Some Physical, Chemical and Electrical Properties of the Polyphosphate $LiM^{II}_2(PO_3)_5$ (M=Cu, Zn, Cd, Ba, Pb) Glasses

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Abstract: The polyphosphate glasses with the general formulae $LiM^{II}_2(PO_3)_5$ (M=Cu, Zn, Cd, Ba, Pb) were prepared by using the melt-quench technique. They are characterized by X-ray diffraction (XRD), density measurements and differential thermal analysis (DTA). The results show that the glass transition temperature and molar volume increase nonlinearly with increasing of the bivalent cation atomic weight in the sequence Cu<Zn<Cd<Pb<Ba. Measurements of the ionic conductivity were made in the frequency range of 20 - 10^6 Hz and the temperature range 25 - 300°C. It is found that the Conductivity of the $LiZn_2(PO_3)_5$ and $LiCu_2(PO_3)_5$ glasses are much lower than those of the other samples. The differences in conduction properties are discussed based on the structural and atomic properties of the glass components.

Keywords: Phosphate, glasses, chemical durability, electrical conductivity.

1. INTRODUCTION

Phosphate glasses are of potential interest because of their high thermal expansion coefficient [1] and low melting temperature relative to silicate glasses [2]. However, their relatively poor chemical durability [3-4] to water limits their practical use. Recently, phosphate glasses have been developed for a variety of specialty applications [5].

Phosphate glasses can be made with a range of structures, from a cross-linked network tetrahedra (vitreous P_2O_5) to polymer-like metaphosphate chains of tetrahedra to 'inevert' glasses based on the O/P ratio as set by glass composition. The addition of a modifying oxide to P_2O_5 results in the creation of non-bridging oxygens (NBO) at the expense of bridging oxygens (BO).

Several properties and data on phosphate glasses had been presented elsewhere [5]. Among phosphate families, metaphosphate is the less complicated glass structure. It contains tetrahedra with two bridging oxygens that form chains and rings. The chains and rings are attached by ionic bonds between various metal cations and the non-bridging oxygens. The lithium ions in metaphosphate glasses are tetrahedrally coordinated [6].

The present work was undertaken for the purpose of determining the relative importance of some bivalent cations to the physical and chemical properties of the polyphosphate $LiM^{II}_2(PO_3)_5$ (M=Zn, Pb, Cu, Ba, Cd) glasses. We will relate the obtained results to modification in the phosphorus chemical environments caused by cations with different counter ion potentials.

2. EXPERIMENTAL PROCEDURE

Chemical reagents Li_2CO_3, CuO, ZnO, $BaCO_3$, PbO, CdO and $NH_4H_2PO_4$ were used as starting materials. The vitreous samples were prepared by mixing and grinding together appropriate amounts in an agate mortar. The platinum crucible containing the mixture was initially heated in a furnace at 360°C for 12 hours to remove NH_3 and CO_2 gases. Then, the temperature is increased to 900°C for 15 min before quenching the melt. The molten glasses were then quenched to room temperature under air atmosphere.

Powder X-ray diffraction was used to examine all the as-quenched glasses to confirm their amorphous state. Differential thermal analysis was carried out by a Seiko-DTA analyzer on powder samples at a heating rate of 10 °C min^{-1} in order to determine the glass transition temperature (Tg). Density measurements were carried out at room temperature, using

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E-ISSN: 2409-5826/14

Table 1: Some Physical And Chemical Parameters Of The Glasses

formula	ρ (g/cm^3)	V_m (cm^3/mol)	V_c (cm^3/mol)	ΔV (cm^3/mol)	$D_R \times 10^5$ (g/(cm^2.min))	$\sigma \times 10^8$ (Ω^{-1}.cm^{-1})	s	β	ΔE_a (eV)	ΔE_f (eV)
$LiBa_2(PO_3)_5$	3.49	38.96	41.31	2.35	1.76	0.70	-	-	0.38	0.37
$LiPb_2(PO_3)_5$	4.72	39.05	40.63	1.58	2.18	0.66	-	-	0.43	0.42
$LiCd_2(PO_3)_5$	3.3	36.93	37.51	0.58	1.53	0.53	0.54	0.68	0.53	0.52
$LiCu_2(PO_3)_5$	3.33	36.04	36.14	0.1	2.05	0.41	0.53	0.65	1.08	1.01
$LiZn_2(PO_3)_5$	2.91	36.69	37.04	0.35	1.17	0.39	0.51	0.63	1.3	1.28

Archimedes' method with using CCl_4 as an immersion liquid. The molar volume (V_m) was calculated using the formula: $V_m = \sum y_i M_i / \rho$, where y_i is the molar fraction of the oxide (i) and M_i is its molecular weight. The dissolution rate of the glasses in water was evaluated from the weight loss of samples immersed in deionised water at 90 °C for 2 days. Duplicate measurements were made for each glass and the average dissolution rate (D_R), normalized to the glass surface area and the corrosion time, was calculated from the weight loss using the following equation: $D_R = \Delta W(g)/[A(cm^2) \times t(min)]$, where *A* is the surface area (cm^2) of the sample and *t* is the time (min) that the sample was immersed in the test solution at 90 °C. The weight loss (ΔW) is $W_i - W_t$, where W_i is the initial weight and W_t is the weight of the same sample after a time t in solution at 90 °C. The electrical measurements of the $LiM^{II}_2(PO_3)_5$ (M=Cu, Zn, Cd, Ba, Pb) glasses are carried out using a LCR- meter HP4284. The measurements were realized in the frequency range 20–10^6 Hz and over thermal 298-573K range.

3. RESULTS AND DISCUSSION

3.1. Density and Molar Volume

The measured densities for the different vitreous compositions $LiM^{II}_2(PO_3)_5$ (M=Cu, Zn, Cd, Ba, Pb) are shown in Table **1**. Depending on the bivalent cation, the density value lies between 2.9 and 4.7. Presenting these data as a function of the metal atomic number Z (Figure **1**), one can see that the density increases with the atomic weight (or Z). The molar volume of the glasses is listed in Table **1** and its variation according to the atomic weight of the bivalent metals is shown in Figure **1**. It is seen that the molar volume increases with the ionic radius of the bivalent metal. Based on the molar weight of the M^{2+} cation, the observed increase of the density with the atomic number Z is understandable as the lighter oxide is replaced by the heavier one.

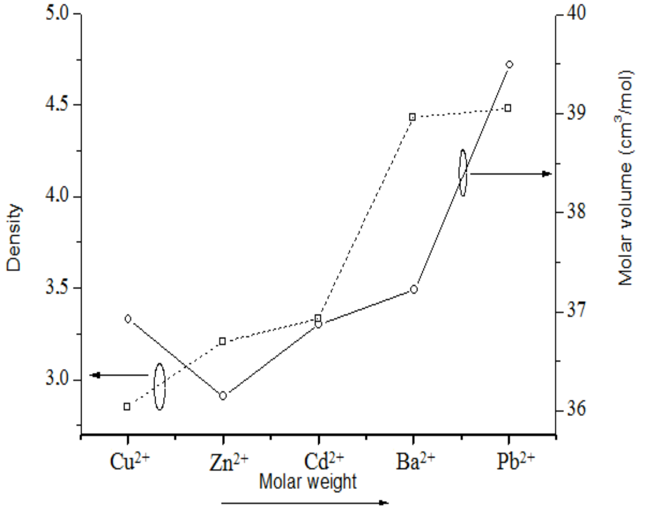

Figure 1: Compositional dependence of density and molar volume of the $LiM_2(PO_3)_5$ glasses.

Moreover, the observed variations of density and molar volume could be related to the nature of the chemical bonds formed in the glassy network. From the chemical formulae of the glasses it is understood that their network is composed mainly by the metaphosphate structural units (since the ratio O/P=3). The phosphorous nearest-neighbor environment in each glass is nominally the same, i.e, two bridging oxygens and two non-bridging oxygens per P. The next-nearest-neighbor environment of the phosphorous could include the metal cation (P-O-M). Now, any change of oxygen bonding in the glass network, such as the replacement of bivalent ion by an alkaline earth cation in P-O-M bonds, changes some physical properties of the glasses (such as density and glass transition temperature) since they are influenced by the oxygen bond strength in the glass forming network [2]. Indeed, in glass the parameter that is most commonly used to classify metal cations is Dietzel's field strength [7-8]. This parameter measures the electrostatic energy between the metal cations and the neighboring oxygen atoms. Using atomic properties of each bivalent cation we found that the bond strength of M-O link increases in the order: Ba(0.26)<Pb(0.28)<Cd(0.38) <Cu(0.39)<Zn(0.45). This sequence indicates that the strength of the antagonist P-O bond in the P-O-M linkage increases in the order: Zn<Cu<Cd<Pb<Ba. Therefore, one can state that the density and the P-O bond strength are correlated.

The corresponding molar volume for ideal close packing network for the glasses (V_c) is calculated (Table **1**) by considering the network formed by the closeness packing of the oxides Li_2O, MO, and P_2O_5. This is done simply by summing up the relative molar volumes of the crystalline Li_2O (14.84 cm^3), MO: M=Zn (14.52 cm^3), Cu (12.26 cm^3), Ba (25.18 cm^3), Cd (15.7 cm^3), Pb (23.5 cm^3) and P_2O_5 (59.5 cm^3). These values are both listed in Table **1** for comparison. The large difference (ΔV) between the experimental molar volume and the molar volume for ideal close packing (Table **1**) shows that all the bivalent Cu^{2+}, Zn^{2+}, Ba^{2+}, Pb^{2+} and Cd^{2+} cations could reticulate the network of the glass by contracting the arrangement of oxygen ions. From this difference, one can state that the Pb^{2+} cation is the most efficient in packing the structure network.

3.2. Chemical Durability

The dissolution rate in deionized water at 90°C for $LiM_2(PO_3)_5$ (M= Ca, Cu, Zn, Cd, Ba, Pb) glasses are given in Table **1**. The results show that the dissolution rate increases in the order $Pb^{2+}>Cu^{2+}>Ba^{2+}>Cd^{2+}>Zn^{2+}$. The D_R value is the lowest for $M=Zn^{2+}$ while it is the highest for $M=Pb^{2+}$. The comparison of the dissolution rate of $LiPO_3$ glass and $LiM_2(PO_3)_5$ glasses shows that $D_R(LiPO_3)>D_R(LiM_2(PO_3)_5$ whatever the bivalent cation. According to the fact that the $LiM_2(PO_3)_5$ glasses could be obtained from the combination of $LiPO_3$ and MO components, the observed decrease in the dissolution rate of $LiM_2(PO_3)_5$ suggests that doping $LiPO_3$ by MO oxide increases the cross-link density between the (PO_4) units. Compared to the lithium ions, divalent cations, like Zn^{2+}, Cd^{2+}, Ba^{2+}, Cu^{2+}, Pb^{2+}, can form stronger iono-covalent cross-links between the non-bridging oxygens of two (PO_4) chains which decrease the dissolution of the glasses. This type of metal chelate structure between (PO_4) chains has been reported elsewhere [5,9-11].

The Pb- and Cu- doped $LiPO_3$ glasses have a dissolution rates which are close to each other (see Table **1**). In the same way, the Zn-, Cd- and Ba-based glasses have a similar dissolution rate value. The D_R for glasses containing Zn and Cd is lower than that for the corresponding sample containing Pb due probably to the greater field strength of the Zn^{2+}, Cd^{2+} ions as compared to that of Pb^{2+} ion. On the contrary, the D_R of Cu^{2+}-glass is higher than that of Ba^{2+}-glass thought the field strength of the copper ion is the lower. Therefore, the field strength of the metal cation couldn't explain the over all variations of the dissolution rate of the glasses.

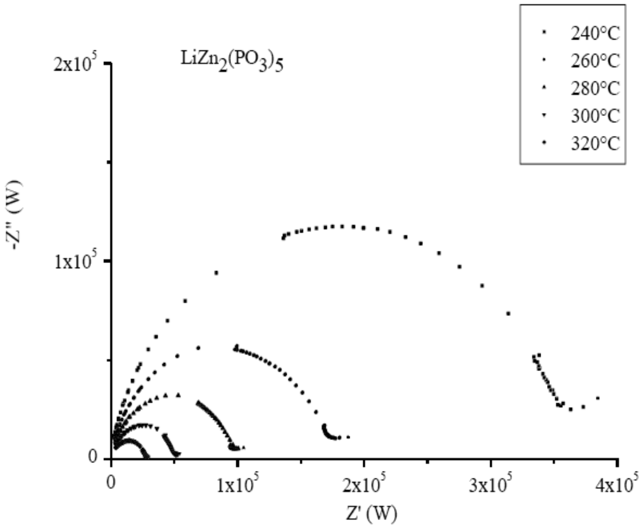

Figure 2: Typical impedance plots for $LiZn_2(PO_3)_5$ glass at different temperatures.

3.3. Electrical Conductivity

The impedance plots of all the samples were found to exhibit semicircles. A typical impedance plots for $LiZn_2(PO_3)_5$ glass at different temperatures is shown in Figure **2**. The dc conductivity was calculated by taking the intersection points of the semicircle on real axis. Variations of the dc conductivity as a function of temperature for $LiM_2(PO_3)_5$ ($M^{2+}=Zn^{2+}$, Cu^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+}) glasses are shown in Figure **3**. For each glass, single linear variation of log (σT) versus 1000/T has been observed and the conductivity dependence temperature exhibits consequently an Arrhenius behaviour $\sigma=\sigma_0 \exp(-E_a/kT)$, where σ_0: pre-exponential factor, Ea: activation energy. The calculated activation energy for the glasses is found to depend on the nature of the bivalent oxide present in the glass (Table **1**). The conductivity of the glasses is due to the presence of lithium ions as charge carriers. The analysis of the conductivity values of the glasses showed that those of Li^+ in lead- and barium-glasses are the highest. The values of the conductivity for copper and zinc based glasses are the lowest. Even though, there is not a direct dependence of the conductivity on the bivalent ion radius, it seems that the higher the radius of the

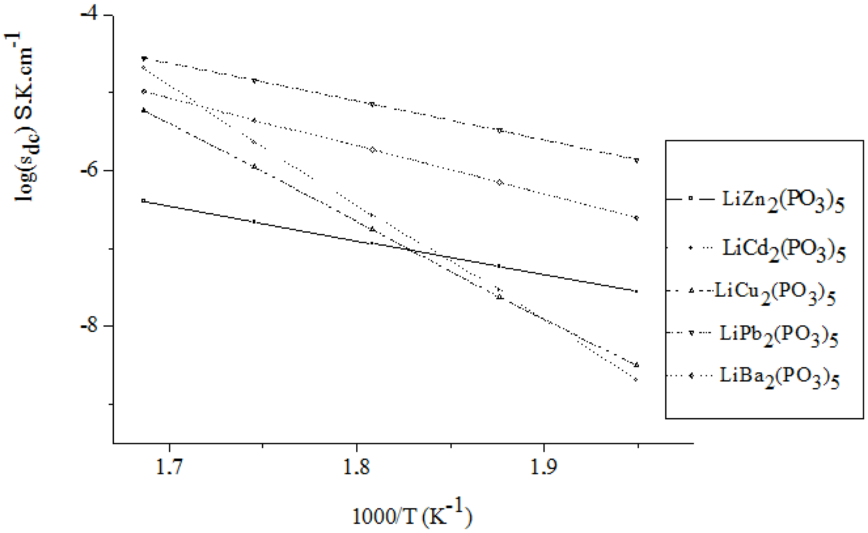

Figure 3: Variation of log($T\sigma_{dc}$) versus 1000/T for $LiM_2(PO_3)_5$ glasses (M=Cu, Zn, Cd, Pb, Ba).

bivalent ion is, the higher the conductivity of the glass is. When a larger cation is introduced in the glass matrix, it favors the formation of an open network which in turn enhanced the migration of Li^+ ion from site to site.

A typical plot of ac conductivity as a function of frequency for $LiZn_2(PO_3)_5$ glass is shown in Figure **4**. The ac conductivity exhibits a change of slope to higher values as the frequency is increased. A similar behaviour is observed for the other glasses. A nearly flat portion at lower frequencies is associated with the *dc* conductivity. The *ac* conductivity has been analyzed using Almond-West type power frequency dependence of conductivity [12-13]: $\sigma(\omega)=\sigma_{dc}+A\omega^s$, where σ_{dc} is the frequency independent *dc* conductivity, $\omega=(2\pi f)$ is the angular frequency. It can be seen from Figure **4** that as temperature decreases, σ becomes a strong function of frequency at the high frequency end, and the *dc* plateau eventually becoming unobservable.

The power law exponent (*s*) obtained from power law fit for each glass is listed in Table **1**. It is found that (*s*) values are temperature independent and significantly lower than unity, and generally lie in a narrow range of 0.5–0.6. These values of the power low exponent for the glasses under study are in agreement with the Jonscher assumption [14].

The electrical modulus formalism has been used to analyze the conductivity data. Typical plots of the normalized M''/M''_{max} of the complex modulus versus

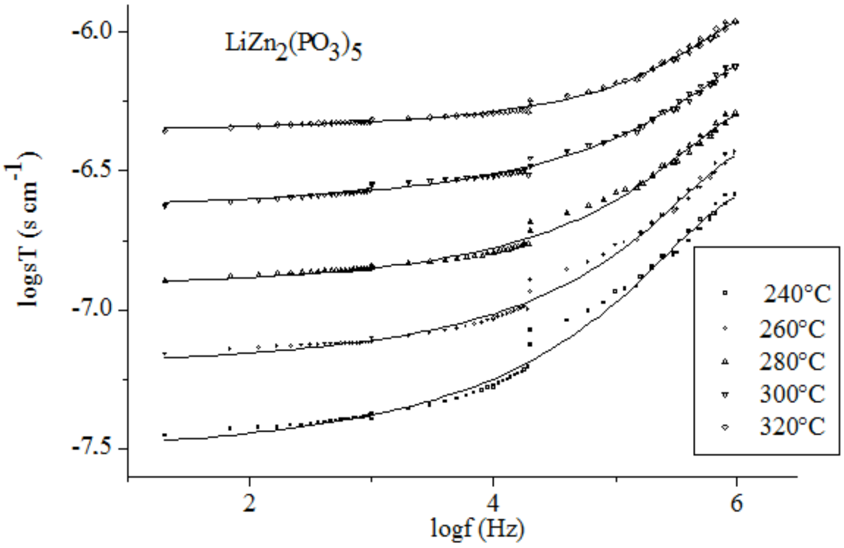

Figure 4: Variation of log ($T\sigma_{dc}$) versus frequency for the $LiZn_2(PO_3)_5$ glass at different temperatures. A line corresponds to the power law fitting data.

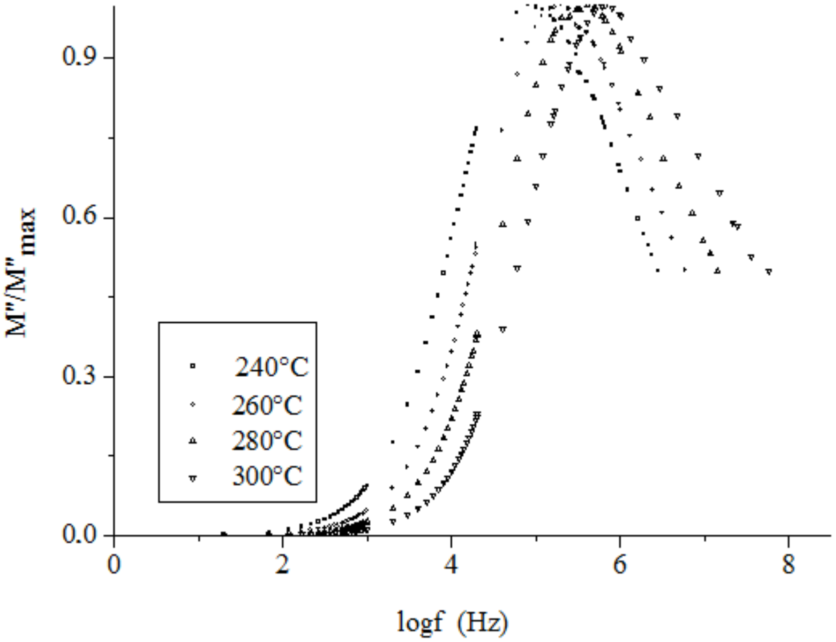

Figure 5: Typical plots of the modulus (M") variation with frequency for $LiCu_2(PO_3)_5$ glass at different temperatures.

log (f) are given in Figure **5** at various temperatures for the $LiCu_2(PO_3)_5$ glass. It is evident from the latter that M" values exhibit characteristically asymmetric peaks. The asymmetric M" peak originates from the nature of the relaxation behaviour. The maximum of the relaxation peak is characterized by a relaxation frequency (f_0). Figure **5** shows that the M" peak shifts systematically towards higher frequencies with increasing temperature. M" peaks are reasonably well fitted using Kohlrausch–Williams–Watts (KWW) or stretched exponential function for relaxation [15-16]: $\Phi=\Phi_0[-(t/\tau)^\beta]$, where τ is the characteristic relaxation time and β is the stretched exponent and its value lies between 0 and 1. The relaxation time τ_p was calculated using the relaxation frequency (ω_p); $\tau_p=1/\omega_p$. The relaxation time also systematically shifts to higher values with increasing temperature. The spectra of the normalized modulus, M''/M''_{max}, are non-symmetric in agreement with the non-exponential behaviour of the Kohlrausch function [15-16]. The full width at the half maximum (FWHM) of the M''/M''_{max} spectrum is wider than the breadth of a Debye-peak (1.14 decades) and it results in a value of β=1.14 /FWHH for the Kohlrausch parameter. Values of β relative to the glasses studied are given in Table **1**. The obtained value of β<1 can be attributed to the existence of a distribution of relaxation times inside the glasses. Such an interpretation is known to occur in the electronic glasses [17] as well as in the ionic ones [18]. When the temperature increases, the modulus peak maxima shifts to higher frequencies. The frequency dependence of M", shows that the frequency of the M" maximum shifts in frequency with about the same activation energy (ΔE_f) as *dc* conductivity (ΔE_σ), see Table **1**. This result suggests that the mechanism of the transport in these glasses is probably due to a hopping process [19]. Furthermore, in the temperature range studied the *β* exponent is temperature independent.

The *β* values which are smaller than unity as obtained from KWW fits of modulus spectra (Table **1**) are consistent with the dispersion of the *ac* conductivity in the glasses under study. Such dispersion can be influenced by both disorder of the glassy network and interactions between charge carriers [19].

CONCLUSION

Some physical and chemical properties of the $LiM_2(PO_3)_5$ M^{2+} (Cu, Zn, Cd, Pb, Ba) such as density, electrical conductivity and chemical durability have been determined and their compositional dependencies were investigated. The following conclusions can be drawn from this work: (i) the molar volume and the density of the glasses increases in the order Cu<Zn<Cd<Ba<Pb; (ii) the rate dissolution increases in the sequence order Ba<Zn<Cd<Pb<Cu; (iii) the ionic conductivity is influenced by the nature of the bivalent metal ion M^{2+} (Cu, Cd, Ba, Pb, Zn). It is found that the glasses corresponding to the compositions $LiM_2(PO_3)_5$ (M^{2+}= Ba, Pb) present the high ionic conductivity.

ACKNOWLEDGEMENTS

The authors are grateful to the Swedish Research Council and the FCT-CNRST committee for the financial support of this work.

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Received on 31-10-2014 Accepted on 10-11-2014 Published on 09-01-2015

DOI: http://dx.doi.org/10.15377/2409-5826.2014.01.02.3