intervals of the mean model prediction according to Equation (9).

The information matrices  $X^T \cdot X$  in the Tables 3–5 were calculated as follows: first, the factor matrix  $X$  was developed. The factor matrix  $X$  contained all experimental datasets from all investigators in rows and all chemical glass melt components in columns. All outlying datasets and all insignificant glass components were deleted. Table 6 shows a part of the factor matrix  $X$  of the model at 1000°C. Next, the transpose of  $X$  is formed by converting the first column of  $X$  to the first row of  $X^T$ . Likewise, the second column of  $X$  becomes the second row of  $X^T$ , etc. The information matrix  $X^T \cdot X$  can be determined through common mathematics programs, including Excel.

The matrices in Tables 3–5 show interesting information about the data distribution within the source data. For example, the first row displays the sum of all concentrations of the specific factor, e.g. the sum of all Al<sub>2</sub>O<sub>3</sub> concentrations for the model at 1200°C is 327.2, and for MgO, it is 126.1 (Table 4). MgO is not much represented within the source data of the model at 1200°C, i.e. future experiments could be

concentrated in the influence of MgO. The matrices in Tables 3–5 also show which component combinations were not investigated so far, for instance, Table 4 does not include Li<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O–CaO, Li<sub>2</sub>O–MgO.

The example below demonstrates the prediction of the density and thermal expansion coefficient of a glass melt as well as the determination of the prediction errors, confidence intervals, and  $t$ -values. For example, it may be required to estimate properties of a soda–lime–silica container glass with the following composition in mol%: 74.42SiO<sub>2</sub>, 0.75Al<sub>2</sub>O<sub>3</sub>, 0.3MgO, 11.27CaO, 12.9Na<sub>2</sub>O, 0.19K<sub>2</sub>O, 0.01Fe<sub>2</sub>O<sub>3</sub>, 0.01TiO<sub>2</sub>, 0.16SO<sub>3</sub>. First, the density at 1400°C is determined with the help of the coefficients in Table 2

$$\begin{aligned} \text{Density at 1400°C in g/cm}^3 &= 2.20989 + 0.00207 \\ &\times 0.75 - 0.00049 \times 12.9 - 0.00194 \times 0.19 + 0.00781 \times 0.3 \\ &+ 0.00971 \times 11.27 - 0.000035 \times 11.27^2 + 0.000167 \\ &\times 0.75 \times 12.9 = \mathbf{2.314} \end{aligned}$$

Density values of 2.354 g/cm<sup>3</sup> and 2.415 g/cm<sup>3</sup> are obtained at 1200°C and 1000°C, very close to the experimental findings by Clare *et al.*<sup>(35)</sup> as seen in Figure 1. For comparison, for the same composition, the glass melt density models by Kucuk<sup>(3)</sup> and Ghiorso *et al.*<sup>(36)</sup> result in predictions of 2.326 and 2.319 g/cm<sup>3</sup>, respectively, at 1400°C, and the model by Stebbins *et al.*<sup>(37)</sup> results in the same prediction as in this work of 2.314 g/cm<sup>3</sup> at 1400°C. The density function between 1000°C and 1400°C can be calculated by linear regression: Density in g/cm<sup>3</sup> = 2.6636 – 0.00025234 × temperature in °C. For estimating the errors and confidence intervals of the mean model predictions according to Equation (9) the factor 1-column matrix of interest  $x_0$  and its transpose  $x_0^T$  must be determined. Following the example above,  $x_0^T$  is given in Table 7. Table 8 shows the inverse of the matrix in Table 3 (inverse information matrix).

The result of the matrix product for the mentioned example  $x_0^T \cdot (X^T \cdot X)^{-1} \cdot x_0$  is 0.0364. Consequently, the error of the mean model prediction PE in g/cm<sup>3</sup> at 1000°C for the chosen example is as follows: PE = 0.0538 × (0.0364)<sup>1/2</sup> = **0.0103**. If PE is multiplied with the  $t$  distribution value  $t_{a,DF}(100 \times (1-a)) = \text{desired confidence, DF} = \text{degree of freedom} = n - p - 1$ , the confidence interval of the mean model prediction is obtained. The degree of freedom for the model at 1000°C is as follows: DF =  $n - p - 1 = 136 - 6 - 1 = 129$ . The  $t$  distribution

Table 3. Information matrix  $X^T \cdot X$ , density model at 1000°C

	Intercept	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	PbO	(PbO) <sup>2</sup>	CaO	K <sub>2</sub> O
Intercept	136	283.759	364.168	2304.93	103131.83	342.79	284.179
Al <sub>2</sub> O <sub>3</sub>	283.759	2675.39	790.531	442.089	22334.313	1876.62	4.11344
B <sub>2</sub> O <sub>3</sub>	364.168	790.531	7410.96	442.089	22334.313	36.9008	103.749
PbO	2304.93	442.089	442.089	103132	4794206.9	442.089	6534.11
(PbO) <sup>2</sup>	103132	22334.3	22334.3	4794207	228223296	22334.3	225309
CaO	342.79	1876.62	36.9008	442.089	22334.313	3042.16	32.5836
K <sub>2</sub> O	284.179	4.11344	103.749	6534.11	225308.93	32.5836	4643.66

Table 4. Information matrix  $X^T \cdot X$ , density model at 1200°C

	Intercept	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Li <sub>2</sub> O	MgO	PbO	(PbO) <sup>2</sup>
Intercept	211	327.2	288.37	509.42	663.13	778.4	126.1	2006.5	92052.974
Al <sub>2</sub> O <sub>3</sub>	327.199	3174.5	859.08	2045.1	2.6726	0	72.989	442.09	22334.313
B <sub>2</sub> O <sub>3</sub>	288.372	859.08	4961.6	782.43	104.19	0	54.866	442.09	22334.313
CaO	509.417	2045.1	782.43	5478.3	190.83	0	229.92	442.09	22334.313
K <sub>2</sub> O	663.127	2.6726	104.19	190.83	16899	250	178.53	2086	75509.421
Li <sub>2</sub> O	778.397	0	0	0	250	26665	0	2253.6	102668.56
MgO	126.097	72.989	54.866	229.92	178.53	0	1554.2	442.09	22334.313
PbO	2006.47	442.09	442.09	442.09	2086	2253.6	442.09	92053	4352672.3
(PbO) <sup>2</sup>	92053	22334	22334	22334	75509	102669	22334	4352672	209839005

values for various confidence levels and a degree of freedom of 129 are:  $t=1.000$  (68.1% confidence),  $t=1.979$  (95.0% confidence),  $t=3.025$  (99.7% confidence). Finally, for the density at 1000°C and a 95% confidence level, we can state:

$$\text{Density}=(2.415 \pm 0.020) \text{ g/cm}^3$$

The 95% confidence interval of the mean model prediction at 1200°C is 0.022, and at 1400°C, it is 0.037. The error and confidence interval of the mean model prediction depend on the glass melt composition of interest that needs to be predicted.

The error and the confidence interval of the mean model prediction in this study are a measure of the confidence of the predicted value to be accurate. In other words: the error and the confidence interval of the mean model prediction reflect the confidence that the mean result obtained from multiple measurements in several laboratories will be within the confidence interval of the mean. The confidence in single future experiments (Equation (10)) is significantly lower than the confidence in the mean model fit, i.e. the confidence in several values is higher than in a single value.

In this work, for conservative estimations of the confidence interval, the deviations from a linear

density fit between 1000°C and 1400°C were added to the initially calculated confidence interval, as seen in Figure 1 and Ref. 28.

From the temperature–density curve, the thermal expansion coefficient can be determined through the Equations (2) and (3). The coefficient of the volume thermal expansion (CTE<sub>V</sub>) for the example above is 109 ppm/K, and the coefficient of the linear thermal expansion (CTE<sub>L</sub>) is 36 ppm/K. For comparison, Ghiorso *et al*<sup>(36)</sup> is predicting CTE<sub>V</sub>=74 ppm/K for the same glass melt composition, while the experimental result<sup>(35)</sup> is CTE<sub>V</sub>=91 ppm/K.

The  $t$ -value of a specific coefficient is a measure of the coefficient significance (see introduction). For example, the  $t$ -value of CaO in the model at 1000°C can be calculated in the following way using Equation (7): the coefficient  $b$  for CaO from Table 2 is 0.01241, the standard error  $S$  is 0.0538, and the diagonal element  $C_{jj}$  for CaO in the inverse information matrix  $(X^T \cdot X)^{-1}$  from Table 8 is 0.0009445. All  $C_{jj}$  in Table 8 are underlined. Consequently, the standard error of the coefficient for CaO  $S_b$  in the model at 1000°C is 0.00165 (13% error), and its  $t$ -value is 7.51. CaO has an extremely significant influence on the glass melt density at 1000°C.

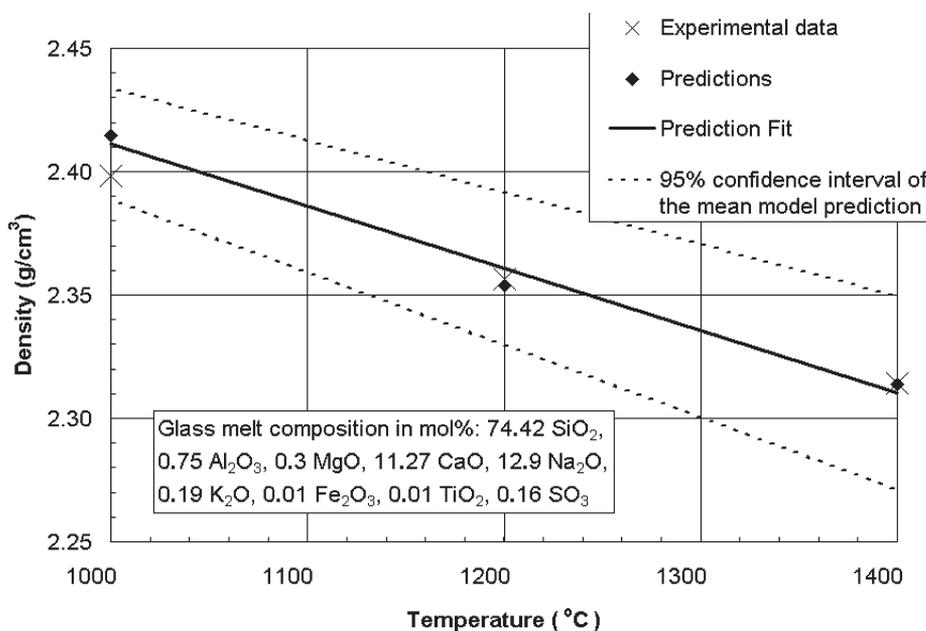


Figure 1. Example density curve, soda–lime–silica container glass

Table 5. Information matrix  $X^T \cdot X$ , density model at 1400°C

	Intercept	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	CaO	(CaO) <sup>2</sup>	K <sub>2</sub> O	Li <sub>2</sub> O	(Li <sub>2</sub> O) <sup>2</sup>	MgO	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub> .Na <sub>2</sub> O
Intercept	264	616.38	214.32	2236.33	73072.644	868.63	1159.94	40092.93	449.57	3779.3	5463.88
Al <sub>2</sub> O <sub>3</sub>	616.38	5831	856.77	12215.2	437535.74	257.24	0	0	994.81	5463.9	58118.2
B <sub>2</sub> O <sub>3</sub>	214.32	856.77	3787.2	162.723	2831.732	9.5971	0	0	59.726	2668.9	10618.5
CaO	2236.3	12215	162.72	73072.6	2876338.4	410.74	175.543	3170.31	7089.4	8828.4	23317.5
(CaO) <sup>2</sup>	73073	437536	2831.7	2876338	122393675	10920	1706.28	30815.42	217437	100186	212476
K <sub>2</sub> O	868.63	257.24	9.5971	410.741	10919.68	23642	400	8000	421.97	1549.1	860.915
Li <sub>2</sub> O	1159.9	0	0	175.543	1706.2799	400	40092.9	1607171	175.54	2975.1	0
(Li <sub>2</sub> O) <sup>2</sup>	40093	0	0	3170.31	30815.415	8000	1607171	71890675	3170.3	52316	0
MgO	449.57	994.81	59.726	7089.41	217436.98	421.97	175.543	3170.31	7072.3	3075.7	857.587
Na <sub>2</sub> O	3779.3	5463.9	2668.9	8828.36	100186.08	1549.1	2975.07	52315.95	3075.7	112693	101939
Al <sub>2</sub> O <sub>3</sub> .Na <sub>2</sub> O	5463.9	58118	10619	23317.5	212476.21	860.91	0	0	857.59	101939	1099941

Discussion

Modelling approach

The multiple regression slack-variable modelling technique using polynomial functions appeared to describe the density data well for all silicate glass melts studied. It was not observed that most glass melts within a specific composition area were outlier suspects, i.e. sharp property extrema did not seem to exist that could not be described through polynomial functions. Nevertheless, caution is advised; future experimental findings may require modifications of the model Equation (4).

Model accuracy

Since to the best of the authors' knowledge all data available in the scientific literature were included in this work, and over-fitting as well as under-fitting were avoided (see introduction), the overall modelling result can be considered as accurate as the source data allow. More precisely, the model accuracy can be assumed to be close to the standard confidence intervals of the mean model prediction following Equation (9) multiplied by the appropriate *t* distribution value *t*<sub>a,DF</sub> which may be determined using the density calculator based on this work.<sup>(28)</sup> Since the number of experimental data is finite, future experimental findings could necessitate modifications of this model. The user should be cautious, especially about predictions in glass melt composition areas where few experimental data exist. For sensitive applications, the confidence level in the density and thermal expansion coefficient calculator<sup>(28)</sup> may be increased from 95% to 99.7%.

In this work, it is suggested to consider the ex-

Table 6. Part of the factor matrix *X*, density model at 1000°C

Intercept	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	PbO	(PbO) <sup>2</sup>	CaO	K <sub>2</sub> O
1	0.75	0	0	0	11.27	0.19
1	2.92	2.89	0	0	8.97	0.54
1	0	0	46.29	2143	0	7.41
1	0.75	0	0	0	8.79	1.99
1	0	4.48	0	0	2.45	3.31
1	0	7.88	0	0	0	10.07
...	...	...	...	...	...	...
136 rows total						

perimental and predicted density data at 1200°C and 1400°C as more accurate than at 1000°C, based on the standard errors and coefficient consistency of the models. Future experimental findings may improve the accuracy considerably. At 800°C, many glass melt density data may not be reliable due to the difficulty of measurements on relatively highly viscous liquids.

Among the previously established glass melt density models,<sup>(3,36-40)</sup> the model by Kucuk<sup>(3)</sup> (glass melt density at 1400°C) and Ghiorso *et al*<sup>(36)</sup> stand out, because they are based on more data (404 and density-composition datasets at 1400°C, and 628 datasets at 428-1800°C respectively) than any glass melt density model known to the authors.

Kucuk did not summarise application limits of his model and the source data references in detail, but it is clear in his work<sup>(3)</sup> that he considered all data available from the older version 3.5 of the SciGlass information system.<sup>(1)</sup> Kucuk did not establish models for glass melt density at 1000°C and 1200°C. It is not possible to recognise how the coefficient for PbO was derived because no published data to support a PbO term are known to the authors. Within the application limits of the models in this work, the model by Kucuk predicts densities generally within the error limits of this study.<sup>(28)</sup> This is not surprising because of the similar source of data. In more detail, the standard error of the model at 1400°C in this work is 0.0204 (Table 2), and the standard deviation of the residuals is 0.0200 (see Equation (8) and following description). The standard deviation of the residuals of the model by Kucuk is 0.0973 (Table 9). If the model by Kucuk is applied exactly to the same source data as in this study, its standard deviation of the residuals is 0.0423. Therefore, it can be concluded that the model in this work at 1400°C (Table 2) is about twice as accurate as the model by Kucuk (Table 9). On the other hand, the application limits of the model by Kucuk are much wider than in this study, which may be one reason for

Table 7. Example composition 1-column matrix transpose  $x_o^T$

Intercept	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	CaO	PbO	(PbO) <sup>2</sup>
1	0	0.75	0.19	11.27	0	0

Table 8. Inverse information matrix ( $X^T \cdot X$ )<sup>-1</sup>, density model at 1000°C

	Intercept	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	PbO	(PbO) <sup>2</sup>	CaO	K <sub>2</sub> O
Intercept	0.03907	-0.000906	-0.001749	-0.001628	1.806E-05	-0.003709	-0.000911
Al <sub>2</sub> O <sub>3</sub>	-0.000906	0.0007165	-3.15E-05	3.536E-05	-3.94E-07	-0.000342	2.727E-05
B <sub>2</sub> O <sub>3</sub>	-0.001749	-3.15E-05	0.0002208	7.793E-05	-9.21E-07	0.0002089	3.57E-05
PbO	-0.001628	3.536E-05	7.793E-05	0.0006606	-1.3E-05	0.000162	-0.000204
(PbO) <sup>2</sup>	1.806E-05	-3.94E-07	-9.21E-07	-1.3E-05	2.646E-07	-1.89E-06	4.334E-06
CaO	-0.003709	-0.000342	0.0002089	0.000162	-1.89E-06	0.0009445	7.946E-05
K <sub>2</sub> O	-0.000911	2.727E-05	3.57E-05	-0.000204	4.334E-06	7.946E-05	0.000346

the larger error. Other causes for Kucuk's relatively large error could be based on the fact that he did not perform a correlation or an outlier analysis (see introduction). For comparison, the model by Kucuk can be applied using the Excel-based calculator based on this work.<sup>(28)</sup>

Ghiorso *et al* also did not specify application limits for their work, but they can be derived from very detailed references with partially listed source data including all 628 temperature–density–silica molar fraction datasets and the glass systems employed.<sup>(36)</sup> The model by Ghiorso *et al* is centred at 1400°C; densities at lower and higher temperatures are calculated through linear approximation based on the source data. The standard deviations of the residuals for the model by Ghiorso *et al* are 0.2332 (overall), 0.2139 (interpolated to 1400°C), 0.1803 (excluding 209 glasses containing iron oxides), and 0.1507 (interpolated to 1400°C and excluding 209 glasses containing iron oxides). Compared to the standard deviation of the residuals in this work at 1400°C of 0.0200, the model by Ghiorso *et al* seems to be less reliable, which is partially caused by not performing an outlier analysis. Some predictions in the model by Ghiorso *et al* deviate as much as 1 g/cm<sup>3</sup> from the experimental data and possibly influence the whole model inappropriately. However, it is a big advantage that the model by Ghiorso *et al* can be applied over a very wide temperature range (428–1800°C, considering narrower limits set by the knowledgeable user) to all glasses containing iron oxides, taking into account the iron oxide oxidation state. Those properties make the model by Ghiorso *et al* very interesting for use in geology, as long as the more specialised model in this work can not be applied instead.

The glass melt density model by Priven<sup>(40)</sup> can only be employed through the updated SciGlass program 4.0 or higher<sup>(1)</sup> and Priven's doctoral thesis<sup>(41)</sup> (in Russian) because the calculation details are not published otherwise. For the authors of this work Priven's model was not available. It is stated by Mazurin<sup>(4)</sup> that within the limits of the models by Stebbins *et al*<sup>(37)</sup> and Bottinga *et al*,<sup>(39)</sup> the model by Priven<sup>(40)</sup> is less accurate. Therefore, comparisons of the models by Stebbins *et al* and Bottinga *et al* to this work allow conclusions regarding the model by Priven. Overall, the model by Priven<sup>(40)</sup> ( $\sigma=0.106$  g/cm<sup>3</sup>) appears to have a similar accuracy at 1400°C to the model by Kucuk ( $\sigma=0.0973$  g/cm<sup>3</sup>).

The models by Ghiorso *et al*,<sup>(36)</sup> Stebbins *et al*,<sup>(37)</sup> Kucuk,<sup>(3)</sup> Mo *et al*,<sup>(38)</sup> by Bottinga *et al*<sup>(39)</sup> and this study (Table 2) were used for predicting all 264 density values in this work at 1400°C, minus 56 values of glasses containing B<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O (B<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O fall outside the range of the models by Ghiorso, Stebbins, Mo, and Bottinga). The standard deviation of the residuals  $\sigma$  of Ghiorso's model was 0.0322,  $\sigma$  of Stebbins' model was 0.0295,  $\sigma$  of Kucuk's model was 0.0441,  $\sigma$  of Mo's model was 0.0388,  $\sigma$  of Bottinga's model was 0.0355, and  $\sigma$  of the model in this work was 0.0196. This means that even though all models appear more accurate for soda–lime–silica glasses than Kucuk's, the model in this study is, by far, the most accurate. It is still surprising that the relatively low number of source data of Stebbins' model (exact number not known) leads to a better accuracy than the models by Ghiorso *et al* and Kucuk that are based on as many as 628 and 404 source data, respectively. Obviously, a high number of data does not guarantee a high accuracy; a careful handling of the data is required as well.

Figure 2 displays the experimental data and the model fit for the binary system SiO<sub>2</sub>–Na<sub>2</sub>O at 1400°C. It can be seen that the experimental data by Shartsis *et al*<sup>(42)</sup> and Coenen<sup>(6)</sup> are surprisingly similar and systematically different from other investigators. It is

Table 9. Glass melt density model by Kucuk,<sup>(3)</sup> 1400°C

Factors	Coefficients, 1400°C
Intercept	4.3464759
SiO <sub>2</sub>	-0.0212910
B <sub>2</sub> O <sub>3</sub>	-0.0257820
Al <sub>2</sub> O <sub>3</sub>	-0.0140990
Li <sub>2</sub> O	-0.0247570
Na <sub>2</sub> O	-0.0246630
K <sub>2</sub> O	-0.0233130
CS <sub>2</sub> O	0.0147320
MgO	-0.0148380
CaO	-0.0129100
SrO	0.0039526
BaO	0.0154421
PbO	0.0423592
FeO	0.0056412
SiO <sub>2</sub> .Na <sub>2</sub> O	0.0000451
Al <sub>2</sub> O <sub>3</sub> .Na <sub>2</sub> O	0.0004011
Al <sub>2</sub> O <sub>3</sub> .MgO	0.0004238
Standard deviation of residuals* in g/cm <sup>3</sup>	0.0973
R <sup>2</sup>	0.9889

Excluded insignificant factors: Rb<sub>2</sub>O, MnO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>\*Li<sub>2</sub>O, SiO<sub>2</sub>\*K<sub>2</sub>O, CaO\*PbO, SiO<sub>2</sub>\*MgO, SiO<sub>2</sub>\*CaO, SiO<sub>2</sub>\*Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>\*B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>\*BaO, SiO<sub>2</sub>\*PbO, Al<sub>2</sub>O<sub>3</sub>\*CaO, Al<sub>2</sub>O<sub>3</sub>\*B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>\*BaO, Na<sub>2</sub>O\*B<sub>2</sub>O<sub>3</sub>. \*The standard deviation of residuals is very close to the standard error of the model due to the high degree of freedom (see introduction)

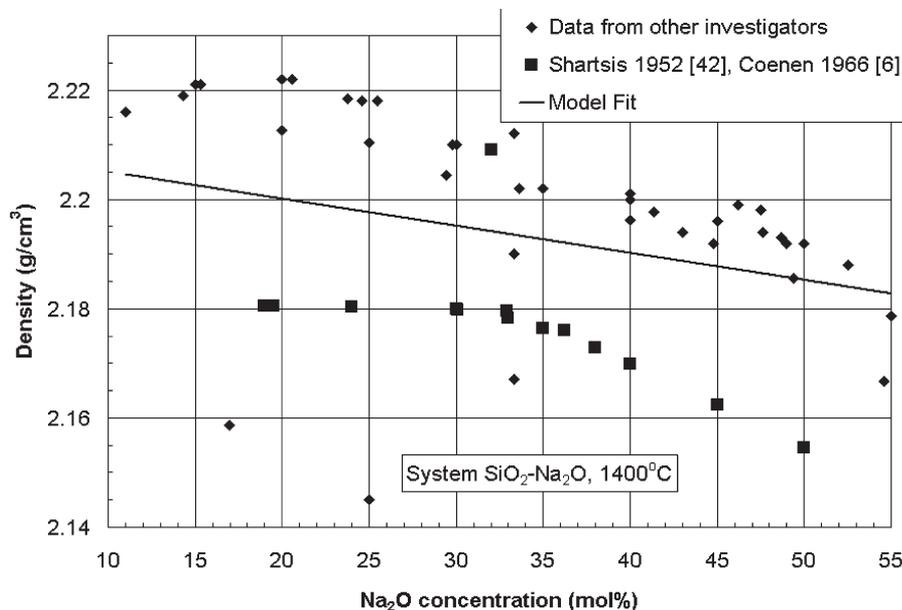


Figure 2. Experimental data and model fit for the binary system  $\text{SiO}_2\text{-Na}_2\text{O}$  at  $1400^\circ\text{C}$

possible that Coenen in 1966 used the experimental data by Shartsis *et al* from 1952 for calibration, even though it is not stated in Coenen's publication.<sup>(6)</sup> The similarities between Shartsis' and Coenen's findings appear too close to be explained by using the same measurement technique only. The same trends of Shartsis' and Coenen's data are observed at other temperatures in the system  $\text{SiO}_2\text{-Na}_2\text{O}$ , as well as in the binary system  $\text{SiO}_2\text{-K}_2\text{O}$  at  $1200\text{-}1400^\circ\text{C}$ . In this work, it did not appear beneficial to try to correct systematic errors mathematically<sup>(25,26)</sup> because strong correlations between assumed systematic errors and some coefficients in Table 2 exist based on the few experimental data available, i.e. the difference between the influences of a glass component and a systematic error often can not be resolved satisfactory.

From Figure 2, it can be estimated that the error of repeated density measurements at  $1400^\circ\text{C}$  considering several investigators is approximately  $0.02\text{ g/cm}^3$ . At  $1200^\circ\text{C}$ , an error of  $0.03\text{ g/cm}^3$  can be assumed, and at lower temperature, no approximations are possible at the present time. The error of repeated density measurements of one investigator using one experimental technique is approximately  $0.002$  to  $0.01\text{ g/cm}^3$ <sup>(4)</sup> for solid glass and glass melts (excluding the glass transition range). The difference between the error of one investigator compared to the overall error of several investigators is caused by small systematic errors that can not currently be resolved.

#### *Effects of the composition on the silicate glass melt density and thermal expansion*

The models in this study were developed in the way that the coefficients in Table 2 directly reflect the density change caused through an exchange of silica by

$1\text{ mol\%}$  of the considered glass melt component. For example, if  $1\text{ mol\% CaO}$  is introduced into a silicate glass melt in exchange for silica, the density ( $\text{g/cm}^3$ ) would increase  $0.0124$  at  $1000^\circ\text{C}$ ,  $0.0103$  at  $1200^\circ\text{C}$ , and  $0.0097$  at  $1400^\circ\text{C}$ , plus further changes due to component interactions (not applicable to  $\text{CaO}$ ) and squared influences. The model intercepts in Table 1 are supposed to represent the density of the residual comprising mainly  $\text{SiO}_2$  and all insignificant components, beyond the application limits of this work.

For an accurate interpretation of model coefficients, the factor correlation<sup>(26)</sup> must be considered. Unfortunately, none of the factors (glass melt component concentrations, concentration products) are absolutely statistically independent, i.e. all factor influences interfere mutually. It is recommended that the model coefficients in this paper be used as preliminary findings until further experimental data become available. Nevertheless, as long as all concentration limits summarised in Ref. 28 are followed, accurate predictions are possible.

The influences of components on the glass melt density at a given temperature are related to four factors:

- (1) The atomic mass, i.e. components with high density increase the glass density more than components with low density;
- (2) The influence of the component on the thermal expansion of the glass melt, i.e. components that cause a high thermal expansion decrease the density during temperature increase;
- (3) Component interaction effects, i.e. components that develop strong bonds with others generally increase the density;
- (4) The ionic size of the component, i.e. small ions can be incorporated into small interstices of the

glass melt structure that would be empty otherwise and increase the density.

The thermal expansion is influenced by anharmonic thermal oscillation of the atoms, i.e. with increasing temperature, the glass expands. In glass melts, the thermal expansion is increased additionally through structural changes (e.g. coordination numbers, bonding angles) that may not occur below the glass transition.<sup>(4)</sup>

### Boron oxide, B<sub>2</sub>O<sub>3</sub>

Boron oxide decreases the density of silicate glass melts based on its low molecular mass. Boron oxide interactions could not be analysed in this work because of data scatter, but it should be noted that the well-known boron anomaly (B<sub>2</sub>O<sub>3</sub>–alkali oxide interaction) leads to an increase of the density of solid borosilicate glasses.<sup>(43,44)</sup> Because the influence of the boron anomaly decreases with increasing temperature, it is possible that at glass melting temperature the boron anomaly plays a relatively insignificant role.

Boron oxide seems to increase the silicate glass melt thermal expansion coefficient if introduced in exchange for silica.

Some interesting experimental results are reported by Coenen,<sup>(6)</sup> especially for a glass melt with the following high boron composition in mol%: 60SiO<sub>2</sub>, 24B<sub>2</sub>O<sub>3</sub>, 8Na<sub>2</sub>O, 8Al<sub>2</sub>O<sub>3</sub>. For this glass, the density at 1200°C was found to be 2.12 g/cm<sup>3</sup>, and at 1400°C, it was 2.17 g/cm<sup>3</sup>,<sup>(1)</sup> i.e. the density increases significantly with increasing temperature. The models in this work, to the contrary, result in a density of 2.15 g/cm<sup>3</sup> at 1200°C and 2.13 g/cm<sup>3</sup> at 1400°C. Unfortunately, few experimental data are available for comparison. According to Clare *et al.*,<sup>(35)</sup> the density of industrial E-glass and low expansion borosilicate glass melts decrease with increasing temperature. Similarly, a borosilicate glass melt density curve by Volff<sup>(17)</sup> shows a decrease of the density with increasing temperature. It is either possible that the model in this study is inaccurate concerning the prediction of Coenen's composition or that Coenen made a systematic error during his experiments (e.g. B<sub>2</sub>O<sub>3</sub> evaporation). Coenen explains his findings with the simultaneous presence of B<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in the glass melt because he did not observe the density increase with increasing temperature for an Al<sub>2</sub>O<sub>3</sub>-free borosilicate glass.

### Alumina, Al<sub>2</sub>O<sub>3</sub>

Alumina clearly increases the glass melt density at high temperatures (1200 to 1400°C). At lower temperatures (1000°C), the opposite appears to be the case; however, the negative coefficient for Al<sub>2</sub>O<sub>3</sub> at 1000°C may be questionable because it is based on

very few experimental data.

If alumina and sodium oxide are simultaneously present in a silicate glass melt at 1400°C, the Al<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O interaction leads to an increase of the density. At the same time, Al<sub>2</sub>O<sub>3</sub> seems to permit the sodium ions an increased mobility by reducing nonbridging oxygen sites.<sup>(25,45)</sup> It is possible that the Al<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O interaction results in a stronger Si–O–Al bonding than without the presence of sodium ions because sodium donates electrons to the Si–O–Al bond and allows Al to act as network former ([AlO<sub>4/2</sub>]<sup>−</sup> tetrahedra). A stronger Si–O–Al bonding increases the density.

At 1000°C and 1200°C, the Al<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O interaction could not be analysed because of a very strong correlation between Al<sub>2</sub>O<sub>3</sub>.Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>. Future experiments are required to clearly separate the influences of Al<sub>2</sub>O<sub>3</sub> and the Al<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O interaction at 1000°C and 1200°C.

It is possible to obtain a better model fit at 1400°C by assuming an Al<sub>2</sub>O<sub>3</sub>–MgO interaction that increases the density. However, many data correspond to one specific investigator (Winterhager *et al.*<sup>(46)</sup>). Therefore, it is not clearly possible at present to conclude whether an Al<sub>2</sub>O<sub>3</sub>–MgO interaction exists that increases the density significantly or whether Winterhager *et al.* made a systematic error during their measurements. Measurements by several investigators would increase the reliability.

Alumina appears to decrease the thermal expansion coefficient of silicate glass melts.

### Lithium oxide, Li<sub>2</sub>O

In accordance with its low molecular weight and small influence on the thermal expansion, lithium oxide slightly decreases the density of silicate glass melts.

### Sodium oxide, Na<sub>2</sub>O

Sodium oxide does not have a strong influence on the glass melt density within the studied temperature range because of the interplay between its medium molecular weight, its influence on the thermal expansion, and component interactions. At 1400°C, adding Na<sub>2</sub>O appears to decrease the density, whereas at lower temperatures the influence of Na<sub>2</sub>O addition is not readily recognised.

In the binary system SiO<sub>2</sub>–Na<sub>2</sub>O, the thermal expansion coefficient derived from this work<sup>(28)</sup> is higher than that reported by Shartsis *et al.*<sup>(42)</sup> Based on the numerous experimental data of glasses that were considered containing Na<sub>2</sub>O, it is possible that the findings in this study are more accurate than those by Shartsis *et al.* For soda–lime–slica glasses, observations similar to the thermal expansion derived from this work<sup>(28)</sup> are given by Haggerty & Cooper.<sup>(16)</sup>

### Potassium oxide, K<sub>2</sub>O

Despite the relatively high molecular weight of potassium oxide, it significantly decreases the density of silicate glass melts. It is possible to explain this effect with a strong increase of the thermal expansion coefficient upon introduction of K<sub>2</sub>O that is observed in most industrial glasses below the glass transition temperature  $T_g$ .<sup>(47)</sup>

The low coefficient for K<sub>2</sub>O at 1000°C is questionable because it is based on very few experimental data.

It should be noted that, in this work, K<sub>2</sub>O does not seem to increase the thermal expansion of silicate glass melts (above  $T_g$ ) more than Na<sub>2</sub>O, which is in contradiction to Shartsis *et al.*<sup>(42)</sup> Based on the few available data and error levels in this study, it can not be concluded at this point whether this effect is real. In addition, the experimental findings of Shartsis *et al.*<sup>(42)</sup> may be systematically different from others as described above, i.e. the accuracy of Shartsis' data could be questionable.

It is interesting to note that all alkali oxides increase the density of solid glass,<sup>(42)</sup> but for glass melts, the opposite seems to be the case. It appears that in solid glass, the alkali oxides are incorporated into small interstices of the silica network without expanding them significantly. In glass melts, on the other hand, the thermal expansion is increased and the increased thermal oscillation of the alkali ions forces a dilatation of the interstices. An intermediate temperature region presumably exists (~1000°C for Li<sub>2</sub>O or Na<sub>2</sub>O and <800°C for K<sub>2</sub>O) where the incorporation of alkali oxides in glass melts in exchange for silica does not change the density.

The thermal expansion of most glass melts increases with increasing alkali content.

### Magnesium oxide, MgO

Magnesium oxide might not decrease the glass melt density despite its low molecular weight, because it does not appear to increase the thermal expansion coefficient significantly.

### Calcium oxide, CaO

Calcium oxide increases the glass melt density due to its relatively high molecular weight and the moderate influence on the thermal expansion coefficient.

### Lead oxide, PbO

Lead oxide has a very high molecular weight; therefore, it increases the glass melt density significantly.

From the model by Kucuk<sup>(3)</sup> (Table 9) and the experimental data in SciGlass 6.5,<sup>(1)</sup> it can be concluded that SrO and especially BaO increase the glass melt density. Likewise, according to Kucuk,<sup>(3)</sup>

Cs<sub>2</sub>O increases the density. The influences of FeO and Fe<sub>2</sub>O<sub>3</sub> are well described by Ghiorso *et al.*<sup>(36)</sup> over wide temperature ranges. The effects of MnO and Rb<sub>2</sub>O appear uncertain at the present time.

The interpretation of the significant and insignificant interaction coefficients in the model by Kucuk (Table 9) may not always lead to correct conclusions. Kucuk did not perform a correlation analysis (Equation (6)); the factors of the investigated interaction coefficients could strongly interfere with others.

Given the glass melt density, it is possible to estimate the heat capacity based on the kinetic theory.<sup>(37,48–50)</sup> Experimental data and models<sup>(37)</sup> for the heat capacity are available in SciGlass.<sup>(1)</sup> In papers by van der Tempel<sup>(51)</sup> a relation was established between the density, the heat capacity, and the thermal (phonon) conductivity of glass melts up to 1000°C. In future, it would be interesting to evaluate if the model in this work could improve predictions for the thermal conductivity of glass melts because measurements of this property are difficult.

### Recommendations for model application

The authors recommend using the models in this paper for predicting density and thermal expansion coefficient because it appears to be more accurate than models published previously. For glass melts containing SrO, BaO, and other uncommon components not covered by Ghiorso *et al.*,<sup>(36)</sup> the experimental data in SciGlass<sup>(1)</sup> and the models by Kucuk<sup>(3)</sup> and Priven<sup>(1,40,41)</sup> can be a guide for initial estimates, while iron oxide containing and all other melts are best described by Ghiorso *et al.*<sup>(36)</sup> The model by Ghiorso *et al.* can be applied over wide temperature ranges. The models by Kucuk and Priven appear to be less accurate compared to the other models known to the authors.

For glass design through property modelling, evaporation losses during glass batch melting and possible influences of the oxidation states of transition metal oxides must be taken into account.

Because of the complexity of the calculations, it is strongly advised to use the density and thermal expansion coefficient calculator based on this study,<sup>(28)</sup> which, in addition, includes the model by Kucuk.<sup>(3)</sup> The calculator evaluates automatically the appropriate concentration and component combination limits, and it shows the density and thermal expansion coefficient predictions, the prediction confidence intervals, and the linear fit to the density–temperature curve. The calculator also performs conversions from mol% to wt% and vice versa.

### Conclusions

Models based on multiple regression using polynomial functions are provided for estimating the

high temperature density and thermal expansion coefficient of silicate glass melts from their chemical composition with high accuracy. The model can quantify the influences of specific glass melt components and component interactions. Some important glass melt components are not included as yet because of insufficient published data. A number of interactions are correlated too strongly for analysis within the composition ranges covered. Notwithstanding these shortcomings, success in the estimation of the density and thermal expansion coefficient from the chemical composition has been demonstrated.

To reduce errors in predictions, the authors recommend targeted verification experiments according to the data and data-series leverage (Cook-values<sup>(26)</sup>) in the present model, i.e. preferably those values should be verified that contribute the most information.

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## References

1. SciGlass 6.5 Database and Information System, 2005.
2. International Glass Database System INTERGLAD ver.6; New Glass Forum, Tokyo, Japan
3. Kucuk, A. Doctoral Thesis, Alfred University, New York, 1999.
4. Mazurin, O. V. in *Properties of Glass-Forming Melts* ed. by D. L. Pye, I. Joseph & A. Montenegro, CRC Press, Boca Raton, Florida, 2005.
5. Bockris, J. O'M., Tomlinson, J. W. & White, J. L. *Trans. Faraday Soc.*, 1956, **52**, 229.
6. Coenen, M. *Glastech. Ber.*, 1966, **39**, 81. (In German.)
7. Maksimov, N. N., Shashkin, V. S., Kuznetsona, M. G. & Gribkova, V. I. *Sov. J. Opt. Technol. (Engl. Transl.)*, 1984, **51**, 469.
8. Kucuk, A., Clare, A. G. & Jones, L. E. *Ceram. Trans.*, 1998, **82**, 287.
9. Clare, A. G. *Glass Res.*, 2001, **10–11**, 30–32+52.
10. Clare, A. G., Wing, D., Jones, L. E. & Kucuk, A. *Glass Technol.*, 2003, **44**, 59.
11. Clare, A. G., Landcastle, C. A. & Jones, L. E. *Phillips-TNO (Netherlands Organization for Applied Scientific Research) Seminar Proceedings*, Eindhoven, Netherlands, 1997, 8.1.
12. Passerone, A., Sangiorgi, R. & Valbusa, G. *Ceram. Int.*, 1979, **5**, 18.
13. Merker, L. *Glastech. Ber.*, 1959, **32** (12), 501. (In German.)
14. Barrett, L. R. & Thomas, A. G. *J. Soc. Glass Technol.*, 1959, **43**, 179.
15. Klyuev, V. P. *Fiz. Khim. Stekla*, 1997, **23**, 137. (In Russian.)
16. Haggerty, J. S. & Cooper, A. R. *Physics of non-crystalline solids, proceedings of the international conference*, Delft, 1964, North Holland Publishing Co. Amsterdam 1965, 436.
17. Richards, E. A. & Bergeron, C. G. *Phys. Chem. Glasses*, 1985, **26**, 177.
18. Basin, A. S., Baginskii, A. V. & Provodnikov, V. L. *Issledovanie Teplofizicheskikh Svoistv Rasvorov i Rasplavov*, Novosibirsk, 1974, 135. (In Russian.)
19. Ejima, T. & Kameda, M. *Jpn. Inst. Met.*, 1967, **31**, 120.
20. Taylor, R. E. *Thermal Expansion of Solids*, CINDAS Data Series on Material Properties, Vol. I-4, ASM International, 1998
21. Montgomery, D. G. *Design and Analysis of Experiments*, John Wiley & Sons, 2001.
22. Dowdy, S. & Wearden, S. *Statistics for Research*, John Wiley & Sons, 1983.
23. Draper, N. R. & Smith, H. *Applied regression analysis*, John Wiley & Sons, 1998.
24. *User guide of the MCA software*, Haller Information Technology System, Harold S Haller & Company, Cleveland, Ohio.
25. Fluegel, A., Earl, D. A., Varshneya, A. K. & Öksoy, D. Chapter 9 in: *High temperature glass melt property database for process modeling*, Eds. T. P. Seward & T. Vascott, The American Ceramic Society, Westerville, Ohio, 2005.
26. Fluegel, A. *Glass Technol., Eur. J. Glass Sci. Technol.*, 2007, **48**, 13–30.
27. Myers, R. H. & Montgomery, D. C. *Response surface methodology*, second edition, John Wiley & Sons, Inc. 2002, 40.
28. Microsoft Excel based prediction program available at: <http://glass-properties.com/density>
29. Scheffé, H. *Ann. Math. Stat.*, 1953, **40**, 87. Scheffé, H. *The analysis of variance*, Wiley, New York, 1959, 68.
30. Leko, V. K., Gusakova, N. K., Meshcheryakova, E. V. & Prokhorova, T. I. *Glass Phys. Chem.*, 1977, **3**, 204.
31. Hunold, K. & Brückner, R. *Glastech. Ber.*, 1980, **53**, 149.
32. Leko, V. K., Mazurin, O. V. *Glass Phys. Chem.*, 2003, **29**, 16.
33. Dreyfus, C. & Dreyfus, G. *J. Non-Cryst. Solids*, 2003, **318**, 63.
34. Shakhmatkin, B. A., Vedishcheva, N. M. & Wright, A. C. *J. Non-Cryst. Solids*, 2001, **293–295**, 220.
35. Clare, A. G., Kucuk, A., Wing, D. R. & Jones, L. E. Chapter 6 in: *High temperature glass melt property database for process modeling*, Eds. T. P. Seward & T. Vascott, American Ceramic Society, Westerville, Ohio, 2005.
36. Ghiorso, M. S. & Kress, V. C. *Am. J. Sci.*, 2004, **304**, 679.
37. Stebbins, J. F., Carmichael, I. S. E. & Moret, L. K. *Contributions to mineralogy and petrology*, 1984, 131.
38. Mo, X. X., Carmichael, I. S. E., Rivers, M. & Stebbins, J. *Miner. Mag.*, 1982, **45**, 237.
39. Bottinga, Y., Richet, P. & Weill, D. F. *Bull. Miner.*, 1983, **106**, 129.
40. Priven, A. I. *Glass Technol.*, 2004, **45**, 244.
41. Priven, A. I. *Fundamentals of the calculation of concentration-temperature-time dependencies of properties of oxide glass-forming substances in wide composition areas and temperature ranges*, Doctoral Thesis, St. Petersburg, 2002. (In Russian.)
42. Shartsis, L., Spinner, S. & Capps, W. J. *Am. Ceram. Soc.*, 1952, **35**, 155.
43. Biscoe, J. & Warren, B. E. *J. Am. Ceram. Soc.*, 1938, **21**, 287.
44. Vogel, W. *Glass Chemistry*, Springer-Verlag, 1994, 138.
45. Isard, J. O. *J. Soc. Glass Technol.*, 1959, **43**, 113T.
46. Winterhager, H., Greiner, L. & Kammel, R. *Forschungsberichte des Landes Nordrhein-Westfalen*, 1966, 1630. (In German.)
47. Seward, T. P. & Vascott, T. *High temperature glass melt property database for process modeling*, American Ceramic Society, Westerville, Ohio, 2005.
48. Kittel, C. *Introduction to Solid State Physics*, fourth ed. 1971, New York: John Wiley & Sons, Fig. 27, 231.
49. Kingery, W. D., Bowen, H. K. & Uhlmann, D. R. *Introduction to Ceramics* second ed., Wiley Series on the Science and Technology of Materials. 1976, New York, NY, John Wiley & Sons, 1032.
50. Varshneya, A. K. *Fundamentals of Inorganic Glasses*, Academic Press Inc., San Diego, CA, 1994, ISBN 0-12-714970-8, Chapter 11.
51. van der Tempel, L. *Glass Phys. Chem.*, 2002, **28**, 147.