J Mater Sci (2007) 42:4772–4777
DOI 10.1007/s10853-006-0766-4

Formation and properties of SnO–MgO–P_2O_5 glasses

Jiin-Jyh Shyu · Chih-Hsien Yeh

Received: 16 August 2005 / Accepted: 7 August 2006 / Published online: 19 March 2007
© Springer Science+Business Media, LLC 2007

Abstract A new glass system SnO–MgO–P_2O_5 with low viscosity has been developed by a melt-quenching method. Formation, thermal properties, and chemical durability of these glasses have been investigated. For a constant P_2O_5 concentration, the glass formation ability is enhanced with the increasing Sn/(Sn + Mg) ratio. The glasses exhibit low glass transition temperature (T_g = 270–400 °C), low dilatometric softening temperature (T_{DS} = 290–420 °C), and high thermal expansion coefficient ($CTE = 110–160 \times 10^{-7}$ K^{-1}). With the increasing Sn/(Sn + Mg) ratio, T_g and T_{DS} decrease, and *CTE* increases. When Sn/(Sn + Mg) ratio is varied, the relationship between chemical durability and thermal properties of the present glasses is not consistent with what expected in general cases. It is noted that the glasses with 32–32.5 mol% P_2O_5 exhibit excellent chemical durability and tunable T_g, T_{DS}, and *CTE* (by varying Sn/(Sn + Mg) ratio).

Introduction

In comparison to silicate glasses, phosphate glasses have unique properties, e.g., low melting temperatures, low softening-temperatures [1], high thermal-expansion [2, 3], and optical characteristics [4, 5]. Thus, low-melting phosphate glasses are candidate materials for applications such as IC packaging, thick-film technology, glass-metal sealing, flat panel display sealing, host matrix for the vitrification of radioactive waste, and host materials for lasers [2–9]. From the environment viewpoint, lead-free, P_2O_5-based glasses are also alternatives to the PbO-containing glasses [10]. However, the practice use of phosphate glasses is limited due to their relatively poor chemical durability [11, 12]. Several efforts have been made to improve the chemical durability while retain the low softening-temperature of phosphate glasses [1, 2, 4, 5, 7, 8, 10, 13–19]. SnO-containing phosphate glasses [1, 7, 10, 13–22], e.g., SnO–ZnO–P_2O_5 system, were found to possibly fulfill these requirements [7, 15–19].

In the present study, a new glass system SnO–MgO–P_2O_5 with low viscosity was developed. Effect of Sn/(Sn + Mg) ratio on the formation and properties of the glasses were investigated. The present glass system was shown to have low softening temperatures and good chemical durability.

Experimental procedures

Preparation of glass

Glasses with nominal compositions shown in Fig. 1 were prepared from reagent-grade $Sn_2P_2O_7$, $NH_4H_2PO_4$, and MgO. The MgO powder was obtained from calcining $Mg(OH)_2$ powder at 700 °C for 1 h. Well-mixed powder containing 10–15 g of the above chemicals and 1 wt% of sugar was placed in an alumina crucible. The batch was put directly into a furnace at 950–1200 °C in a nitrogen atmosphere. Nitrogen atmosphere and sugar was able to provide a reducing atmosphere during melting to inhibit the oxidation of Sn^{2+} to Sn^{4+}. After

---

J.-J. Shyu (✉) · C.-H. Yeh
Department of Materials Engineering, Tatung University, Taipei 104, Taiwan
e-mail: jjshyu@ttu.edu.tw

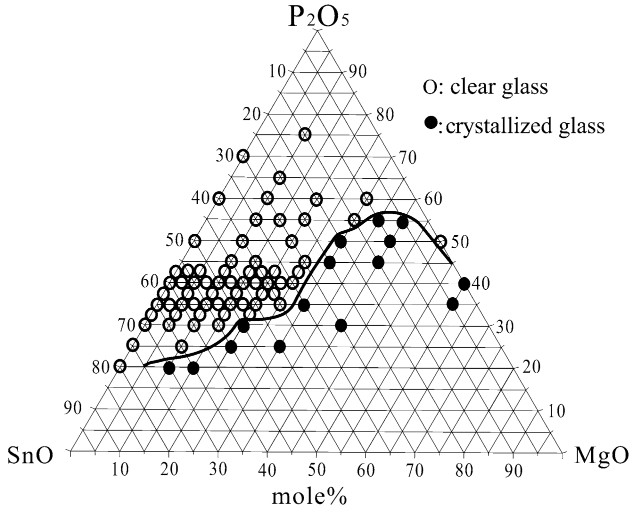

Fig. 1 Compositions investigated and glass formation region of the SnO–MgO–P_2O_5 system

heating for 10–30 min, the melt was quenched by pouring it onto a copper plate. The glass was then annealed at 300 °C for 1–3 h and then furnace-cooled to room temperature. In general, higher temperatures for melting and annealing were required for the compositions with more MgO content. Chemical analysis of the glasses indicated that the difference between nominal composition and real composition for each component was less than 2 mol%.

Characterization

Glass transition temperature (T_g), dilatometric softening temperature (T_{DS}), and coefficient of thermal expansion (*CTE*, 50 °C to T_g) of the glasses were measured by thermomechanical analysis (TMA) (Model SETSYS-1750, Setaram Inc., France), using quartz as push rod. The heating rate was 10 K/min. The Fourier transform infrared (FTIR) spectra of the glasses were recorded between 1,400 and 400 cm^{-1} (resolution 4 cm^{-1}) on a spectrophotometer (Model 300E, Jasco Co., Tokyo, Japan). For chemical durability test, the glasses were cut by diamond saw and ultrasonic cutter to yield disc-shaped samples (diameter 7.9 mm and thickness 2.5 mm). The samples were polished with No.1200 SiC paper and then ultrasonically cleaned with acetone, deionized water, and alcohol. The glass samples were placed in covered polypropylene flasks containing 100 mL of deionized water (initial pH = 7) at 90 ± 1 °C for 6 h. At least three samples were used from each composition glass. Then, the dissolution rate, defined as the weight loss per unit surface area per unit time, was calculated.

Results

Glass formation

Figure 1 shows the glass formation region (the hatched area). The content of the glass former P_2O_5 should be at least 25 mol% to form glassy state. When the content of the glass former P_2O_5 is higher than 55 mol%, glasses with any Sn/(Sn + Mg) ratio can be formed. When the P_2O_5 content is in the range of 25–55 mol%, the Sn/(Sn + Mg) ratio that is required for glass formation must be increased when the content of the network former P_2O_5 is decreased (except for the binary MgO–P_2O_5 compositions). It is also noted that the glass formation region of the binary system SnO–P_2O_5 (upto 80 mol% SnO) is much wider than that of the MgO–P_2O_5 system (50 mol% MgO).

Several literatures [23–25] have been reported on the preparation of SnO–SiO_2 glasses. The melts are inhomogeneous due to the reaction of some Sn^{2+} to Sn^0 and Sn^{4+}. The SnO_2 floats to the surface of the melt and Sn metal sinks to the base. It was found in the present study that, if the batch did not contain suitable amounts of sugar and was melted in air, a significant amount of SnO_2 crust will form on the melt surface. The utilization of sugar and nitrogen atmosphere was found to be useful for minimizing the oxidation of Sn^{2+} to Sn^{4+} during melting, although the melts with a P_2O_5 content of around 25 mol% and a higher SnO content still revealed a small amount of crust on the melt surface. No metal tin was found in the glass melt. In addition, there are several works on the enhancement of chemical durability by nitridation of the phosphate glasses [26]. Although the present glasses were melted in nitrogen atmosphere, the possible nitridation effect was not taken into account in the present study.

It is noted that the glasses with P_2O_5 contents exceed ~40 mol% were easily attacked by humidity, and that the glasses with P_2O_5 contents lower than ~25 mol% became less stable during glass formation. Therefore, glasses with P_2O_5 contents between 30 and 42.5 mol% were investigated in the following experiment. The concentrations of SnO and MgO are 32.5–70 and 0–25 mol%, respectively (see Fig. 1).

Thermal mechanical analysis

Figure 2a–c show the variations of glass transition temperature (T_g), dilatometric softening temperature (T_{DS}), and coefficient of thermal expansion (*CTE*) of the glasses with the Sn/(Sn + Mg) ratio, respectively. It can be seen that the glasses exhibited low glass transition temperature (T_g = 270–400 °C), low dilatometric

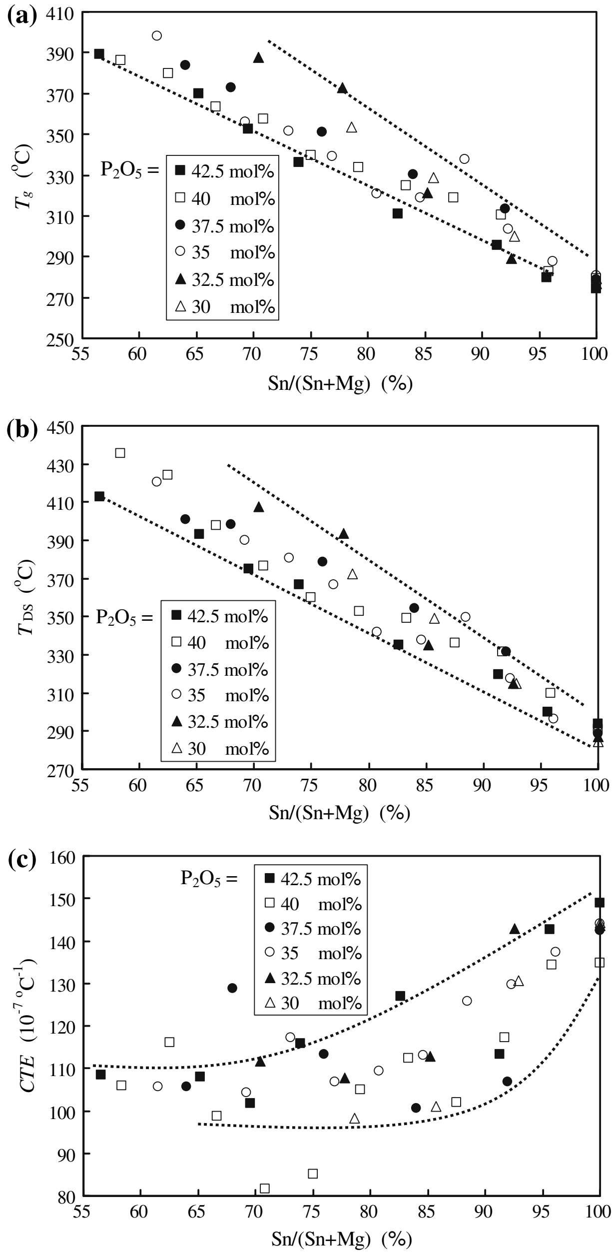

Fig. 2 Effect of Sn/(Sn + Mg) ratio on the (**a**) glass transition temperature, (**b**) dilatometric softening temperature, and (**c**) coefficient of thermal expansion of the glasses

softening temperature (T_{DS} = 290–420 °C), and high thermal expansion coefficient (CTE = 110–160 × 10^{-7} K^{-1}).

In general, increase in the content of divalent cation is expected to increase the degree of cross-linking between chains or rings which are constructed by PO_4^{3-} tetrahedra, resulting in increase in T_g and T_{DS}, and decrease in CTE [27]. However, in the present study, we cannot explore definite relationships between the above properties and the P_2O_5 content. On the other hand, when the Sn/(Sn + Mg) ratio is increased, T_g and T_{DS} decrease, and CTE essentially increases.

Chemical durability

Figure 3 shows the dissolution rate (DR) as a function of Sn/(Sn + Mg) ratio for the glasses immersed in 90 °C water for 6 h. The DR values range from 3 to 328 × 10^{-5} g/cm^2 min. It can be seen that increase in the P_2O_5 content resulted in the increase in DR. The glasses with 30–32.5 mol% P_2O_5 exhibited chemical durability comparable with a sintered commercial PbO-based sealing glass and were still transparent after the test.

As shown in Fig. 3, the variation of DR with the Sn/(Sn + Mg) ratio shows two regions with the opposite trends. The whole curves for 30–37.5 mol% P_2O_5 and the left parts of the curves for 40–42.5 mol% P_2O_5 are in region I, characterized as the nearly constant or decreased DR with increasing Sn/(Sn + Mg) ratio. For P_2O_5 content of 30–32.5 mol%, DR is nearly constant with the Sn/(Sn + Mg) ratio. For P_2O_5 content of 35–42.5 mol%, increase in Sn/(Sn + Mg) ratio results in the decrease in DR, and this trend becomes remarkable for the higher P_2O_5 contents. Moreover, it is noted that for the glasses in this region, addition of SnO is helpful to reduce the viscosity and improve chemical durability. The glasses with 32–32.5 mol% P_2O_5 in this region exhibit excellent chemical durability and tunable T_g, T_{DS}, and CTE (by Sn/(Sn + Mg) ratio).

On the other hand, the right-hand sides of the curves for 40 and 42.5 mol% P_2O_5 are in region II, characterized as the increased DR with increasing Sn/(Sn + Mg) ratio. An abrupt increase in DR is observed at the “transition” point (marked by the arrow)

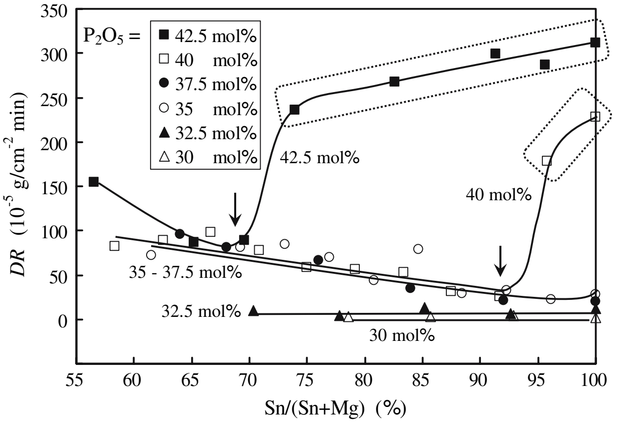

Fig. 3 Variation of dissolution rate with Sn/(Sn + Mg) ratio for the glasses immersed in 90 °C deionized water for 6 h. Compositions in region II are indicated by the *dotted line*. Other compositions are in region I

between region I and region II. The transition point shifts to a lower Sn/(Sn + Mg) ratio when the P_2O_5 content is increased from 40 to 42.5 mol%.

In summary, lower P_2O_5 contents or higher P_2O_5 contents + lower Sn/(Sn + Mg) ratios favor region I. For P_2O_5 contents ≥40 mol% and Sn/(Sn + Mg) ratios higher than the transition point, region II is observed.

Infrared (IR) spectra

Figure 4a–c show the typical IR spectra of the glasses (P_2O_5 concentration = 42.5, 37.5 and 30 mol%, respectively). The high-frequency bands at 1240–1280 cm^{-1} may be associated with the asymmetric stretching vibrations of the two non-bridging oxygen atoms bonded to phosphorus atoms, the PO_2 units, in the Q^2 tetrahedra forming the polyphosphate chains [28, 29]. The bands at 1100 and 1000 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of the PO_3^{2-} terminal groups (Q^1 tetrahedra), respectively [30]. The bands at 900 and 700–780 cm^{-1} can be attributed to asymmetric (in phosphate chains) and symmetric (in phosphate rings) stretching modes of the P–O–P bonds, respectively [28, 29, 31]. The band at 500–530 cm^{-1} can be assigned to the bending modes of the PO_4 groups [31, 32]. It is noted that when the Sn/(Sn + Mg) ratio was increased, the absorption associated with Q^2 decreased while those due to Q^1 increased.

Discussion

As shown in Fig. 1, for a constant P_2O_5 concentration, the glass formation ability is enhanced with the increasing Sn/(Sn + Mg) ratio. It is also noted that the glass formation region of the binary $SnO–P_2O_5$ system (upto 80 mol% SnO) is much wider than that of the $MgO–P_2O_5$ system (50 mol% MgO). This result suggests that Sn^{2+} ion acts as not only a glass modifier but a glass former. It has been reported in glasses based on $SnO–P_2O_5$ [20, 21, 33] that Sn^{2+} acts as a modifier when P_2O_5 is the dominating glass forming oxide. With increasing SnO concentration, Sn^{2+} tends to behave as a glass former. In $Na_2O–SnO–P_2O_5$ glasses [20], for example, Sn^{2+} acts as a modifier up to about 27 mol% of nominal composition. Above this concentration, Sn^{2+} acts as a network former. On the other hand, Mg–O bond is ionic in nature and the MgO content (0–25 mol%) is not high in the present study, suggesting that Mg^{2+} always acts as a network modifier. The improved glass stability in the present study for higher Sn/(Sn + Mg) ratio seems consistent with the above structural mechanism.

As shown in Fig. 2a–c for thermal properties, with increasing Sn/(Sn + Mg) ratio, T_g and T_{DS} decrease, and *CTE* increases. This result implies that increase in the concentration of SnO relative to MgO would weaken the average bond-strength of the glass structure. It is suggested that the larger size of Sn^{2+} ion (1.12 Å) than Mg^{2+} ion (0.65 Å) would result in the weaker Sn–O bond relative to the Mg–O bond.

As shown in Fig. 3 for chemical durability, the increase in the P_2O_5 content results in the increase in *DR*, due to the increased amount of P–O–P bonds which is easily attacked by water molecules [12]. On the other hand, when Sn/(Sn + Mg) ratio is varied, the relationship between chemical durability and thermal properties of the present glasses is not consistent with what is expected in general cases, i.e., decreased viscosity and improved chemical durability are mutually exclusive [3]. As previously discussed on thermal properties, increase in Sn/(Sn + Mg) ratio would weaken the glass structure, thus at first an increased trend of *DR* is expected. However, for the glasses in region I, addition of SnO to replace MgO is helpful to reduce the viscosity and improve chemical durability. Namely, these glasses show an “abnormal” relationship between chemical durability and thermal properties. On the other hands, the glasses in region II show a “normal” relationship between chemical durability and thermal properties, i.e., the viscosity and chemical durability are both reduced with increasing Sn/(Sn + Mg) ratio.

According to the FTIR results (Fig. 4a–c), the glass structure was changed from Q^2 to Q^1 when the Sn/(Sn + Mg) ratio was increased. Takebe et al. [34] have reported that when the structure of x ZnO – (100 – x) P_2O_5 glasses (in mol%, x = 50–70) was changed from Q^2 to Q^1 due to the increase in the ZnO content, the chemical durability was significantly improved (i.e., a reduced *DR*). Moreover, for cations of the same charge, the polarizability of the cation increases with the increasing cation radius [35]. The larger size of Sn^{2+} ion (1.12 Å) than Mg^{2+} ion (0.65 Å) indicates the larger polarizability of Sn^{2+} ion with respect to Mg^{2+} ion. He et al. [27] found that addition of cations with a high polarizability into a phosphate glass reduced glass viscosity and improved chemical durability. Therefore, it is suggested that the abnormal behavior of region I in the present study can be explained by the above-mentioned structure change as well as the larger polarizability of the Sn^{2+} ion.

On the other hand, with the increasing Sn/(Sn + Mg) ratio, the glass structure is continuously weakened because of the lower bond energy of the Sn–O bond relative to Mg–O bond, as previously discussed for the

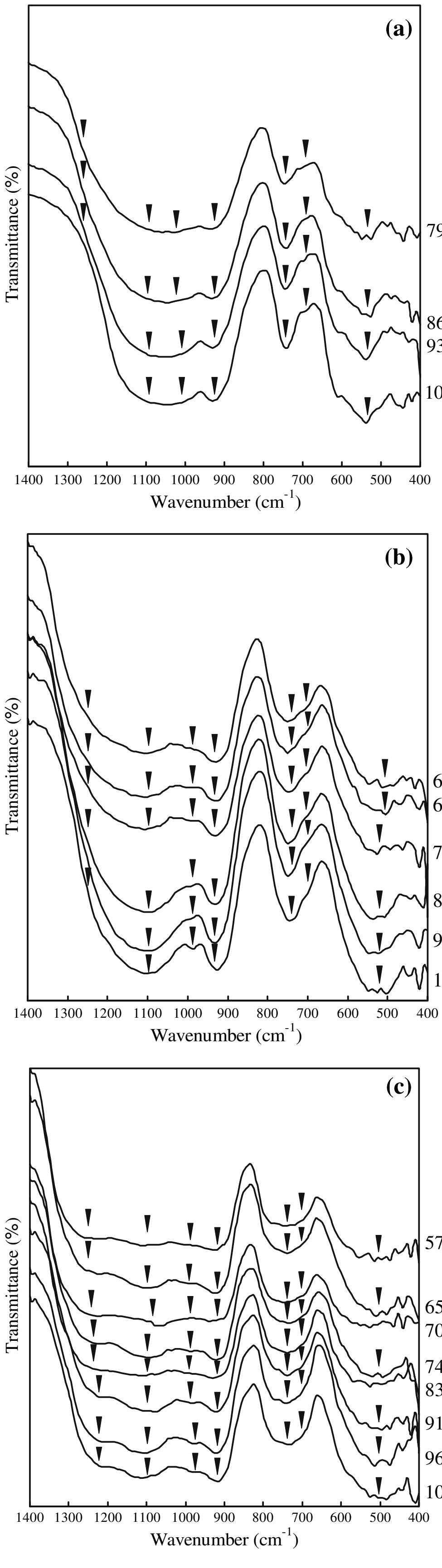

Fig. 4 Typical infrared spectra of the glasses with P_2O_5 concentrations of (**a**) 42.5, (**b**), 37.5, and (**c**) 30 mol%. The value associated with each curve is the Sn/(Sn + Mg) ratio (%)

thermal properties. This would tend to reduce the chemical durability (i.e., an increased *DR*). It is suggested that the normal behavior of region II was caused by this mechanism.

Conclusions

A new glass system $SnO–MgO–P_2O_5$ with low viscosity has been developed. For a constant P_2O_5 concentration, the glass formation ability is enhanced with the increasing Sn/(Sn + Mg) ratio. The properties of the glasses with P_2O_5 contents between 30 and 42.5 mol% were further investigated. The glasses exhibit low glass transition temperature (T_g = 270–400 °C), low dilatometric softening temperature (T_{DS} = 290–420 °C), and high thermal expansion coefficient (*CTE* = 110–160 × 10^{-7} K^{-1}). With the increasing Sn/(Sn + Mg) ratio, T_g and T_{DS} decrease, and *CTE* increases. When Sn/(Sn + Mg) ratio is varied, the relationship between chemical durability and thermal properties of the present glasses is not consistent with what expected in general cases. For the glasses with lower P_2O_5 contents (30–37.5 mol%) or higher P_2O_5 contents (40–42.5 mol%) plus lower Sn/(Sn + Mg) ratios, addition of SnO is helpful to reduce the viscosity and improve chemical durability, i.e., these glasses show an ''abnormal'' relationship between chemical durability and thermal properties. On the other hands, the glasses with ≥40 mol% P_2O_5 and higher Sn/(Sn + Mg) ratios showed reduced chemical durability with increasing Sn/(Sn + Mg) ratio. These glasses show a ''normal'' relationship between chemical durability and thermal properties. It is noted that the glasses with 32–32.5 mol% P_2O_5 exhibit excellent chemical durability and tunable T_g, T_{DS}, and *CTE* (by varying Sn/(Sn + Mg) ratio).

References

1. Marino AE, Arrasmith SR, Gregg LL, Jacobs SD, Chen G, Duc Y (2001) J Non-Cryst Solids 289:37
2. Peng YB, Day DE (1991) Glass Technol 32:166
3. Peng YB, Day DE (1991) Glass Technol 32:200
4. Hunt JT, Speck DR (1989) Opt Eng 28:461
5. Brow RK (2000) J Non-Cryst Solids 263–264:1
6. Brow RK, Tallant DR (1997) J Non-Cryst Solids 222:396

7. Aitken BC, Bookbinder DC, Greene ME, Morena R (1993) USP 5,246,890
8. Day DE, Wu Z, Ray CS, Hrma P (1998) J Non-Cryst Solids 241:1
9. Campbell JH, Suratwala TI (2000) J Non-Cryst Solids 263–264:318
10. Morinaga K, Fujino S (2001) J Non-Cryst Solids 282:118
11. Gray PE, Klein LC (1983) Glass Technol 24:202
12. Bunker BC, Arnold GW, Wilder JA (1984) J Non-Cryst Solids 64:291
13. Tick PA (1984) Phys Chem Glasses 25:149
14. Shaw CM, Shelby JE (1988) Phys Chem Glasses 29:87
15. Morena R (2000) J Non-Cryst Solids 263–264:382
16. Francis GL, Morena R (1994) USP 5,281,560
17. Morena R (1996) USP 5,514,629
18. Morena R (1996) USP 5,516,733
19. Morena R (2000) USP 6,048,811
20. Bhat MH, Berry FJ, Jiang JZ, Rao KJ (2001) J Non-Cryst Solids 291:93
21. Brow RK, Phifer CC, Xu XJ, Day DE (1992) Phys Chem Glasses 33:33
22. Matusita K, Osawa N, Koide M, Sato R, Komatsu T (1994) J Non-Cryst Solids 177:216
23. Sears A, Holland D, Dowsett MG (2000) Phys Chem Glasses 41:42
24. Karim MM, Holland D (1995) Phys Chem Glasses 36:206
25. Bent JF, Hannon AC, Holland D, Karim MMA (1998) J Non-Cryst Solids 232–234:300
26. Pascual L, Duran A (1996) Mater Res Bull 31:77
27. He Y, Day DE (1992) Glass Technol 33:214
28. Hudgens JJ, Martin SW (1993) J Am Ceram Soc 76:1691
29. Kurkjian CR (2000) J Non-Cryst Solids 263–264:207
30. Efimov AM (1997) J Non-Cryst Solids 209:209
31. Sammet M, Bruckner R (1987) Glastech Ber 60:55
32. Samuneva B, Tzvetkova P, Gugov I, Dimitrov V (1996) J Mater Sci Lett 15:2180
33. Xu XJ, Day DE (1990) Phys Chem Glasses 31:183
34. Takebe H, Baba Y, Kuwabara M (2006) J Non-Cryst Solids 352:3088
35. Wolf MB (1984) In: Glass science and technology, vol 7. Elsevier, Amsterdam