Original Paper

Influence of mixed alkali oxides on some melt properties of TV screen glass

Jong-Hee Hwang[1)] and Jeong-Hyun Park

Department of Ceramic Engineering, Yonsei University, Seoul (Korea)

Ki-Dong Kim

Department of Materials Science & Engineering, Kunsan National University, Kunsan (Korea)

Sang-Sam Choi

Photonics Research Center, Korea Institute of Science and Technology, Seoul (Korea)

The influence of K_2O/R_2O ($R_2O = Na_2O+K_2O$) on some melt properties was studied in alkali–alkaline earth–silicate TV screen glasses. Viscosity, surface tension, electrical resistivity, volatilization and devitrification of glass melts were determined. No mixed alkali effect was observed in viscosity, surface tension and liquidus temperature. They showed a linear behavior with increase of K_2O/R_2O. On the other hand, electrical resistivity and weight loss by volatilization showed a strong mixed alkali effect against relative alkali concentration. According to the dependence of viscosity, electrical resistivity and volatilization on K_2O/R_2O, the slope change of those properties took place at $K_2O/R_2O = 0.4$ to ≈ 0.5. The compositional dependence of viscosity, surface tension and liquidus temperature was discussed in terms of field strength, polarizability and material diffusion, respectively. A correlation was also discussed between the dependence of properties on K_2O/R_2O and the production process of TV screen glass. In conclusion, from the viewpoint of both production and application of TV glasses it was suggested that the mole fraction of K_2O/R_2O should lie between 0.2 and 0.5.

Einfluß von Mischalkalioxiden auf einige Eigenschaften der Schmelzen von Fernsehschirmgläsern

Der Einfluß von K_2O/R_2O ($R_2O = Na_2O + K_2O$) auf Eigenschaften der Schmelzen von Alkali-Erdalkali-Silicatgläsern für die Fernsehschirmherstellung wurde untersucht. Viskosität, Oberflächenspannung, elektrischer Widerstand, Verflüchtigung und Entglasung von Glasschmelzen wurden bestimmt. Hinsichtlich Viskosität, Oberflächenspannung und Liquidustemperatur wurde kein Mischalkalieffekt festgestellt. Sie zeigten bei einer Erhöhung des Wertes für K_2O/R_2O ein lineares Verhalten. Der elektrische Widerstand und der Gewichtsverlust durch Verdampfung zeigten dagegen einen starken Mischalkalieffekt in Abhängigkeit von der relativen Alkalikonzentration. Viskosität, elektrischer Widerstand und Verdampfung zeigten in Abhängigkeit vom K_2O/R_2O-Verhältnis bei $K_2O/R_2O = 0.4$ bis ≈ 0.5 eine nichtlineare Änderung ihrer Eigenschaftswerte. Die Abhängigkeit von Viskosität, Oberflächenspannung und Liquidustemperatur von der Zusammensetzung wurde hinsichtlich Feldstärke, Polarisierbarkeit und Komponentendiffusion diskutiert. Die Beziehung zwischen der Abhängigkeit der Eigenschaften von K_2O/R_2O und dem Herstellungsprozeß von Fernsehschirmglas wurde ebenfalls behandelt. Im Hinblick auf den Herstellungsprozeß sowie die Anwendung von Fernsehschirmglas wurde vorgeschlagen, daß der Molenbruch von K_2O/R_2O zwischen 0.2 and 0.5 liegen sollte.

1. Introduction

Mixed alkali glasses exhibit interesting characteristics, in particular the nonlinear dependence of their properties on the relative concentration of two network-modifying alkali oxides. The properties of an alkali oxide glass, which are associated with alkali ion transport such as electrical conductivity, show a strong minimum in an intermediate mixed alkali composition, when one alkali is replaced by another. The viscosity shows sometimes a pronounced minimum with alkali replacement. This mixed alkali effect has been found to occur in a large number of glass forming systems. According to the two review papers [1 and 2], the magnitude of the effect increases with the increase of radius difference (or difference of field strength) of the alkali ion pair and depends on the temperature. No mixed alkali effect occurs at low alkali concentration (< 10 mol%). In the reviews several industrial applications of this effect have been also suggested. With respect to the mechanism of the mixed alkali effect many models and theories have been suggested. Now it seems persuasive that the mixed alkali effect should be retained for properties relating to alkali ion mobility [3 and 4].

In relation to the industrial applications of the mixed alkali effect, it is very interesting to investigate this effect on the properties of commercial glasses. The main commercial glasses investigated were, however, soda-lime-

Received 11 March 1999, revised manuscript 19 July 1999.

[1)] Now with: Samsung Corning Co., Suwon (Korea).

silicate glasses that contain practically only one alkali oxide [5 and 9]. Commercial TV screen glass is a typical mixed alkali glass containing two alkali oxides (Na_2O and K_2O) half-and-half in wt%. Schaeffer [10] mentioned briefly that the mixed alkali effect was applied intentionally to TV glass in order to increase its electrical resistivity. In the present work the properties such as viscosity, surface tension, electrical resistivity, volatilization and devitrification were investigated in mixed alkali glass melts whose compositions are similar to those of TV screen glasses. The main objective of this work is to examine the influence of the mixed alkali oxides on the melt properties and, from the viewpoint of TV glass production to discuss the correlation between the results and the commercial compositions.

2. Experimental

2.1 Preparation of glasses

The base glass composition in mol% was $72SiO_2$, $(14-x)Na_2O$, xK_2O, $10(SrO+BaO)$ and other inevitable minor components for TV screen glass such as ZrO_2, TiO_2, Al_2O_3, CeO_2 with $x = 0$, 3.5, 5.5, 7, 10.5 and 14, in which the K_2O/R_2O ($R_2O = Na_2O + K_2O$) mole fraction takes the value of 0, 0.25, 0.39, 0.5, 0.75 and 1. The raw materials used were sand and reagent grade carbonate chemicals, etc. As a fining agent sodium antimonate ($Na_2O \cdot Sb_2O_5$) was used. The batches were mixed thoroughly and melted in a Pt/20Rh crucible at temperatures between 1500 and 1550 °C in an electric furnace, depending on the composition. Sufficient time (4 to 6 h) was allowed for the melts to become visibly homogeneous. The glasses were remelted at 1550 °C after casting on a graphite plate and homogenized by using a Pt/Rh stirrer, and bubble-free homogeneous glass melts were prepared.

A linear X-ray absorption coefficient μ of each glass is very important for TV screen glass and should be normally more than 28 cm^{-1} [11]. It was calculated by equation (1) [12 and 13]

$$\mu = \omega_g \, d = (\Sigma \, \omega_{XO} f_{XO}) \, d \qquad (1)$$

where, ω_{XO} is the mass absorption coefficient of each corresponding oxide at 0.06 nm, f_{XO} the weight fraction of each oxide, and d the density of the glass at room temperature. Table 1 shows the composition, density and linear X-ray absorption coefficient of the experimental glasses. Although the glass density decreases with replacement of Na_2O by K_2O, the linear X-ray absorption coefficient increases due to higher mass absorption coefficient of K_2O. Among these compositions, the commercial TV glass composition "M" lies between glass no. 2 and no. 3, where the value of K_2O/R_2O is 0.39 approximately.

2.2 Measurements

The glass properties in the molten state were measured by using a vertical tube furnace in which various accessories are installed and the measuring system can be computerized.

The viscosity η of glass melts was determined by a rotating viscometer. The viscometer (RotoVisco "RV30" Hakke Co., (Germany)) was calibrated using DGG (Deutsche Glastechnische Gesellschaft) standard glass I in the temperature range from 1450 to about 1000 °C. An apparatus constant was determined as 1.01 at the 30 mm immersion depth of the spindle. The viscosity of each glass melt was measured at 100 K temperature intervals within a temperature range of 1400 to 1000 °C. The softening point ($10^{7.6}$ dPa s) was measured by using a penetration method (SP III, Harrop Industry, Ohio (USA)). The transition temperature corresponding to the viscosity of $10^{13.3}$ dPa s was determined using a horizontal dilatometer (Netz 402 D, Selb (Germany)) with a heating rate of 5 K/min for the finely annealed glasses.

The surface tension of glass melts in the viscosity range between 10^2 and 10^3 dPa s was determined in air atmosphere by maximum pull using the cylinder method. The overall design of the present apparatus is generally similar to that of the previous one [14]. The apparatus consists of a Pt/20Rh cylinder connected to a digital recording microbalance (D-101, Cahn, USA) by platinum wire and an alumina crucible filled with glass melt. The measuring system for surface tension was at first calibrated directly at a temperature between 1400 and 1100 °C with a $7.5Na_2O \cdot 17.5Rb_2O \cdot 75SiO_2$ (composition in mol%) glass melt, of which surface tension values at high temperature were already determined by Frischat and Beier [15]. The correction factor was applied to the measurements in the temperature range of 1400 to 1200 °C. The maximum force (F_{max}) was detected by a microbalance while descending the alumina crucible after the melt in the crucible had been in contact with the bottom of the platinum cylinder. The surface tension, σ, of glass melts was calculated by equation (2),

$$\sigma = F_{max}/(4 \, \pi \, r \, g) \qquad (2)$$

where r is the radius of the platinum cylinder and g the gravitational constant. The reproducibility of surface tension appeared to be within ±2 %.

For the electrical measurement of glass melts, a dipping electrode arrangement was applied. The resistivity cell consists of an alumina crucible filled with glass melt and two Pt/30Rh electrodes immersed at 10 mm depth from melt level. Electrical resistivity was measured between two electrodes separated by 15 mm. As measurement bridge, a precision LCR meter (Hewlett Packard 4284A, USA) was used. The resistivity measurements were performed at 1 MHz. The resistivity of a melt is related to its resistance by the following equation (3),

$$\varrho = R_0/K \qquad (3)$$

Table 1. Compositions in mol%, density and linear x-ray absorption coefficient of the experimental glass melts of the mixed alkali system $(14-x)\ Na_2O-xK_2O-10(SrO+BaO)-72SiO_2$

	composition in mol% of glass no.					
	1	2	M[1)]	3	4	5
Na_2O	14	10.5	8.5	7	3.5	0
K_2O	0	3.5	5.5	7	10.5	14
$m = K_2O/R_2O$	0	0.25	0.39	0.5	0.75	1
SrO			6			
BaO			4			
SiO_2			72			
CeO_2			0.11			
ZrO_2			1.0			
TiO_2			0.35			
Al_2O_3			1.6			
Sb_2O_3			0.08			
ZnO			0.39			
density in g/cm^3	2.7784	2.7645	2.7627	2.7552	2.7447	2.7291
linear x-ray absorption coefficient in cm^{-1} at 0.06 nm	28.21	28.57	28.74	28.96	29.32	29.61

[1)] Commercial TV glass (composition in wt%): $62.0SiO_2$, $7.5Na_2O$, $7.4K_2O$, 8.85SrO, 8.73BaO, $0.27CeO_2$, $1.76ZrO_2$, $0.4TiO_2$, $2.33Al_2O_3$, $0.33Sb_2O_3$, 0.45ZnO.

Table 2. Temperatures in °C at five fixed viscosities for six glasses, $m = K_2O/R_2O$

viscosity in $\lg\eta$ (η in dPa s)	$m = 0$	$m = 0.25$	$m = 0.39$	$m = 0.5$	$m = 0.75$	$m = 1$
2	1446	1459	1465	1479	1510	1532
3	1190	1201	1208	1221	1256	1285
4	1014	1023	1030	1043	1077	1111
7.6	706	707	708	718	746	789
13.3	518	510	517	519	536	594

where ϱ is the specific electrical resistivity, R_0 the measured resistance and K the cell constant which is determined by measuring the resistance when the cell is filled with a liquid of known resistivity. The cell was calibrated directly at temperatures between 1000 and 1300 °C with several molten glasses. Binary alkali silicate glass melts, $20Na_2O \cdot 80SiO_2$ and $20K_2O \cdot 80SiO_2$, were used for the calibration. The cell constant K was determined as 1.02. The details of the cell and the calibration are described elsewhere [16]. After calibration of the cell, resistivities of glass melts were measured at 100 K temperature intervals in the range of 1400 to 1000 °C. Melt resistivity was reproducible within ±5 %.

Volatilization experiments of glass melts were carried out by a simple thermal gravimetric method in air atmosphere. The overall design is similar to that of surface tension determination, except the cylinder, a Pt20Rh bucket with about 6 cm^3 volume, which can contain maximum 5 g of glass was hung on the digital recording microbalance. A mullite tube was used as a closed reaction tube. The vaporization products were carried with helium gas to the outlet of the tube. A small piece of glass (about 4 g) was placed in a bucket and then inserted into a furnace. The weight loss at 1400 °C versus time was continuously detected by the microbalance. The measurements ran for 12 h. The experiment was reproducible within the range of ±10 % and the results showed the same tendency. The vaporization products of some melts were collected and analyzed qualitatively by EDX (Link Oxford 6232, (UK))

The liquidus temperature (or devitrification temperature) of the glasses was measured by using a gradient furnace (Siliconit, Japan) according to the ASTM method [17]. The calibration of the gradient furnace was checked with NBS 773 standard reference glass. The glass powders placed into the platinum boat were soaked for 12 h. The primary phase was examined by a polarizing microscope and the liquidus temperature was determined. The liquidus temperature was reproducible within ±0.5 %. The analysis for the crystals at liquidus temperature was performed quantitatively by EPMA (Jeol JXA-8900R, (Japan)).

3. Results

3.1 Viscosity, surface tension and devitrification

Figure 1 shows the temperature dependence of viscosity for six glasses in the range of between 10^2 and 10^4 dPa s.

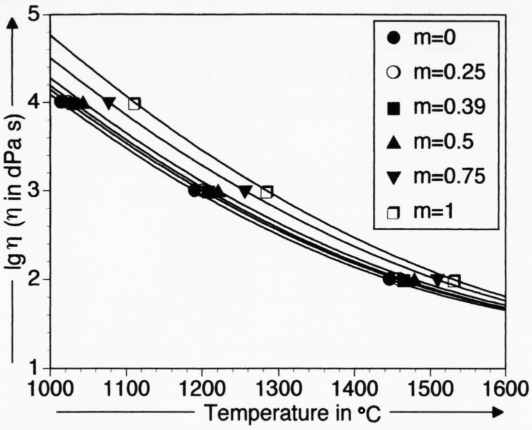

Figure 1. Viscosity-temperature curves of six glasses, $m = K_2O/R_2O$ (see table 1).

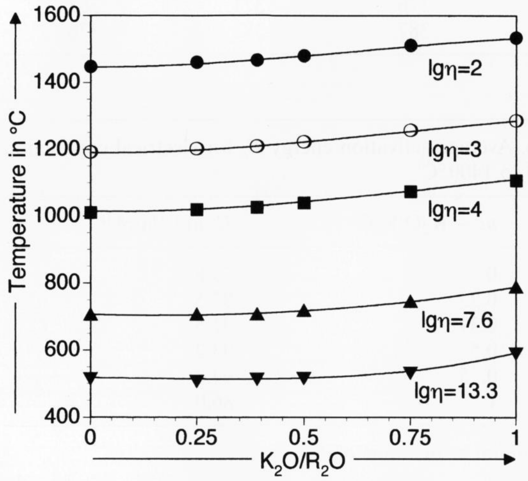

Figure 2. Isoviscosity curves against K_2O/R_2O.

Table 2 shows their temperatures at five fixed viscosities. As shown in table 2, the temperatures at a fixed viscosity within the range of 10^2 and $10^{7.6}$ dPa s increase with K_2O/R_2O, in other words an increase of viscosity occurs, whereas at $10^{13.3}$ dPa s, namely at transformation temperature, another behavior prevails as plotted in figure 2. The temperature dependence of the viscosity in high and low temperature ranges was calculated by the Vogel-Fulcher-Tammann (VFT) equation, $\lg\eta = A + B/(T - T_0)$, where A, B, T_0 are constants, and T is given in °C. Table 3 contains the constants in low (10^2 to 10^4 dPa s) and high (10^4 to $10^{13.3}$ dPa s) viscosity ranges for the six glasses, respectively. In figure 2 the dependence of five fixed viscosities on K_2O/R_2O is shown. The four isoviscosity curves show no extreme but linearity. A weak slope change is observed near $K_2O/R_2O \approx 0.4$ for four viscosities. In the case of $\lg\eta = 13.3$, however, a very slight minimum occurs near $K_2O/R_2O = 0.25$ that is also shown in table 2.

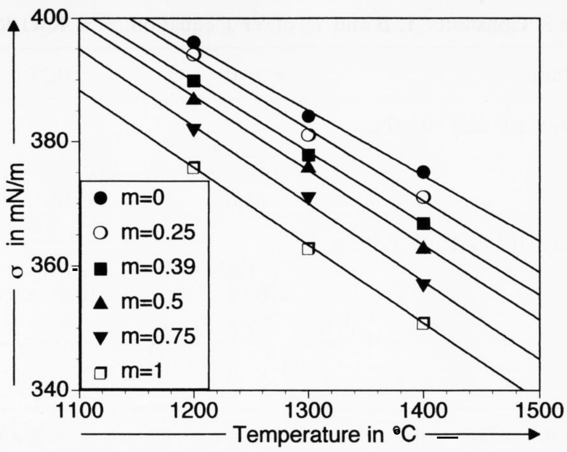

Figure 3. Temperature dependence of surface tension for six glasses, $m = K_2O/R_2O$.

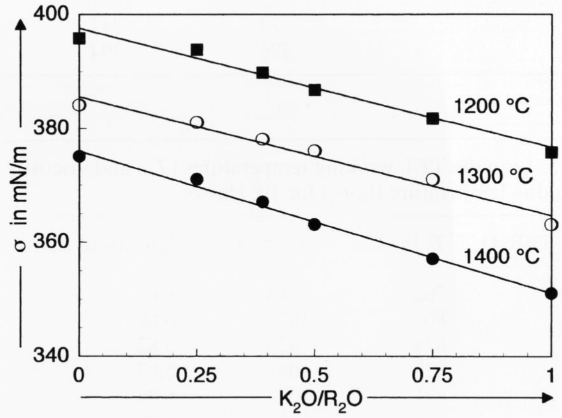

Figure 4. Surface tension isotherms against K_2O/R_2O.

Table 4 shows the surface tension values of six glass melts at 1400, 1300 and 1200 °C and the temperature dependence of surface tension is plotted in figure 3. The surface tension σ has a linear relation to the temperature T as $\sigma = a + b\,T$, where a and b are constants. Surface tension against the relative alkali concentration gives also a linear relation. In figure 4 the surface tension is plotted as a function of K_2O/R_2O at 1200, 1300 and 1400 °C, where it decreases linearly with increase of K_2O/R_2O. There are no minima or maxima in surface tension like the results in the melt viscosity in figure 2.

Table 5 contains liquidus or devitrification temperatures (T_l) and their related data of six glasses. The liquidus temperature increases slightly with increase of K_2O/R_2O and lies below its working temperature (T_w) corresponding to 10^4 dPa s. The viscosity at each liquidus temperature was calculated by using the VFT equation with the constants of table 3, and the values (η_{T_l}) were about 10^6 dPa s. The morphology of the crystal phase observed by polarizing microscope was leaflet shape. It was identified by using EPMA that two crystal phases ($BaO \cdot 2SiO_2$ and $SrO \cdot SiO_2$) coexist near the liquidus temperature irrespective of K_2O/R_2O.

Table 3. Constants A, B and T_0 of VFT equation, $m = K_2O/R_2O$

constant	$m = 0$	$m = 0.25$	$m = 0.39$	$m = 0.5$	$m = 0.75$	$m = 1$
between 10^2 and 10^4 dPa s						
A	−2.400	−2.450	−2.506	−2.450	−2.773	−2.767
B	6082.5	6257.1	6377.0	6257.1	6999.7	6790.7
T_0	63.6	52.9	49.9	72.9	43.5	107.5
between 10^4 and $10^{13.3}$ dPa s						
A	−1.834	−2.040	−1.571	−1.864	−2.218	−1.760
B	4709.4	5110.8	4570.2	5010.7	5613.2	4822.5
T_0	206.8	176.8	209.7	188.6	174.3	273.8

Table 4. Surface tension σ (in mN/m) for six glasses, $m = K_2O/R_2O$

	σ in mN/m					
temperature in °C	$m = 0$	$m = 0.25$	$m = 0.39$	$m = 0.5$	$m = 0.75$	$m = 1$
1400	375	371	367	363	357	351
1300	384	381	378	376	371	363
1200	396	394	390	387	382	376

Table 5. Liquidus (T_l), working temperatures (T_w) and viscosity at liquidus temperature ($\lg\eta_{T_l}$) for six glasses

$m = K_2O/R_2O$	T_l in °C	T_w in °C	$\lg\eta_{T_l}$ (η in dPa s)
0	762	1014	6.65
0.25	806	1023	6.08
0.39	828	1030	5.82
0.5	828	1043	5.97
0.75	871	1077	5.84
1	889	1111	6.08

Table 6. Average activation energy E_a for electrical conduction at 1000 to 1400 °C

$m = K_2O/R_2O$	E_a in kJ/mol[3)]
0	75.8
0.25	87.5
0.39	91.5
0.5	93.2
0.75	94.8
1	86.0

3) Maximum error range of E_a is ±2%.

3.2 Electrical resistivity and volatilization

The temperature dependence of the resistivity ϱ for the six glass melts is presented in figure 5. These glass melts exhibit non-Arrhenius behavior in the investigated temperature range. The non-Arrhenius behavior in resistivity for the melts can be expressed best by a least-squares curve fitting as a second-degree polynomial of the type $\lg\varrho = A + B/T + C/T^2$, where A, B and C are constants for a given melt. By differentiating this equation, it is possible to calculate the activation energy for ionic conduction. Table 6 contains the average activation energy (E_a) in the temperature range from 1000 to about 1400 °C. The order of the resistivity values at each temperature in figure 5 and the activation energies in table 6 seems to indicate their nonlinear dependence on the relative alkali concentration (K_2O/R_2O) as shown in figures 6 and 7.

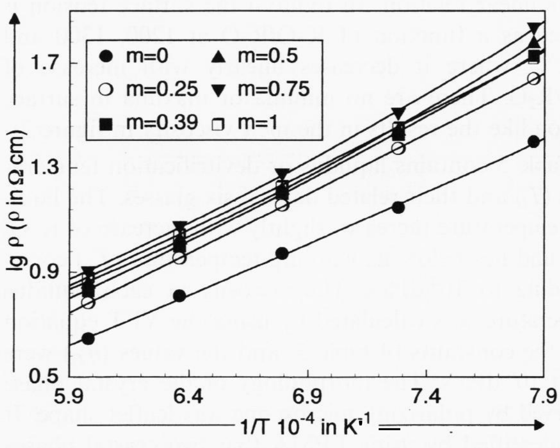

Figure 5. Temperature dependence of electrical resistivity for six glasses, $m = K_2O/R_2O$.

Figures 6 and 7 display the resistivity isotherms at three temperatures and the activation energies, respectively, as a function of K_2O/R_2O. They show maxima which are usually called the mixed alkali effect. The slope changes slightly at $K_2O/R_2O \approx 0.5$. The resistivity maxima are positioned between $K_2O/R_2O = 0.65$ and 0.75, and the magnitude of the mixed alkali effect diminishes with increasing temperature.

In figure 8 the volatilization behavior of six glass melts at 1400 °C is plotted as a function of heat treatment time. The weight loss increases with increasing

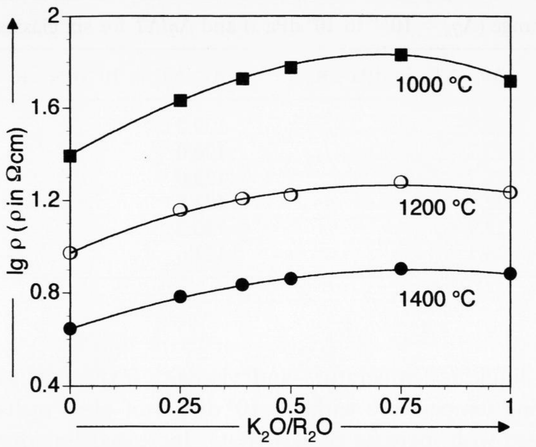

Figure 6. Resistivity isotherms of glass melts against K_2O/R_2O.

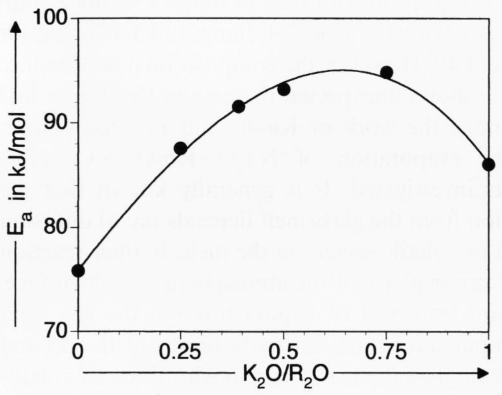

Figure 7. Average activation energy for electrical conduction in the temperature range between 1000 and 1400 °C as a function of K_2O/R_2O.

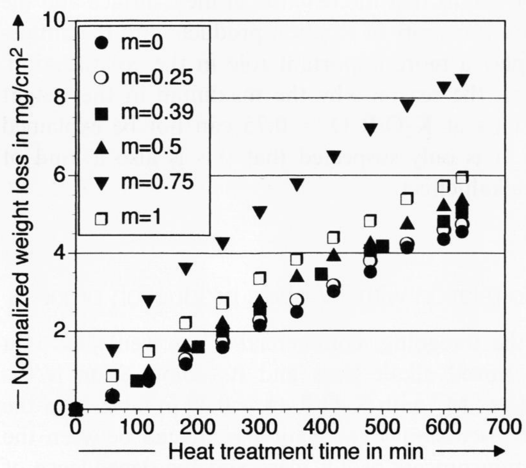

Figure 8. Normalized weight loss at 1400 °C for six glasses, $m = K_2O/R_2O$.

time, but the order at constant time does not follow the K_2O/R_2O mole fraction. The glass melt with $K_2O/R_2O = 0.75$ shows the largest weight loss and its value approaches to about 8 mg/cm^2 at 600 min of heat treatment time. From this a nonlinear dependence of the volatilization on K_2O/R_2O is expected. Figure 9 shows

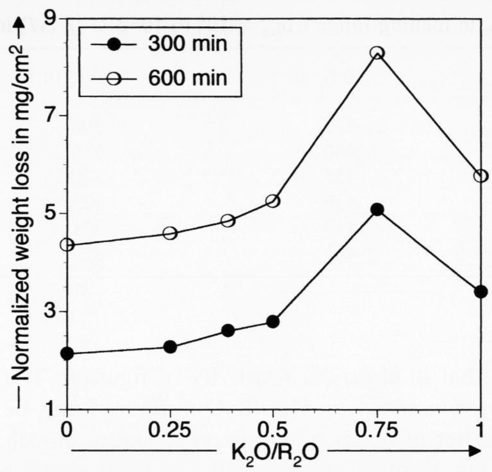

Figure 9. Normalized weight loss at 1400 °C against K_2O/R_2O.

compositional dependence of the weight loss at two different heat treatment times of 300 and 600 min. The weight loss increases slightly with increase of K_2O/R_2O, and after passing through $K_2O/R_2O = 0.5$ mole fraction a dramatic increase occurs to $K_2O/R_2O = 0.75$ and then it decreases steeply. Hence, the two curves exhibit extreme values at $K_2O/R_2O = 0.75$. The EDX analysis indicated that the collected vaporization products consist of alkali and antimony.

4. Discussion

4.1 Dependence of properties on K_2O/R_2O

Although minima in viscosity curves against relative alkali concentration have been found in some mixed alkali silicate glasses/melts [18 and 21] and some mixed alkali borate glasses [22 and 23], they show different behavior from the properties depending on the mobility of the alkali ions, for example electrical conductivity. The studies on the influence of various alkali ion pairs on the electrical conductivity [24 to 26] showed that the mixed alkali effect increases with increase in the difference of ionic radii between the alkali ion pair. In contrast, the order of the alkali ion pair which affects viscosity is independent of the difference of ionic radii, for example the nonlinearity increases in the order of Na−K<Li−Na<Li−K<Na−Rb in the melt state [20 and 21] and K−Rb<K−Cs<Na−Cs<Na−Rb<Na−K in the transformation range [19 to 23]. Recent studies [4 and 27] on mixed-alkali aluminosilicate glasses have demonstrated two distinct differences: first, with replacement of SiO_2 by Al_2O_3, namely with decreasing nonbridging oxygen content, the mixed alkali effect in the electrical resistivity increases and the minimum in the viscosity disappears; second, the mole fractions at a viscosity minimum and at a resistivity maximum in the mixed alkali glasses are different from each other.

From those differences between both properties it can be deduced that the slight minimum shown in the $10^{13.3}$ dPa s isoviscosity curve of figure 2 is a different

Table 7. ΔT_m in melting range ($\Delta\eta_m$ = 10^4 to 10^2 dPa s), ΔT_s in shaping range ($\Delta\eta_s$ = $10^{7.6}$ to 10^4 dPa s) and $\Delta\eta/\Delta T$ for six glasses

$m = K_2O/R_2O$	ΔT_m in K	ΔT_s in K	$\Delta\eta_m/\Delta T_m$ in dPa s/K	$\Delta\eta_s/\Delta T_s$ in 10^3 dPa s/K
0	432	308	22.9	129.2
0.25	436	316	22.7	126.0
0.39	435	322	22.7	123.6
0.5	436	325	22.7	122.5
0.75	433	331	22.9	120.2
1	421	322	23.5	123.6

effect from that in electrical resistivity of figure 6. The dependence of viscosity on K_2O/R_2O in figure 2 can be explained rather in terms of a general structure model. The field strength of K^+ (F_{K-O} = 0.13 · 10^2 nm^{-2}) for the neighboring oxygen is lower than that of Na^+ (F_{Na-O} = 0.17 · 10^2 nm^{-2}) and thus the overall glass network is bonded tightly by substitution of the K^+ ions for Na^+ ions. This may result in an increase of viscosity. On the other hand, the resistivity results in figure 6 show a typical mixed alkali effect and are similar to those reported previously for the melts [8 and 27], particularly at the mole fraction of the extreme values.

There have been few studies on the surface tension measurements of the mixed alkali glasses. The surface tension is also an independent property of the alkali ion mobility. No mixed alkali effect is observed in the present work as shown in figure 4. The results of the surface tension show the same tendency as those of $Na_2O-Rb_2O-SiO_2$ mixed alkali glass melts of a previous study [15]. In general, the surface tension of alkali silicate glass melts is related to the polarizability of alkali ions [28]. The polarizability of K^+ with a large ion radius is greater than that of Na^+ and thus the surface tension of glass melts decreases with increase of K_2O/R_2O.

There have also been few studies related to the effect of mixed alkali oxide on the devitrification of glasses. Because the present glasses consist of several components, it is very complicated to explain the increase of the liquidus temperature with replacement of Na_2O by K_2O in table 5. In general, it has been suggested that a reduction of viscosity by compositional change results in an increase of material diffusion and then the crystallization rates in glasses can be enhanced. According to [29] in which the effects of small water concentration on the crystallization behavior of lithia silicate glasses is investigated the increase in the OH ion concentration displaced the temperature (T_{max}) corresponding to the maximum crystal growth rate towards lower temperature. The work reported that a reduction of viscosity due to the increase of the OH ion concentration contributed partly to a lowering of T_{max}. A similar relation between viscosity and liquidus temperature exists also in the present glasses. Liquidus temperature (T_l), working temperature (T_w) and viscosity at liquidus temperature ($\lg\eta_{T_l}$) by using the data of table 5 are plotted as a function of K_2O/R_2O in figure 10; $\lg\eta_{T_l}$ is about 6 (η_{T_l} in d Pa s). Both liquidus temperature and viscosity (expressed as working temperature with $\eta = 10^4$ dPa s) of glass melts increase with increase of K_2O/R_2O. Increased liquidus temperature of the present glass melts may be partly due to the increase in viscosity.

The volatilization with time in figure 8 shows a similar tendency with the work of Jiang and LaCourse for TV glasses [30]. However, the compositional dependence of figure 9 shows unexpected maxima in the weight loss curves unlike the work of Kassis and Frischat [31], in which the evaporation of $Na_2O-Rb_2O-SiO_2$ glass melts was investigated. It is generally known that the evaporation from the glass melt depends on: a) diffusion transport of volatile species in the melt, b) their reaction rate with vapor phase of the atmosphere at melt surface, c) diffusion transport of vapors through the gas layer [32]. Comparison of the resistivity results of the present mixed alkali glass melts in figure 6 with those of volatilization in figure 9 indicates that the role of alkali diffusion in the melt may be small for volatilization. This agrees with the suggestion of Conradt and Scholze [33], who studied the volatilization from glass melts extensively. It seems that the reaction at melt surface and the diffusion transport of reaction products into the atmosphere play a more important role in the volatilization. However, the reason why the maximum in the weight loss occurs at K_2O/R_2O = 0.75 can not be explained clearly. It is only suspected that this is also a kind of mixed alkali effect.

4.2 Correlation with TV glass production process

From the foregoing, commercial TV screen glass is a typical mixed alkali glass and its composition is expressed as "M" with K_2O/R_2O = 0.39 in table 1. In the present discussion a correlation is treated between the production process of TV glass and the dependence of melt properties on K_2O/R_2O.

The viscosity of glass and its variation with temperature is a very important property in the overall glass manufacturing process, especially the shaping process. Two temperature differences, ΔT_m in the melting range (10^2 to 10^4 dPa s) and ΔT_s in the shaping range (10^4 to $10^{7.6}$ dPa s) in table 7 are characterized by using the data of table 2. ΔT_m and ΔT_s are almost constant. $\Delta\eta/\Delta T$ in both ranges is also constant irrespective of the K_2O/R_2O

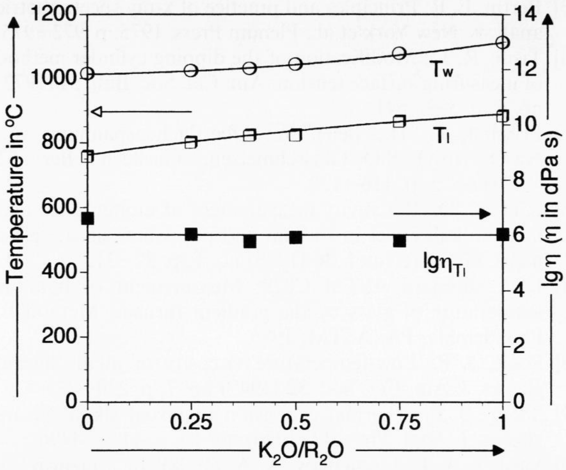

Figure 10. Liquidus (T_l), working temperature (T_w) and viscosity at liquidus temperature ($\lg\eta_{T_l}$) against K_2O/R_2O.

mole fraction. It is hence expected that the temperature control condition of the furnace for the melting and shaping process is the same in spite of the replacement of Na_2O by K_2O. However, the isoviscosity curves of figure 2 show a slight increase in viscosity after passing through $K_2O/R_2O = 0.4$. This means that in the case of $K_2O/R_2O > 0.4$, the furnace operation temperature should be higher for good fining and homogenization of melts. It is thus desirable that the K_2O/R_2O mole fraction is below 0.4.

The surface tension of the glass melt is a property contributing to the refining process in which the dissolution of seeds by shrinkage is dominant [34 and 35]. The more the surface tension of glass melt increases, the greater the possibility of seed removal becomes. As shown in figure 4 the melt surface tension at constant temperature decreases linearly with increase of K_2O/R_2O. Therefore, the increase of K_2O/R_2O may diminish the degree of the refining in TV glass.

Devitrification is very important for the glass-shaping processes. Premature devitrification, occurring during the shaping of the glass, is highly undesirable and must be avoided. In the present experiments as the Na_2O was replaced by K_2O, the liquidus temperature increased. However, as shown in table 5 and figure 10, the liquidus temperatures of each glass melt lie below its working temperature and their difference is greater than 200 K. Therefore, the stability of the glass against devitrification is secured. Especially the viscosity values at the liquidus temperature (η_{T_l}) are more than 10^5 dPa s. This is of practical importance since $\eta_{T_l} > 10^5$ dPa s in TV glasses means also the stability of the glass against devitrification. However, the increase of K_2O/R_2O causes the working temperature increase that can damage the glass shaping machine inclusive mold.

The electrical resistivity of glass melts is important to optimize the operation of furnaces heated by electric boosting with immersed electrodes in the glass melt. In determining the total electric power of the booster the resistance between the electrodes in the glass melts plays a decisive role. It depends on the resistivity of glass melt, the number of electrodes in the melt, the permissible surface current density of the electrodes, and the layout and the dimensions of the electrodes [36]. Under the assumption that the above parameters except the melt resistivity are fixed, the resistance between the electrodes in the glass melts with increase of K_2O/R_2O will be increased due to the increase of electrical resistivity as shown in figure 6. This will result in an increase of total power output of the booster which can be a maximum at $K_2O/R_2O = 0.75$.

Vaporization of alkali from glass melts is important due to its influence on glass homogeneity and refractory corrosion. Especially, the reaction of the atmospheric water with the molten glass surface results in considerably higher concentration of alkali volatile species as ROH which corrodes the refractory materials and thus the service life of the glass melting tank is decreased. For the commercial TV glasses it has been reported that KOH vapor concentrations in the atmosphere exceed NaOH [37]. The present results for volatilization of figure 9 show that with replacement of Na_2O by K_2O the weight loss increases, its slope is changed steeply at $K_2O/R_2O = 0.5$ and its maximum occurs at $K_2O/R_2O = 0.75$. These results imply that it is undesirable for TV glasses to be $K_2O/R_2O \geq 0.5$.

Through the above discussion, from the viewpoint of production it seems to be better for TV glasses not to contain K_2O. However, in designing a glass composition not only the production technology must be considered but also the applications of the glass product. Considering that TV glasses are used as an electronic component, it is desirable that glass has a higher resistivity for good insulating. According to the several works [38 and 39] in which the resistivity below transformation temperature was investigated, in mixed alkali silicate glasses the resistivity maxima occur at $K_2O/R_2O = 0.5$ to ≈ 0.65. In addition to the resistivity, other properties of glass can be considered, for example chemical durability which shows a maximum at $K_2O/R_2O = 0.2$ to ≈ 0.5 in mixed alkali silicate glasses [7 and 40]. Melt properties such as viscosity, electrical resistivity and volatilization depending on K_2O/R_2O in the present work showed the slope change at $K_2O/R_2O = 0.5$ approximately. Therefore, it is valuable that the mole fraction of K_2O/R_2O should lie between 0.2 and 0.5 to satisfy both production and application of TV glasses. The commercial TV screen glass with $K_2O/R_2O = 0.39$ is in accord with this suggested range.

5. Conclusions

The commercial TV screen glass is a typical mixed alkali glass with $K_2O/R_2O = 0.39$ mole fraction ($R_2O = Na_2O + K_2O$). In the present work, the dependence of some melt properties on K_2O/R_2O was studied in TV screen glasses.

The viscosity, the surface tension and the liquidus temperature of melts showed no extreme values but linear behavior with increase of K_2O/R_2O. On the other hand, the mixed alkali effect occurred in electrical resistivity and the weight loss by volatilization. Therefore, it can be concluded that the mixed alkali effect should be retained for properties relating to alkali ion mobility.

Relating those results with the TV glass production process, it seems to be undesirable for TV glasses to contain K_2O. However, for the application of glass products some amount of K_2O (K_2O/R_2O = 0.2 to $\approx$0.65) is needed to improve the glass properties, for example resistivity and chemical durability. The problem is how to combine production of glass with its application. The compositional dependence of the viscosity, the resistivity and the volatilization in the present work showed a slope change at K_2O/R_2O = 0.4 to $\approx$0.5 approximately. It is expected that the influence of K_2O on the production process is worse at $K_2O/R_2O > 0.5$. From the viewpoint of both production and application of TV glasses it is concluded that the mole fraction of K_2O/R_2O should lie between 0.2 and 0.5.

*

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998.

6. References

[1] Day, D. E.: Mixed alkali glasses – Their properties and uses. J. Non-Cryst. Solids **21** (1976) p. 343–372.
[2] Dietzel, A.: On the so-called mixed alkali effect. Phys. Chem. Glass. **24** (1983) no. 6, p. 172–180.
[3] Matusita, K.; Watanabe, T.; Kamiya, K. et al.: Viscosities of single and mixed alkali borate glasses. Phys. Chem. Glasses **21** (1980) no. 2, p. 78–84.
[4] Kim, K.-D.; Lee, S.-H.: Viscosity behavior and mixed alkali effect of alkali aluminosilicate glass melts. J. Japan. Ceram. Soc. **105** (1997) no. 10, p. 827–832.
[5] Sen, S.; Tooley, F. V.: Effect of Na_2O/K_2O ratio on chemical durability of alkali-lime-silica glasses. J. Am. Cer. Soc. **38** (1955) no. 5, p. 175–177.
[6] Prasad, R. S.; Isard, J. O.: The dielectric properties of some glasses at 40 Gc/s. Phys. Chem. Glasses **8** (1967) no. 6, p. 218–223.
[7] Dilmore, M. F.; Clark, D. E.; Hench, L. L.: Chemical durability of $Na_2O-K_2O-CaO-SiO_2$ glasses. J. Am. Cer. Soc. **61** (1978) no. 9–10, p. 439–443.
[8] Baucke, F. G. K.; Werner, R. D.: Mixed alkali effect of electrical conductivity in glass-forming silicate melts. Glastech. Ber. **62** (1989) no. 5, p. 182–186.
[9] Yue, Y.; Brückner, R.: Influence of homologous substitution of chemical components on the rheological properties and on isochomal workability of silicate glass melts. Glastech. Ber. Glass. Sci. Technol. **69** (1996) no. 7, p. 204–215.
[10] Schaeffer, H. A.: Allgemeine Technologie des Glases, Grundlagen des Schmelzens und der Formgebung. Erlangen: Institut für Werkstoffwissenschaften, 1988. p. 13–16.
[11] McLellan, G. W.; Shand, E. B.: Glass engineering handbook. 3rd ed. New York et al.: McGraw-Hill, 1984.
[12] Brewster, G. F.: Calculated X-ray mass absorption coefficients of glass components. J. Am. Cer. Soc. **35** (1952) no. 8, p. 194–197.
[13] Bertin, E. P.: Principles and practice of x-ray spectrometric analysis. New York et al.: Plenum Press, 1975. p. 972–975.
[14] Tiede, R. L.: Modification of the dipping cylinder method of measuring surface tension. Am. Cer. Soc. Bull. **51** (1972) no. 6, p. 539–541.
[15] Frischat, G. H.; Beier, W.: Oberflächenspannung von $Na_2O-Rb_2O-SiO_2$-Glasschmelzen. Glastech. Ber. **52** (1979) no. 5, p. 116–120.
[16] Kim, K.-D.: Resistivity measurement of molten glass and mixed alkali effect in sodium and potassium silicate glass melts. Glass Technol. **36** (1995) no. 1, p. 27–31.
[17] USA standard ASTM C829: Measurement of liquidus temperature of glass by the gradient furnace. Method B. Philadelphia, PA: ASTM, 1986.
[18] Poole, J. P.: Low-temperature viscosity of alkali silicate glasses. J. Am. Cer. Soc. **32** (1949) no. 7, p. 230–233.
[19] Shelby, J. E.: Thermal expansion of mixed-alkali silicate glasses. J. Appl. Phys. **47** (1976) no. 10, p. 4489–4496.
[20] Vasiliev, A. I.; Lisenenkov, A. A. (1978): In: Mazurin, O. V.; Streltsina, M. V.; Shvaiko-Shvaikovskaya, T. P. (eds.): Handbook of Glass Data. Part C. Ternary silicate glasses. Amsterdam et al.: Elsevier, 1983. p. 32.
[21] Frischat, G. H.; Herr, K.; Barklage-Hilgefort, H.: Probleme bei der Vorbereitung glastechnischer Untersuchungen im Weltraum. Projekt "Reaktionskinetik in Glasschmelzen". Glastechn. Ber. **53** (1980) no. 1, p. 1–9.
[22] Kuppinger, C. M.; Shelby, J. E.: Viscosity and thermal expansion of mixed-alkali sodium- potasium borate glasses. J. Am. Cer. Soc. **68** (1985) no. 9, p. 463–467.
[23] Kuppinger, C. M.; Shelby, J. E.: Viscosity and thermal expansion of mixed-alkali borate glasses. J. Am. Cer. Soc. **69** (1986) no. 12, C292–C293.
[24] Tickle, R. E.: The electrical conductance of molten alkali silicate. Pt. 1. Experiments and Results. Phys. Chem. Glasses **8** (1967) no. 3, p. 101–112.
[25] Hakim, R. M.; Uhlmann, D. R.: On the mixed alkali effect in glasses. Phys. Chem. Glasses **8** (1967) no. 5, p. 174–177.
[26] Wakabayashi, H.; Terai, R.; Watanabe, H.: Alkali ion mobility in mixed cation glasses. Pt. 1. Mixed alkali glasses. J. Cer. Soc. Japan **94** (1986) no. 7, p. 677–682 .
[27] Kim, K.-D.: Electrical conductivity in mixed alkali aluminosilicate melts. J. Am. Ceram. Soc. **79** (1996) no. 9, p. 2422–2428.
[28] Scholze, H.: Glas. Natur, Struktur und Eigenschaften. 3rd ed. Berlin et al.: Springer, 1988. p. 297–305.
[29] McMillan, P. W.: Glass-ceramics. 2nd ed. London et al.: Academic Press, 1979. p. 48–57.
[30] Jiang, H.; LaCourse, W. C.: The effects of atmospheres on volatilization and surface tension. In: Clare, A. G.; Jones, L. E. (eds.): Advances in Fusion and Processing of Glass II. Proc. 5th Int. Symp. on the Advances in Fusion and Processing of Gbss, Toronto 1997. Westerville, OH: The American Ceramic Society, 1997. p. 233–238. (Ceramic Transactions. Vol. 82.)
[31] Kassis, N.; Frischat, G. H.: Dampfdrücke von Glasschmelzen des Mischalkalisystems $Na_2O-Rb_2O-SiO_2$. Glastech. Ber. **54** (1981) no. 4, p. 89–98.
[32] Hlavac, J.: The technology of glass and ceramics, an introduction. Amsterdam et al.: Elsevier, 1983. p. 135–141.
[33] Conradt, R.; Scholze, H.: Zur Verdampfung aus Glasschmelzen. Glastech. Ber. **59** (1986) no. 2, p. 34–52.
[34] Subramanian, R. S.; Weinberg, M. C.: The role of surface tension in glass refining. In: Proc. XIII. Internationaler Glaskongreß, Hamburg 1983. Glastech. Ber. **56K** (1983) Bd. 1., p. 76–81.
[35] Kim, K.-D.: The effect of ZnO as a minor component on the refining of alkali-alkaline earth-silicate glassmelts. Fundamentals of Glass Science and Technology 1997. In: Proc. 4th Conf. European Society of Glass Science and Technology, Växjö 1997. Växjö: Glafo 1997. p. 135–140.
[36] Stanek, J.: Electric Melting of Glass. Amsterdam et al.: Elsevier, 1977. p. 318–337.

[37] Winder, S. M.; Gupta, A.: Ongoing investigation of oxy-fuel firing impact on corrosion of nonglass contact refractories. Pt. 2. Proc. 56th Conference on Glass Problems, Illinois, 1995.
[38] Moynihan, C. T.; Saad, N. S.; Tran, D. C. et al.: Mixed-alkali effect in the dilute foreign-alkali region. Failure of the strong electrolyte/cationic interaction model. J. Am. Cer. Soc. **63** (1980) no. 7–8, p. 458–464.
[39] Lapp, J. C.; Shelby, J. E.: DC electrical conductivity in sodium and potassium galliosilicate glasses. Adv. Ceram. Mater. **1** (1986) no. 2, p. 174–178.
[40] Wu, Z.; Zhou, N.; Mao, B. et al.: Study of the mixed alkali effect on chemical durability of alkali silicate glasses. J. Non-Cryst. Solid. **84** (1986) p. 468–476.

0100P002

Addresses of the authors:

J.-H. Hwang, J.-H. Park
Dept. of Ceramic Engineering
Yonsei University
134 Shinchin-Dong, Sudaemoon-Ku
120-749 Seoul
Korea

K.-D. Kim
Dept. of Materials Science & Engineering
Kunsan National University
Miryong-Dong
Kunsan, 573-701, Chun-Buk
Korea

S.-S. Choi
Photonics Research Center
Korea Institute of Science and Technology
P.O. Box 131 Cheongryangri
130-650 Seoul
Korea