Understanding Glass Formation

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➤ **Understanding the structures and calculated properties of glasses is necessary when developing a glaze system for use as a coating on a ceramic body.**

Glass can be described as a transparent product possessing the properties of hardness, rigidity and brittleness. Some oxides can be obtained in the form of glasses when they are cooled, and the ability to form a glass depends on the oxygen ions' arrangement in forming the unit cell of the crystal structure. Understanding the structures and calculated properties of glasses is necessary when developing a glaze system for use as crystal, opaque, transparent or matte coatings on ceramic bodies.

Oxides and Structure

Oxides, which form glasses when melted and cooled, are termed glass-forming or network-forming. In silicate glasses, the network-forming oxides are based on SiO_4-tetrahedral interconnected through oxygen atoms at the corners. Conventional wisdom implies that alkaline and alkaline-earth orthosilicate materials cannot be vitrified because they do not contain sufficient network-forming SiO_2 to establish the needed interconnectivity.

The most important glass-forming oxides are silica, boric acid and phospho-

rous pentoxide. Silica glass is well known due to its low coefficient of thermal expansion and high softening temperature. Boric acid and phosphorous pentoxide glasses are easily attacked by water and have no practical application.

When considering glass structure, it is necessary to differentiate two other types of oxides in terms of their function—network-modifying and intermediate oxides. Alkali oxides and alkaline earth oxides are considered modifiers and play an active role in defining the mechanical, chemical and optical properties of the glass. A modifying glass is not able to build up the glass network and instead weakens the glass structure. For example, sodium oxide forms sodium silicate glass but results in changes to the viscosity and thermal expansion properties, which can be attributed to the weakening of the bonds within the glass network.

An intermediate oxide is not capable of forming a glass, but it can take part in the glass network. While these compounds don't form glasses on their own, they participate in the tangled networks initiated by other compounds such as silica. Alumina (Al_2O_3) is a good example. Adding alumina to an alkali glass or glaze gives strength,

chemical resistance and higher devitrification resistivity. On the other hand, the addition of alumina also raises the softening and melting point of the glass.

Elements like titanium and zircon can also be considered network co-formers. Glasses that feature a higher amount of cations do not vitrify very easily (e.g., zinc and cadmium-containing glasses). The addition of zinc to a glaze provides increased strength and chemical resistivity. If the zinc level has reached a maximum, it reacts like a network modifier.[1]

Melting Behavior

Problems concerning the furnace refractory can develop if the melting temperature of the glass is too high. Adding certain glass ingredients can lower the melt viscosity and thus speed up the melting. Alkali metal oxides like Li_2O, Na_2O and K_2O are considered useful fluxes in the melting process.

Lead is a glass constituent that contributes to the transparency, fusibility and high refractive power of the glass. Lead can easily form a glass with a small amount of glass former (e.g., SiO_2, B_2O_3). The ratio between PbO and B_2O_3 determines the relative solubility of lead and

Table 1. Factors for oxides used in the thermal expansion calculation.

Oxides	αi	See Notes	Oxides	αi	See Notes
Li_2O	27(27)	1	ZnO	5	
Na_2O	39.5(41)	1	PbO	13 to 19	6
K_2O	46.5(50)	1, 2	B_2O_3	-5 to 0	3
MgO	6		Al_2O_3	-3	
CaO	13		SiO_2	0.5 to 3.8	4
SrO	16		TiO_2	-1.5 to +3	5
BaO	20		ZrO_2	-6	

Notes

1. Values indicated in parentheses are valid for a R_2O-SiO_2 glass system.
2. If the Na_2O content is > 1%, factor for K_2O = 46.5 in all other cases K_2O = 42.5.
3. αB_2O3 = -1.25*b where b = sum p(R_2O) + sum p(RO)-p(Al_2O_3) divided by p(B_2O_3). If b > 4, then B_2O_3 = -5.0. Otherwise, the factor for B_2O_3 will be according to the formula as above.
4a. If p(SiO_2) is between 67% and 100%, then the factor for SiO_2 is αSiO_2 = 10.5 - 0.1*p(SiO_2).
4b. If p(SiO_2) = or < 67, then the factor for SiO_2 is 3.8.
5. If SiO_2 content is 50 to 80%, the factor for TiO_2 will be αTiO_2 = 10.5 - 0.15*p(SiO_2).
6. αPbO = 13 for glasses: a. without Na_2O, K_2O and Li_2O; b. alkali-lead-silicate glass with sum p(R_2O) < 3; or c. other glasses, if sum p(RO) + sum p(RmOn) divided by sum p(R_2O) is > 0.33. If the conditions a., b., and c. are not fulfilled, then the factor for PbO will be αPbO = 11.5 + 0.5*sum p(R_2O).

Table 2. Factors for the individual oxides used in the calculation of flux factor.

Oxide	Factor	
ZrO_2	0.32	= X
Al_2O_3		
SiO_2	0.38	
TiO_2	0.38	
MgO	0.54	
CaO	0.58	
BaO	0.60	
ZnO	0.60	= RO = Y
K_2O	0.88	
Na_2O	0.88	
B_2O_3	1.00	
PbO	2.00	

Calculated thermal expansion.

Oxides	Mol%	Factor	Mol%*Factor
Na_2O	7.12	39.5	281.24
K_2O	0.19	46.5	8.84
MgO	1.87	6.0	11.22
CaO	14.24	13.0	185.12
Al_2O_3	6.09	-3.0	-18.27
SiO_2	57.53	3.8	218.61
B_2O_3	12.97	-1.67	-21.66

Total: $665.10 = 6.65 \times 10^{-6}$

Measured thermal expansion

Figure 1. Calculated (table, left) and measured (graph, right) thermal expansion for Frit F 280 (base: CaO-B_2O_3-SiO_2).
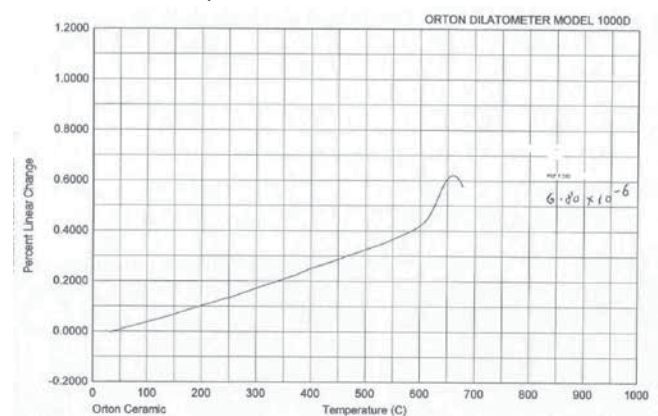
boric acid in a lead borate glass, and it is affected by other ingredients (like alkalis). If the ratio is greater than 2:5, the lead oxide is easily extracted and can be optimized by progressively varying the ingredients.

Higher silica and alumina content in a glass tends to decrease the solubility level. The most effective solution is to develop two glass systems—one with lead but without alkalis and boric acid, and the second with alkalis and boric acid but without lead. Using these two glasses in a glaze batch can reduce the solubility of lead.[2]

Adding a network-forming oxide such as PbO or Na_2O continuously to a silica glass produces glass property changes. Boric acid, however, produces a change comparable to the silica glass but with an increased concentration of B_2O_3 in the glass system.

Glass Properties

Most glass properties are sensitive to chemical composition. In this paper, we are going to discuss only those properties that are closely related to the use of glass in creating a coating that will be used on diverse ceramic bodies. These properties include surface tension, thermal expansion, flux factor and acidity.

Surface tension (ST) is measured as the energy required to increase the surface area of a liquid by a unit of area. Low surface tension favors the elimination of gas bubbles during glaze firing, whereas high surface tension favors the reabsorption of the bubbles during the cooling of glaze. High surface tension also causes the glaze to crawl. Dietzel proposed the following factors to calculate the ST of a glaze from the oxide composition:[3]

Na_2O	1.5
K_2O	0.1
BaO	3.7
Li_2O	4.6
ZnO	4.7
CaO	4.8
Al_2O_3	6.2
SiO_2	3.4
B_2O_3	0.8

The ST of the glass is calculated according to the formula: oxide % x ST factor. It is expressed as dynes per centimeter.

Many tables of oxide *thermal expansion* have been published over the years; the first system was suggested by Winkelman

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Table 3. The relationship between flux factors and glass systems.

Temperature (ºC)	Flux Factor	Glass System
1100	75	Crystal
1040	68	Matte
1120	60	Matte
1250	45	Matte
1120	50	Glossy
1200 and above	35	Vitreous

Table 4. The ratio of the alkaline and acid oxides determines the structure of glass systems.

Alkaline	Acid	Structure
1	0.8	Matte and Crystal
1	1.5	Transparent
1	1.8	Vitreous Glass

& Schott.[4] All of the known methods for calculating the thermal expansion of glasses from composition are based on additive formulae that represent the expansion as a linear function of oxide concentration. However, the majority of glass and melt properties are not linear over a wider composition range.

Accordingly, Appen has taken this fact into consideration in defining the factors of expansion for oxides.[5] The formula for the calculation of thermal expansion is: $\alpha i = \alpha 1^* p1 + \alpha 2^* p2 + \ldots + \alpha N^* pn$, where αi = factors for the oxides (see Table 1, p. 27), and $p1, p2 \ldots \ldots pN$ = amount of oxides of a glass expressed in molar percentage. The expansion coefficient is expressed in 10^{-8}. Figure 1 (p. 27) shows a comparison of measured vs. calculated thermal expansion values.

Both *flux factor* and *acidity* are calculated from the molar composition of a glass based on each individual factor. The formula for the calculation of flux factor is: $F = 100^*Y/(X+Y)$, where $X = [1.18^*(Al_2O_3+ZrO_2) + SiO_2]^*0.38$, and $Y = RO + (B_2O_3)$. Factors for the individual oxides used in the calcu-

lation of flux factor are shown in Table 2 (p. 27),[6] while Table 3 illustrates the relationship between flux factors and glass systems.

The ratio of the alkaline and acid oxides determines the structure of glass systems used as a coating on a ceramic body. It can be easily modified by changing the alkaline and acid oxides according to the application temperature (see Table 4).

Defeating Defects

Glaze defects like crazing and crawling are the result of a thermal expansion mismatch between the glaze and the body. Likewise, high surface tension in a glaze can lead to crawling, and too low of an ST causes the glazes to run.

The proper calculation of thermal expansion and surface tension, among other factors, is important to consider in glaze formulation to guarantee the proper fit of the glaze to the body. The calculation methods described here can be used as effective tools to develop glaze compositions with specified physical and chemical properties, which will

help manufacturers better understand the structure and properties of their glaze systems.   **c**

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