Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Wookyung Sung [a], Juyeon Won [a], Jungki Lee [a] & Hyungsun Kim [a]

[a] School of Materials Engineering, Inha University, Incheon, Korea

Version of record first published: 18 Mar 2009

To cite this article: Wookyung Sung, Juyeon Won, Jungki Lee & Hyungsun Kim (2009): Properties and Structure of P_2O_5-V_2O_5-ZnO/B_2O_3 Glasses, Molecular Crystals and Liquid Crystals, 499:1, 234/[556]-241/[563]

To link to this article: http://dx.doi.org/10.1080/15421400802619891

Mol. Cryst. Liq. Cryst., Vol. 499, pp. 234/[556]–241/[563], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802619891

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Properties and Structure of P_2O_5-V_2O_5-ZnO/B_2O_3 Glasses

Wookyung Sung, Juyeon Won, Jungki Lee, and Hyungsun Kim
School of Materials Engineering, Inha University, Incheon, Korea

Glasses in the P_2O_5-V_2O_5-ZnO/B_2O_3 (PVZ/B) system, were investigated on the thermal properties such as glass transition temperature, dilatometer softening point and coefficient of thermal expansion, and chemical properties (aqueous durability) in order to determine their applicability as barrier-ribs in plasma display panels that can be fired at low temperatures ($\leq 500^{\circ}C$). The glass transition temperature, dilatometer softening point and coefficient of thermal expansion of the PVZ/B glasses ranged from $340 \sim 375^{\circ}C$, $380 \sim 410^{\circ}C$ and $120 \sim 132 \times 10^{-7}/K$, respectively. The aqueous durability was improved through the addition of some additives such as Al_2O_3 and TiO_2. The FT-IR spectra revealed that the length of the phosphate chains was changed by changing the glass composition.

Keywords: aqueous durability; low firing temperature; phosphate glass; thermal property

INTRODUCTION

Display industries such as PDP, LCD and OLED, have developed rapidly owing to the information-oriented society based on digital technology. Many studies on component materials in the display area have been carried out to replace commercial materials with new materials for lower cost and improved product quality [1]. The barrier ribs located on the rear substrate in PDPs are a collection of fluorescent lamps in sub-millimeter scale discharge cells (red, green, and blue). Many studies have been conducted over the last several years in an attempt to replace lead oxide containing borosilicate glasses with

This work was supported by the Ministry of Commerce, Industry and Energy (MOCIE) through the New Growth Engine Project.

Address correspondence to Prof. Hyungsun Kim, School of Materials Engineering, Inha University, Yonghyun-dong, Nam-gu, Incheon 402-751, Korea (ROK). E-mail: kimhs@inha.ac.kr

lead-free glasses, due to harmful effect of lead oxide on health and environment [1,2].

Another technical issue in the PDP industry is to lower the processing temperature in order to reduce the manufacturing cost and allow the use of relatively cheap soda-lime glasses as a substrate in PDP. Phosphate based glass compositions have attracted considerable recent attention for applications to electronic devices compared with other glass system because of the low melting temperature, ultraviolet transmission, thermal expansion coefficients and an eco-friendly material [1–4]. However, such glasses are restricted to apply to electric devices because of the low chemical durability and hydration.

Bunker *et al.* reported the first comprehensive examination of phosphate glass durability and pH values in 1984 [5]. Since then, several other papers have published various mechanisms for aqueous attack on phosphate glass systems [6–8]. According to these reports, there are two different mechanisms for the reaction between the glass surface and water. Those are the hydrolysis of the P-O-P band and hydration of the modifier cations that ruptures the ionic cross-linking bond between the P-O-P chains. Many reports on phosphate glasses were based mainly on the binary or ternary system. In addition, there are very few reports on phosphate glasses containing vanadium oxide. In this study, the thermal properties such as glass transition temperature, dilatometer softening point and coefficient of thermal expansion and aqueous durability of a P_2O_5-V_2O_5-ZnO/B_2O_3 glass system were investigated with the aim of developing a new glass system for the matrix of the barrier-ribs in PDP as an initial stage work.

EXPERIMENTAL

All compositions of the PVZ/B (P_2O_5-V_2O_5-ZnO/B_2O_3) glasses were prepared from chemically pure reagents, P_2O_5 (98%, Junsei Chemical Co., Japan), V_2O_5 (99.6%, Aldrich Chemical Co., USA), ZnO (99.9%, Aldrich Chemical Co., USA), H_3BO_3 (99.99%, Aldrich Chemical Co., USA). The glass compositions were shown in Figure 1. All the batches were 40 g and all batch components were weighed to within ± 0.0001 g. The mixed powders were melted in a platinum crucible at 1000–1200°C for 2 h and then quenched. The properties of some glass compositions were measured in both solid (bulk) and powdered (frit) form. The quenched cullets using a stainless roller were pulverized to make the frits with a mean particle size of $\leq 45\,\mu m$, and the bulk samples were annealed at 350–380°C to evaluate several properties.

Two different compositions in the PVZ/B glasses were analyzed quantitatively by inductively coupled plasma – atomic emission spectrometer

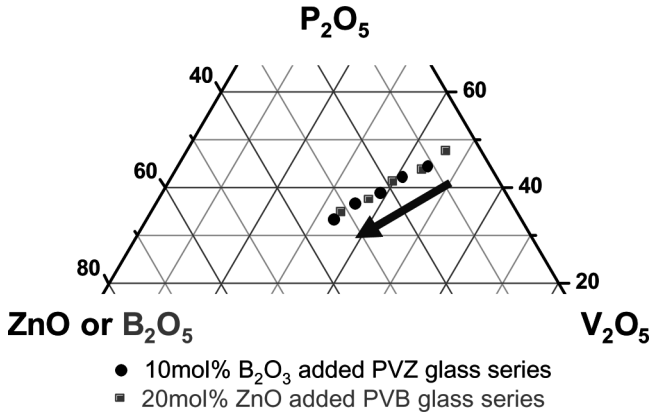

FIGURE 1 The glass composition of P_2O_5-V_2O_5-ZnO/B_2O_3.

(ICP-AES, IRIS Interpid II, Thermo Electron, USA). The glass transition temperature (T_g) was measured by differential thermal analyzer (DTA, Thermo Plus TG-8120, Rigaku, Japan) at a heating rate of 10°C/min. The dilatometer softening point (T_{dsp}) and coefficient of thermal expansion of the PVB/Z glasses were measured using a thermo dilatometer (Dilatometer PT-1600, Linseis, Germany). The aqueous durability of the PVZ/B glasses and commercially used glass composition was determined by measuring the weight change as a function of the immersion time in 90°C de-ionized water. All the weight changes were reported on a normalized basis with respect to the surface area (i.e., mg/cm^2). The contact angle of water on the various glass systems was measured using a contact angle meter (cam200, KSV, USA). For the structural interpretation, the glass powder screened through a 500 sieve was used for the IR spectra measurement (Fourier transform-Infrared spectroscopy, IRPrestige-21, Shimadzu, Japan).

RESULTS AND DISCUSSION

Several properties of the glass compositions were examined by increasing the ZnO or B_2O_3 content in the P_2O_5-V_2O_5-ZnO/B_2O_3 glass system (Fig. 1). Besides, the concentration of P_2O_5 and V_2O_5 was fixed at the specific ratio, which has a low melting temperature in the phase diagram of the P_2O_5-V_2O_5 binary system for low firing glasses [9]. It is well known that phosphate is highly hygroscopic. Therefore, phosphate glasses with high phosphorus oxides are unstable to humidity in air. A few ppm of water can alter the viscosity and structure of

TABLE 1 Comparison of the Composition Between the Batched and Analyzed Glass Powder

	P_2O_5 (mol%)	V_2O_5 (mol%)	B_2O_3 (mol%)	ZnO (mol%)
PVZ5 (batched)	30	30	10	30
PVZ5 (analyzed)	30.2	30.2	9.1	30.5
PVB5 (batched)	28	27	25	20
PVB5 (analyzed)	29.5	28.1	22.2	20.2

glass [10]. Therefore, inductively coupled plasma – atomic emission spectroscopy was used to confirm the precise compositions after melting compared with batched compositions.

Two glass compositions were analyzed, as shown in Table 1. From the ICP results, the concentration of B_2O_3 decreased and the concentration of the other oxides (P_2O_5, V_2O_5 and ZnO) increased in both the PVZ5 and PVB5 glasses after melting compared with the batched compositions. The decrease in B_2O_3 might be the result of sublimation or evaporation during high temperature melting [11]. However, it was found that the properties of these glasses were not influenced by a composition change because it is a negligible quantity.

The glass transition temperature (T_g), dilatometer softening point (T_{dsp}) and coefficient of thermal expansion (CTE) of P_2O_5-V_2O_5-ZnO/B_2O_3 were examined as a function of the ZnO or B_2O_3 concentration (Fig. 2). The T_g and T_{dsp} decreased gradually with increasing ZnO and B_2O_3 content, respectively, indicating that these glasses have different rearrangement properties in the glass structure. However, the CTE values of theses glasses were in the range of $130 \sim 140 \times 10^{-7}$/K without any special tendency.

The structure of phosphate glass basically consists of tetrahedral PO_4 groups by P^{5+} with a similar structure to Si^{4+}. However, P^{5+} has a double bond that can be a reason for the less cross-linked structure. Therefore, this weak ionic cross-link can be easily attacked by water [6]. A direct method for improving the chemical durability of glass is to strengthen the cross-linking between the phosphate chains by adding other oxides. Figure 3 shows the contact angle of de-ionized water on phosphate glass, lead glass and borate glass. The driving force for wetting of these glasses was also calculated from the contact angle. The driving force for wetting of the phosphate glass was significantly higher than the lead and borate glasses, indicating an extremely hydrophilic composition.

The aqueous durability of glass was investigated quantitatively by measuring the weigh loss by dissolution in water. Figure 4 shows

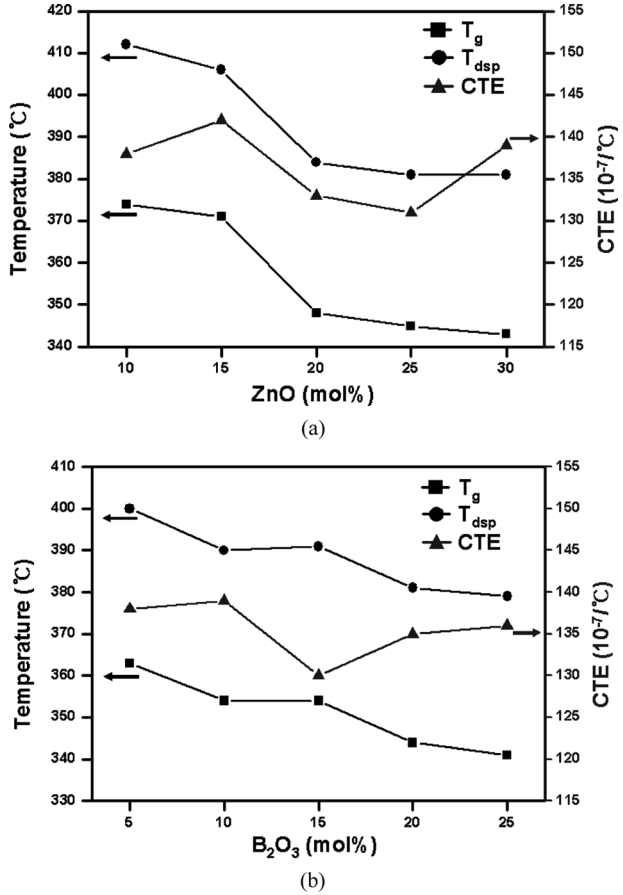

FIGURE 2 Distribution of the glass transition temperature (Tg), dilatometer softening point (Tdsp) and coefficient of thermal expansion (CTE) with increasing (a) ZnO and (b) B_2O_3 content.

the aqueous durability of the PVB3 glass, PVB3 glasses containing some additives such as Al_2O_3 and TiO_2, and B_2O_3-ZnO based glass, which is commercially used, as the weight loss (normalized to surface area) as a function of the immersion time in 90° de-ionized water. PVB3 has a pure aqueous durability compared with the commercial B_2O_3-ZnO based glass, as shown in Figure 4.

However, there was an increase in aqueous durability when additives such as Al_2O_3 and TiO_2 were added to the PVB3 glass. Moreover, this result shows that Al_2O_3 is more effective in improving the aqueous durability than TiO_2. The chemical durability of the glass increases

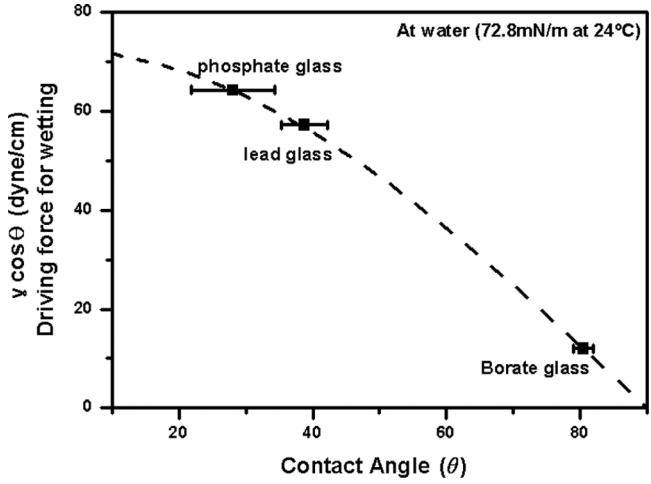

FIGURE 3 Wetting behavior of water on phosphate glass, lead glass and borate glass.

with the addition of modifying cations. In particular, the addition of cations with a high valence (Al^{3+}) increases the amount of cross-linking within the glass network. It is necessary to understand the structural mechanisms responsible for this durability improvement.

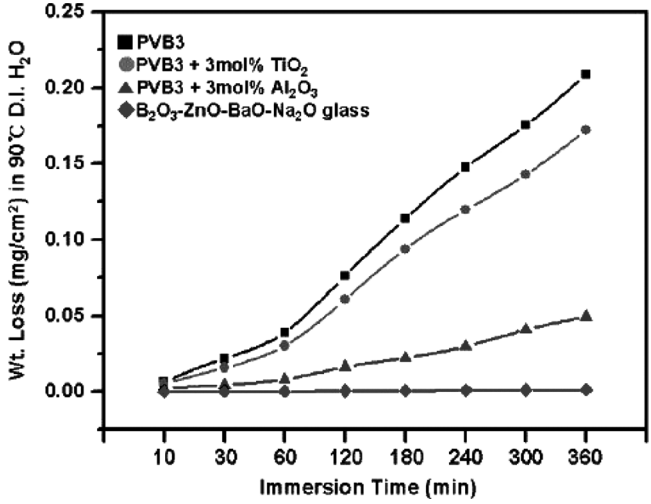

FIGURE 4 Aqueous durability in H_2O at 90°C for PVB3 glasses with several additives and B_2O_3-ZnO based glass.

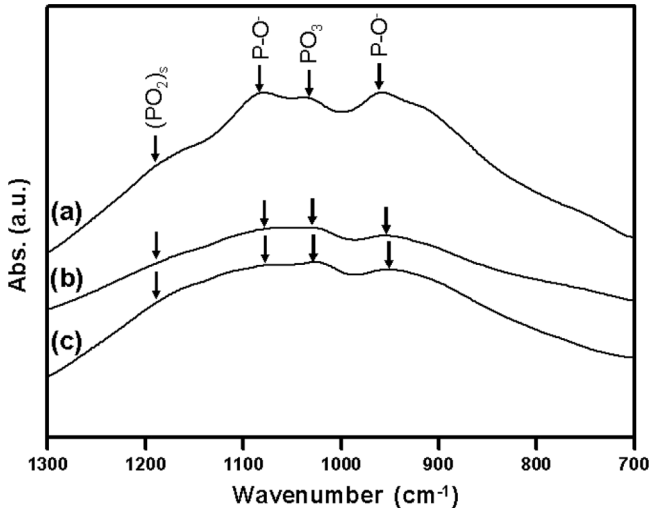

FIGURE 5 FTIR spectra of the (a) only PVB3 glass, (b) PVB3 glass with 3 mol% TiO_2 and (c) PVB3 glass with 3 mol% Al_2O_3.

Figure 5 shows the FTIR spectra of the PVB3 glass and 3 mol% TiO_2 or Al_2O_3 added PVB3 glasses, respectively. The band at approximately 1190 cm^{-1} is assigned to the symmetric stretching vibration of PO_2. The P-O absorption band is present near 1100 cm^{-1}. The two bands near 1030 and 980 cm^{-1}, which are attributed to the PO_3 end groups and $P\text{-}O^-$ stretching band, respectively, are also present in the spectra [12,13]. The FTIR spectra of these glasses show the changes in the $P\text{-}O^-$ and PO_3 bands. The shifts of the P-O absorption bands near 1100 cm^{-1} to a lower frequency were attributed to the formation of P-O-M linkages through the addition of TiO_2 or Al_2O_3. Besides, the amplitude of the PO_3 bands decreases by adding additives such as TiO_2 and Al_2O_3. PO_3 is the end group of the phosphate chain. When a modifier cation is incorporated into chain-like phosphate glasses, it will shorten the chain by disrupting the P-O-P bond and increase the end group simultaneously. The improved durability of PVB3 containing TiO_2 or Al_2O_3 is attributed to the replacement of the easily hydrated P-O-P bonds by P-O-M bonds [12,14].

CONCLUSIONS

The thermal properties, chemical properties and structure of the P_2O_5-V_2O_5-ZnO/B_2O_3(PVZ/B) glass system were mainly investigated with the aim of developing a new glass system as a matrix in barrier-ribs.

These PVBZ glasses had low thermal properties such as T_g and T_{dsp} that can be fired above 500°C. Some additives such as Al_2O_3 and TiO_2 were added to the PVZ/B glass in order to improve the aqueous durability of PVZ/B glasses. The length of the phosphate chains changed with different compositions indicating an improvement in aqueous durability.

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