

## $V_2O_5$ - $P_2O_5$ -ZnO- $Sb_2O_3$ Glass Frit Materials with BaO and $Al_2O_3$ for Large-sized Dye-sensitized Solar Cell Sealing

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### ABSTRACT

$V_2O_5$ - $P_2O_5$ -ZnO- $Sb_2O_3$  glasses modified with BaO and  $Al_2O_3$  are synthesized as a sealing material for large-scale dye-sensitized solar cells (DSSCs). A compositional study is performed in order to determine the glass that can be sintered below 500°C with a high chemical stability against the electrolyte. The flow size of the glasses after the heat treatment and the glass stability are increased with the addition of  $Al_2O_3$  and BaO, while the glass transition temperature is decreased. After the reaction with the electrolyte at 60°C for 72 h, the addition of 5 mol% of BaO and 2 mol% of  $Al_2O_3$  considerably enhances the chemical stability of the glass. X-ray diffraction (XRD) and scanning electron microscope (SEM) are used to examine the reaction between the electrolyte and glasses. The structural contribution of the additives is also investigated and discussed.

**Key words :** Glass, Sealing, Frit, Vanadate, DSSC

### 1. Introduction

Extensive studies have been performed on dye-sensitized solar cells (DSSC) due to their several benefits over the present semiconducting photovoltaic cell, such as an easy processing method, better color and lower production cost<sup>1,2)</sup>. They also can generate an electricity under low illumination condition such as indoor environment and can be applied as a building integrated photovoltaic cell<sup>3,4)</sup>. DSSC consists of  $TiO_2$  electrode doped with Ru-dye, liquid electrolyte and transparent FTO (fluorine doped tin oxide) electrode. Organic surlyn is conventionally used as a hermetic sealant to separate each cell of DSSC and to support glass substrates<sup>5)</sup>. Surlyn, however, suffered from its poor thermal stability and hermetic sealing property against moisture and gas from outside of the cell<sup>6,7)</sup> which reduces the DSSC efficiency and hinders the outdoor deployments.

Glass is an amorphous inorganic material, which has good thermal, chemical and mechanical properties as well as excellent hermetic property. The glass frit has long been used as sealing materials for a cathode-ray tube (CRT), plasma display panel (PDP) and active matrix organic light emitting diodes (AMOLED). Recently, applications of glass frit materials as a DSSC sealant to substitute surlyn have been reported<sup>8,9)</sup>. In order to be used for the dye-sensitized solar cell, glass frit materials should not react with the liquid electrolyte and can be sealed below 500°C to prevent

from any damage on DSSC substrate during the fabrication process. Moreover, they should have a similar thermal expansion to the substrate along with the strong bonding strength to the substrate for large scale production. PbO- $SiO_2$  based glasses have been used as a sealing materials for CRT or PDP due to their low melting temperature, but they cause a damage to the counter electrode coated with Pt in DSSC<sup>10)</sup>. Moreover, heavy content of lead also prohibits their practical applications. Lee *et al.*<sup>8)</sup> reported that the glasses containing  $Bi_2O_3$  reacted with  $I/I_3^-$  ions in DSSC electrolyte, and Bi ions have been easily reduced when applied to DSSC. Cho *et al.*<sup>9)</sup> recently studied a glass system based on  $V_2O_5$ -BaO-ZnO- $B_2O_3$  containing  $TeO_2$  for laser sealing process. However, the production cost of laser sealing for large sized DSSC is much higher than conventional processes and the glass showed a crystallization tendency when heat-treated.

In this study, thus, we prepared glass frit materials based on  $V_2O_5$ - $P_2O_5$ -ZnO- $Sb_2O_3$  system for a large sized DSSC which can be fabricated with conventional sintering process.  $Al_2O_3$  and BaO were added to improve glass stability and their effects on fluidity, chemical stability to the electrolyte and glass stability were investigated. XRD, SEM and Raman spectroscopy were examined to discuss the role of additives to glass structure and chemical resistivity.

### 2. Experimental Procedure

The glass compositions based on  $V_2O_5$ - $P_2O_5$ -ZnO- $Sb_2O_3$  system were fabricated varying their composition of  $V_2O_5$ ,  $P_2O_5$  and  $Sb_2O_3$  + ZnO within 20 ~ 60 mol% range, respectively. Among the fabricated glasses, glasses with 25 ~ 35 mol% of

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$V_2O_5$  and  $P_2O_5$  and 20 ~ 35 mol% of  $Sb_2O_3$  + ZnO showed stable glass formation and the nominal glass composition for the present study was selected as shown in Table 1. VPSZ0 glass sample contains 61.5 mol% and 38.5 mol% of  $V_2O_5$ + $P_2O_5$  and  $Sb_2O_3$ +ZnO, respectively. 3, 5 and 7 mol% of BaO substituted  $Sb_2O_3$  in VPSZ0 (VPSZ1~VPSZ3), and 1 and 2 mol% of  $Al_2O_3$  were added to the VPSZ2 glass (VPSZ4, VPSZ5). Raw materials with high purity (over 99.9%) were weighed and mixed with a ball mill. The glass batch was melted in an alumina crucible at 1100°C for 30 minutes, and the melt was quenched in a brass mold followed by pulverization less than 50  $\mu$ m in size.

A disc sample (diameter of 12 mm) with 4 g of glass powders was formed with uniaxial press followed by heat treatment at 500°C for 30 minutes to examine the glass stability and flowability. Chemical resistance against the electrolyte were tested by soaking the sintered glass in a commercial DSSC electrolyte solution (NPN-15) which maintained the temperature at 60°C for 72 h using water bath. Glass transition temperature ( $T_g$ ) was determined by a differential scanning calorimeter (DSC-60, Shimadzu, Japan) and crystalline phase after heat-treatment of the glass were determined by XRD (Mini flex 600, Rigaku, Japan. SEM (TESCAN, MIRA LMN, Czech) and energy dispersive X-ray spectroscopy were applied to examine the reaction product on the glass surface. Raman spectroscopy (ARAMIS, Horba Jobin Yvon, France) was used to investigate glass structure.

### 3. Results and Discussion

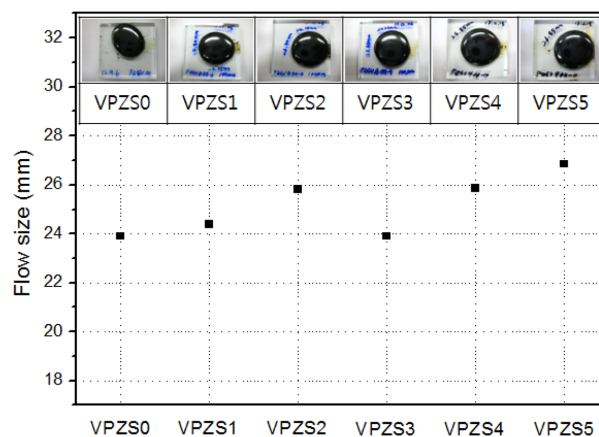
When various glasses were synthesized and examined by varying the amount of  $V_2O_5$ ,  $P_2O_5$  and  $Sb_2O_3$  + ZnO within glass forming range for 500°C sealing application,  $T_g$  was decreased while the crystallization tendency was increased when the content ratio of  $Sb_2O_3$ +ZnO to  $V_2O_5$ + $P_2O_5$  decreased. The optimum composition for this study, thus has been determined as 61.5 mol% and 38.5 mol% of  $V_2O_5$  +  $P_2O_5$  and  $Sb_2O_3$ +ZnO, respectively (VPZS0) which showed relatively stable glass formation with the heat treatment at 500°C. BaO and  $Al_2O_3$  were added to improve the glass stability as well as chemical stability against the electrolyte. Fig. 1 shows the results of flow-button test. Glass discs with different glass composition were sintered at 500°C for 30 minutes and the size of buttons was mea-

**Table 1.** Composition of  $V_2O_5$ - $P_2O_5$ - $ZnO$ - $Sb_2O_3$  Glasses for DSSC Sealing (in mol%)

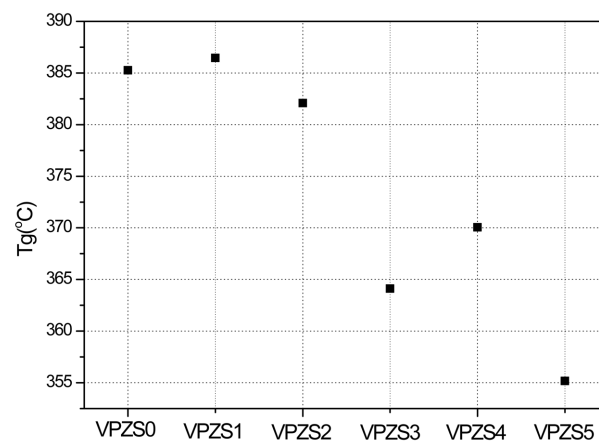
Sample ID	Composition			
	$V_2O_5$ + $P_2O_5$	ZnO+ $Sb_2O_3$	BaO	$Al_2O_3$
VPZS0	61.5	38.5	0	0
VPZS1	61.5	35.5	3	
VPZS2	61.5	33.5	5	
VPZS3	61.5	31.5	7	
VPZS4	61.5	32.5	5	1
VPZS5	61.5	31.5	5	2

sured. Small amount of surface crystallization has been detected for the BaO free glass and the glass containing 7 mol% of BaO. The glass VPZS2 containing 5 mol% of BaO showed the largest flow-button size. This indicates that the glass stability of VPSZ0 glass is enhanced by the addition of BaO, but addition of more than 7 mol% of BaO promotes devitrification of the glass. When  $Al_2O_3$  was added to the glass VPSZ2, the flow-button size increased further. This indicates that the addition of BaO and  $Al_2O_3$  to the glass VPSZ0 enhances glass fluidity suppressing crystallization when sintered at 500°C, which is promising as a DSSC sealing material. Glass stability and viscosity normally increase at the same time when networking of the glass structure is increased within the glass<sup>11</sup>). In the present glass system, however, the substitution of  $Sb_2O_3$  with BaO and  $Al_2O_3$  lowered glass viscosity as well as improving glass stability. This is due to the special role of BaO and  $Al_2O_3$  in the glass structure which will be discussed later.

Figure 2 illustrates the variation of glass transition temperature of VPSZ glasses with the addition of BaO and  $Al_2O_3$ . All glass samples have glass transition temperatures lower than 385°C supporting the possibility of present



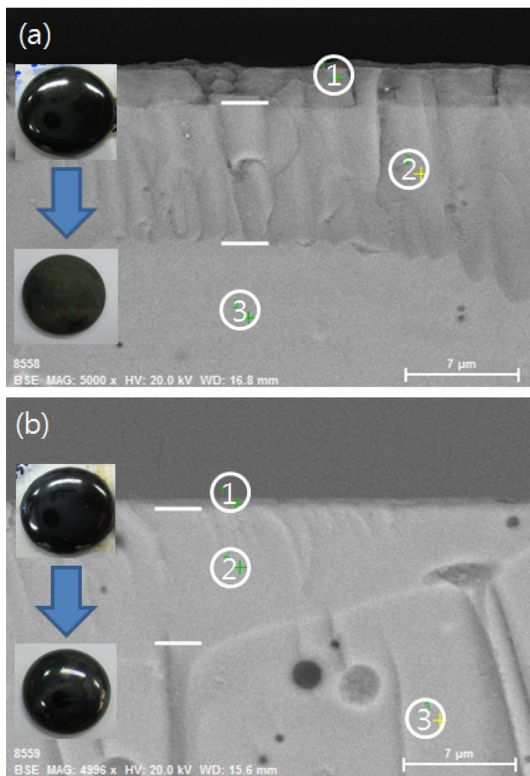
**Fig. 1.** Flow button size change of VPZS glasses which are sintered at 500°C for 30 min. The inset figure shows their surface images after the sintering.



**Fig. 2.** Glass transition temperature change of VPZS glasses.

glasses as a low temperature sealing material. It should be mentioned that  $T_g$  decreased with the increase of BaO and  $Al_2O_3$  content, which is consistent to the result of flow button test. Viscosity of glasses generally decreases as  $T_g$  decreases due to the improved structural flexibility. It seems, thus that BaO and  $Al_2O_3$  improved the structural flexibility of the present vanadate glass system.

In order to examine the chemical resistance of the glasses obtained, VPSZ2 and VPSZ5 glasses were soaked in a liquid electrolyte at 60°C for 72 h, and each glass surface was examined under SEM. The dull surface of VPSZ2 glass can be clearly distinguished from the shiny surface of VPSZ5 glass under bare eye. Fig. 3 shows the SEM morphology of the cross-section for each glass sample and their EDS results are summarized in Table 2. Three layers were clearly observed in the cross-section of VPSZ2 glass as shown in Fig. 3(a). Concentration of P and Zn decreased significantly from the inside of sample to its surface as summarized in Table 2. This can be attributed to the serial

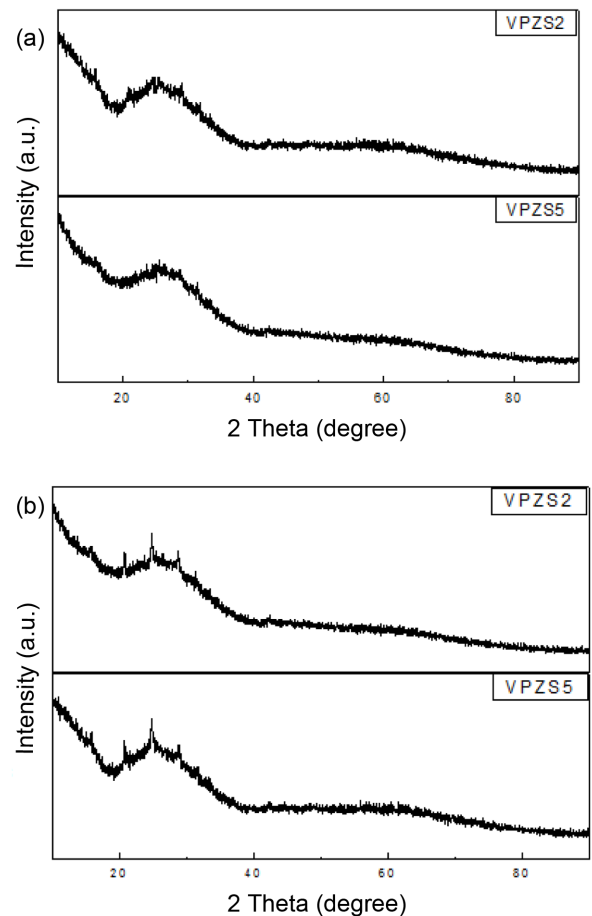


**Fig. 3.** Surface and cross-sectional SEM image of (a) VPZS2 and (b) VPZS5 glasses after the reaction with liquid electrolyte.

**Table 2.** EDS Results of Phosphorous and Zinc in VPZS Glasses in wt% After Reaction with DSSC Electrolyte

Location	VPZS2		VPZS5	
	P	Zn	P	Zn
1	9.29	4.12	11.95	9.94
2	12.86	14.77	15.55	17.89
3	14.41	17.16	16.85	19.43

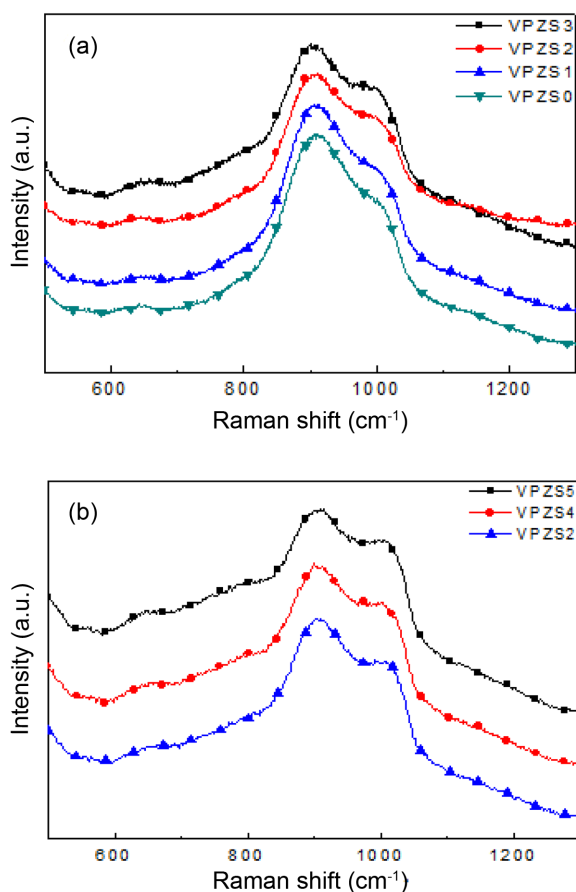
destruction of glass network from the surface with the reaction of  $I/I_3^-$  ions in the liquid electrolyte along with the diffusion of P and Zn ions residing within the glass matrix. The leaching rate of Zn ion was even higher than that of P ion. This is due to the structural role of P ions forming glass network based on  $[PO_4]$  structural units while Zn ions act as a modifier within the glass structure. On the contrary, the glass VPSZ5, as found in Fig. 3(b), exhibited a very thin and the limited reaction layer on the surface and it showed also limited leaching concentration of P and Zn for each layer when compared to VPSZ2. The results suggest that 2 mol% of  $Al_2O_3$  in VPSZ5 effectively strengthened the glass structure. Fig. 4 illustrates the XRD result of the glass surface before and after the reaction with liquid electrolyte. Characteristic diffuse scattering patterns due to amorphous phase were observed before the reaction but small crystalline peaks appeared for both glasses after the reaction. XRD analysis determined those peaks as  $\beta$ -barium zinc phosphate ( $Ba_2Zn(PO_4)_2$ ) crystal phase (JCPDS# 160635) which is believed to be precipitated on the glass surface by the leached Zn and P ions. Based on the peak intensity and full width at half maximum of the peak, the formed crystals are believed in nanometer size. The EDS and XRD results



**Fig. 4.** XRD results of VPZS2 and VPZS5 glasses (a) before and (b) after the reaction with liquid electrolyte.

clearly suggest that the VPSZ5 glass also react with the electrolyte but the reaction rate can be effectively retarded by  $Al_2O_3$  addition.

Raman spectroscopy investigated the structural role of BaO and  $Al_2O_3$  in VPZS glasses and the results were illustrated in Fig. 5. All glasses showed characteristic Raman spectra of  $V_2O_5$ - $P_2O_5$  glasses and their peak assignments were summarized in Table 3. As shown in Fig 5.(a), the peak intensity of  $920\text{ cm}^{-1}$  increased while that of  $1013\text{ cm}^{-1}$  decreased with the increase of BaO content. It implies that  $Q^1$  unit decreases while O-V-O chain or  $(PO_4)^{3-}$   $Q^0$  unit increase as BaO substitutes  $Sb_2O_3$ .  $Q^n$  stands for a unit having n number of bridging oxygens (BO) in  $[PO_4]$  tetrahedral unit. That is, BaO modifies the glass network breaking the O-P-O bond more effectively than  $Sb_2O_3$  and leads to decrease in glass transition temperature and viscosity.



**Fig. 5.** Raman spectra of VPZS glasses (a) varying BaO content and (b) varying  $Al_2O_3$  content.

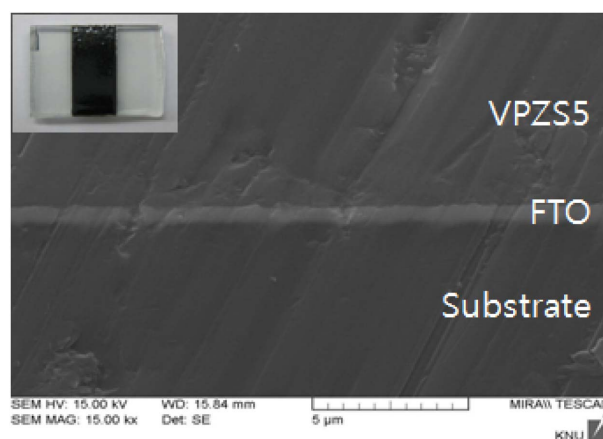
**Table 3.** Raman Peak Assignments of VPZS Glasses

Raman peaks ( $cm^{-1}$ )	Assignments	Ref.
~670	Vibrations of V-O-V, V-O-P, P-O-P stretching modes	12, 13, 14
~920	Stretching vibration of V = O in $VO_4$ , O-V-O in metavanadate chain or vibration of $(PO_4)^{3-}$ $Q^0$ units	12, 13, 14
~1013	P-O stretching and $(PO_3)_{sym}$ stretching vibration in $Q^1$ units	15, 16

$Q^n$ : Phosphate tetrahedral classification based on the number of bridging oxygen n

However, noticeable structural change has not been observed when  $Al_2O_3$  was added with fixed amount of BaO at 5 mol% (Fig. 5.(b)). It should be reminded that the glass viscosity and transition temperature decreased with  $Al_2O_3$  addition as shown in Fig. 1 and 2. This indicates that  $Al_2O_3$  also acts as a network modifier in VPZS glass breaking V-O-V or P-O-P bonds. Moreover, it should be also recalled that the small amount of  $Al_2O_3$  effectively delayed the reaction with the corrosive electrolyte. These behavior can be understood by the size and bonding characteristics of Al ion which substitutes the  $Sb_2O_3$  as a network modifier. The smaller ionic size of  $Al^{3+}$  decreases the glass transition temperature and viscosity while stronger bonding strength of Al-O than Sb-O improves network stability during the reaction with electrolyte. Ionic size dependent change of viscosity and glass transition temperature can be found in alkali silicate glasses.<sup>11)</sup> Formation of strong bonds or increased coordination number of Al ion with neighboring oxygens which are left over within the glass structure by the reaction with  $I^-$  ions may also contribute to the improvement of chemical resistance but more detailed study such as coordination number or local structure change is required. It should be also mentioned that the addition of BaO and  $Al_2O_3$  weakened the glass network but promoted glass stability after heat treatment. Formation of multi-component phase equilibria by the addition of BaO and  $Al_2O_3$  into VPSZ glass system may hinder the crystallization, which also requires further study.

Figure 6 exhibits the SEM morphology of the sample which was heat treated at  $500^\circ C$  for 30 minutes after apply-



**Fig. 6.** Cross-sectional SEM image of FTO glass substrate pasted and sintered with VPZS5 glass powders at  $500^\circ C$  for 30 min.

ing VPSZ5 glass powder on the silicate glass substrate coated with FTO thin film. VPSZ5 glass was uniformly and well bonded to the FTO layer, and no second phases including any crystalline phase were detected at the interface between FTO and glass. It clearly suggests the practical feasibility of the present glass system as a hermetic sealing material for the large sized DSSC.

#### 4. Conclusion

Glasses based on  $V_2O_5$ - $P_2O_5$ - $ZnO$ - $Sb_2O_3$  system containing BaO and  $Al_2O_3$  were prepared as an amorphous inorganic sealant to substitute the conventional organic surlyn for a large sized DSSC. Glass transition temperature and viscosity were decreased with the addition of BaO and  $Al_2O_3$ . After accelerated reaction test with commercial liquid electrolyte at 60°C for 72 h, it is found that  $Al_2O_3$  effectively retarded the corrosion reaction of the glass. Throughout the study, we developed a glass frit material which has good flowability and low sealing temperature along with the high chemical durability against DSSC electrolyte. The 40 inch large sized DSSC has been successfully fabricated using the developed sealing glass and a reliability test is now undergoing. Further study, however, is required to understand the role of Al ion in the glass structure and its influence on the chemical durability.

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