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Strengthening Thermal Stability in V_2O_5 -ZnO-BaO- B_2O_3 - $M(PO_3)_n$ Glass System (M = Al, Mg) for Laser Sealing Applications

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Abstract: Today, the most common way of laser sealing is using a glass frit paste and screen printer. Laser sealing using glass frit paste has some problems, such as pores, nonuniform height, imperfect hermetic sealing, etc. In order to overcome these problems, sealing using fiber types of sealant is attractive for packaging devices. In this work, $(70-x)V_2O_5-5ZnO-22BaO-3B_2O_3-xM(PO_3)_n$ glasses (mol%) incorporated with $xM(PO_3)_n$ concentration (where M = Mg, Al, n = 2, 3, respectively) were fabricated and their thermal, thermomechanical, and structural properties were investigated. Most importantly, for this type of sealing, the glass should have a thermal stability (ΔT) of $\geq 80^\circ C$ and the coefficient of thermal expansion (CTE) between the glass and panel should be $1.0 \text{ ppm}/^\circ C$. The highest thermal stability ΔT of the order of $93.2^\circ C$ and $112.9^\circ C$ was obtained for the 15 mol% of $Mg(PO_3)_2$ and $Al(PO_3)_3$ doped glasses, respectively. This reveals that the bond strength and connectivity is more strongly improved by trivalent $Al(PO_3)_3$. The CTE of a $(70-x)V_2O_5-5ZnO-22BaO-3B_2O_3-xAl(PO_3)_3$ glass system (mol%) (where $x = 5-15$, mol%) is in the range of $9.5-15.5 (\times 10^{-6}/K)$, which is comparable with the CTE ($9-10 (\times 10^{-6}/K)$) of commercial DSSC glass panels. Based on the results, the studied glass systems are considered to be suitable for laser sealing using fiber types of sealant.

Keywords: V_2O_5 glass; metaphosphate; thermal stability; laser sealant

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1. Introduction

Laser hermetic sealing is an excellent way to protect delicate components in harsh environments for reliable packaging [1,2]. The sealing industry has focused more attention on laser sealing as it is very effective and reliable in packaging systems, including dye-sensitized solar cells (DSSC), organic light-emitting diodes (OLEDs), solid oxide fuel cells, etc., that should be highly stable and maintain initial efficiency for more than 10 years under a harsh environment. To improve the durability of the DSSC modules, the long-term stability should be assured without electrolyte leakage after laser sealing [3–5]. Furnace-based thermal sealing and laser-assisted sealing using glass frit have been popular processes until now. In the case of laser sealing using glass frit, on one hand, glass material should show a relatively low glass transition temperature and high absorption efficiency at laser wavelength. On the other hand, the coefficient of thermal expansion between the sealing glass and the substrate should be matched to maintain high durability after sealing. However, the laser sealing process using glass frit has the disadvantage that pores are present and the sealed surface is not uniform in thickness due to evaporation of resin applied by screen printing, which cause the durability to diminish. In view of this, laser sealing using fiber types of sealant has received significant interest, owing to its ability to

reduce the defect rate by improving the sealant thickness [6]. It also controls the shape to prevent the formation of internal defects, such as pores and gas, during the process. Thus, fewer pores, uniform height of the sealed surface, and low-cost sealing can be achieved using fiber types of sealant [6]. There are several requirements for materials of fiber types of sealant. In the process of glass frit, the thermal stability (ΔT) of glass frit materials is not the main factor for the laser sealing process, but the ΔT of fiber types of sealant needs to be 80 °C or more for the glass fiber to be able to be drawn to a thickness of hundreds of microns without crystallization. Further, the sealing glass material should have a low glass transition temperature and, thereby, a low thermal energy transfers to packaging devices. Moreover, the coefficient of thermal expansion (CTE) of sealing glass material should be similar to that of the panel. The CTE difference between the glass panel and sealing glass should be lower than $1.0 \times 10^{-6} \text{ K}^{-1}$.

In the case of laser sealing glass, it started with major compositions containing PbO in the early 1990s. However, due to environmental regulations, vanadium-based glass as a sealant has been considered a more promising candidate [7,8]. Among the candidate compositions, V_2O_5 - P_2O_5 -based glasses have been studied a lot in order to overcome the narrow glass-forming area of vanadium-based glass. It was reported that, when P_2O_5 is added into V_2O_5 -based glass systems, the glass formation stability is improved [9,10]. However, there is a limit to its application as a sealing glass due to poor chemical durability and low water resistance [11]. Therefore, the addition of third and fourth components are required to overcome these limitations.

In this work, $(70-x)\text{V}_2\text{O}_5$ - 5ZnO - 22BaO - $3\text{B}_2\text{O}_3$ - $x\text{M}(\text{PO}_3)_n$ glass system (mol%) (where $\text{M} = \text{Al}, \text{Mg}, \text{Na}$, $n = 3, 2, 1$, respectively, mol%) was prepared by the melting and casting method. The $\text{Al}(\text{PO}_3)_3$ and $\text{Mg}(\text{PO}_3)_2$ metaphosphates were used as a source for trivalent Al_2O_3 and divalent MgO [12]. Incorporation of $\text{Al}(\text{PO}_3)_3$ increases the degree of structural polymerization through forming crosslinked P-O-Al bonds. The $\text{Al}(\text{PO}_3)_3$ plays a role in increasing the thermal stability and reducing the crystallization tendency in the glass network. The glass transition temperature (T_g), glass thermal stability (ΔT), the coefficient of thermal expansion (CTE), and structural properties with respect to metaphosphate contents were determined for the purpose of fiber types of sealant. For the laser sealing process, we selected workable glass compositions with a low glass transition temperature of <300 °C, higher glass thermal stability of above 80 °C, and CTE matching with DSSC panels having 9–10 ($\times 10^{-6}/\text{K}$) of CTE. In addition, the glass composition with low glass transition temperature and higher glass thermal stability was further optimized in order to convert into fiber types of sealant, rather than the conventional laser sealing using glass frit for sealing DSSC panels.

2. Experimental Details

2.1. Glass Fabrication

Table 1 shows the mole fractions of chemical constituents of V_2O_5 - ZnO - BaO - B_2O_3 - $\text{M}(\text{PO}_3)_n$ (where $\text{M} = \text{Al}, \text{Mg}, \text{Na}$, $n = 3, 2, 1$, respectively, mol%) based glasses. The glasses were prepared by the melt-quenching method. Reagent grade chemicals of V_2O_5 (99.9%), ZnO (99.9%), BaO (99.99%), B_2O_3 (99.9%), and $\text{M}(\text{PO}_3)_n$ (99.9%) were used as raw materials to fabricate the glass ingots. The batch chemicals (about 50 g) were weighed using a microbalance and then crushed using a ball mill with zirconia balls for 30 min to get a homogeneous mixture. Then, the well-mixed powder was transferred into an alumina crucible and kept in an electric furnace for the melting process. For the preparation of glasses, a two-step melting process was applied, i.e., in the 1st step, the glass composition was melted at 550 °C for 30 min, and in 2nd step, the temperature was raised to 700 °C and the glass composition was then heated under N_2 atmosphere for 30 min (see Figure 1). Then, the melt was poured onto a preheated brass mold and transferred to another electric furnace for the annealing process to remove internal stress. The glass ingots were annealed at 280 °C for 3 h. The glass ingots were used to examine the feasibility for laser sealing through physical, thermal, and structural properties.

Table 1. Chemical composition of the present glasses, $(\text{Al}(\text{PO}_3)_3)_x = \text{xAP}$, $(\text{Mg}(\text{PO}_3)_2)_x = \text{xMP}$ and $\text{NaPO}_3 = \text{xNP}$ (where $x = 2.5, 5, 7.5, 10, 12.5, 15$) (mol%).

Glasses	V_2O_5	ZnO	BaO	$\text{Al}(\text{PO}_3)_3$	B_2O_3
VZBB	70	5	22	0	3
AP2.5	67.5	5	22	2.5	3
AP5.0	65	5	22	5	3
AP7.5	62.5	5	22	7.5	3
AP10.0	60	5	22	10	3
AP12.5	57.5	5	22	12.5	3
AP15.0	55	5	22	15	3
Glasses	V_2O_5	ZnO	BaO	$\text{Mg}(\text{PO}_3)_2$	B_2O_3
MP2.5	67.5	5	22	2.5	3
MP5.0	65	5	22	5	3
MP7.5	62.5	5	22	7.5	3
MP10.0	60	5	22	10	3
MP12.5	57.5	5	22	12.5	3
MP15.0	55	5	22	15	3
Glasses	V_2O_5	ZnO	BaO	NaPO_3	B_2O_3
NP2.5	67.5	5	22	2.5	3
NP5.0	65	5	22	5	3
NP7.5	62.5	5	22	7.5	3
NP10.0	60	5	22	10	3
NP12.5	57.5	5	22	12.5	3
NP15.0	55	5	22	15	3

Figure 1. Thermal profile of $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ glass system (mol%) (where $\text{M} = \text{Al}, \text{Mg}, \text{Na}$, $n = 3, 2, 1$, respectively, mol%), and inset depicts photographs of glass samples.

2.2. Characterization

Density was measured at room temperature by the Archimedes' method with an electronic densimeter (Qualitest USA, MD-300S). The amorphous nature of glasses was evaluated by means of X-ray diffractometer (X'pert Pro, Panalytical) with $\text{CuK}\alpha$ ($\lambda = 1.542 \text{ \AA}$) used as source. Differential scanning calorimetry (DSC 204 F1, NETZSCH) was used for thermal behavior of the glass samples. The measurement was carried out in the range of $25-550 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ and under N_2 atmosphere. Thermomechanical analysis (TMA) was carried out using a dilatometer (DIL402F3, NETZSCH) in the range of $25-450 \text{ }^\circ\text{C}$, with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ under N_2 atmosphere. Glass samples with a dimension of $5 \times 5 \times 8 \text{ mm}^3$ were used for the measurement. Raman data were acquired in the range from 50 to 1600 cm^{-1} , with 0.5 cm^{-1} resolution by the spectrometer (Horiba Jobin-Yvon, France). A diode laser operating at 515 nm was used as an excitation source. The X-ray photoelectron spectroscopy analysis was carried out by a spectrometer (NEXSA, Thermo Fisher Scientific, Waltham, MA, USA). The product of Gaussian and Lorentzian functions was used for the curve fitting.

3. Results and Discussion

3.1. Density and Molar Volume

Density of glass is a property of interest where it reflects any structural variations in a glass network, and the measured density of a glass is usually used to calculate molar volume. Density was measured for different $M(\text{PO}_3)_n$ contents in $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ (mol%) (where $M = \text{Al}, \text{Mg}$ mol%, $n = 3, 2$, respectively) a glass system. Figure 2a shows that the density of $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ glass system (mol%) decreased from 3.53 g/cm^3 to 3.43 g/cm^3 and 3.25 g/cm^3 with an increase in $\text{Mg}(\text{PO}_3)_2$ and $\text{Al}(\text{PO}_3)_3$ contents up to 15 mol%, respectively. In other word, a reduction of density for substituting 15 mol% $\text{Mg}(\text{PO}_3)_2$ and 15 mol% $\text{Al}(\text{PO}_3)_3$ instead of V_2O_5 was found to be 3.36% and 8.49%, respectively. Generally, variation of density can be easily explained by molecular weight and atomic density, i.e., as the elements of the lower molecular weight and atomic density were replaced with the elements with a heavier molecular weight and atomic density, the density of the glass system would be increased. Several studies reported these trends, i.e., the increase of the density in the $\text{P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-BaO-La}_2\text{O}_3$ and $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-TeO}_2$ glass system by replacing elements with those of a heavier molecular weight [13,14]. Our current results on density are in opposition to this trend. To analyze the variation of the density in terms of atomic density in the current glass system, we compared the atomic density among the three elements, i.e., V_2O_5 , $\text{Al}(\text{PO}_3)_3$, $\text{Mg}(\text{PO}_3)_2$ (atomic density: 3.36, 2.78, 2.74, respectively). Replacement with a relatively lighter atomic density coincided with the decreasing trend of density. However, although the atomic densities of $\text{Mg}(\text{PO}_3)_2$ and $\text{Al}(\text{PO}_3)_3$ are very similar, the reduction widths of the two values of density could not be explained. In other words, discussion of density based on molecular weight and atomic density could not be completely applied to all glass systems.

Figure 2. Variation of (a) Density and (b) Molar volume with respect to $\text{M}(\text{PO}_3)_n$ concentration in $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ (where $M = \text{Al}, \text{Mg}$, $n = 3, 2$, respectively, mol%) glass system.

The molar volume (V_m) was calculated using Equation (1) as shown below [15]:

$$V_m = \frac{M}{d} \left(\text{in } \text{cm}^3 \text{mol}^{-1} \right) \quad (1)$$

where M is the molar mass and d is the density of the glass. As shown in Figure 2b, the molar volume was plotted as a function of $x\text{M}(\text{PO}_3)_n$ (where $M = \text{Al}, \text{Mg}$ mol%, $n = 3, 2$, respectively) in the $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ (mol%) glass system. It was founded that molar volume increased from $47.39 \text{ cm}^3/\text{mol}$ to $49.05 \text{ cm}^3/\text{mol}$ and $55.60 \text{ cm}^3/\text{mol}$, with an increase in $\text{Mg}(\text{PO}_3)_2$ and $\text{Al}(\text{PO}_3)_3$ contents up to 15 mol%, respectively. The basic building units of a phosphate glass system are the PO_4 tetrahedra. These tetrahedrons are connected through bridging oxygen to form different phosphate structures. The chains and rings are linked through terminal oxygen bonded with the modifying cations [15]. It can be seen that the volume of $\text{M}(\text{PO}_3)_n$ (where $M = \text{Al}, \text{Mg}$, $n = 3$,

2, respectively, mol%) is larger than that of V_2O_5 . The number of tetrahedrons in the current system is proportional to the ionic status of cation, i.e., divalent ($M = Mg$) and trivalent ($M = Al$) metal ions. A similar study by Tsuchida et al. presented that the substitution of $Pb(PO_3)_2$ by $Al(PO_3)_3$ creates a more open glass structure, leading to an increase in molar volume of the glass system [16]. In other words, the molar volume of a $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $15Al(PO_3)_3$ glass system is larger than that of a $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $15Mg(PO_3)_2$ (mol%) glass system, indicating that $Al(PO_3)_3$ has more capability for connecting and corner sharing PO_4 tetrahedra than $Mg(PO_3)_2$. This will be discussed in more detail by Raman analysis in Figure 6 and X-ray photoelectron spectroscopy (XPS) analysis in Figure 7.

3.2. Thermal Properties

One of the most important characteristics for evaluating the glassy state and thermal properties is glass transition temperature. Figure 3a presents the differential scanning calorimetry (DSC) traces, measured in the range of 25–550 °C, for the $(70-x)V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $xM(PO_3)_n$ glass system (mol%) (where $M = Al, Mg$ mol%, $n = 3, 2$, respectively). The traces were obtained for different metaphosphates at various concentrations. The distinctive temperatures, such as the glass transition temperature (T_g), crystallization onset temperature (T_x), and peak crystallization temperature (T_p), were evaluated from the DSC curves as shown in Figure 3b. The T_g is obtained by drawing the tangent to the endothermic peak, while the T_x is taken as the temperature at which heat flow starts to increase from its constant value. We investigated the effect of monovalent ($M = Na$), divalent ($M = Mg$), and trivalent ($M = Al$) metal ions of $xM(PO_3)_n$ on thermal properties, such as T_g , T_x , and T_p , as shown in Figure 3b. When the concentration of $xM(PO_3)_n$ was increased up to 15 mol% ($M = Mg, Al$), it was observed that the T_g increased from 263 °C to 289 °C and 302 °C, respectively. However, the T_g of the $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $xNaPO_3$ glass system was not considerably changed with respect to $NaPO_3$ concentration. The T_x increased linearly from 293 °C to 383 °C and 405 °C, respectively, with an increase in $Mg(PO_3)_2$ and $Al(PO_3)_3$ contents up to 15 mol%. The increased $NaPO_3$ content up to 15 mol% led to the slight increase of T_x from 263 °C to 274 °C. In brief summary, this concludes that the T_g and T_x increased in the order of $Al(PO_3)_3$, $Mg(PO_3)_2$, and $NaPO_3$ added in the $(70-x)V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $xM(PO_3)_n$ (mol%) glass system.

Figure 3. Effect of $M(PO_3)_n$ concentration on thermal properties in V_2O_5 - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $xM(PO_3)_n$ (where $M = Al, Mg, Na$ mol%, $n = 3, 2, 1$, respectively) glass system. (a) DSC curves, (b) glass transition temperature (T_g), crystallization onset temperature (T_x) and peak crystallization temperature (T_p).

This behavior can be related to the bond strength of the glass network which can be explained in terms of the cation field strength (which is the charge divided by the square of the cation oxygen distance). In other words, thermal properties of glass could be influenced by various metaphosphate species, because $M(PO_3)_n$ with different metal cations showed different cation field strength depending on their charge, as shown in Table 2 [17,18]. It can

be seen that the Z/α increases in the order of cation, i.e., monovalent ($M = \text{Na}$), divalent ($M = \text{Mg}$), and trivalent ($M = \text{Al}$) metal ions. The reason behind trivalent $\text{Al}(\text{PO}_3)_3$ with a high Z/α having the highest T_g and T_x was analyzed. As plotted in Figure 3b, it was observed that the degree of increase in T_g , T_x , and T_p is closely related to the Z/α of cation, in order, in the present glass system. Muñoz-Senovilla et al. reported that the increase in T_g with Z/α was described according to different cation in alkali and alkaline earth phosphate glasses. It might then be due to the rise of the glass network strength and connectivity [15]. The trends on increase of T_g according to Z/α coincide with other studies mentioned above in the current study. In considering the effect of the divalent and trivalent metal cation in $M(\text{PO}_3)_n$, Schneider et al. studied the short-range structure and cation bonding in a $(1-x)\text{Ca}(\text{PO}_3)_2-x\text{Al}(\text{PO}_3)_3$ glass system. Increasing $\text{Al}(\text{PO}_3)_3$ led to the increase in T_g , which can be understood in terms of the replacement of Ca-O bonds by stronger Al-O bonds, i.e., bridging neighboring phosphate chains. In this way, the mobility of the phosphate segments become more restricted, causing an increase in T_g [18]. Tsuchida et al. reported that an increase of $\text{Al}(\text{PO}_3)_3$ in a $(1-x)\text{Pb}(\text{PO}_3)_2-x\text{Al}(\text{PO}_3)_3$ glass system leads to the increase of T_g . This phenomenon stems from the fact that Al atoms established stronger, more covalent bonds with nonbridging oxygen. Crosslinking of phosphate chains through Al-O-Al bridges restricts the mobility of these groups, increasing the T_g of the glass [16]. Based on those references, the divalent ($M = \text{Mg}$) and trivalent ($M = \text{Al}$) metal cations cause structural changes, leading to different thermal properties. As a result, the effect of Al-O bonds or crosslinking of phosphate chains through Al-O-Al bridges by $\text{Al}(\text{PO}_3)_3$ was more dominant than that of $\text{Mg}(\text{PO}_3)_2$, causing higher T_g and T_x than that of $\text{Mg}(\text{PO}_3)_2$ in the $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ (mol%) glass system.

Table 2. Ratio between charge, ionic radius, and cation field strength in Na, Mg, and Al [17].

Cation (M)	Charge (Z)	Ionic Radius (α)	Ratio (Z/α)	Cation Field Strength (Z/α^2)
Na	1	1.02 Å	0.980 Å ⁻¹	0.961 Å ⁻²
Mg	2	0.72 Å	2.778 Å ⁻¹	3.858 Å ⁻²
Al	3	0.53 Å	4.615 Å ⁻¹	10.679 Å ⁻²

Thermal stability (ΔT) is frequently characterized by the difference between T_g and T_x , $\Delta T = T_x - T_g$. It has been well known that the higher the thermal stability for a glass composition, the higher the crystallization resistance during heat treatment [19]. Figure 4 shows the variation of quantitative values of ΔT with respect to $x\text{M}(\text{PO}_3)_n$ concentration in a $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ glass system (mol%) (where $M = \text{Al}$, Mg , Na , $n = 3, 2, 1$, respectively mol%). When increasing the concentration of $\text{M}(\text{PO}_3)_n$ up to 15 mol% ($M = \text{Mg}$, Al), it was observed that the ΔT increased from 30.4 °C to 93.2 °C and 112.9 °C, respectively. However, the ΔT remained almost constant regardless of NaPO_3 concentration, incorporated up to 15 mol%. Per review on the thermal effect of phosphate content in a glass system, Armando Mandlule et al. reported that, in a $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O}$ glass system, network connectivity, chain length, and molar volume increase in structural behavior as P_2O_5 increases [20]. Ahmed et al. and Amos et al. suggested that the density of phosphate glasses is also affected by the phosphate chain length [21,22]. As explained above in Figure 3, structural changes and thermal properties are affected according to the ionic status of cation, i.e., monovalent ($M = \text{Na}$), divalent ($M = \text{Mg}$), and trivalent ($M = \text{Al}$) metal ions. The enhanced glass stability is caused by a lower mobility of longer phosphate chains in the glass network, resulting in a higher energy barrier for rearrangement and subsequent crystallization. The effect of $\text{Al}(\text{PO}_3)_3$ was stronger than that of $\text{Mg}(\text{PO}_3)_2$ on a lower mobility of longer phosphate chains, leading to a higher exhibited ΔT in a $(70-x)\text{V}_2\text{O}_5-5\text{ZnO}-22\text{BaO}-3\text{B}_2\text{O}_3-x\text{M}(\text{PO}_3)_n$ (mol%) glass system.

Figure 4. Variation of thermal stability with respect to $xM(PO_3)_n$ concentration (where $M = Al, Mg, Na, n = 3, 2, 1$, respectively, mol%) in $(70-x)V_2O_5-5ZnO-22BaO-3B_2O_3-xM(PO_3)_n$ glass system (mol%).

3.3. Thermomechanical Properties

CTE is one of the important properties to assess the feasibility of the glass material for laser sealing application. Well-matched CTE can guarantee its lifetime during the sealing process, along with long-term operation from thermal shock [23–25]. It is well known that the expansion of a glass material depends mainly on the internal network structure, the arrangement of the constituting building units, and the bond strength between the atoms involved. Thermomechanical analysis of the present glasses was carried out by using the dilatometer in the range of 25–450 °C. The dilatometer is used for characterizing the dimensional changes (length or volume) of glass material as a function of temperature. The coefficient of thermal expansion is obtained by linear fitting the dilatometric curves. Figure 5 shows the variation of CTE in $(70-x)V_2O_5-5ZnO-22BaO-3B_2O_3-xM(PO_3)_n$ (mol%) (where $M = Al, Mg, n = 3, 2$, respectively, mol%) glass as a function of metaphosphate concentration. The results show that as $xM(PO_3)_n$ (where $M = Al, Mg, n = 3, 2$, respectively, mol%) concentration increases, the CTE reached the highest values of $13.88 \times 10^{-6}/K$ and $9.991 \times 10^{-6}/K$ at $x = 12.5$ mol%, respectively.

Figure 5. Variation of coefficient of thermal expansion (CTE) in $(70-x)V_2O_5-5ZnO-22BaO-3B_2O_3-xM(PO_3)_n$ (mol%) (where $M = Al, Mg, n = 3, 2$, respectively, mol%) glass as a function of metaphosphate concentration.

According to Tsutomu et al., it was reported that the increase of CTE is due to a decrease in the cation field strength, along with the increase of radius of alkali cations in a $R_2O-Al_2O_3-P_2O_5$ and $R_2O-P_2O_5-WO_3$ glass system, analogous to the case of silicate glasses [26]. However, it can be seen that cation field strength is in the order of $Na(0.961 \text{ \AA}^{-2}) < Mg(3.858 \text{ \AA}^{-2}) < Al(10.679 \text{ \AA}^{-2})$ as listed in Table 2. Accordingly, it is expected that the CTE of $Mg(PO_3)_2$ should be higher than that of $Al(PO_3)_3$ in a $(70-x)V_2O_5-5ZnO-22BaO-3B_2O_3-xM(PO_3)_n$ (mol%) (where $M = Al, Mg, n = 3, 2$, respectively, mol%) glass system, because the cation field strength of Mg was lower than that of Al. However, the opposite trend of CTE was observed. Bingham et al. studied the effect of monovalent and divalent modifiers in a $((1-x)-(0.6P_2O_5-0.4Fe_2O_3))-xR_ySO_4$ glass system ($x = 0 - 0.5$ in increments of 0.1 and $R = Li, Na, K, Mg, Ca, Ba$, or Pb and $y = 1$ or 2). They reported that the increase of monovalent and divalent modifier contents elevates the CTE ($50-300^\circ C$), T_g , T_d , and T_{liq} in a $((1-x)-(0.6P_2O_5-0.4Fe_2O_3))-xR_ySO_4$ glass system. It was assumed that the addition of alkaline earth, such as MgO , depolymerizes the glass structure ($P-O-P$ bonds $\rightarrow$ $P-O-M$ bonds), resulting in the increase of T_g and T_d [26,27]. In the present study, the effect of monovalent $NaPO_3$ on T_g was less dominant compared to those of divalent $Mg(PO_3)_2$ or trivalent $Al(PO_3)_3$ in $(70-x)V_2O_5-5ZnO-22BaO-3B_2O_3-xM(PO_3)_n$ (mol%) (where $M = Al, Mg, Na, n = 3, 2, 1$, respectively, mol%), as explained in Figure 3. In terms of the thermomechanical properties, the substitution of $Al(PO_3)_3$ in the current glass system led to a strong effect on CTE compared to $Mg(PO_3)_2$. As discussed in several studies, it indicates that the network bonding and connectivity is more strongly influenced by divalent $Mg(PO_3)_2$ or trivalent $Al(PO_3)_3$ than monovalent $NaPO_3$, and is consistent with the greater field strength and $M-O$ bond strength of divalent $Mg(PO_3)_2$ or trivalent $Al(PO_3)_3$. However, the increase in CTE with increasing modifier content would appear to dispute this structural assertion, as thermal expansion is also strongly influenced by the strength of network bonding, its connectivity, and the interactions between cations and nonbridging oxygen [28]. The CTE can also be explained based on the density. It is well known that the decreasing trend of density causes an increase in volume expansivity, resulting in an increase in the CTE of glass. Accordingly, in the present study, the density of the glasses decreased with respect to metaphosphate content at various concentrations, causing an increase in the CTE (see Figures 2 and 5).

3.4. Structural Properties

Vibrational spectroscopy, namely Raman spectroscopy in this work, can supply useful information about the structure of non-crystalline materials. In comparison with IR spectroscopy, Raman spectroscopy is more sensitive to vibrations of bonds with a high covalence, which is advantageous for the study of changes in the structure of the phosphate backbone ($P-O$ bonds) and the vibrations of $V-O$ bonds in which a higher content of covalence (higher polarizability) is also assumed, contrary to the higher ionicity of $Zn-O$ bonds. Figure 6 shows the Raman spectra of a $55V_2O_5-5ZnO-22BaO-3B_2O_3-15M(PO_3)_n$ (where $M = Al, Mg, Na, n = 3, 2, 1$, respectively, mol%) glass system modified with $M(PO_3)_n$ concentration up to 15 mol%. As is seen from the spectra, all the studied glasses showed the characteristic vibration bands of vanadium and phosphate. The peak position and assignment of the vibrational bands observed at around 275, 491, 706, 991, 1120, and 1326 cm^{-1} are shown in Table 3. The distinctive bands related to the V_2O_5 are observed at 291, 399, 665, 799, and 1154 cm^{-1} which are assigned as shown in Table 3. The short-range order of phosphate glasses has been commonly described by the concepts of four different phosphate structural units derived from PO_4 tetrahedra, labeled as Q^n , where the superscript $n = 0, 1, 2$, and 3 denotes the number of bridging oxygen per tetrahedron [29]. Q^0 represents the orthophosphate groups, Q^1 indicates the terminal units of chains or pyrophosphate groups (Q^1-Q^1), Q^2 corresponds to metaphosphate groups, and Q^3 attributes to ultraphosphate groups. As shown in Figure 6, it is clear that the intensity and bandwidth of the Raman bands increased with the substitution of different metaphosphates, as compared to that of base VZBB glass. It is worth mentioning that the intensity and bandwidth of the distinctive

bands observed at around 275, 706, and 991 cm^{-1} significantly increased when $\text{Al}(\text{PO}_3)_3$ metaphosphate substituted for V_2O_5 due to the formation of strong V–O–Al coupling and a broadening and merging of bands. The decrease in broadening of the bands is clearly observed, with decreasing charge and covalence of the ions from Al^{3+} through Mg^{2+} to Na^+ . Furthermore, Raman spectra also showed the shift of the P–O–P band to lower energies, with decreasing charge and covalence of the ions from Al^{3+} through Mg^{2+} to Na^+ . This indicates that the Al bands merge together with the phosphate network deformation bands due to coupling of Al–O–P. Other bands also show some degree of merging. This behavior is validated from the XPS studies in a $\text{M}(\text{PO}_3)_n$ modified $(70-x)\text{V}_2\text{O}_5$ –5ZnO–22BaO–3B₂O₃– $x\text{M}(\text{PO}_3)_n$ (mol%) (where M = Al, Mg, Na, $n = 3, 2, 1$, respectively, mol%) glass system.

Figure 6. Comparison of the Raman spectra in $55\text{V}_2\text{O}_5$ –5ZnO–22BaO–3B₂O₃–15M(PO₃)_n (where M = Al, Mg, Na, $n = 3, 2, 1$, respectively, mol%) glass system and $70\text{V}_2\text{O}_5$ –5ZnO–22BaO–3B₂O₃ glass system. Refer to Table 1.

Table 3. Assignment of observed Raman bands of V_2O_5 –5ZnO–22BaO–M(PO₃)_x–3B₂O₃ (where M = Al, Mg, Na, $n = 3, 2, 1$, respectively, mol%) glasses.

Raman Vibrational Bands (cm^{-1})				Attributed Vibrational Modes
VZBB	VA#1-6	VM#1-6	VN#1-6	
291	275	289	279	Bending modes of PO ₄ tetrahedra units or bending vibrations of V ₃ –O, V–O–V, and V=O bonds
399	491	494	496	Bending modes of PO ₄ tetrahedra units or stretching vibration of V ₃ –O bonds
665	-	626	633	Stretching vibrations of V–O–V, V–O–P, P–O–P bonds
799	706	685	689	Stretching vibrations of V–O–V, V–O–P, P–O–P bonds
1154	991	984	979	V=O vibrations in VO ₄ tetragonal pyramid or PO ₄ vibrations of Q ⁰ units
-	1120	-	1127	PO ₂ symmetric stretching in O–P–O groups of corner sharing PO ₄ tetrahedra
-	-	1326	1327	Symmetric stretching modes of P=O bonds of Q ³ units

Structural analysis via X-ray photoelectron spectroscopy (XPS) was carried out to identify the correlation between the change in thermal properties and the structural change depending on M(PO₃)_n in a $(70-x)\text{V}_2\text{O}_5$ –5ZnO–22BaO–3B₂O₃– $x\text{M}(\text{PO}_3)_n$ (mol%) (where

M = Al, Mg, $n = 3, 2$, respectively, mol%) glass system. A nonlinear, least-squares algorithm was employed to determine the best fit to the O 1s spectra, with three Gaussian–Lorentzian curves in order to distinguish various oxygen bonding sites (such as BO and NBO). The fraction (relative abundance) of various oxygen bonding sites was determined from the respective area ratios obtained from optimized fits. Figure 7 shows the high-resolution XPS spectra along with their deconvoluted curves for the O 1s core level for AP15 and MP15. The resulting peak positions and area under the peaks of the different oxygen sites from the curve fitting of O 1s core levels for specimens are displayed in Table 4. Typically, the 1s O peak of oxide glass consists of two components: bridging oxygen (BO) at a higher energy and nonbridging oxygen (NBO) at a lower energy [30,31]. In particular, it has been reported that the XPS spectra of a P_2O_5 - V_2O_5 -based glass system was deconvoluted into more than three curves [32,33]. In this work, the area of the BO peak at 532.55 eV shows 33.95 % and 32.46 % for $Mg(PO_3)_2$, and $Al(PO_3)_3$, respectively. The area of the BO peak indicating P-O-P bonds is not significantly distinguished by the type of $Mg(PO_3)_2$ and $Al(PO_3)_3$. On the other hand, the areas of BO peaks at 531 eV are 29.55 % and 40.24 % for $Mg(PO_3)_2$ and $Al(PO_3)_3$, respectively, as shown in Figure 7.

Figure 7. Comparison of the XPS spectra of (a) $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $15Al(PO_3)_3$, and (b) $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $15Mg(PO_3)_2$.

Table 4. Peak positions and area from the curve fitting of O 1s core levels for $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $15Al(PO_3)_3$ and $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $15Mg(PO_3)_2$ glasses (mol%).

	15 mol% $Al(PO_3)_3$		15mol% $Mg(PO_3)_2$	
	Area (%)	Centroid (eV)	Area (%)	Centroid (eV)
NBO	27.3	530.09	36.49	529.97
BO	40.24	531.17	29.55	531.07
BO	32.46	532.55	33.95	532.24

XPS studies on vanadium phosphate-based glasses reported that the P-O-P bonds as a BO structure would have the strongest covalent bonds, since the Pauling electronegativity is in the order of P (2.19), V (1.63), Al (1.61), Mg (1.31), and Ba (0.89). Consecutively, the binding energy would be weakened in the order of P-O-V, P-O-Al, V-O-V, and V-O-Al bonds as intermediate BO structures, and P-O-Mg, V-O-Mg, P-O-Ba, and V-O-Ba bonds as NBO structures [32,33]. The area of BO peak at 531 eV by $Al(PO_3)_3$ is larger than that by $Mg(PO_3)_2$, which means that $Al(PO_3)_3$ preferentially formed intermediate BO, such as P-O-Al bonds in the current glass system. On the other hand, it is believed that the area of NBO peak from $Mg(PO_3)_2$ means the forming of major P-O-Mg and V-O-Mg bonds, as well as the V-O-Ba and P-O-Ba bonds in a $55V_2O_5$ - $5ZnO$ - $22BaO$ - $3B_2O_3$ - $Mg(PO_3)_2$ (mol%) glass system. A similar effect by Al^{3+} -ions reported that the relative fractions of P-O-P bonds (BO) and P-O-Na bonds (NBO) decrease, and the fraction of P-O-Al bonds (BO) increases

with an increase of Al_2O_3 content in an Al_2O_3 - NaPO_3 glass system [34]. Moreover, Al^{3+} -ions, when added to phosphate glass, have been known to increase the degree of structural polymerization via forming the crosslinked P-O-Al structure within the glass networks. The substitution of AlPO_4 for NaPO_3 consumes both P-O-P and P-O- Na^+ bonds to form P-O-Al bonds, which crosslink and shorten the P-O-P chains in the $\text{Al}(\text{PO}_3)_3$ - $\text{Na}(\text{PO}_3)$ system [35,36]. On the other hand, it is believed that the area of NBO peak from $\text{Mg}(\text{PO}_3)_2$ means the forming of major P-O-Mg and V-O-Mg bonds, as well as the V-O-Ba and P-O-Ba bonds in $55\text{V}_2\text{O}_5$ - 5ZnO - 22BaO - $3\text{B}_2\text{O}_3$ - $\text{Mg}(\text{PO}_3)_2$ (mol%). This trend can be described as a role of the alkaline earth within the glass. Generally, the incorporation of alkaline earth, such as MgO, CaO, SrO, and BaO, within the glass matrix results in depolymerization of glass structure. Indeed, it was reported that Mg^{2+} -ions break the glass network and can take a position in the vanadate or phosphate chain within the MgO - V_2O_5 and MgO - P_2O_5 systems [26,27]. Consequentially, the trivalent Al-ion within the glass is well-known as a network intermediate which plays a role in increasing thermal/chemical stability, melting temperature, and viscosity, and reducing crystallization tendency [37]. Therefore, it could be assumed that Al^{3+} -ions from $\text{Al}(\text{PO}_3)_3$ contributed to the enhancement of T_g by reducing the fraction of NBO by preferentially forming intermediate BOs, such as the P-O-Al and V-O-Al bonds [35]. As explained in Figures 3 and 4, these results supported that the network bonding and connectivity being more strongly improved by trivalent $\text{Al}(\text{PO}_3)_3$ led to an increase in T_g and, in turn, the thermal stability.

4. Conclusions

The $(70-x)\text{V}_2\text{O}_5$ - 5ZnO - 22BaO - $3\text{B}_2\text{O}_3$ - $x\text{M}(\text{PO}_3)_n$ glass system (mol%) incorporated with different $\text{M}(\text{PO}_3)_n$ at various concentrations (where M = Mg, Al, n = 2, 3, respectively) was prepared to observe its aptness for fiber types of sealant. The thermal stability of the $(70-x)\text{V}_2\text{O}_5$ - 5ZnO - 22BaO - $3\text{B}_2\text{O}_3$ - $x\text{M}(\text{PO}_3)_n$ glass system in $x = 15$ mol% (where M = Mg, Al, n = 2, 3 respectively, mol%) increased from 30.4 °C to 93.2 °C and 112.9 °C, respectively. Incorporation of $\text{Al}(\text{PO}_3)_3$ increased the degree of structural polymerization through forming crosslinked P-O-Al bonds. The $\text{Al}(\text{PO}_3)_3$ plays a role in increasing thermal stability and reducing crystallization tendency. The coefficient thermal expansion of the $(70-x)\text{V}_2\text{O}_5$ - 5ZnO - 22BaO - $3\text{B}_2\text{O}_3$ - $x\text{Al}(\text{PO}_3)_3$ glass system (mol%) (where $x = 5\sim 15$, mol%) is in the range of 9.5–15.5 ($\times 10^{-6}/\text{K}$). These developed glass compositions are tunable for matching the thermal expansion coefficient with DSSC panels having 9–10 ($\times 10^{-6}/\text{K}$) of CTE. The considerable variation in the thermal stability and CTE with the substitution of $\text{Al}(\text{PO}_3)_3$ indicates that the network bonding and connectivity being more strongly improved led to an increase in the T_g and, in turn, the thermal stability. The Raman and XPS studies also confirm the network connectivity and bond strength with the substitution of $\text{Al}(\text{PO}_3)_3$ in the present system. The results clearly indicate that the $55\text{V}_2\text{O}_5$ - 5ZnO - 22BaO - $3\text{B}_2\text{O}_3$ - $15\text{Al}(\text{PO}_3)_3$ glass system (mol%) is a potential candidate for the development of fiber types of sealant in laser sealing applications.

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