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Influence of BaO/(SrO+BaO) on melt properties in $R_2O-RO-SiO_2$ glasses for plasma display panel substrates

Ki-Dong Kim

Department of Materials Science & Engineering, Kunsan National University, Kunsan 573-701, Korea

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The influence of the BaO/(SrO+BaO) ratio on the viscosity, liquidus temperature and electrical resistivity of melts was studied in $R_2O-RO-SiO_2$ glasses for a plasma display panel (PDP) substrate. SrO was substituted progressively by BaO at fixed concentrations of alkaline earth oxides. The dependence of the viscosity and liquidus temperature on BaO/(SrO+BaO) showed a continuous decrease. However, the compositional dependence of resistivity showed minima that may be a kind of mixed mobile ion effect. Comparison of these results with those of previous work suggests that a full replacement of SrO by BaO is desirable from the viewpoint of raw material cost and practical glass production.

BaO and SrO are frequently used in display glasses for CRT (cathode ray tube)⁽¹⁾ and LCD (liquid crystal display).⁽²⁾ According to recent patents^(3–5) commercial substrate glasses for PDP (plasma display panel) also contain BaO and SrO. The compositions of these glasses belong to alkali-alkaline-earth silica system. An example of a PDP device is shown in Figure 1. Components including dielectric paste, seal, electrode, phosphor and barrier rib are processed with a front or rear glass substrate at 550–580°C. The substrate glass should be free from thermal mismatch with those components and from thermal deformation during processing. Therefore, the most important thermal properties of substrate glass are the thermal expansion coefficient and strain point.^(6–10) The constituents of PDP glass substrates are similar to those of CRT glass including SiO_2 , R_2O (Na_2O+K_2O), RO ($MgO+CaO+SrO+BaO$) and minor additives such as ZrO_2 , Al_2O_3 , B_2O_3 . The glasses are typical mixed alkali compositions which also contain mixed alkaline earth oxides. The glass substrates are produced by a float process because their surface should be mirror quality to exclude optical distortion.

In a previous study,⁽¹¹⁾ the effect of replacement of SrO by BaO on some thermal properties of glasses at low temperatures was studied in alkali alkaline earth silicate

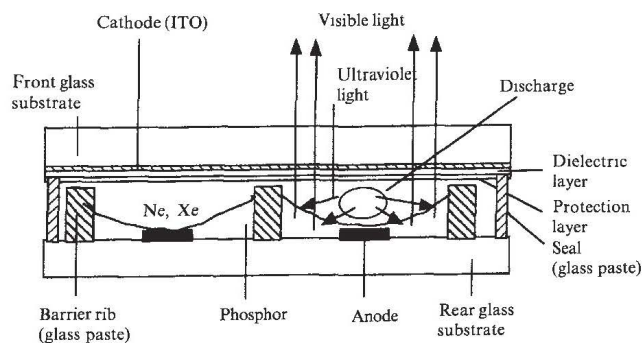


Figure 1. Construction of ac plasma display panel

PDP substrate glass compositions.⁽¹²⁾ Four viscosity fixed points and the thermal expansion coefficient were determined. The results showed no mixed alkaline earth effect but a linear relation against BaO/(SrO+BaO). This behaviour has been discussed in terms of a general structure model based on the modifier field strength. According to the results of that study complete replacement of SrO by BaO also satisfies the requirements of PDP glass substrates with an expected reduction of raw material cost. In the present work the influence of the ratio of BaO/(SrO+BaO) on viscosity, liquidus temperature and electrical resistivity of melts was further studied in the same PDP substrate glass compositions.

Glass preparation and measurements of melt properties

The compositions (mol%) were 68.2 SiO_2 , 9.04(Na_2O+K_2O), 13.4 RO ($MgO+CaO$), 4.5 RO ($SrO+BaO$) and a small amount of ZrO_2 , Al_2O_3 in which the Na_2O/K_2O and the MgO/CaO mole ratios are fixed at 1. The BaO/ RO ($RO=SrO+BaO$) mole fraction is 0.07, 0.2, 0.4, 0.5, 0.8 or 0.98. Table 1 lists the compositions of the experimental glasses.

The viscosity was determined by the rotating cylinder method. The viscometer (RotoVisco "RV30" Hakke Co., Germany) was calibrated using DGG soda-lime-silica standard glass I in the temperature range 1450–1000°C. The viscosity of each glass melt was measured

(e-mail: kdkim@kunsan.ac.kr)

Table 1. Compositions (mol%) of experimental glasses

Glass No.	1	2	3	4	5	6
SiO ₂			68.2			
ZrO ₂			3.3			
Al ₂ O ₃			1.35			
Na ₂ O+K ₂ O			9.04			
MgO+CaO			13.4			
SrO	4.5	3.62	2.71	2.26	0.9	*0.1
BaO	*0.33	0.9	1.81	2.26	3.62	4.53
m=BaO/RO	0.07	0.2	0.4	0.5	0.8	0.98

*introduced as impurity

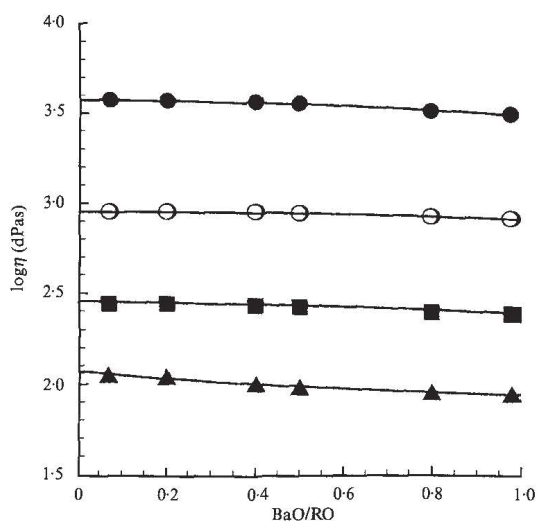
at 100 K intervals within the temperature range 1500 to 1000°C. The measurement of liquidus temperatures (or devitrification temperatures) was performed using a gradient furnace. Calibration of the gradient furnace was checked using a NIST 773 standard reference glass. The glass powders placed into the platinum boat were soaked for 12 h. The primary phase was examined by a polarising microscope and the liquidus temperature determined. Analysis of the crystals at the liquidus temperature was performed qualitatively by the electron probe x-ray microanalyser (EPMA: Jeol, JXA-8900R).

A dipping electrode arrangement was used for the electrical measurement of the melts. The resistivity cell consists of an alumina crucible filled with melt and two Pt/30Rh electrodes immersed to a length of 10 mm. Electrical resistivity was measured between two electrodes separated by a distance of 15 mm. A precision LCR meter (Hewlett Packard 4284A, USA) was used as a measurement bridge. Resistivity measurements were performed at 100 kHz. The cell was calibrated at temperatures between 1000 and 1300°C with two alkali silica glass melts, i.e. 20Na₂O.80SiO₂ and 20K₂O.80SiO₂. Details of the cell and the calibration process are described elsewhere.⁽¹³⁾ After calibration of the cell, resistivities were measured at 100 K temperature intervals within the temperature range 1100–1400°C.

Results and discussion

Viscosity and liquidus temperature

Plots of $\log \eta$ versus $1/T$ exhibit a linear or Arrhenian relationship. Figure 2 shows the dependence of the viscosity on the BaO/RO mole fraction at four tempera-

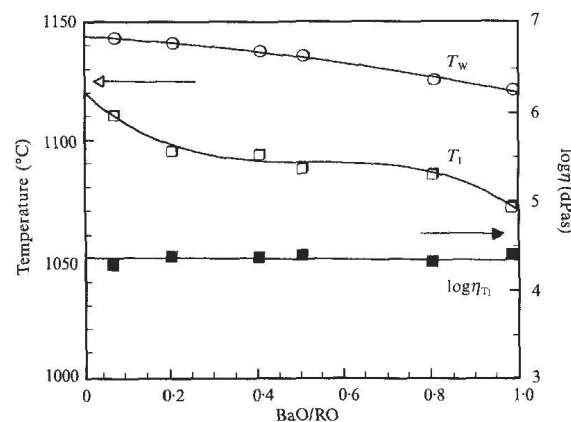
**Figure 2.** Dependence of viscosity on BaO/RO
● 1200°C ○ 1300°C ■ 1400°C ▲ 1500°C**Table 2.** Constants A , B and T_0 of VFT equation determined by working, softening and transition temperature

Constant	$m=0.07$	$m=0.2$	$m=0.4$	$m=0.5$	$m=0.8$	$m=0.98$
A	-3.485	-3.376	-3.452	-3.433	-3.808	-3.338
B	6822.637	6679.370	6885.731	6833.954	7224.178	6576.941
T_0	232.537	235.466	214.954	216.587	200.720	225.701

Softening and transition temperatures of six glasses were taken from Ref. 11

tures. With replacement of SrO by BaO, the viscosity decreases slightly like the four viscosity fixed points of the previous work.⁽¹¹⁾ This tendency is consistent with the results in the alkaline earth aluminosilicate glasses⁽¹⁴⁾ in which the transition temperature corresponding to $10^{13.3}$ dPas decreases in sequence of CaO, SrO and BaO. It has been generally proposed that alkaline earth ions act as traditional modifier ions like alkali ions. In the case of silicate glasses containing alkali oxide, however, the viscosity decreases in the order of $K_2O > Na_2O > Li_2O$, namely the order of alkaline earth ions affecting the viscosity is contrary to that of alkali ions. Therefore, the lowering of viscosity by substitution of Ba²⁺ for Sr²⁺ cannot be explained simply in terms of the field strength or polarisability of the modifier.

Liquidus temperatures (T_l), working temperatures (T_w) and viscosity at the liquidus temperature ($\log \eta_{T_l}$) of six glasses are plotted as a function of BaO/RO in Figure 3. The viscosity at each liquidus temperature ($\log \eta_{T_l}$) was calculated by using the Vogel–Fulcher–Tamann (VFT) equation, $\log \eta = A + B/(T - T_0)$, where A , B , T_0 are constants and T temperature in °C. Table 2 contains VFT constants determined between 10^4 and $10^{13.3}$ dPas for the six melts. T_l lies below its T_w , corresponding to 10^4 dPas. $\log \eta_{T_l}$ occurs at about 4.3 (η_{T_l} in dPas). The liquidus temperature decreases continuously with an increase of BaO/RO. It is very difficult to explain the decrease of liquidus temperature with increase of BaO/RO since the present glasses consist of several components. It has been generally suggested that a reduction of viscosity by compositional change results in increase of material diffusion and consequently crystallisation rates in glasses can be enhanced.⁽¹⁵⁾ As shown in Figure 3, T_l also decreases with a decrease of viscosity (expressed as T_w with $\eta = 10^4$ dPas) of these melts. A decrease of liquidus temperature of the present melts

**Figure 3.** Liquidus temperatures (T_l), working temperature (T_w) and viscosity at liquidus temperature ($\log \eta_{T_l}$) as a function of BaO/RO

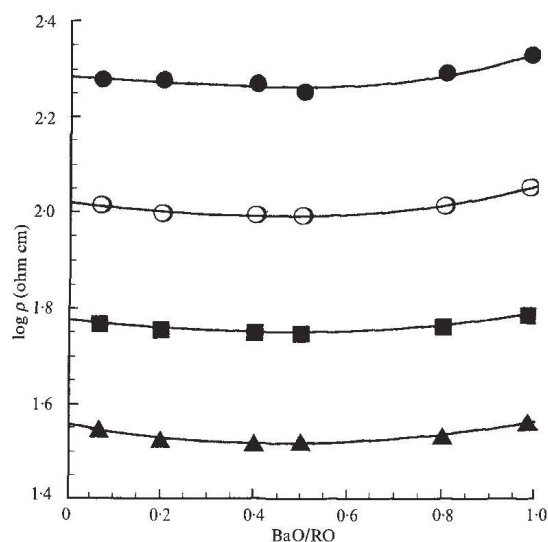


Figure 4. Isothermal resistivity as a function of BaO/RO
● 1100°C ○ 1200°C ■ 1300°C ▲ 1400°C

may be partly due to a decrease of viscosity. The crystal phase observed by polarising microscope was plate shaped. According to the results of EPMA the crystal phase near the liquidus temperature was identified as Akermanite ($2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) irrespective of BaO/RO mole fraction.

Electrical resistivity

Figure 4 shows resistivity isotherms at four temperatures as a function of BaO/RO. The curves show slight minima. The resistivity minima are positioned at BaO/RO ≈ 0.45 and the magnitude of nonlinearity is independent of the temperature. The occurrence of minima or maxima in some properties except resistivity against relative concentration of two alkaline earth oxides has been reported in several works^(16–18) and is called the mixed alkaline earth effect. The resistivity minima in the present work show an opposite behaviour compared with the resistivity maxima in the mixed alkali effect.^(13,19) However, both effects have a common feature of extreme values in the ion conductivity. According to Ingram⁽²⁰⁾ such anomalies of ion conductivity with replacement of one ion by another are collectively called mixed mobile ion effects. The mixed alkaline earth effect in resistivity of the present work may belong to the mixed mobile ion effect. The existing theories for ion conduction mechanisms, however, cannot explain the interactions between SrO and BaO that may be responsible for this effect. Extensive investigations for various alkaline earth ion pairs are necessary to establish the mixed alkaline earth effect on conductivity.

Comparison with thermal properties at low temperature

In a previous study⁽¹¹⁾ the influence of replacement of SrO by BaO on some thermal properties of glasses was studied in the same glass compositions. The previous and present results are summarised in Table 3. A PDP is processed at about 580°C and thus the strain point must be higher than the processing temperature. In order to avoid thermal mismatch with another component of the PDP, the thermal expansion coefficient

Table 3. Strain point, thermal expansion coefficient (α), relative glass batch cost, high temperature viscosity, liquidus temperature (T_l), electrical resistivity (ρ) of the experimental glasses and specification of PDP substrate glasses

Glass no.	1	2	3	4	5	6	Spec.
Properties							
m=BaO/RO	0.07	0.2	0.4	0.5	0.8	0.98	
Strain point (°C)*	593	590	586	584	582	579	>580
α ($\times 10^{-7}$)*	84.3	84.6	84.7	84.9	86.0	87.1	83–88
40/350°C							
Relative glass batch cost (unitless)*	1	0.97	0.95	0.93	0.90	0.87	
Temperature (°C)							
at 10^2 dPas	1514	1510	1501	1495	1489	1486	
at 10^4 dPas	1144	1141	1139	1136	1126	1122	
T_l (°C)	1111	1096	1095	1089	1087	1073	
$\log \eta_{Tl}$ at T_l (dPas)	4.28	4.38	4.37	4.40	4.34	4.42	
$\log \rho$ at 1400°C (ohm cm)	1.547	1.526	1.517	1.519	1.532	1.559	

* data from Ref. 11

(α) of the substrate glass should be $83\text{--}88 \times 10^{-7}/\text{K}$. In the previous work it was found out that these two thermal properties required for PDP glass substrate could be satisfied by full substitution of SrO by BaO. This result indicates that the total glass batch cost can be reduced to approximately 13%.

The viscosity and the liquidus temperature found in the present study exhibit positive effects for glass manufacturing. With replacement of SrO by BaO, the temperature at 10^2 dPas where melting, homogenisation and fining occur decreases continuously. The working temperature at 10^4 dPas, where shaping occurs, shows the same behaviour. The lowering of furnace operation temperature by a complete replacement of SrO by BaO contributes to energy saving and reduction of refractory corrosion. When the molten glass is shaped into plate form on a tin bath by the float process, it is expected that the tin vaporisation will reduce due to decrease of the working temperature. The liquidus temperature is of practical importance since devitrification during the shaping of the glass is highly undesirable. In the present study a decrease of the liquidus temperature with increase of BaO/RO was found. As shown in Table 3 and Figure 3 the liquidus temperature of each melt lies below its working temperature. In the case of glass no. 6 with a BaO/RO = 0.98, the viscosity at the liquidus temperature ($\log \eta_{Tl}$) is 4.42. This value is higher than that of glass no. 1 that contains almost no BaO, i.e. the stability against devitrification is better.

If the melting tank is heated partly by electric boosting consisting of immersed electrodes in the glass melt, the melt resistivity is valuable in optimising the operation of furnaces. In determining the total electric power of the booster, knowledge of the resistance between the electrodes in the glass melts is essential. The resistance depends on the resistivity of the melt, number of electrodes in the melt, permissible surface current density of the electrodes and layout and dimensions of the electrode.⁽²¹⁾ If all parameters except the resistivity of glass melt are fixed, the resistance between the electrodes in the glass melts will be decreased with an increase of the BaO/RO ratio due to a decrease in melt

resistivity. After passing through BaO/RO=0.45, however, the resistance will increase as shown in Figure 4. This increase will result in an increase of total power output of the booster which can be a minimum at BaO/RO=0.45. It is thus expected that the total power output of the booster in melts with BaO/RO=0.98 increases slightly compared with those of mixed alkaline earth glasses containing BaO and SrO.

Summary

Influence of the BaO/RO ratio on viscosity, liquidus temperature and specific electrical resistivity was studied in alkali-alkaline earth-silica plasma display panel substrate glasses. Results of the viscosity and the liquidus temperature show a continuous decrease with increase of BaO/RO. On the other hand minima in compositional dependence of resistivity occur. It is postulated to be a kind of mixed mobile ion effect. By comparing the present results with previous work it is concluded that a full replacement of SrO by BaO is desirable for not only the reduction of raw material cost but also practical glass production.

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