Thermochimica Acta 496 (2009) 93–96

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Wetting and surface tension of bismate glass melt☆

Seung-Bo Shim, Dong-Sun Kim, Seongjin Hwang, Hyungsun Kim*

School of Materials Engineering, Inha University, 253 Younghyun-dong, Incheon 402-751, Republic of Korea

ARTICLE INFO

Article history:
Received 28 July 2008
Received in revised form 22 June 2009
Accepted 14 July 2009
Available online 21 July 2009

Keywords:
Glass frit
Surface tension
Thermophysical property
Work of adhesion

ABSTRACT

Lead oxide glass frits are used widely in the electronics industry for low-temperature firing. On the other hand, one of the low-sintering and low-melting lead-free glass systems available, the bismate glass system, is considered to be an alternative to lead oxide glass. In order to extend the applications of Bi_2O_3 glasses, this study examined the thermophysical properties of low-melting Bi_2O_3–B_2O_3–ZnO–BaO–Al_2O_3–SiO_2 glass frits with various ZnO/B_2O_3 ratios. The fundamental thermal properties, such as glass transition temperature and softening point, were examined by differential thermal analysis and a glass softening point determination system. The wetting angles, viscosities and surface tension of the various bismate glasses on an alumina substrate were measured using hot-stage microscopy and the sessile drop method. These thermophysical properties will be helpful in understanding the work of adhesion and the liquid spread kinetics of glass frits.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Electronic applications, such as information displays, multilayer ceramic capacitors, low-temperature co-fired ceramics, and solar cells, all require various types of glasses that are fired as frits. Such devices are produced as a thick film using methods, such as screen printing, green-sheet lamination and die coating with pastes followed by firing. The firing of pastes is generally performed in a furnace, which involves the sintering and fusing of pastes. Thick films after firing often require good optical, electrical, thermal, or mechanical properties [1]. Indeed, the thermophysical properties of a frit, such as glass transition temperature, softening point, wetting angle, viscosity, and surface tension, affect the work of adhesion and the spread kinetics of the glass [2,3].

Lead oxide glass frits are used widely in low-temperature sintering and melting processes in the electronics industry. However, lead oxide glass systems should be replaced with lead-free glasses due to the environmental pollution. One of the low-sintering and low-melting lead-free glass systems, the bismate glass system, has been considered as an alternative to lead oxide glasses. This is because bismate glasses have similar thermal and optical properties to lead oxide glasses [1,4]. The surface tension of Bi_2O_3-containing glass melts have been studied to extend their applications. The following binary systems have mainly been investigated: $x$$Bi_2O_3$–$(100-x)$$B_2O_3$ ($x = 0$–100 mol.%) [5,6], $50Bi_2O_3$–$50SiO_2$ (mol.%) [7], and $x$$Bi_2O_3$–$(1-x)$$GeO_2$ [8]. However, bismate glasses have been found to be unsatisfactory compared to commercial lead oxide glasses due to their different thermal and physical characteristics [1].

This study examined the surface tension of Bi_2O_3–B_2O_3–ZnO–BaO–Al_2O_3–SiO_2 glasses containing minor oxide components as well as the effect of temperature on the work of adhesion of the Bi_2O_3 glasses. The viscosities, surface tension, and wetting angles of Bi_2O_3–B_2O_3–ZnO–BaO–Al_2O_3–SiO_2 frits with various component ratios (ZnO/B_2O_3 = 0.67, 0.86 and 1.3) were measured using hot-stage microscopy and the sessile drop method [2,9].

2. Experimental procedure

Bismate glass systems were prepared by mixing powders at various ZnO/B_2O_3 ratios (0.67, 0.86 and 1.3) with Bi_2O_3, B_2O_3, ZnO, BaO, Al_2O_3, and SiO_2 (Aldrich, USA) with >99% of purity (Table 1). The mixed batches were melted in an alumina crucible at 1200 °C for 1 h and then quenched on a ribbon roll. During the first crush, the cullet was crushed manually using an agate mortar and pestle. It was then sieved using a 140 mesh (<106 μm) and pulverized in a planetary mono-mill (Fritsch, Pulverisette-7, Germany). The glass transition temperature (T_g) of each glass composition was determined by thermogravimetry-differential thermal analysis (TG-DTA, Rigaku, Japan) at a heating rate of 10 °C/min to 1200 °C. The Littleton softening point (T_s) was measured using a glass softening point determination system (Orton, SP-3A, USA).

The fusion behavior of the bismate glass frits was analyzed using an automatic hot-stage microscope (HSM, Ajeon Co. Korea) [10,11]. The measurements were taken in air at a heating rate of 10 °C/min. The samples for these HSM measurements were made using a

☆ This paper was presented at 8th Symposium of the Korean Society of Thermophysical Properties held at POSTECH, Korea from April 24–25, 2008.

* Corresponding author. Tel.: +82 2 860 7545; fax: +82 2 864 3730.
E-mail address: kimhs@inha.ac.kr (H. Kim).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.07.005

Table 1
Compositions of the Bi_2O_3–B_2O_3–ZnO glass frits (in mol.%)[a].

Samples	Bi_2O_3	B_2O_3	ZnO
$ZnO/B_2O_3 = 0.67$	11	40	27
$ZnO/B_2O_3 = 0.86$	11	36	31
$ZnO/B_2O_3 = 1.3$	11	29	38

[a] The summation of 10BaO, $4Al_2O_3$, and $8SiO_2$ is 22 mol.% of the total composition.

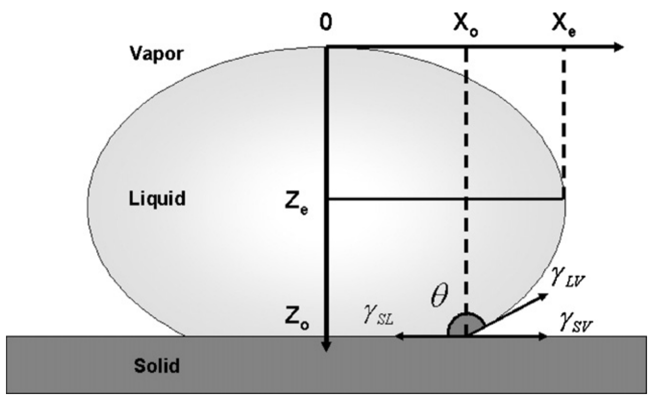

Fig. 1. Sessile drop of solid–liquid–vapor system in equilibrium on a substrate [12].

hand press to compress the frits (<26 μm), which were contained within a small cylindrical metal mold (about 3 mm × 3 mm). An alumina plate (5 mm × 5 mm × 0.7 mm) was used as the substrate. A computerized image analysis system automatically recorded and analyzed the sample geometry during heating. The wetting process between the bismate glasses and alumina was measured using HSM to help understand the sintering and fusion behavior of the frits at elevated temperatures.

The surface tension for each composition of bismate frits melted on an alumina substrate was determined using the sessile drop method (Fig. 1). A drop with a wetting angle >90° was regarded as a spheroidal-type drop. The surface tension of each sample was determined easily using the tables produced by Bashforth and Adams [9]. However, only the surface tension of droplets with wetting angles >90° could be determined due to the limitations of the sessile drop method [2].

3. Results and discussion

The bismate glass frits did not show any exothermic peaks up to 900 °C in the DTA curve, which indicates an amorphous

Table 2
Glass transition point (T_g), Littleton softening point (T_s)[a] and half ball point (T_h)[b].

Samples	T_g (°C)	T_s (°C)	T_h (°C)
$ZnO/B_2O_3 = 0.67$	502	558	700
$ZnO/B_2O_3 = 0.86$	494	547	684
$ZnO/B_2O_3 = 1.3$	484	537	675

[a] Littleton softening point (T_s) is defined as the temperature at which the viscosity of the glass is in the vicinity of $\log\eta = 7.6$ (dPa s) [13].
[b] Half ball point (T_h) is the temperature at which the sample forms a half shape during the HSM analysis [14].

phase without crystallization up to a melting temperature for each composition. The T_g, T_s, and T_h values decreased with increasing ZnO/B_2O_3 ratio (0.67 → 0.86 → 1.3), (Table 2). The T_g, T_s, and T_h values are obviously related to the viscosity of the bismate glass systems: $\eta = 10^{13.3}$ dPa s at T_g; $\eta = 10^{7.6}$ dPa s at T_s; $\eta = 10^{4.6}$ dPa s at T_h.

The sintering and fusion reactions were divided into three stages in terms of the change in pellet shape, which are the HSM samples (Fig. 2). In the 1st stage (RT (537–558 °C)), the pellet changed from a square to a trapezoid shape and then to a square shape. The glass particles that existed on the top of the pellet and heat energy first reacted at the corner with the largest surface area. Therefore, it appears that the corner of the pellet contracts rapidly to reduce the surface energy. This process is related to the rearrangement and contraction of the glass particles. The fusion of the glass actually began after stage 1. The 2nd stage proceeded in the temperature range of (537–558 °C) to (675–700 °C). The pellet was eventually formed into a swollen sphere in the lateral direction and maintained its longitudinal height in the 2nd stage. The corners of the pellet first reacted, resulting in a rounded shape. This is known as the softening point. The glass particles on the surface first melted due to the fastest thermal conductivity from the outside. The internal solid phase changed gradually into a liquid phase with the continuous supply of heat energy. Thus, the shape of the pellet changed into an ellipsoid with an angle >90°. In the 3rd stage, the wetting angle of the molten glass was <90°. The molten glass spread over the substrate due to viscous flow resulting from the high temperature conditions.

The wetting starting temperature, the starting and ending temperatures of the 3rd stage, and the hemisphere temperature decreased significantly with increasing ZnO/B_2O_3 ratio. The wetting angles of the frits in the temperature range, 570–700 °C, were recorded using the HSM measurements (Fig. 3). In the case of each composition, the end point of the 1st stage is related to the softening point. Therefore, the lower temperature of the ending point of

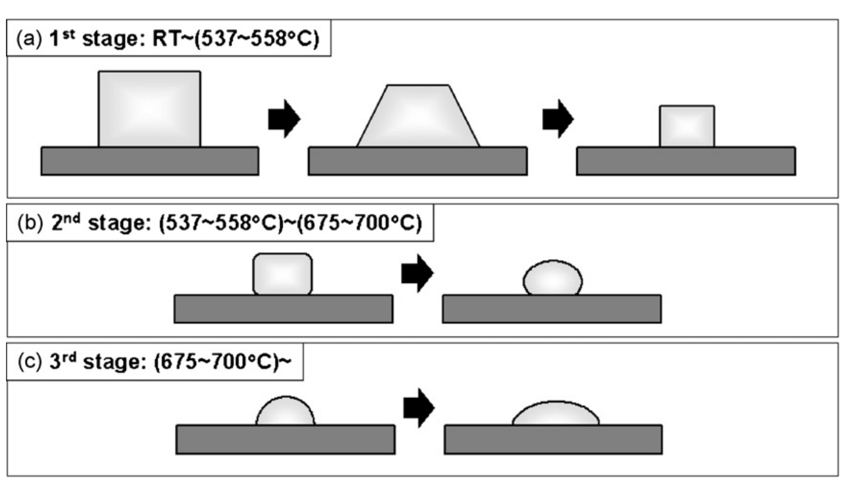

Fig. 2. Schematic diagrams for the sintering and fusion reaction of Bi_2O_3–B_2O_3–ZnO frits on a substrate: (a) 1st stage, (b) 2nd stage, and (c) 3rd stage.

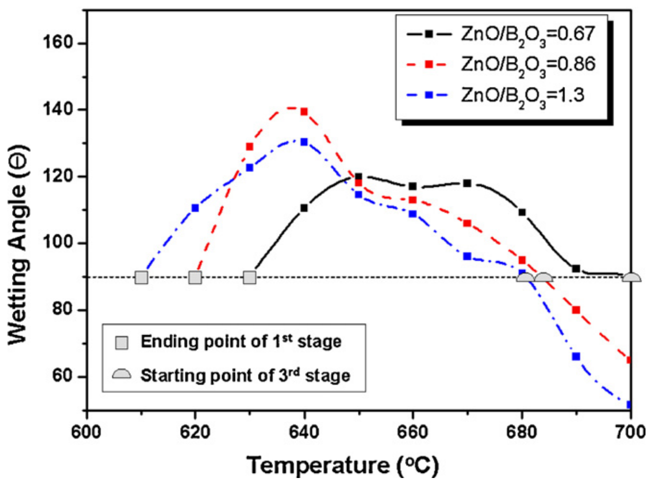

Fig. 3. Wetting angles of Bi_2O_3–B_2O_3–ZnO glass frits on an alumina substrate [15].

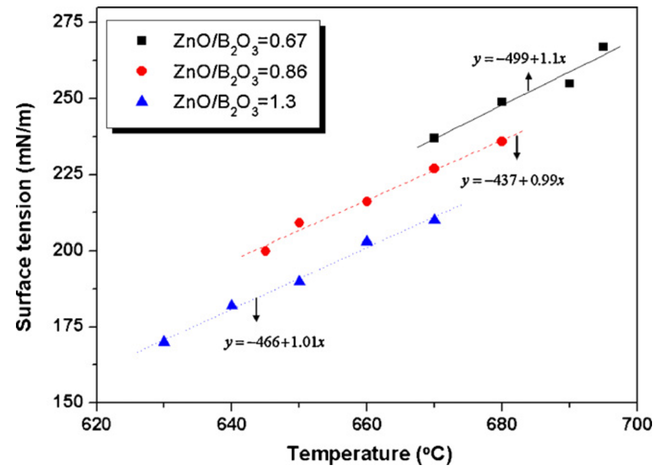

Fig. 5. Surface tensions of the Bi_2O_3–B_2O_3–ZnO glass frits on an alumina substrate [15].

the 1st stage and the start point of the 3rd stage was induced by the higher ZnO/B_2O_3 ratio in the samples.

The viscosity curves of the bismate glasses were determined as a function of temperature to quantify the wetting behavior of the glasses. The viscosity curves were calculated using the Vogel–Fulcher–Tamman (VFT) equation: $\log\eta = A + B/(T - T_0)$ [13]. Fig. 4 shows the three constants in the VFT equation, A, B and T_0, for the glass frits. The viscosity of the melted glasses was estimated from the HSM measurements based on the three known reference points (T_g, T_s and T_h). The 2D images of the HSM and the viscosity values at elevated temperatures showed the expected variations in wetting behavior with composition ratios. The melting viscosity of the bismate glasses decreased with increasing ZnO/B_2O_3 ratio.

The surface tension of the bismate glass frits decreased slightly with increasing ZnO/B_2O_3 ratio (Fig. 5). In the Bi_2O_3–B_2O_3 binary melts, pure Bi_2O_3 and B_2O_3 have surface tensions of 216.1 and 84.8 mN/m, respectively, at 900 °C [5]. Increasing the B_2O_3 content decreases the surface tension of the binary melts significantly because B_2O_3 has a parallel arrangement of triangular planes of three-oxygen-coordinated BO_3 at the melt surface. This leads to a weak binding force perpendicular to the surface [5,13]. On the other hand, regarding the effect of ZnO on the surface tension of the BaO–ZnO–P_2O_5 melts, the surface tension decreased with increasing ZnO content up to 30 mol.% ZnO. It showed a constant value of 220 mN/m at more than 40 and 50 mol.% ZnO in the temperature range of 1050–1300 °C [16]. However, the effect of the two components (ZnO, B_2O_3) from those studies cannot explain the change in surface tension in our glass system.

Previous studies reported that the surface tension of bismuth silicate glass ($50Bi_2O_3$–$50SiO_2$, mol.%), and lead borosilicate glass (63PbO–$25B_2O_3$–$12SiO_2$, wt%) was 136–144 mN/m (in the range 1030–1060 °C) [7] and 168–225 mN/m (in the range of 635–733 °C) [17], respectively. The latter viscosity range is close to the present results. As shown in Fig. 6, the temperature coefficient of the surface tension ($d\gamma/dT$) of the Bi_2O_3–B_2O_3–ZnO melt is positive (0.0011×10^{-3} N/m)/K, while the $d\gamma/dT$ values of many glasses are negative [5]. According to Hwang et al. [5], the temperature coefficient of the surface tension of a Bi_2O_3–B_2O_3 binary mixture changed from positive to negative in the range of 30–80 mol.% Bi_2O_3: $d\gamma/dT = 0.0367 \times 10^{-3}$ N/m/K for $10Bi_2O_3$–$90B_2O_3$ and $d\gamma/dT = -0.0193 \times 10^{-3}$ N/m/K for $60Bi_2O_3$–$40B_2O_3$. A similar temperature dependence of the surface tension was reported for xBi_2O_3–$(1-x)GeO_2$ [8]; $d\gamma/dT$ changed from positive to negative at $x \approx 0.38$. The change in $d\gamma/dT$ was explained by changes in the structural units, changes in the arrangement of the structural units, and changes in the surface concentrations of the constituents [5]. Future studies will examine the effect of temperature on the surface tension of glass systems.

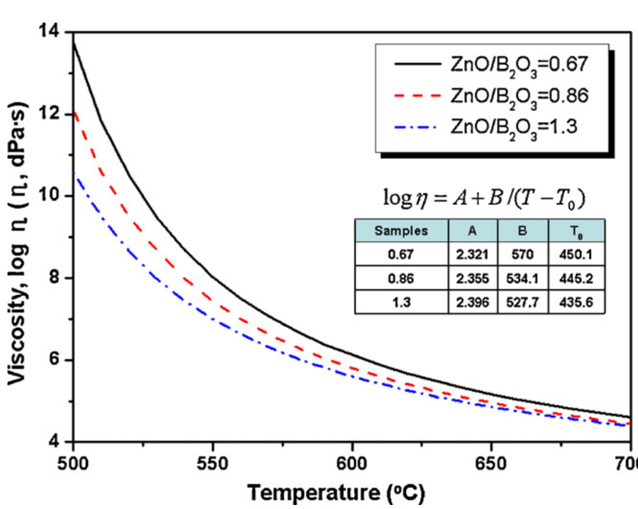

Fig. 4. Predicted viscosities of the Bi_2O_3–B_2O_3–ZnO frits from using the VFT equation.

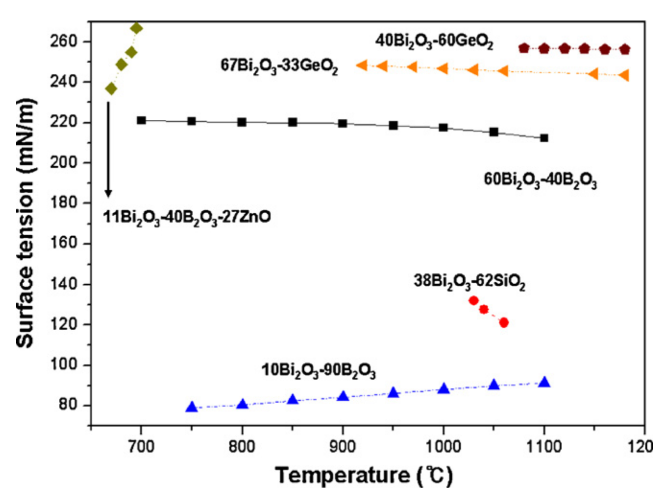

Fig. 6. Temperature dependence of the surface tension for Bi_2O_3 glasses ($38Bi_2O_3$–$62SiO_2$ [17], $10Bi_2O_3$–$90B_2O_3$, $60Bi_2O_3$–$40B_2O_3$ [5], $40Bi_2O_3$–$60GeO_2$, $67Bi_2O_3$–$33GeO_2$ [8], $10Bi_2O_3$–$40B_2O_3$–27ZnO).

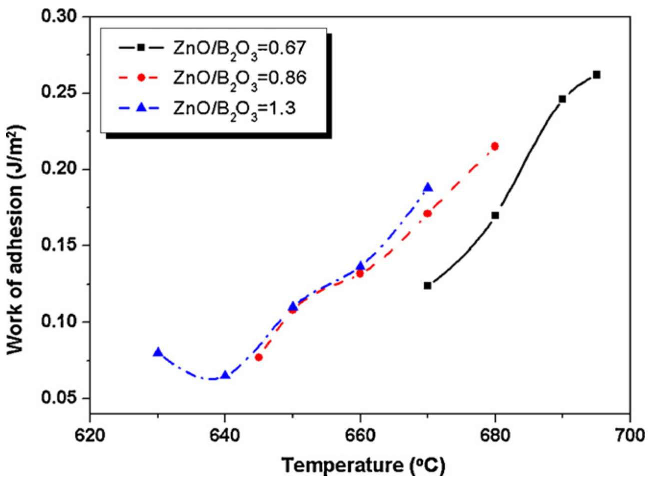

Fig. 7. Works of adhesion of the Bi_2O_3–B_2O_3–ZnO frits on an alumina substrate.

Determining the physical properties (e.g., viscosity and surface tension) of glasses is important for controlling and predicting their wetting behavior [3]. For example, the physical properties of a glass will affect its work of adhesion and spread kinetics. The work of adhesion gives an indication of the interfacial adhesion between the melt and the substrate. The work of adhesion values ($W = \gamma(1 + \cos\theta)$, where γ is the surface tension and θ is the wetting angle) for glasses with ZnO/B_2O_3 ratios of 0.67, 0.86 and 1.3 were found to be 0.124–0.262, 0.08–0.215, and 0.08–0.19 J/m^2, respectively. As shown in Fig. 7, the work of interfacial adhesion between the bismate glass systems and alumina substrate decreased with increasing ZnO/B_2O_3 ratio.

4. Conclusion

This study examined the wetting behavior of Bi_2O_3–B_2O_3–ZnO–BaO–Al_2O_3–SiO_2 glasses with various ZnO/B_2O_3 ratios at elevated temperatures. The surface tension of the bismate glass frits decreased slightly with increasing ZnO/B_2O_3 ratio. The temperature coefficient of the surface tension ($d\gamma/dT$) of the Bi_2O_3–B_2O_3–ZnO–BaO–Al_2O_3–SiO_2 melt was positive. The work of interfacial adhesion between the bismate glass systems and alumina substrate decreased with increasing the ZnO/B_2O_3 ratio. Overall, knowledge of the fundamental thermophysical properties of glass frits is important for predicting their work of adhesion and surface tension.

Acknowledgements

This work is financially supported by the Ministry of Education and Human Resources Development (MOE), the Ministry of Commerce, Industry and Energy (MOCIE) and the Ministry of Labor (MOLAB) through the fostering project of the Lab of Excellency.

References

[1] Y.J. Kim, S.J. Hwang, H.S. Kim, Mater. Sci. Forum 510–511 (2006) 578–581.
[2] F.S. Shyr, J. Mater. Sci. Lett. 10 (1991) 946–948.
[3] M. Tomut, H. Chiriac, Mater. Sci. Eng. A 304–306 (2001) 272–276.
[4] M.I. Zargarova, T.C. Kurbanov, M.F. Kasumova, Thermochim. Acta 93 (1985) 449–452, 1.
[5] C. Hwang, S. Fujino, K. Morinaga, J. Ceram. Soc. Jpn. 112 (2004) S1200–1205.
[6] S. Fujino, C. Hwang, K. Morinaga, J. Mater. Sci. 40 (2005) 2207–2212.
[7] N.P. Bansal, R.H. Doremus, Handbook of Glass Properties, Academic Press, London, 1985, p. 124.
[8] R. Tan, Q. Wang, L. Wang, C. Li, K. Lu, S. Peng, L. Hu, J. Am. Ceram. Soc. 90 (2007) 2837–2842.
[9] F. Bashforth, J.C. Adams, An Attempt to Test the Theories of Capillarity, Cambridge University Press, Cambridge, 1883.
[10] D.A. Earl, M. Ahmed, Ceram. Eng. Sci. Proc. 24 (2003) 1–12.
[11] A.R. Boccaccini, B. Hamann, J. Mater. Sci. 34 (1999) 5419–5436.
[12] M. Danesuk, Cronin, J.P. Zelinski, B.J.J. Kreidl, D.R. Uhlmann, Phys. Chem. Glasses 34 (1993) 203–211.
[13] H. Scholze, Glass: Nature, Structure Properties, Springer-Verlag, New York, 1991.
[14] M.J. Pascual, L. Pascual, A. Duran, Phys. Chem. Glasses 42 (2001) 61–66.
[15] S.B. Shim, S.W. Lee, S.J. Hwang, H.S. Kim, Proceedings of the Asian Thermophysical Properties Conference, 2007, pp. 135–140.
[16] S. Fujino, C. Hwang, K. Morinaga, Shigen-to-Sozai 119 (2003) 423–426.
[17] N.P. Bansal, R.H. Doremus, Handbook of Glass Properties, Academic Press, London, 1985, p. 108.