

Thermal Expansion and Glass Transition Temperatures of Y-Mg-Si-Al-O-N Glasses

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The thermal expansion coefficients and glass transition temperatures of Y-Mg-Si-Al-O-N glasses were measured using dilatometry. The thermal expansion coefficients of these glasses could be calculated on the basis of composition, using experimentally determined thermal expansion prefactors.

I. Introduction

Thermal expansion coefficients and glass transition temperatures have been reported for several Mg-Si-Al-O-N¹ and Y-Si-Al-O-N² glasses. However, these have not resulted in simple equations to describe the properties of the glass as a function of chemical composition. This makes design of a glass with given properties difficult. To develop descriptive equations, glass-forming compositions in the system Y,Si,Al,Mg/N,O were selected for this study. Oxynitride glasses in the Y, Si, Al, Mg/N, O system are found at the grain boundaries in many silicon nitride ceramics. Therefore, the properties of glasses in these systems are of interest because of their influence on the mechanical properties of silicon nitride ceramics.

The glass transition temperature and Young's modulus depend on the coordination number of elements in the glass and the strength of attraction between elements in the glass. Cations which have high coordination numbers and nondirectional bonds raise the glass transition temperature.³ For example, IR investigations⁴ on oxynitride glasses showed that Mg²⁺ participates in the formative network, while Ca²⁺ is a network modifier. Drew *et al.*⁵ found that oxynitride glasses which contained Ca²⁺ (in 6-fold coordination) had higher glass transition temperatures than those which contained Mg²⁺ (in 4-fold coordination).

When different cations which have the same coordination number are used, the glass transition temperature increases as the ionic field strength of the cation increases. For example, replacement of Nd³⁺ by the smaller Y³⁺ raises the glass transition temperature.⁵ Drew *et al.* replaced Mg²⁺ by Y³⁺, which has both a higher field strength and higher coordination number than Mg²⁺, and found that the glass transition temperature of the glass increased, as expected.⁵

The glass transition temperature is also affected by the structure of the glass. Mulfinger⁶ suggested that the presence of nitrogen would change the structure of the glass, because each nitrogen was able to bond to three silicon atoms, while oxygen could bond to only two silicon atoms. As a result, the number of bonds between Si(O, N)_x tetrahedra in the network would increase. Measurement by X-ray photoelectron spectroscopy, raman spectroscopy, and ²⁹Si NMR spectroscopy indicate that

nitrogen bonds to silicon in the glass network, as Mulfinger suggested.⁷⁻⁹ NMR spectroscopy has revealed evidence of some Al-N bonding, although it is not as prevalent as Si-N bonding.^{10,11}

An increase in the number of bonds between tetrahedral structural units would be expected to increase the density of the glass. Homeny and McGarry¹² measured a linear increase in density with increasing nitrogen content in Mg-Si-Al-O-N glasses.

Since the substitution of nitrogen for oxygen increases the coordination number of the anion in the glass structure, the glass transition temperature would be expected to increase as the nitrogen content of the glass increased. Large increases in the glass transition temperature have been observed as the amount of nitrogen increases in many compositions, including Mg-Si-Al-O-N, Ca-Si-Al-O-N, Y-Al-Si-O-N, Nd-Si-Al-O-N and Ba-Al-Si-O-N compositions.^{5,13-17} When the cation ratios in the glass are held constant, the T_g increases linearly with the atomic percent nitrogen in the glass.^{5,16}

The thermal expansion coefficient of the glass depends on the asymmetry of the amplitude of thermal vibrations in the glass. The amplitudes of the thermal vibrations are small when there are many strong bonds present in the network. As a result, the thermal expansion coefficient decreases as the rigidity of the glass network increases.

Modifying cations decrease the rigidity of the glass network by introducing nonbridging oxygen ions, and therefore increase the thermal expansion coefficient of the glass. Other changes in the structure or chemistry of the glass also change the thermal expansion coefficient of the glass. The change in the thermal expansion coefficient of the glass which is caused by different additives is often directly proportional to the amount of additive. If the change in the thermal expansion coefficient of the glass, $\Delta\alpha$, caused by the additive is divided by the amount of additive, x , the result is the thermal expansion prefactor for that additive, α_i .

The thermal expansion coefficient of the glass can be calculated from the weighted sum of the thermal expansion prefactors of the constituents of the glass, as expressed in Eq. (1):

$$\alpha = \sum \alpha_i X_i \quad (1)$$

where X_i is the mole fraction of the constituent and α_i is the empirically determined thermal expansion coefficient prefactor.¹⁷

Takahashi¹⁸ had determined the thermal expansion coefficient prefactors for Al₂O₃ and MgO. Appen¹⁹ had determined the prefactors for MgO and SiO₂. Using their prefactors, the unknown prefactors for Y₂O₃ and Si₃N₄ were determined.

II. Experimental Procedures

The glasses were synthesized from the starting powders, Al₂O₃, Si₃N₄, SiO₂, Y₂O₃, and MgO. The compositions prepared are listed in Table I. The powders were mixed by hand with isopropyl alcohol with an agate mortar and pestle, dried, and cold pressed into pellets. The pellets were melted at 1650°C for 2 h under 10 atm of nitrogen. The samples were quenched by turning off the power to the furnace and cooled to room temperature in approximately 3 h. The presence of crystalline

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Table I. Glass Compositions (in Moles)

SiO ₂	Al ₂ O ₃	Y ₂ O ₃	MgO	Si ₃ N ₄	α _{Measured} × 10 ⁶ /°C
0.55	0.22	0	0.22	0	4.0
0.54	0.22	0	0.21	0.02	3.7
0.53	0.21	0	0.21	0.05	3.6
0.53	0.22	0	0.22	0.02	4.2
0.50	0.22	0	0.22	0.04	4.0
0.47	0.22	0	0.23	0.06	3.1
0.52	0.24	0.01	0.21	0	4.1
0.52	0.23	0.01	0.20	0.02	4.5
0.49	0.22	0.01	0.20	0.05	4.0
0.51	0.25	0.02	0.20	0	4.1
0.50	0.26	0.03	0.19	0	4.3
0.48	0.27	0.05	0.19	0	4.6
0.46	0.28	0.06	0.19	0	5.1
0.44	0.29	0.07	0.18	0	5.2
0.42	0.31	0.08	0.17	0	5.3
0.38	0.34	0.11	0.15	0	5.3
0.61	0	0.30	0	0.08	6.3
0.87	0	0.12	0	0	5.1
0.60	0.06	0.33	0	0	7.5

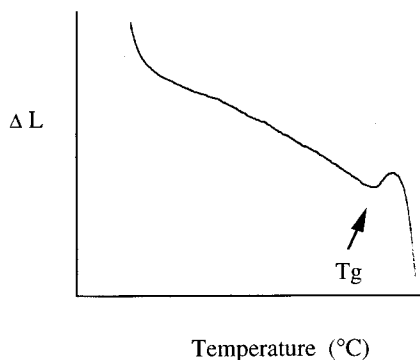
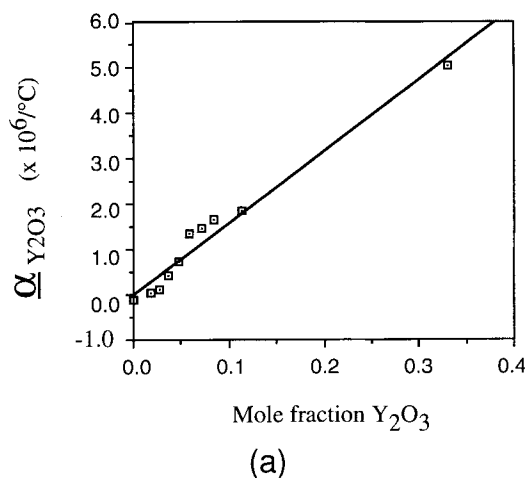
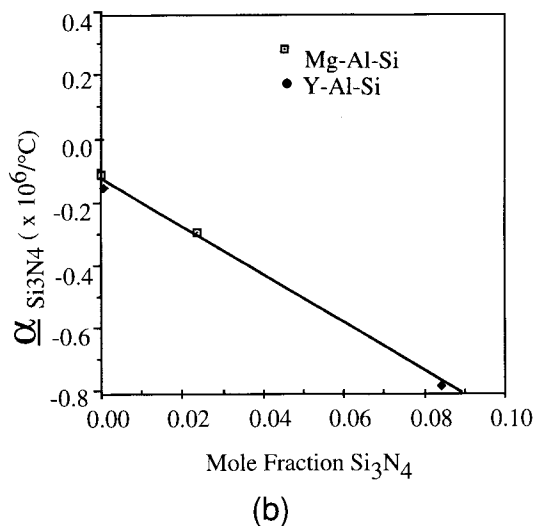


Fig. 1. Typical dilatometer trace.



(a)



(b)

Fig. 2. (a) Thermal expansion coefficient of the glass increases when Y₂O₃ is added. The slope of this plot is the thermal expansion prefactor of Y₂O₃, α_{Y₂O₃}. (b) The thermal expansion coefficient of the glass decreases when Si₃N₄ is added. The slope of the plot is the thermal expansion prefactor for Si₃N₄, α_{Si₃N₄}.

$$\alpha_{Y_2O_3} = \alpha_{Y_2O_3} X_{Y_2O_3} \tag{3}$$

(Equation (2) is an expansion of Eq. (1).) The thermal expansion prefactor of Si₃N₄ was determined using the glass compositions in Table I. The amount of thermal expansion which was due to Si-N bonds, called α_{Si₃N₄}, was calculated using Eq. (4):

phases was determined by X-ray diffraction. Only samples which did not show any crystalline peaks were used to determine the thermal expansion coefficient and T_g of the glass. The compositions of the glasses were verified using EPMA.

The thermal expansion coefficient was measured from room temperature to 1200°C, using an alumina single-rod dilatometer calibrated with a fused silica standard. The heating rate was 2°C/min. The value of the thermal expansion coefficient from room temperature to 515°C was calculated. The T_g was determined from the dilatometer trace. A typical dilatometer trace is shown in Fig. 1, with the T_g indicated.

The thermal expansion coefficient prefactor for Y₂O₃ was determined from glasses which contained MgO, Al₂O₃, SiO₂, and Y₂O₃ only. The amount of the thermal expansion which was due to Y-O bonds, called α_{Y₂O₃}, was determined from Eq. (2) below:

$$\alpha_{Y_2O_3} = \alpha_{\text{Measured}} - \{ \alpha_{MgO} X_{MgO} + \alpha_{SiO_2} X_{SiO_2} + \alpha_{Al_2O_3} X_{Al_2O_3} \} \tag{2}$$

where

Table II. Thermal Expansion Prefactors

	This study (α _i × 10 ⁶ /°C)	Takahashi ¹⁸ (α _i × 10 ⁶ /°C)	Appen ¹⁹ (α _i × 10 ⁶ /°C)
SiO ₂	3.8		3.8
Al ₂ O ₃	3.1	3.1	
Y ₂ O ₃	15.7		
MgO	6.0	6.0	6.0
Si ₃ N ₄	-7.5		
SrO			16
CaO			14.5

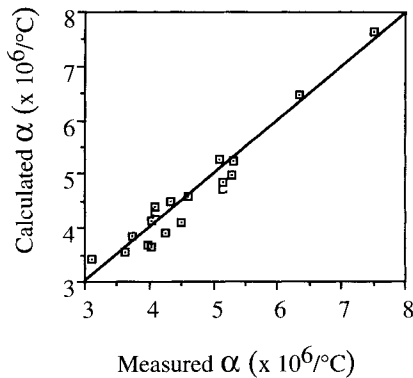


Fig. 3. Comparison of calculated and measured thermal expansion coefficients.

$$\alpha_{\text{Si}_3\text{N}_4} = \alpha_{\text{Measured}} - \{ \alpha_{\text{MgO}} X_{\text{MgO}} + \alpha_{\text{Al}_2\text{O}_3} X_{\text{Al}_2\text{O}_3} + \alpha_{\text{SiO}_2} X_{\text{SiO}_2} + \alpha_{\text{Y}_2\text{O}_3} X_{\text{Y}_2\text{O}_3} \} \quad (4)$$

where

$$\alpha_{\text{Si}_3\text{N}_4} = \alpha_{\text{Si}_3\text{N}_4} X_{\text{Si}_3\text{N}_4} \quad (5)$$

III. Results and Discussion

The thermal expansion coefficients and the glass compositions are listed in Table I. The error in the thermal expansion coefficient measurements is about $2 \times 10^{-7}/^\circ\text{C}$, based on the calibration of the dilatometer. The error in temperature measurements is $\pm 2^\circ\text{C}$, according to the calibration of the dilatometer thermocouple.

Using previously reported α_i values for MgO, Al₂O₃, and SiO₂,^{18,19} α_i values for Si₃N₄ and Y₂O₃ were determined. The α_i values are listed in Table II. The α_i value for SiO₂ is valid only when the mole fraction of SiO₂ is less than 0.67. The α_i values were determined from plots of α_i as a function of X_i . Figure 2(a) shows the plot of $\alpha_{\text{Y}_2\text{O}_3}$ as a function of $X_{\text{Y}_2\text{O}_3}$. The slope of the plot in Fig. 2 is $\alpha_{\text{Y}_2\text{O}_3}$. Figure 2(b) shows the plot of $\alpha_{\text{Si}_3\text{N}_4}$ as a function of $X_{\text{Si}_3\text{N}_4}$. The slope of the plot in Fig. 2(b) is $\alpha_{\text{Si}_3\text{N}_4}$.

Using the α_i values listed in Table II, the expected values of the thermal expansion coefficient were calculated. Figure 3 shows the excellent agreement between the calculated and measured values—the maximum error is 10%.

The addition of Y₂O₃ and Al₂O₃ in a 3:5 ratio (YAG) to the original Mg-Si-Al-O-N had little effect on the glass transition temperature of the oxide glass, as shown in Fig. 4.

Figure 5 shows the glass transition temperature as a function of silicon nitride content for MgO–Al₂O₃–SiO₂–Si₃N₄ and Y₂O₃–MgO–Al₂O₃–SiO₂–Si₃N₄ glasses. A best-fit line through the data in Fig. 5 results in an empirical equation for the glass

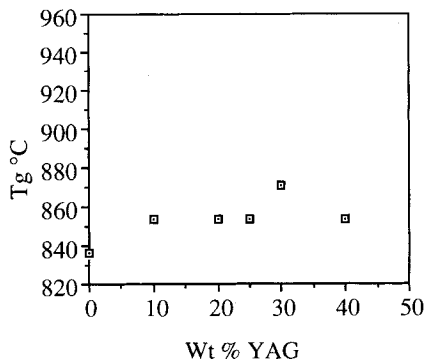


Fig. 4. Small additions of Y₃Al₅O₁₂ to Mg-Si-Al-O oxide glasses show no effect on T_g .

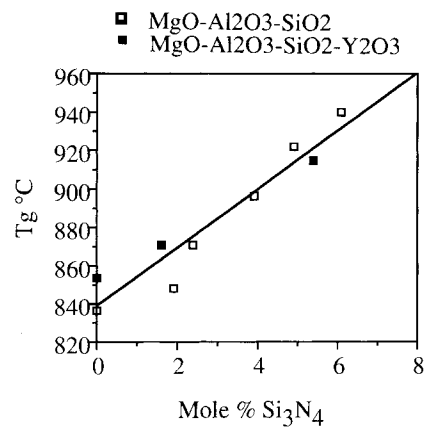


Fig. 5. Si₃N₄ additions raise the T_g of oxynitride glass.

transition temperature. The glass transition temperature can be expressed in Eq. (6):

$$T_g (^\circ\text{C}) = 839 + 15.3 (\text{mol}\% \text{Si}_3\text{N}_4) \quad (6)$$

The thermal expansion coefficients and glass transition temperatures of Y-Mg-Si-Al-O-N glasses can be predicted from simple equations. The thermal expansion prefactors also correspond with the role of the ion in the glass structure. The thermal expansion prefactor of MgO is much smaller than that of CaO as expected from both the structural roles and the relative field strengths of the Mg²⁺ and Ca²⁺. The high thermal expansion prefactor found for Y₂O₃ is consistent with the position of Y³⁺ as a network modifier but not with its high field strength.

References

- R. E. Loehman, "Oxynitride Glasses," *J. Non-Cryst. Solids*, **42**, 433–46 (1980).
- R. E. Loehman, "Preparation and Properties of Yttrium-Silicon-Aluminum Oxynitride Glasses," *J. Am. Ceram. Soc.*, **62** [9–10] 491–94 (1979).
- A. Buri, D. Caferra, F. Branda, and A. Marotta, "Relationship between Composition and Glass Transition Temperature in Na₂O–M₂O₃–SiO₂ Glasses (M = Ga, In, Sc, Y, La)," *Phys. Chem. Glasses*, **23**, 37–40 (1982).
- J. Videau, J. Etourneau, C. Garnier, P. Verdier, and Y. Laurent, "Structural Influence of Nitrogen in Alkaline Earth Aluminosilicate Glasses: IR Absorption Spectroscopy," *Mater. Sci. Eng. B*, **14**, 249–54 (1992).
- R. Drew, S. Hampshire, and H. Jack, "Nitrogen Glasses"; pp. 119–32 in *Special Ceramics 7*, Proceedings of the British Ceramic Society (June 1981). Edited by D. Taylor and P. Popper. British Ceramic Society, Shelton, U.K., 1981.
- H. O. Mulfinger, "Physical and Chemical Solubility of Nitrogen in Glass Melts," *J. Am. Ceram. Soc.*, **49**, 462 (1966).
- J. G. Clabes, R. E. Fern, and G. H. Frischat, "Characterization of Nitrogen Containing Glasses by X-ray Photoelectron Spectroscopy," *J. Vac. Sci. Technol. A*, **4** [3] 1580–84 (1986).
- T. Rouxel, J. Besson, E. Rzepka, and P. Goursat, "Raman Spectra of SiYAlON Glasses and Ceramics," *J. Non-Cryst. Solids*, **122**, 298–304 (1990).
- W. Hater, W. Muller-Warmuth, and G. H. Frischat, "29Si MAS NMR Studies of Alkali Silicate Oxynitride," *Glastech Ber.*, **62** [9] 328–64 (1989).
- G. Leng-Ward and M. H. Lewis, "Oxynitride Glasses and Their Glass-Ceramic Derivatives"; pp. 106–53 in *Glasses and Glass Ceramics*. Edited by C. M. Lewis. Chapman and Hall, London, U.K., 1989.
- R. S. Aujla, G. Leng-Ward, M. H. Lewis, G. F. Seymour, G. A. Styles, and G. W. West, "An NMR Study of Silicon Coordination in Y-Si-Al-O-N Glasses," *Philos. Mag. B*, **54** [2] L51–L56 (1986).
- J. Homeny and D. McGarry, "Preparation and Mechanical Properties of Mg-Al-Si-O-N Glasses," *J. Am. Ceram. Soc.*, **67** [11] C-225–C-227 (1984).
- D. Messier, "Preparation and Properties of Y-Si-Al-O-N Glasses," *Int. J. High Tech. Ceram.*, **3**, 33–41 (1987).
- T. Hayashi and T. Y. Tien, "Formation and Crystallization of Oxynitride Glasses in the System Si, Al, Mg/O,N," *Yogyo Kyokaiishi*, **94** [1] 44–62 (1986).
- R. Loehman, "Oxynitride Glasses"; pp. 119–48 in *Treatise on Materials Science and Technology*, Vol. 26, *Glass IV*. Edited by M. Towozawa and R. Doremus. Academic Press, Orlando, FL, 1985.
- W. K. Tredway and S. H. Risbud, "Multianion Glasses"; p. 203 in *Non-Oxide Technical and Engineering Ceramics*. Edited by S. Hampshire. Elsevier Applied Science, London, U.K., 1986.
- J. M. Stevels, "The Structure and the Physical Properties of Glass"; pp. 511–643 in *Encyclopedia of Physics*, Vol. XIII, *Thermodynamics of Liquids and Solids*. Edited by S. Flugge. Springer-Verlag, Berlin, Germany, 1962.
- K. Takahashi, "Thermal Expansion Coefficients and the Structure of Glass. Part I," *J. Soc. Silikattechnik*, **37**, 3N–7N (1953).
- A. A. Appen, *Silikattechnik*, **3**, 113 (1953).