

Technical Report

Influence of BaO/(SrO + BaO) on some thermal properties of R₂O-RO-SiO₂ glasses for plasma display panel substrate

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An influence of BaO/(SrO + BaO) on some thermal properties was studied in alkali – alkaline earth – silica PDP (Plasma Display Panel) substrate glasses. SrO was replaced progressively by BaO at fixed concentration of alkaline earth oxides. Four viscosity fixed points at low temperature, thermal expansion coefficient and density of glasses were determined. The compositional dependence of those properties was discussed from the viewpoint of the mixed alkaline earth effect and the raw material cost.

Einfluß von BaO/(SrO + BaO) auf einige thermische Eigenschaften von R₂O-RO-SiO₂-Substratgläsern für Plasma-Display-Panels

Der Einfluß von BaO/(SrO+BaO) auf einige thermische Eigenschaften von Alkali-Erdalkali-Silicat-Substratgläsern für Plasma-Display-Panels (PDP) wurde untersucht. SrO wurde bei definierten Erdalkalioxid-Konzentrationen zunehmend durch BaO ersetzt. Vier Viskositätsfixpunkte bei niedriger Temperatur, der Wärmeausdehnungskoeffizient und die Glasdichte wurden bestimmt. Die Abhängigkeit dieser Eigenschaften (Parameter) von der Zusammensetzung wurde unter dem Gesichtspunkt des Misch-Erdalkali-effektes und der Kosten für die Rohstoffe diskutiert.

1. Introduction

BaO and SrO are components used frequently in display glasses for CRT (Cathode Ray Tube) [1] and LCD (Liquid Crystal Display) [2]. They affect several glass properties, especially viscosity and thermal expansion of silicate glasses as a network modifier. The recently developed commercial PDP (Plasma Display Panel) substrate glasses called PD-200 of Asahi and CS-25 of Corning-Saint Gobain also contain BaO and SrO, and their compositions belong to the alkali – alkaline earth – silica system [3 to 5]. PDP is an assembly of many different components as shown in figure 1. Components such as dielectric layer, seal, electrode, phosphor and barrier rib are processed together with the glass substrate three or four times at 550 to 580°C. Since the substrate glass should be free from thermal mismatch with those components and from thermal deformation during processing, its thermal expansion coefficient and strain point are treated as the most important thermal properties, and therefore the commercial PDP substrate glasses have been developed to meet these requirements [6 to 10]. The constituents of PDP substrate glasses are

SiO₂, R₂O (R₂O = Na₂O + K₂O), RO (RO = MgO + CaO + SrO + BaO) and minor additives such as ZrO₂, Al₂O₃, B₂O₃. The glasses are typical mixed alkali glasses and contain also mixed alkaline earth oxides. The substrate glasses must have no optical distortion, in other words should be mirror quality and thus, they are produced by the float process.

Concerning the effect of the mixed alkaline earth oxides on the properties of glasses, it has been investigated in several works [11 to 14]. In those works, with replacement of one alkaline earth oxide by another the chemical durability [11], the glass transition temperature [12 and 13] and the melting rate of raw materials [14]

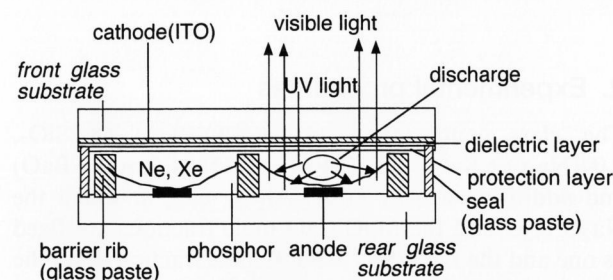


Figure 1. Construction of AC plasma display panel.

Received 23 October, revised manuscript 22 March 1999.

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Table 1. Compositions in mol% of the experimental glasses

component	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 ²⁾
BaO	0.33 ²⁾	0.9	1.81	2.26	3.62	4.53
$m = \text{BaO}/(\text{SrO} + \text{BaO})$	0.07	0.2	0.4	0.5	0.8	0.98

²⁾ BaO of glass no. 1 and SrO of glass no. 6 were introduced as impurity.

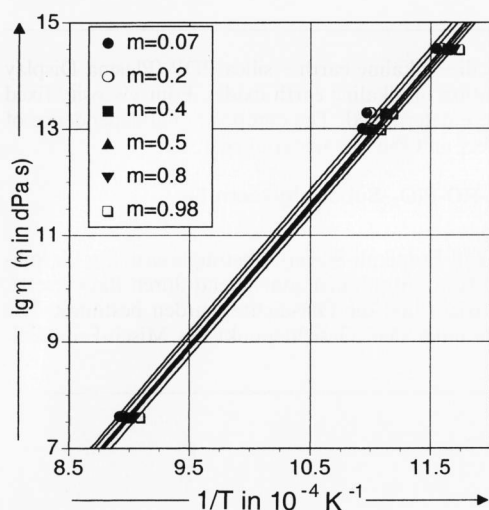


Figure 2. Temperature dependence of the viscosity of six glasses: $m = \text{BaO}/(\text{SrO} + \text{BaO})$ (see table 1).

showed maxima or minima similarly to the mixed alkali effect [15]. As mentioned above, PDP substrate glasses contain four different alkaline earth oxides. Among them SrO is the most expensive component. In the present work, from the viewpoint of the mixed alkaline earth effect and the cost reduction for the raw materials an influence of replacement of SrO by BaO on some thermal properties was studied in alkali – alkaline earth – silica PDP substrate glass compositions developed by the present authors.

2. Experimental procedures

The glass compositions (in mol%) were 68.2SiO₂, 9.04(Na₂O + K₂O), 13.4(MgO + CaO), 4.5(SrO + BaO) and additives such as ZrO₂, Al₂O₃, etc., in which the Na₂O/K₂O and the MgO/CaO mole fractions are fixed as one and the BaO/(SrO + BaO) mole fraction takes the values of 0.07, 0.2, 0.4, 0.5, 0.8, 0.98. The glasses were prepared from high-purity quartz sand, commercial re-

agent-grade Na₂CO₃, K₂CO₃, SrCO₃, BaCO₃, dolomite (MgCO₃ · CaCO₃), Al(OH)₃ and zircon (ZrO₂ · SiO₂). Batches corresponding to about 200 g of glasses were melted in Pt/Rh crucible in an electric furnace and melts were homogenized by using Pt/Rh stirrer. Table 1 contains the compositions of the six experimental glasses.

Four viscosity fixed points (softening, annealing, transition and strain point) were determined. The softening point ($10^{7.6}$ dPa s) was measured by using a penetration method (SP III, Harrop Industry, Ohio (USA)). Annealing and strain points corresponding to the viscosity of 10^{13} and $10^{14.5}$ dPa s were determined by a computerized beam-bending viscometer (Rheotronic, Theta Industries, New York (USA)). The transition temperature T_g corresponding to the viscosity of $10^{13.3}$ dPa s and the thermal expansion coefficient α were simultaneously measured by using a horizontal dilatometer (Netz 402D, Selb (Germany)) with a heating rate of 5 K/min for the finely annealed glasses. Glass density at room temperature was also measured by the Archimedes' method using distilled water.

3. Results and Discussion

The temperature dependence of the viscosity η for the six glasses is shown in figure 2, where plotting of $\lg \eta$ versus $1/T$ exhibits a linear relationship in a temperature range measured. It is generally known that many inorganic glasses show an Arrhenius behavior in a narrow temperature range [16] as follows: $\eta = A \exp(E_\eta/(RT))$ or $\lg \eta = A' + E_\eta/(19.15 T)$, where A and A' are constants, R is the gas constant (8.3143 J/(mol K)) and E_η is the activation energy in J/mol for the viscosity. E_η was calculated from the slope of the plot in figure 2. Table 2 contains the constants A' and E_η .

Figure 3 shows dependence of the softening, the annealing, the transition and the strain points on the BaO/(SrO+BaO) mole fraction. With replacement of SrO by BaO the four viscosity fixed temperatures decrease, in other words the viscosity decrease occurs. The decrease of the viscosity ($\lg \eta$) and the activation energy (E_η) is shown in detail in figure 4, in which the viscosities at 580, 680 and 800 °C calculated by the equation of table 2 are plotted. The viscosity results show no minima but linearity and, thus no mixed alkaline earth effect takes place in the present work. In the studies [11 to 14] relating to the mixed alkaline earth effect, only two alkaline earth oxides were taken and their variable contents were more than 10 mol%. Although the total contents of the alkaline earth oxides in the present glasses are about 18 mol%, the glasses contain four different alkaline earth oxides and among them two alkaline earth oxides (SrO and BaO) are varied in a limited range of 4.5 mol%. Besides, according to the study of Hasegawa [13] the mixed alkaline earth effect at T_g depends on an alkaline earth ion pair, namely the larger the difference in atomic weight between two alkaline earth oxides, the larger the mixed alkaline earth effect. In this work the

Table 2. Constant A' and activation energy E_η of experimental glasses for the equation $\lg \eta = A' + E_{\eta}/(19.15 T)$

	glass no.					
	1	2	3	4	5	6
m = BaO/(SrO+BaO)	0.07	0.2	0.4	0.5	0.8	0.98
A'	-16.17	-16.13	-16.17	-16.14	-16.08	-16.03
E _η in kJ/mol	511.1	508.5	506.6	505.0	502.9	501.2

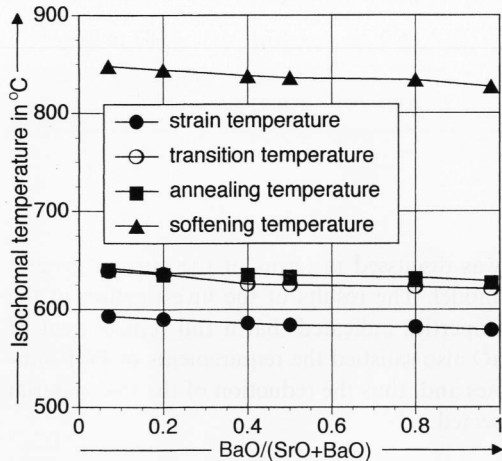


Figure 3. Four viscosity-fixed points (strain, transition, annealing and softening temperature) against the BaO/(SrO + BaO) ratio (see table 3).

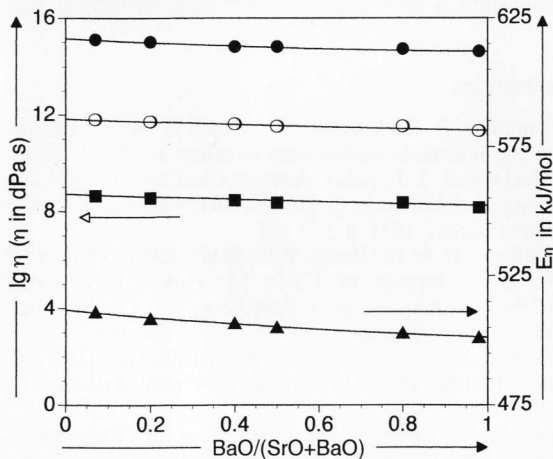


Figure 4. Viscosity isotherms at three temperatures 580 (●), 680 (○), 800 °C (■) and activation energy (▲) against the BaO/(SrO + BaO) ratio (see table 2).

SrO-BaO pair showed the least mixed alkaline earth effect at T_g . Accordingly, the behavior in figures 3 and 4 is reasonable if one considers the current structure model for alkali - alkaline earth - silica glasses [17]. It has been generally proposed that alkaline earth ions act as traditional modifier ions. The field strength of Ba²⁺ ions ($F_{Ba-O} = 0.24 \cdot 10^2 \text{ nm}^{-2}$) for neighboring oxygens is lower than that of Sr²⁺ ions ($F_{Sr-O} = 0.27 \cdot 10^2 \text{ nm}^{-2}$).

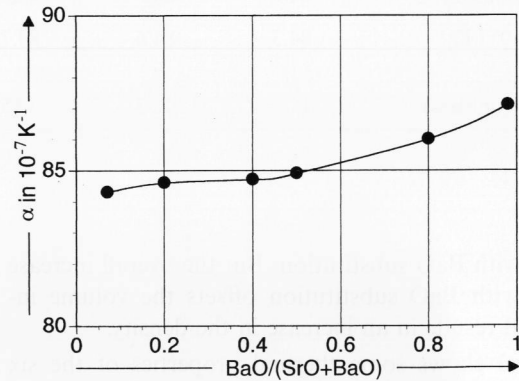
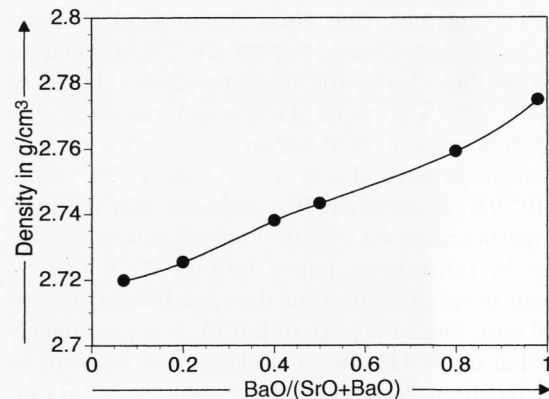

 Figure 5. Effect of BaO concentration on the thermal expansion coefficient α of glasses.


Figure 6. Effect of BaO concentration on the density of glasses.

By substitution of the larger Ba²⁺ ions for Sr²⁺ ions the modifier field strength is lowered and the overall structure is not as tightly bonded, thereby lowering the viscosity.

The effect of the composition on the thermal expansion coefficient α is shown in figure 5. There is also no minima or maxima in α when BaO replaces SrO; it increases slightly with BaO concentration. This behavior is consistent with the above discussion of the modifier ion field strength. The decrease in ion field strength with BaO substitution leads to an increase of α .

Figure 6 shows the compositional dependence of the density at 25 °C. It can be expected that the molar volume of glass increases due to the decrease in ion field

Table 3. Four viscosity fixed points and thermal expansion coefficient α of the experimental glasses, specification of PDP substrate glasses and the relative glass batch cost

properties	glass no.						PDP substrate glasses
	1	2	3	4	5	6	
$m = \text{BaO}/(\text{SrO} + \text{BaO})$	0.07	0.2	0.4	0.5	0.8	0.98	
strain point in °C	593	590	586	584	582	579	>580
transition point in °C	639	636	626	625	623	621	
annealing point in °C	642	637	637	635	633	629	
softening point in °C	848	844	838	836	834	827	
$\alpha_{40/350}$ in 10^{-7} K	84.3	84.6	84.7	84.9	86.0	87.1	83 to 88
relative glass batch cost (unitless)	1	0.97	0.95	0.93	0.90	0.87	

strength with BaO substitution. But the overall increase in mass with BaO substitution offsets the volume increase and results in an increase in the density.

Table 3 shows some thermal properties of the six glasses investigated, the specification of PDP substrate glasses and the relative glass batch cost. As mentioned in section 1, PDP is processed at about 580 °C. No deformation in the substrate glasses which would have a bad influence to the display quality must occur during thermal processing and, thus their strain point must be higher than the processing temperature. The thermal expansion coefficient α of the substrate glasses should be 83 to $88 \cdot 10^{-7}/\text{K}$ to avoid the thermal mismatch with other components of PDP. Strain point and α of glass no. 6 which contains almost no SrO show 579 °C and $87.1 \cdot 10^{-7}/\text{K}$, respectively. It is apparent that the thermal properties required in PDP substrate glasses are also achieved by full substitution of SrO for BaO. This replacement is very beneficial to the reduction of the raw material cost. Since the price of BaCO_3 is approximately half of that of SrCO_3 , the total glass batch cost can be reduced by about 13 % with full substitution of SrO for BaO as indicated in table 3.

As shown in figures 3 and 5, the thermal properties at low temperature are influenced by BaO substitution. Other properties at high temperature such as melt viscosity and liquidus temperature, etc. are expected to be influenced by BaO substitution. These properties will be investigated in the near future.

4. Summary

The influence of $\text{BaO}/(\text{SrO} + \text{BaO})$ on some properties was studied in alkali – alkaline earth – silica substrate glasses for PDP. The viscosities at low temperature, the thermal expansion coefficient and the density were determined. The dependence of those properties on the $\text{BaO}/(\text{SrO} + \text{BaO})$ mole fraction showed no mixed alkaline earth effect, but a linear relation was observed. This

behavior was discussed in terms of the current general structure model. The results of the investigation of the thermal properties indicated that a full replacement of SrO by BaO also satisfied the requirements of PDP substrate glasses and, thus the reduction of the raw material cost is expected.

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The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1997 and they are also grateful to Mr. B. C. Heo of Korea Furnace Development Co. for his cooperation in characterizing glasses.

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