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The Characterization $ZnO-Na_2O-P_2O_5$ Glass System for Dental Restorative Materials

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Abstract. Zinc sodium phosphate glass system with different concentration of zinc and chromium oxide doped have been synthesized using melt quenching technique. These glass system was characterized using X-ray diffraction, Archimedes methods, and UV-Vis spectrofotometer. X-ray diffraction found that these glass system was amorphous structure. Optical absorption was measured at a wavelength of 200-800 nm indicates the absence of a sharp absorption beam. From the results of the optical absorption spectra shows that the value of the gap energy decreases while the urbach energy and refractive index of the glass increases with increasing %mole of ZnO. For preminarily research of dental restorative materials, our system also was doped by Cr_2O_3 and obtain that Cr_2O_3 presence make the range value was smaller for density and molar volume.

1. Introduction

Dental restorative becomes one of the most popular research topics in the field of biomaterials as these associated needs of human dental components and structures. All types of biomaterials basically can be applied to dental restorative; metals, polymers, glasses, ceramics, and composites. However, the materials are selected according to the specific properties which are general guidelines for the study of dental restorative materials. These properties should be considered the biological conditions of the tooth itself, especially the presence of microorganisms. The proper dental restorative materials should build the biological bonding in tissue.

Glasses systems structure have a great impact on biological mechanism and processability, especially antimicrobial properties. Some biomolecules can be replaced by glasses system [1]. On another glasses system polymer combined, the structure of the polymer was transformed to change the bonding and mechanical properties by containing bioactive glass in the glass ionomer cement [2]. For this reason, glass system was chosen for the dental restorative material. This research synthesized zinc sodium phosphate glass system with different chromium oxide concentration using melt quenching technique.

Among the various glasses oxides system, phosphate glass can accommodate active ions without losing its distinctive properties [3,4]. The phosphate glass has other attractive properties, which has a high thermal expansion coefficient, high refractive index, low dispersion, low melting point, high electrical conductivity, and various structures to receive some cation or anion exchange [5]. However, phosphate glass has a weak resistance to chemicals, has a high hygroscopic, and easily vapour [6]. In relation to the dental restorative materials, this research also study the physical properties of Cr_2O_3 doped in $ZnO-Na_2O-P_2O_5$ glass system.

2. Methods

Glass specimens include Zinc Oxide (purity 99.99%), Natrium Oxide (99.99% purity), and Phosphorus Pentaoxide (98% purity). The compositions used are x ZnO - 30 Na_2O - (70 - x) P_2O_5 with x = 0, 5, 10, and 15 %mole shown in Table 1.

Table 1. Chemical Composition of Glass Samples.

Sample Code	Compound (%mole)		
	ZnO	Na_2O	P_2O_5
Sample 1	0	30	70
Sample 2	5	30	65
Sample 3	10	30	60
Sample 4	15	30	55

All the compositions are mixed into the alumina crucible and then furnaced 30 minutes at a temperature 1100°C so all components are completely melted process. Next, mixture was poured into a steel mold with time as fast as possible so that the mixture does not have time to form being crystals. Then the glass sample is transferred into the furnace 3 hours at a temperature 300°C for annealing process to prevent the crack. The last process is cooling the sample at room temperature (cooling down process). The whole process is shown in Figure 1.

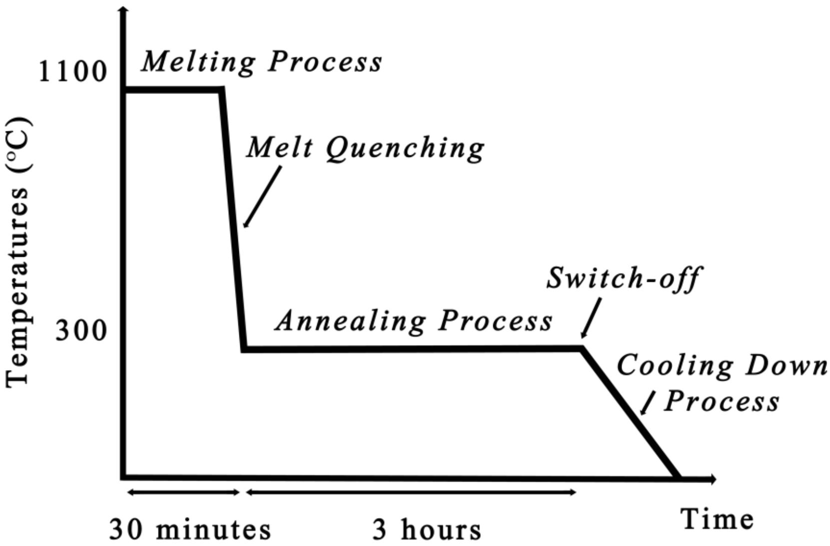

Fig. 1. Glass Making Process Temperature.

The glass samples were tested by X-ray diffraction using a 3kW Rigaku SmartLab 3DW Dexterometric to verify the amorphous properties of glass. The sample was pounded on the mortar until it forms a powder. The Archimedes method is used to determine the glass density. The glass sample was cut and then immersed into the toulene liquid. Toluene fluid was used because it does not readily react with glass samples so it will not affect the properties of the glass. The sample mass is weighed and then fed into a beaker filled with toluene fluid to obtain the sample mass in air and toluene fluid. Glass density is calculated using the equation [7]:

$$\rho = \rho_t \left(\frac{w_a}{w_a - w_t} \right) \tag{1}$$

with ρ_t is toluene density $\left(0.8669 \text{ g/cm}^3\right)$, w_a and w_t respectively the sample mass in the air and toluene. For molar volume calculations using equations [8, 9]:

$$V_m = \frac{M_T}{\rho} \quad (2)$$

with M_T is the total molecular weight of the glass system and is the glass density.

The absorbance of glasss system was recorded at room temperature using the UV-VIS-NIR Shimadzu 3101PC spectrophotometer at 200 - 800 nm wavelength with a 2.5 mm glass thickness. The absorption coefficient for each sample uses Eq. (3) [8, 9].

$$\alpha(v) = 2.303\frac{A}{d} \quad (3)$$

with A the amount of absorbance and d is the thickness of the sample. The energy gap value corresponds to the absorption coefficient using the Eq. (4) [8,9].

$$\alpha(v) = \frac{B(hv - E_g)^s}{hv} \quad (4)$$

with B is a constant, hv is the energy of the photon, E_g is the gap energy, and s is the index which relates to the electronic transition for absorption. On the glass, the value of s is 2, indicating an indirect transition.

The urbach energy calculation based on the equation:

$$\alpha(v) = B\exp\left(\frac{hv}{E_u}\right) \quad (5)$$

with B is a constant, hv is the energy of the photon, E_u is the urbach energy.

The urbach energy value was calculated by determining the gradient of the curve and taking the reciprocals. The calculation of the refractive index value of glass, n was corresponds to the energy gap using the equation:

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_g}{20}} \quad (6)$$

For preliminary research of dental restorative material, also was synthesized glass system doped with Cr_2O_3. The glass system were compound by zinc oxide, natrium oxide, phosphorus pent oxide, and chromium oxide in 99.99% purity. The quantities of these material system based on formula 15 ZnO + 30 Na_2O + 55 P_2O_5 + x wt % Cr_2O_3 where x = 0, 0.002, 0.004, 0.006, 0.008, 0.04 and 0.06 wt %, were mixed together into an alumina crucible and inserted into an electric furnace 30 minutes at a temperature 1100°C and the next process same as the previous glass system. These variation of Cr_2O_3 was intended to analyze and compare the most optimal structure of the system.

3. Results and Discussion

The X-ray diffraction pattern of all zinc oxide-natrium oxide-phosphorus pent oxide glass system samples is shown in Figure 2. From the results of X-ray diffraction analysis it is found that the structure of the glass sample was amorphous (in the absence of a sharp peak). The broad hump is visible at an angle 2θ, i.e. between $15 - 30^\circ$. The facts prove broad hump at a low angle affirms the amorphous glass characteristics [10].

The physical properties (molar density and volume) and optical properties (energy gap, urbach energy, and refractive index) are shown in Table 2.

From the results of physical properties obtained that the density of glass decreased with the increase of %mole ZnO. This is due by the substitution of the molecular weight of ZnO (smaller than the molecular weight of P_2O_5 [10]. The weak connectivity in the glass structure causes decreasing the density value. The weak connectivity in the glass structure shows the value of glass rigidity decreases.

The molar volume is inversely proportional to the density shown in Figure 3. The molar volume of the glass increases with increasing %mole ZnO. This is due to the increasing the free volume by decreasing glass density. The molar volume shows the glass having an open structure. The open structure in question is the breaking of the BO (Bridging Oxygen) bond and the formation of NBO (Non-Bridging Oxygen) bonding [11].

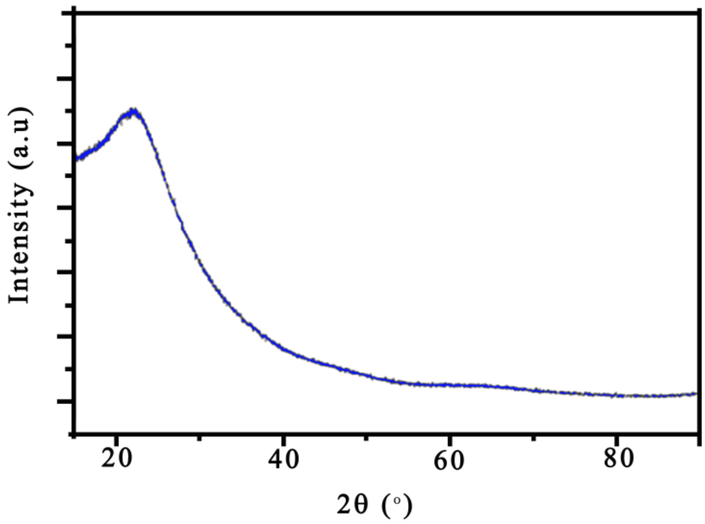

Fig. 2. X-Ray Diffraction pattern.

Table 2. Physical Properties and Optics of Glass Samples.

Sample Code	Density, ρ (g/cm^3)	Molar Volume, V_m (cm^3/mol)	Gap Energy, E_g (eV)	Urbach Energy, E_u (eV)	Recractive Index, n
Sample 1	3.93	28.32	3.45	1.22	2.28
Sample 2	2.40	45.21	3.81	0.92	2.21
Sample 3	2.24	47.03	2.86	1.59	2.44
Sample 4	2.07	49.44	2.27	2.08	2.63

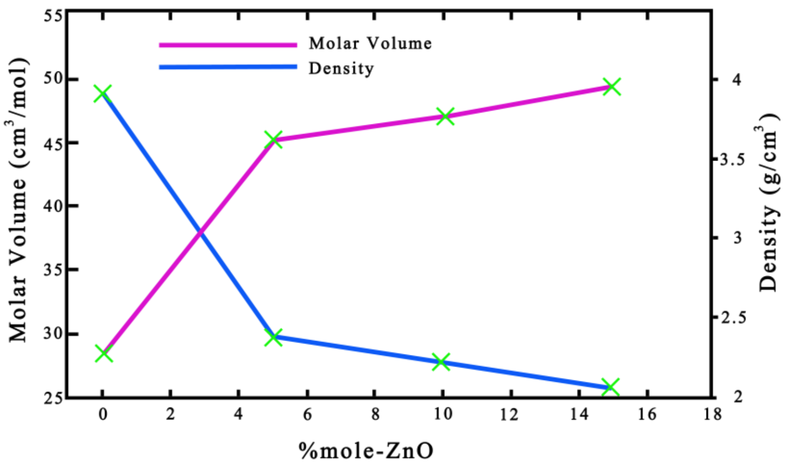

Fig. 3. Relation Between The Density and Molar Volume with mole% ZnO.

Figure 4 shows the absorbance graph as a function of wavelength in the ultra-violet and visible regions. From the graph shows no sharp absorption peak. This is a characteristic of amorphous glass. The optical absorption spectra were methods used to study optical transitions and provide information on bonds, structures, and energy gaps for both amorphous and crystalline materials. At the absorption in the ultraviolet region, visible light, and infrared absorption of atoms occurs. The principle is that the absorption of photons occurs when the electrons in the valence band are excited and heading to the conduction band so that in the conduction band there are free electrons and holes in the valence band. Excitation accompanied by absorption will occur if the photon energy is greater than the gap energy. Optical absorption spectra generally determine the strength of oxygen bonding in glass structures [12].

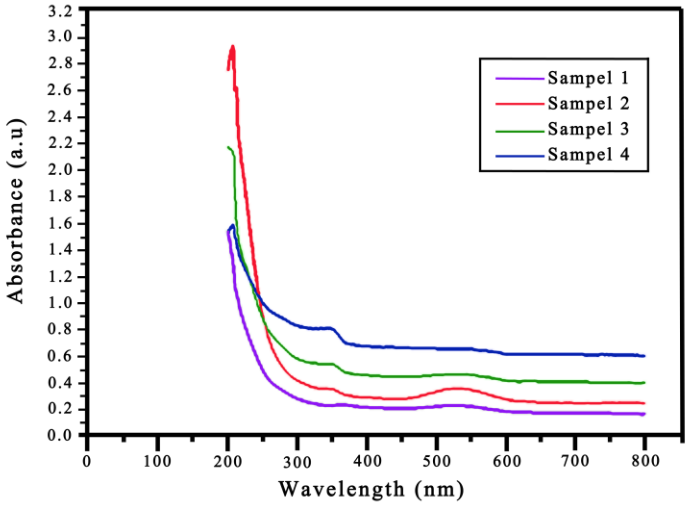

Fig. 4. The Spectrum Absorbance of Glass Samples.

From the optical absorption spectra, can be determined the value of energy gap, urbach energy, and refractive index of glass. The gap energy value was shown in Fig. 5. It can be seen that the gap energy value increases with increasing %mole ZnO only to 5 %mole ZnO. Then, the gap energy value continues to decrease. The increase of gap energy value is caused by the formation of BO on the glass composite matrix. Then, the decrease in gap energy is due to the establishment of NBO formation. This means, increasing the %mole ZnO into the glass matrix causes the BO bond to turn into NBO and it is known that NBO has greater energy than BO. The NBO also has a more negative charge than BO. Therefore, the electrons can easily transfer from the valence band to the conduction band [13].

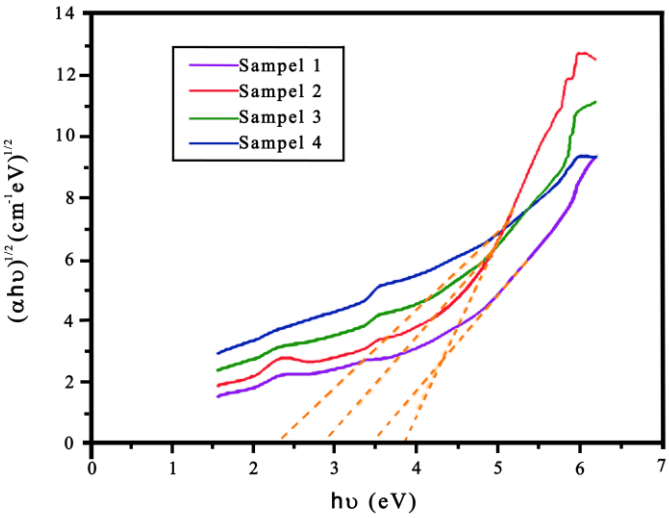

Fig. 5. The Gap Energy Value Determination.

While urbach's energy value is obtained by making a graph of the relationship between shown in Figure 6. Urbach's energy values represent the degree of structural order or disorder (orderness or disorderness) in amorphous materials [13]. Urbach's energy value on glass is inversely proportional to the energy gap.

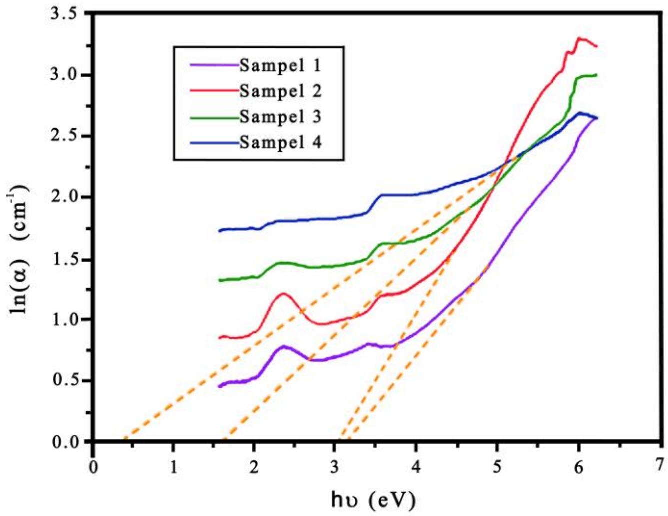

Fig. 6. The Urbach Energy Value Determination.

It can be seen that the value of urbach energy decreases with increasing %mole ZnO only up to 5 %mole ZnO. Then, urbach's energy value keeps increasing. The decrease in urbach energy may be due to increased order of glass tissue as a result of polymerization so that the glass structure becomes more stable and homogeneous [8]. Then, the increase of urbach's energy is due to increased structural irregularity in the glass with the increase of %mole ZnO. Irregularity is caused by increased NBO bond formation due to the decrease in energy gap value. The NBO bond has a weak bond because it has a large inter-atomic distance in the glass structure and an electron that is not strongly bonded with oxygen [21]. The high value of urbach energy also indicates that the glass sample has a low compactness, seen from the decreasing glass density value with the addition of %mole ZnO.

Refractive index values are fundamental to studying the optical properties of the material as they relate to performance or performance and optical device resistance [25]. The value of the refractive index decreases with increasing %mole ZnO only to 5 %mole ZnO. Then, the refractive index value continues to increase shown in Figure 7. The decrease in refractive index value is caused because the Zn atom is starting to form the inside of the glass structure network [21]. Then, the increase of refractive index value is caused by the decrease of gap energy value. Moreover, it is caused by the presence of an electron cloud causing the decrease of light speed in the glass medium. The presence of the electron clouds indicates a high NBO bond formation and indicates a low BO bond on the glass preparation matrix [25,26]. In addition, NBO bonds are more polarized than BO bonds because NBO bonds have larger ionic bonds and less binding energy than BO bonds [26].

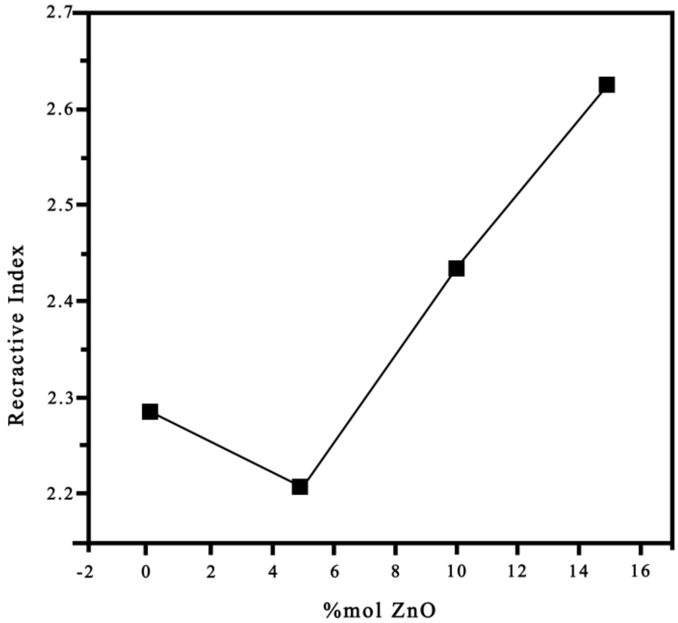

Fig. 7. The Refractive Index Value.

Relation between the density and molar volume with mole %Cr_2O_3, shown in Figure 8. The results obtained the density and molar volume indicate that the Chromium oxide lower the concentration (0.008 wt %) enters the glass network as a modifier by occupying the interstitial space in the network and generating the NBO's to the structure. The comparation with previous glass system, Cr_2O_3 presence make the range value was smaller for density and molar volume.

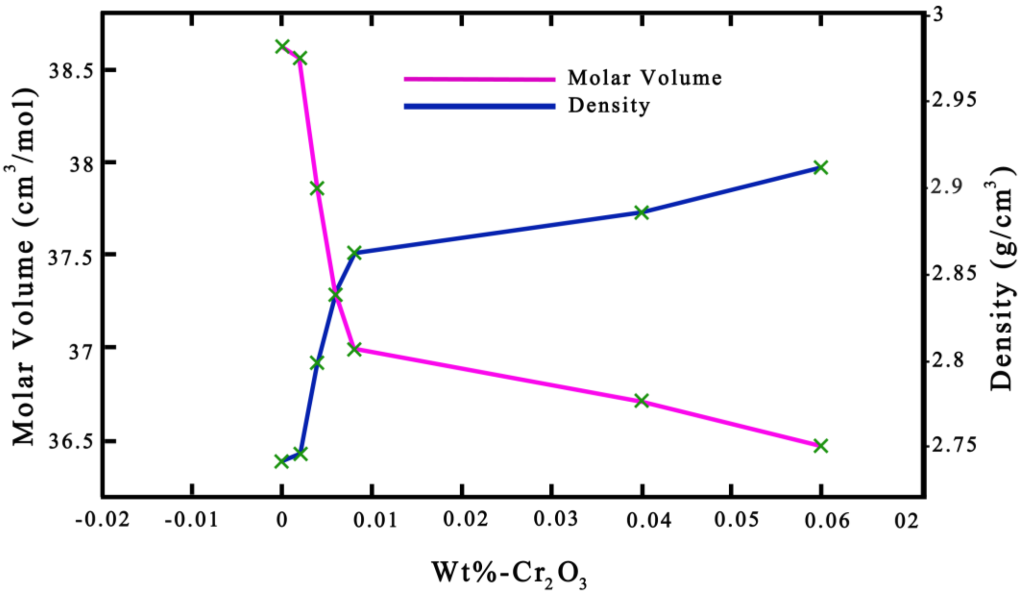

Fig. 8. Relation of the density and molar volume with Cr2O3 wt% for zinc sodium phosphate (NZP) glass system.

4. Summary

The characterization of glass systems x ZnO - 30 Na_2O - (70 - x) P_2O_5 with x = 0, 5, 10, and 15 %mole have been successfully performed using melt quenching technique. The X-ray diffraction pattern shows that the glass made is amorphous. The %mole concentration of ZnO has an enormous influence on the physical properties and optical properties (absorption) of glass. From the study obtained that the value of density and energy gap decreased while the molar volume, Urbach energy, and refractive index increased with increasing %mole ZnO. The optimum value is achieved in Sample 4, with the highest refractive index value, that is 2.63. This is because the refractive index value will be related to performance or optical device performance and resistance. The Cr_2O_3 presence make the range value was smaller for density and molar volume thus making the structure of the system more stable. This Cr doped in system can be used in further research on the utilization of bioglass in future dental restorative research.

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