

Liquidus Prediction in Multicomponent Lithium Aluminosilicate Glasses

Lothar Wondraczek[†] and Lionel Beunet

Corning European Technology Center, Corning S.A.S., Avon, France

An empirical nine-parameter linear mixing model was developed to estimate the liquidus temperature of zirconia-bearing technical lithium aluminosilicate glasses that contain up to 12 major components. The model covers glasses that are suitable as precursor glasses for β -quartz or β -spodumene-type glass ceramics with low coefficients of thermal expansion. Molar coefficients of liquidus temperatures are provided for each component. A self-consistency test results in a standard deviation between predicted and measured liquidus temperatures of 7.5°C, within a range of approximately 200°C and for a typical experimental error of 10°C.

I. Introduction

IN glass technology, the term “liquidus temperature,” T_l , denotes the highest temperature at which a solid phase can exist in equilibrium with the glass melt considered. For technical glasses, T_l generally has two consequences: when T_l is higher than the temperature of the melter, solids can precipitate in the melter. Those can not only accumulate with time and disturb the melter and/or feeder operation but also travel as unmelted residues all the way into the final product. Second, in combination with viscosity characteristics, T_l is usually a crucial parameter in the forming process. That is, while theoretically (physically), for a given forming process (e.g., rolling, drawing, floating), the process window is defined essentially by a viscosity range, technically, the operating temperature is limited by the available forming tools. Then, depending on the cooling and heating rates, if T_l exceeds a temperature pertinent to the forming process, devitrification might occur during forming. For a wide range of simple glasses, T_l can be estimated from thermodynamic phase equilibrium data (e.g., using FactSage¹ or other tools). To assess solution behavior in more complex melts, extended versions of the associate species model (ASM^{2,3}) may be consulted.⁴ However, particularly for multicomponent glasses that lie within the phase field of a minority component, fully empirical models are still necessary to generate data that may help to progress thermodynamic models. In the present study, an empirical linear mixing model was developed to predict T_l of ZrO₂-bearing lithium aluminosilicate melts. Molar coefficients of liquidus temperatures were computed for batches of six to 12 components, and the eventual impact of additional minor components was evaluated.

II. Methodology

Subject of the present study are multicomponent glasses of lithium aluminosilicate compositions (Li₂O–Al₂O₃–SiO₂, LAS) that lie (formally) within the primary phase fields of zirconia and

solid solutions of ZrO₂–HfO₂–SnO₂, respectively. That is, those phases are the first crystalline phases that can be observed after prolonged heat treatment near the liquidus temperature. Such zirconia-bearing glasses with L:A:S close to 1:2:10 are commonly known as precursor glasses for β -quartz or β -spodumene-type glass ceramics with a low coefficient of thermal expansion.⁵ Their liquidus temperatures are notoriously high (often > 1300°C) and, therefore, count among the main targets for compositional optimization.

In order to develop an empirical model that can be used to predict T_l , first, a database was built up, and then this database was used to determine the molar coefficient of liquidus temperature of each batch component for a given compositional range.

(1) Data Acquisition

Experimental T_l data were generated in a straightforward way: liquidus temperatures of a series of conventionally melted glasses were determined via iterations of isothermal heat treatments above and below the estimated T_l . For this, a glass sample was first held at 1480°C, supposedly well above the expected T_l . Optical microscopy was used to confirm that the thus-treated sample was free of crystallites. After that, a second isothermal heat treatment was performed at another temperature, supposedly below T_l , for > 15 h, and the sample was again analyzed for the occurrence of devitrification. Once a temperature below and a temperature above T_l were identified, the absolute location of T_l could be determined by multiple such iterations, for practical reasons, with a final precision of $\pm 10^\circ\text{C}$.

In order to generate an empirical model, an adequate number of datasets must be available, i.e., for a total of N batch components, an N -dimensional space must be covered. If, as discussed later, single components can be excluded from the model because they were shown to have no significant effect on T_l (e.g., because of low concentration), or if two or three components can be combined because their effect on T_l is similar, then the dimensionality of the model can be reduced.

To ensure optimal statistical coverage of the composition space considered, compositional variations were carried out with respect to the following aspects:

- (1) Variation of single components of a baseline composition to identify the linearity or nonlinearity of the component's effect (ZrO₂, TiO₂, HfO₂, Al₂O₃, SnO₂, BaO+SrO).
- (2) Replacing one component with another (ZrO₂/TiO₂, ZrO₂/HfO₂, SiO₂/Al₂O₃).
- (3) Changing several components at a time to best cover the whole compositional range, confirm linearity, and to, eventually, identify (nonlinear) interactions between multiple components.

In total, a set of 45 composition- T_l data was included in the database.

(2) Mixing Model

In a first approximation, T_l as a function of composition n may be described by a linear mixing model,⁶ taking into account

J. Vienna—contributing editor

Manuscript No. 23827. Received October 9, 2007; approved October 29, 2007.

[†]Author to whom correspondence should be addressed. e-mail: wondraczl@corning.com

contributions from all batch components:

$$T_l(n) = \vec{c} \times \vec{x}_n \quad (1)$$

where \vec{x}_n is the molar composition vector of the n th composition and \vec{c} is the vector of molar coefficients of liquidus temperatures for all batch components. For a batch of N components, \vec{x}_n and \vec{c} are N dimensional, and the sum is constrained by

$$\sum_{i=1}^N x_{n,i} = 1 \quad (2)$$

Empirical linear mixing models are historically^{7,8} used to predict a wide range of glass properties, e.g. melt viscosity, density, or refractive index. In recent years, such models have been used frequently to estimate liquidus temperatures of high-level waste glasses,^{9,10} particularly in the phase fields of spinel and zircon. However, it was also acknowledged¹¹ that the liquidus temperature is in fact a much more difficult parameter that does not follow simple linear trends when changing the composition. This is partly based on the fact that even relatively small compositional changes can shift the composition from one phase field to another. For example, the first phase to devitrify in technical soda lime silicate glasses may be devitrite, cristoballite, wollastonite, or one of a series of other phases, depending on the glass composition. Then, maxima, minima, and changes in slope of T_l occur in places where phase boundaries (e.g., eutectics) would be found in the corresponding phase diagram. Backman *et al.*¹¹ studied a range of different approaches to this problem, and eventually found that the best fit between experimental and calculated data results when parameters of higher order were included in a conventional linear mixing model. On the other hand, they also concluded that empirical estimations remain the most suitable as long as thermodynamic parameters are not sufficiently well described. More recently, Dreyfus and Dreyfus¹² demonstrated superior performance of neural regression methods over polynomial fits to predict liquidus temperatures empirically in systems of up to five components.

In some cases, a pragmatic way to approach the problem of nonlinearity of the T_l -composition functions is to know the devitrifying phase and to develop independent models for each possible phase. Then, however, an additional tool is required in order to obtain this knowledge. In the present case, devitrifying phases were first verified experimentally, and the model was then limited to the compositional range that reflects the respective phase fields. Devitrification was observed to generally occur via

the formation of ZrO_2 , HfO_2 , SnO_2 , ZrTiO_4 , or solid solutions of the four. In a first approximation, those phase fields were merged into one, assuming continuous solid solutions between the four components. Throughout the study, it was found that this approximation indeed yields reliable results. Such an approach significantly limits the composition space within which the model can be applied and is therefore only suitable in very specific cases such as the present one.

A statistical multiple regression analysis was performed to fit the $[T_l(n); \vec{x}_n]$ data to a linear model, and to derive the parameter vector \vec{c} . In some cases, the effect of a specific component i on T_l can be estimated by comparing the fitted c_i with the coefficient's standard deviation, SD (t -test, $t = c_i/\text{SD}_{c_i}$), and by comparing c_i with the average value of T_l . Together with the previously discussed considerations, this can be used to separate compositional constituents that have little or no effect on T_l from those that dominate the liquidus. However, to decide clearly whether and how the number of parameters can be reduced (by neglecting or pairing certain batch components), the study of Piepel and Redgate¹³ may be considered. For the present case, it was found that SrO and BaO, and K_2O , Li_2O , and MgO, respectively, could be effectively combined. In the final model, a total of nine parameters were used.

III. Results and Discussion

The final data that were obtained from fitting 45 sets of $[T_l(n); \vec{x}_n]$ to a nine-parameter linear mixing model are summarized in Table I. A goodness-of-fit, r^2 , of 0.9988, was derived after regression, indicating high linearity of the data. The y -intercept of the fit is $\sim 0.2^\circ\text{C}$, what practically corresponds to Eq. (1) (y -intercept at zero). The result of a self-consistency test is shown in Fig. 1: T_l data were calculated and compared with the experimental values of the corresponding compositions. Linear regression of those data yields a slope of experimental versus calculated T_l of 0.998 ($r = 0.9869$). The standard deviation between calculated and experimental values is 7.5°C , and the maximum deviation is 16°C (remember the experimental error of 10°C). The dotted lines in Fig. 1 represent upper and lower 95% confidence bands of the linear regression. From this, it can be concluded that, within the considered composition space, the linear model yields accurate estimates of T_l .

The good accuracy of the model is a result of the fact that the compositional space that it was designed to cover is relatively narrow. However, it covers practically all glasses that are used today, commercially, as precursor glasses for transparent low-expansion glass ceramics for applications such as cooktops,

Table I. Compositional Ranges, Molar Coefficients of Liquidus Temperatures and Statistical Data for 45 Experimental Sets of Composition and Liquidus Temperature

	Range	Mean	c_i ($^\circ\text{C}$)	Error ($^\circ\text{C}$)	t
SiO_2	0.720–0.760	0.736	1366.98	82.9	16.5
Al_2O_3	0.110–0.140	0.127	1281.99	419.6	3.1
Li_2O	0.063–0.086	0.076			
MgO	0–0.020	0.012	378.29 [†]	148.5 [†]	2.5 [†]
K_2O	0–0.015	0.003			
ZnO	0.012–0.029	0.014	2595.47	554.5	4.7
BaO+SrO	0–0.013	0.004	1526.64	580.4	2.6
TiO_2	0.004–0.025	0.013	–546.58	609.7	–0.9
ZrO_2	0.005–0.018	0.011	11 456.35	1207.8	9.5
SnO_2	0–0.002	0.001	8420.31	3285.5	2.6
HfO_2	0–0.010	0.001	15 878.31	1440.7	11.0
Data points	45				
Mean T_l	1397.5 $^\circ\text{C}$				
R^2	0.9988				
R^2 (adj.)	0.9985				
y -intercept	0.2197				
SD (self-consistency)	7.5 $^\circ\text{C}$				

[†]For ($\text{Li}_2\text{O} + \text{K}_2\text{O} + 2\text{MgO}$).

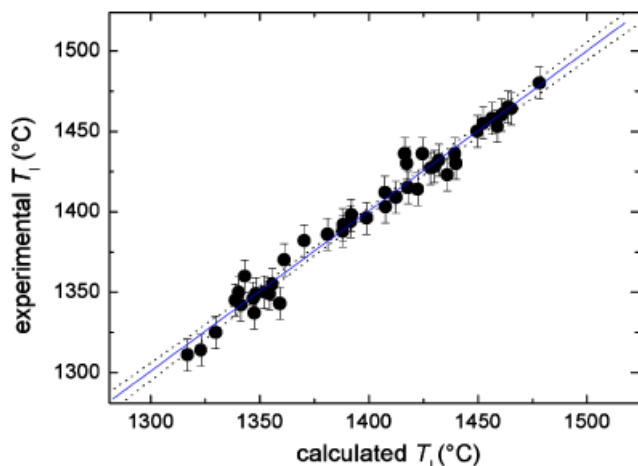


Fig. 1. Comparison of predicted and measured T_l data (see the text for details). The full line represents linear regression of the data; the dotted lines indicate 95% confidence bands.

fireplace windows, or fire protection windows. The liquidus temperature of such glasses strongly increases with increasing additions of HfO_2 , ZrO_2 , and SnO_2 , respectively, whereby the effect of HfO_2 is the strongest and that of SnO_2 is the lowest of the three. If the concentration of either of the three lies in the upper range of the model's boundaries, the first phase to crystallize that is observed experimentally is usually the end member of the solid solution, i.e., zirconia, hafnia, or SnO_2 . HfO_2 accordingly has the lowest molar solubility of all the studied components, followed by ZrO_2 and SnO_2 . This behavior can clearly be quantified with the linear mixing model that is provided in the present study. It is also not surprising that additions of Li_2O , MgO , and K_2O increase the solubility of zirconia, hafnia, and tin oxide, and thus, may decrease the liquidus temperature of the melt. However, while this is true as long as the primary phase field remains the same, the effect can be reversed if a phase boundary is crossed. For example, within the boundaries of the model, additions of Al_2O_3 may result in a decrease of T_l . However, if the alumina concentration is increased considerably, the composition may shift to the phase field of mullite, resulting in increasing values of T_l .

Note that minor additions of As_2O_3 (<0.008), V_2O_5 (<0.004), and B_2O_3 (<0.012) were originally considered, but not found to have statistically relevant effects on T_l (SD, consistency test, maximum deviation). They were thus not included in the final model.

Although extrapolation to compositions that lie outside of the database's boundaries may be possible in some specific cases, the reliability of the computed values of T_l will strongly decrease with increasing distance between those boundaries and the considered composition vector.

IV. Conclusions

A nine-parameter linear mixing model for estimating the liquidus temperature of zirconia-bearing technical lithium aluminosilicate glasses that contain six to 12 major components was derived. The validity range of the model was chosen to cover glasses that are suitable as precursor glasses for β -quartz or β -spodumene-type glass ceramics with low coefficients of thermal expansion. In a self-consistency test, the model is shown to predict values of T_l with a standard deviation of 7.5°C , over a range of approximately 200°C . For the considered compositional range, the model predicts a minimum T_l of 1260°C .

References

- ¹Thermfact/CRCT (Montreal, Canada), GTT-Technologies (Aachen, Germany), www.factsage.com (2007).
- ²D. W. Bonnell and J. W. Hastie, "A Predictive Thermodynamic Model for Complex High-Temperature Solution Phases," *High Temp. Sci.*, **26**, 313 (1989).
- ³B. A. Shakhmatkin, N. M. Vedishcheva, M. M. Shultz, and A. C. Wright, "The Thermodynamic Properties of Oxide Glasses and Glass-Forming Liquids and their Chemical Structure," *J. Non-Cryst. Solids*, **177**, 249 (1994).
- ⁴T. M. Besmann and K. E. Spear, "Thermochemical Modeling of Oxide Glasses," *J. Am. Ceram. Soc.*, **85**, 2887 (2002).
- ⁵W. Pannhorst, "Glass Ceramics: State-of-the-Art," *J. Non-Cryst. Solids*, **219**, 198 (1997).
- ⁶J. A. Cornell, *Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data*, 2nd edition, John Wiley & Sons, New York, 1990.
- ⁷M. B. Volf, *Mathematical Approach to Glass. Glass Science and Technology*, Vol. 9. Elsevier, Amsterdam, 1988.
- ⁸M. Cable "Glasses and Amorphous Materials"; p. 1 in *Materials Science and Technology: A Comprehensive Treatment*, Vol. 9, Edited by J. Zarzycki. VCH, Weinheim, 1991.
- ⁹J. D. Vienna, P. Hrma, J. V. Crum, and M. Mika, "Liquidus Temperature-Composition Model for Multi-Component Glasses in the Fr, Cr, Ni and Mn Spinell Primary Phase Field," *J. Non-Cryst. Solids*, **292**, 1 (2001).
- ¹⁰J. B. Hanni, E. Pressly, J. V. Crum, K. B. C. Minister, D. Tran, P. Hrma, and J. D. Vienna, "Liquidus Temperature Measurements for Modeling Oxide Glass Systems Relevant to Nuclear Waste Vitrification," *J. Mater. Res.*, **20**, 3346 (2005).
- ¹¹R. Backman, K. H. Karlsson, M. Cable, and N. P. Pennington, "Model for Liquidus Temperature of Multi-Component Silicate Glasses," *Phys. Chem. Glasses*, **38**, 103 (1997).
- ¹²C. Dreyfus and G. Dreyfus, "A Machine Learning Approach to the Estimation of the Liquidus Temperature of Glass-Forming Oxide Blends," *J. Non-Cryst. Solids*, **318**, 63 (2003).
- ¹³G. Piepel and T. Redgate, "Mixture Experiment Techniques for Reducing the Number of Components Applied for Modeling Waste Glass Sodium Release," *J. Am. Ceram. Soc.*, **80**, 3038 (1997). □