



Investigation of Partial Replacement of Na₂O on Structural Features and Thermal Properties of Sodium Phosphate Glass System

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Abstract

The urgent need to produce different sealing glass with distinct thermal properties, recommended to study the behaviour of phosphate glass system. Binary alkali phosphate glasses are characterized by low viscosity, low melting temperature, and proper thermal expansion. However, it has poor chemical durability. Therefore, work must be done to improve its chemical properties to suit practical applications. The effect of replacing different proportions of sodium oxide (Na₂O) in equimolar sodium phosphate glass system by equivalent portion of divalent metal oxide on the thermal characteristics was investigated. Thermal expansion coefficients were determined experimentally and theoretically. Careful analysis of dilatometric curves of thermal expansion helps to define both the transition temperature T_g and the softening temperature T_d. It can be found that, both of T_g, T_d temperatures were increased with increasing divalent metal oxide content. This is a clear indication to improve the crosslinking and decrease of the non-bridging oxygen atoms. Also, this observation is consistent with the density results and IR data.

Keywords: Sodium-Phosphate glass; Sealant glasses; Density; Infrared spectroscopies; Thermal Expansion.

1. Introduction

It is well established and acceptable that, the elastic and thermal characteristics of amorphous P₂O₅ and alkali phosphate satisfies the requirements of many applications [1]–[3] such as glass to metal seals. Unfortunately, the poor chemical durability of such phosphate glasses makes them unsuitable for practical applications. On recalling the extensive structure studies in the last few years, dealing with the structure of amorphous P₂O₅ and alkali phosphate glasses, using different techniques (infrared and Raman spectroscopies) it is observed that the most of these studies suggested that the matrix of amorphous P₂O₅ is mainly formed from isolated ring (cyclic) molecules [4], [5]. The basic building unit in these rings is a PO₄ tetrahedron. Also, it was suggested that the addition of modifier oxides leads to

depolymerization of the ring groups, resulting in linear phosphate chain. The chain length together with the accompanying non bridging oxygen atoms depend on the concentration and the type of the modifier oxide [6], [7].

These studies showed that the physical properties such as, density, hardness, rigidity, thermal expansion, and characteristic temperature, T_g and T_d depend largely on the type and concentration of the modifier [8], [9]. Various compositions with several structure of oxide glasses and glass ceramics have been prepared and studied. Phosphate-based glass dropped by Na₂O with content amount vary from 15 to 50 mol % was confirmed. The crystalline chains of the samples were examined via XPS [10]. Calcium oxide (CaO) was added to P₂O₅–Na₂O based glass system to evaluate transition and crystallization

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temperature, XRD and solubility [11]–[13]. Successively, several efforts have been exerted to gain the superior results. A low loading content of TiO₂ (1 mol%) and Mg (2 mol%) were added to P₂O₅–CaO–Na₂O based glass system, as a way to overcome the crystallization phenomenon [14]. The replacement impact of CaO in the 50P₂O₅–20Na₂O–30CaO based glass system by MgO, was investigated. Thus, the results of glass system tool up a distinctive insight into the glass properties [15]–[17]. The glass system with adding of Fe₂O₃ of amount content of 0 to 4 mol% was performed. The glass durability exhibits an enhancing, this may be due to form the Fe–O–P bonds and high density of the cross-link [18], [19]. Boron oxide B₂O₃ was used to equip a glass system based on P₂O₅–CaO–Na₂O–MgO. Where B₂O₃ replaces of Na₂O with a content of 5 and 10 mol%. It was found that, 45P₂O₅–16CaO–5Na₂O–24MgO–10B₂O₃ glass system achieved favorable results in mechanical properties [20]. Metal oxides CuO, ZnO, and CdO were partial exchanged of Na₂O on sodium meta phosphate sealing glass. The IR spectra and density were clarified good results [21].

Planar solid oxide fuel cells were assessed via examining the joint strength of a recent glass sealant. This joint was tested under shear and tensile condition loads at room and extreme temperatures [22]–[24]. Using Spectroscopic techniques, the 45SiO₂–24.5CaO–24.5Na₂O–6P₂O₅ glass system was prepared. SrO with a loading amount of 5 and 10 mol%, was partial exchanged of SiO₂. This system is called glass ionomer cements, which is recognized by corrosion resistance and dissolutions in water [25]. Due to these accomplished results, this glass is preferred to use as a dental restorative material compared to traditional acrylic resin [26]–[30].

In the present study a systematic investigation for the effect of partial replacement of Na₂O in the equimolar sodium phosphate glass system, by each of the divalent modifying oxides CuO, ZnO, and CdO. Moreover, this work is focused to investigate the role of divalent oxide on increasing of density, transition temperature T_g, and softening temperature T_d. This is an indication to improve the crosslinking of the phosphate glass system.

2. Materials and Experimental

2.1. Materials

In current study, sodium-phosphate glass was introduced in the composition of 55 P₂O₅ - (45 - λ) Na₂O - λ MO. Phosphorus pentoxide (P₂O₅) is a white powder color with a particle size of 50-100 μm. Anhydrous sodium carbonate powder (Na₂CO₃), ANALAR reagent, is used to prepare sodium oxide (Na₂O). Metal oxides (MO), which are doped in the composition of this type of glass, are CuO (G1x), ZnO (G2x), and CdO (G3x). All chemical compositions are purchased from Sigma-Aldrich. The content of the Sodium-Phosphate glass composition is displayed in Table 1.

Table 1

Chemical content of Sodium-Phosphate glass

Glass Sample	Composition, mol %		
	P ₂ O ₅	Na ₂ O	MO
G0	55	45	0
G1	55	40	5
G2	55	35	10
G3	55	30	15
G4	55	25	20
G5	55	20	25

2.2. Preparation of Sodium-Phosphate glass

The traditional melt and quenching method were adopted for samples preparation, the weighted component materials were well mixed and carefully transferred to silica crucible. The mixed powders were first heated at 300 °C during the transfer of the batch material in parts. The completely transferred batch was then heated under normal conditions in automatically controlled electric furnace, CF1200 series muffle furnaces - England, for 2 hours at 700-1100 °C depending on the glass composition. The crucible was removed out from the furnace at intervals and swirled to promote good mixing and homogeneity. The melts were casted in an iron mold on an iron plate, and immediately transferred to annealing furnace at appropriate temperature depending on the glass composition. The annealing furnace was then starting self-cooling to room temperature. Cylindrical glass samples of approximately 6 mm in diameter and 15 mm in length with parallel surfaces were prepared to be used for the dilatometry measurement.

2.3. Infrared measurement

Infrared spectroscopy was performed by using a spectrophotometer, Beckman IR 4250 - USA. IR measurement was applied on the samples in powder form and results displayed in the range of 400-2000 cm⁻¹.

2.4. Thermal Expansion

The thermal expansion of samples was determined in the temperature range (25-350) °C using Linseis Dilatometer, with heating rate of 5°C/min. The experimental linear expansion coefficient α was determined from the slope of consecutive length changes (dL/L) experimental data without any curve fitting. The thermal expansion coefficients were also theoretically calculated using Makishima-Mackenzie model [31]. The dilatometric glass transition temperature T_g and softening temperature T_d of the glass were determined following G.Gongyi and C.Yuli procedure [32].

2.5. Density

The density of the glass samples was experimentally determined by Archimedes method using toluene as buoyant liquid, and electric balance with sensitivity 10⁻⁴gm. it was theoretically calculated using the formula

$$d = \frac{1}{\sum a_i/d_i} \quad [1]$$

where the nominator represents the mass of one gram of the sample and a_i is the weight fraction of the oxides used in preparing the samples, d_i is the density of these oxides.

3. Results and Discussion

IR spectra of 55P₂O₅-(45-x) Na₂O-x MO of the three sets glasses containing CuO, ZnO or Cd, respectively, are displayed in Fig. 1. By the diffraction pattern, it is possible to observe that the structural features of the 55P₂O₅-45Na₂O sample almost appears many areas on its IR band are slightly shifted to higher around wave number as 525, 700, 875, 1000, 1050, 1250 and 1600 cm⁻¹.

This may be due to the features of the glass spectrum, where the glass goes through a set of phases, which contains the PO₄ formation mode, symmetric and asymmetric stretching mode of a single P-O-P bond, and symmetric and asymmetric stretching vibration of both of P-O- in PO₄ and P-O- in PO₂. This is in line with the previous research [33],

[34]. Moreover, it is observed that the bands at 1050 cm⁻¹ tends a prominent augmentation in its intensity as result of CuO take the place of Na₂O. This appears to be precise as the phosphate chains react more with copper than with sodium [33]. Thus P-O- bonds linked to Cu ions are longer than P-O(-Na) bonds. While this interference does not occur when Na₂O is replaced by ZnO or CdO [21].

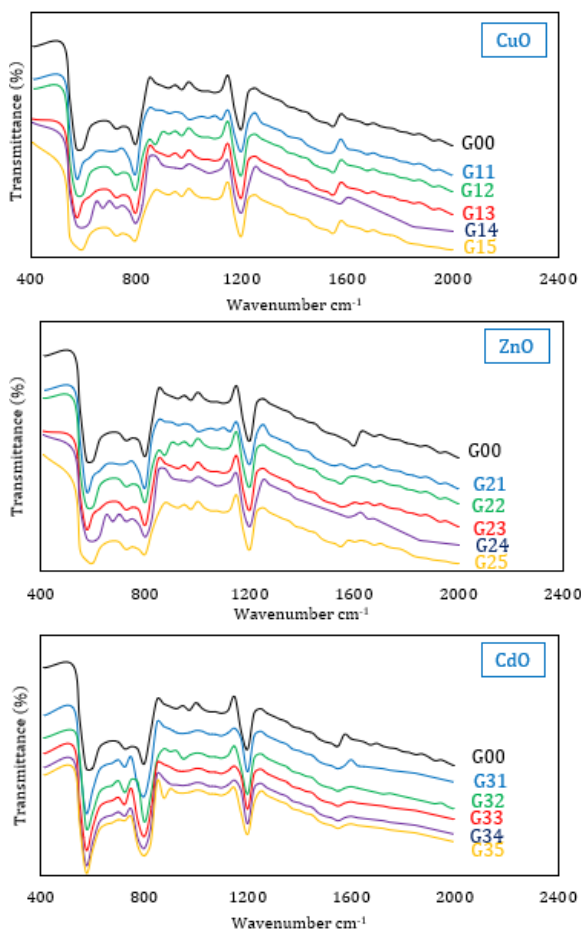


Fig. 1. X IR spectra of 55P₂O₅-(45-x) Na₂O-x MO of the three sets.

Three glass compositions in the sodium meta phosphate sealing glass 55 P₂O₅ - (45 - λ) Na₂O - λ MO were prepared, one with CuO, the second containing ZnO while the third with CdO. The thermal expansion was measured for three sodium meta phosphate glasses compositions. Figure 2 illustrates the thermal expansion curves for sodium meta phosphate as a function of the metal oxide composition amount. It is clearly shown that these experimental curves reflect different slopes at different temperature ranges. From the slopes of the straight part of each of these curves the

corresponding thermal expansion coefficient α_{exp} were estimated.

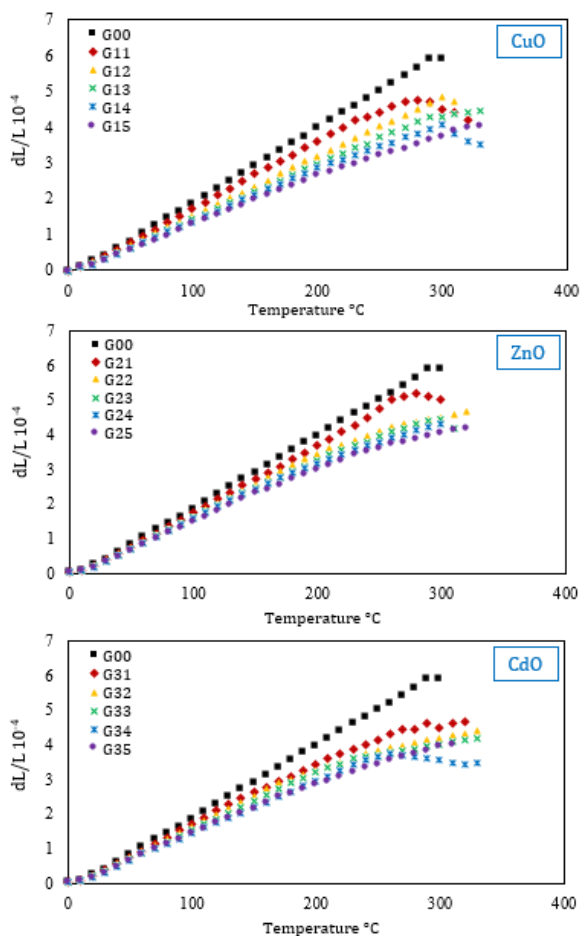


Fig. 2 The relation between MO mol % and the thermal expansion of the three sets

Both experimentally determined values and the theoretical calculated values, as being calculated by Makishima-Mackenzie model (M-M) formula [31] for the three examined systems α_{th} are represented in Fig. 3 for the studied group containing CuO, ZnO, and CdO. It is clear from that both of α_{exp} and α_{th} decrease as Na_2O is replaced by any one of the three oxides CuO, ZnO, and CdO. Moreover, the theoretically calculated α_{th} values are generally higher than the corresponding experimental values for the three groups studied. The parallelism of both two relations reveal that both are similarly affected by replacing Na_2O by any one of the oxides. The values of the glass transition temperature T_g , and the softening temperature T_d as being determined from the thermal expansion curves, are represented in Fig. 4, for the three studied groups reflects also increase in their values as Na_2O is replaced by any one of the

oxides.

Such as changes in the values of α , T_g , T_d as shown in Figures 2-4 may be attributed to one or more of structural alternation expected to occur upon replacing the monovalent cation Na^+ by any one of the three-cation used, due to the relative difference in their electro positivity. One of these changes is the increase in the probability of cross linking as was showed agreement with previous results [35]. In addition to this, the effect of such replacement on the π - bond delocalization with the consequent strengthening of P-O bridging bonds, it appears to be consistent with the results obtained [36]–[39] which used different techniques for studying different phosphate glasses.

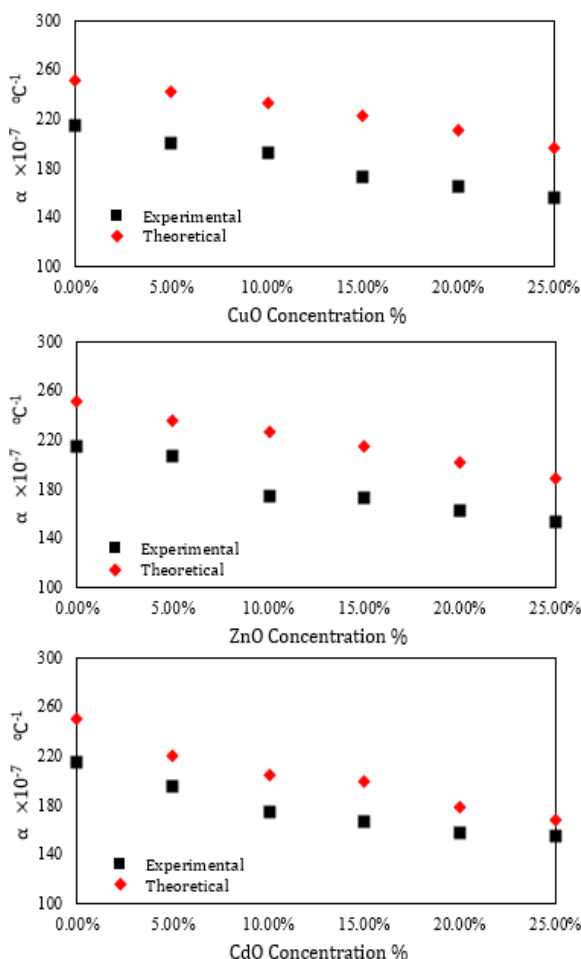


Fig. 3 The relation between MO mol % and both the glass experimental and theoretical thermal expansion coefficient.

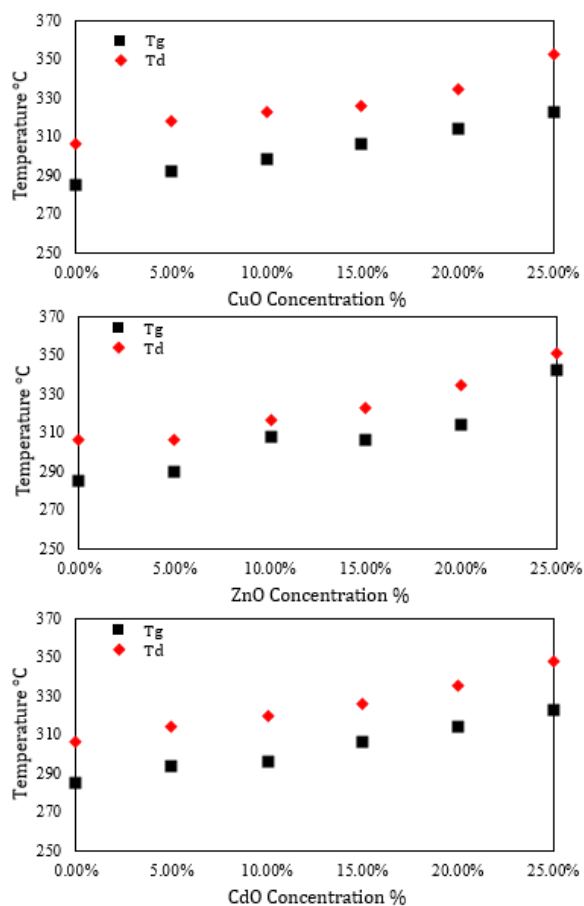


Fig. 4 The relation between MO mol % and both the glass transition temperature T_g and the softening temperature T_d of the three studied glass systems.

Such suggested changes in the covalent character of the lattice bonds supported by the observed increase in the values of both the packing density (V_t) and the dissociation energy (G_i), while the corresponding heat capacity (C_p) decreased as shown in Fig. 5 (a, b, and c) respectively. Now as these three parameters beside the density are functions of compaction i.e., bonding strength and crosslink density, and are included in M-M formula for the theoretical estimation of α_{th} , one can consider the relative lower experimental α_{exp} values reveals that, the real matrix compaction is higher than theoretically estimated one. This again support the suggested changes in the degree of bonds covalency and density of cross link in agreement with [33]. Such suggested higher real matrix compaction is in resonance the negative values of the density deviation $\Delta\rho$ ($\rho_{th} - \rho_{exp}$) as performed in Table [2].

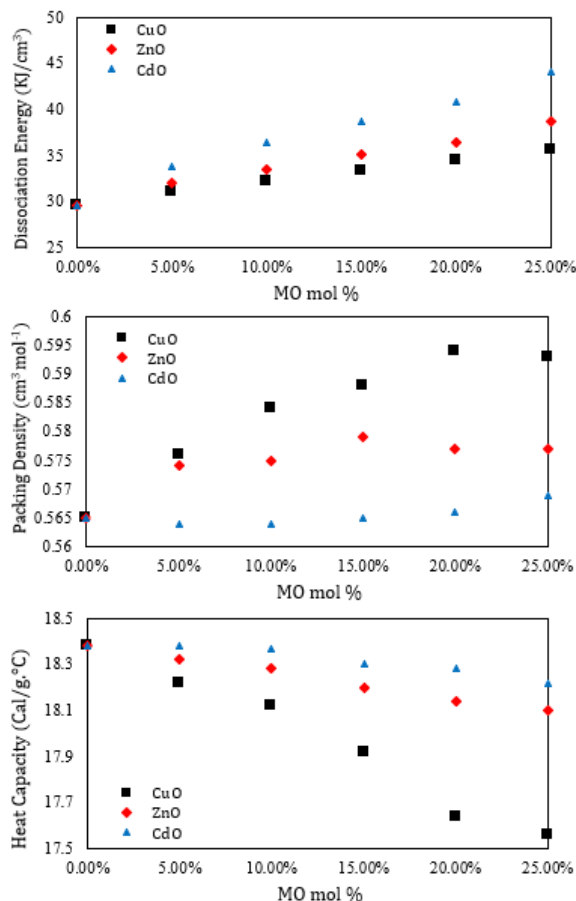


Fig. 5 The relation between MO mol % and (a) the dissociation energy (b) the packing density, (c) the heat capacity

Table 2

The experimental and calculated of the studied glasses

Composition	Density (gm/cm ³)	
	Experimental	Theoretical
P ₂ O ₅ -Na ₂ O-MO		
G00	2.447	2.304
G11	2.538	2.368
G12	2.619	2.436
G13	2.689	2.505
G14	2.761	2.578
G15	2.811	2.654
G21	2.528	2.366
G22	2.587	2.428
G23	2.655	2.493
G24	2.704	2.561
G25	2.758	2.631
G31	2.547	2.417
G32	2.641	2.534
G33	2.743	2.649
G34	2.846	2.772
G35	2.976	2.899

4. Conclusions

In the current study, three types of metal oxides CuO, ZnO, or CdO were used as divalent modifier with different composition fractions to replacement the monovalent modifier Na₂O in Sodium Phosphate Glass System. From the experimental work, the increasing of density, transition temperature T_g and softening temperature T_d, it is a clear indication of the increasing of the crosslinking of the system. Theoretically, the replacement of the monovalent oxide Na₂O by the divalent oxide will increase the crosslinking and decrease of the non-bridging oxygen atoms. All of this agree with IR data. Moreover, replacing 25 moles % in the binary(55P₂O₅-45Na₂O) by equivalent mole ratio from each of CuO, ZnO, or CdO reduces the expansion coefficient by about 25 % and increase both the glass transition temperature T_g, and softening temperature T_d by about 25 %.

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