Journal of Non-Crystalline Solids 390 (2014) 51–58

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

The properties and structure of zinc magnesium phosphate glasses

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ARTICLE INFO

Article history:
Received 26 December 2013
Received in revised form 18 February 2014
Available online 16 March 2014

Keywords:
Zinc phosphate glasses;
Zinc magnesium phosphates;
Thermal properties;
Divalent cations;
Electron configurations

ABSTRACT

Zn–Mg-phosphate (ZMP) glasses, including those with the nominal molar compositions $(50-x)ZnO\ xMgO\ 50P_2O_5$ $(0 \geq x \geq 50)$ and $(60-y)ZnO\ yMgO\ 40P_2O_5 (0 \geq y \geq 60)$, were prepared and properties such as density, refractive index, coefficient of thermal expansion and glass transition temperature (T_g), were measured. The glass transition temperature increases by 100–150 °C and the room temperature dissolution rates in water decrease by 1–2 orders of magnitude when MgO replaces ZnO while maintaining a constant P_2O_5 content. Glass structures were characterized by Raman spectroscopy and there were no significant changes in the phosphate anion distributions when MgO replaces ZnO. The significant changes in properties cannot be explained by a simple cation field strength argument since Mg^{2+} and Zn^{2+} have similar sizes; instead, the effect of 3d electrons on the nature of the bonds between Zn^{2+} ions and non-bridging oxygens on the phosphate tetrahedra must be considered.

1. Introduction

Zinc phosphate glasses have been developed for use as LED light sources [1], and as substrates for optical waveguides written by f-sec lasers [2–5]. These glasses possess a UV-edge below 400 nm, which is useful for some optical applications [6]. Zinc phosphate glasses also tend to have greater coefficients of thermal expansion with low processing temperatures, which make them useful as sealing glasses [7,8].

A drawback to the use of binary zinc phosphate glasses is their susceptibility to chemical attack because of the ease of hydrolysis of the P–O–Zn bonds [9]. It is known that the incorporation of additional oxides can improve the chemical durability of phosphate glasses; one in particular is magnesium oxide which has been shown to reduce corrosion rates in aqueous solutions of zinc phosphate glasses, presumably due to the formation of more chemically resistant P–O–Mg bonds [10].

The properties and structures of binary zinc [9,11–24] and magnesium phosphate [14,18,25–30] glasses have been studied. Both the $ZnO–P_2O_5$ and the $MgO–P_2O_5$ binary systems have been classified as anomalous because of discontinuities in composition–property trends near the metaphosphate (50 mol% P_2O_5) composition [26]. Glasses from the $ZnO–P_2O_5$ binary have a minimum in T_g and CTE near 60 mol% ZnO [13], a behavior that is not found in the $MgO–P_2O_5$ system [19].

The addition of either ZnO or MgO to P_2O_5 results in systematic changes in properties that can be related to changes in the phosphate network structure. Phosphate anionic structures can be described using the Q^n-terminology, where 'n' represents the number of bridging oxygens on a phosphate tetrahedron [31]. For example, changes in the types of phosphate tetrahedra with the addition of MeO (where Me = Zn, Mg) can be described by the reaction:

$$2Q^n + MeO \rightarrow 2Q^{n-1}. \quad (1)$$

Binary phosphate glasses with increasing MeO-content (increasing O/P ratio) have shorter average phosphate anion lengths as nonbridging oxygens replace bridging oxygens on the P-tetrahedra. Evidence for these structural changes can be found in many spectroscopic studies, including Raman and/or infrared (IR) spectroscopies [11,25,28] and ^{31}P nuclear magnetic resonance (NMR) spectroscopy [20,32–34].

Khor and colleagues have described the effects of the composition of ternary zinc–magnesium-phosphate (ZMP) glasses on the optical, dielectric and physical properties [6,10,29,30,35]. They showed that the replacement of P_2O_5 by MgO decreases the aqueous dissolution rates of zinc phosphate glasses [10], although it is unclear if this improvement in chemical durability is due to the replacement of P–O–Zn bonds by P–O–Mg bonds, or to the overall decrease in the P_2O_5 content [9,36,37].

The goal of the present study is to determine the effects of substituting MgO for ZnO, while maintaining a constant P_2O_5 content (constant O/P ratio), on the properties and structures of zinc phosphate glasses, including compositions originally developed as substrates for femto-second processing [2]. A constant O/P ratio fixes the average chain length of the phosphate units in the structure [31] and so property changes can then be related to the nature of the P–O–Me bonds that link neighboring anions. The intent of this paper is to report the glass-forming ranges of several series of $ZnO–MgO–P_2O_5$ compositions, to describe the property trends due to the systematic replacement of ZnO by MgO, and to relate those property trends to the nature of the glass structures.

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.02.010
0022-3093/

2. Experimental

The glasses were prepared by mixing appropriate amounts of MgO (Alfa Aesar, 96%), $NH_4H_2PO_4$ (ACS, 98.0% — Alfa Aesar), and ZnO (reagent grade, ≥99.0% — Sigma Aldrich), calcining the batches in an alumina crucible for ~15 h. at 500 °C, then melting the batches between 1000 and 1500 °C for approximately 2 h in air. Melts were quenched on copper plates, and these glasses were remelted in the alumina crucibles using similar conditions to improve glass homogeneity. The final glass samples were obtained by pouring the melts into a steel mold (10 mm in diameter and 2.5 cm tall), or splat quenching between copper plates if necessary, and annealing near T_g for approximately two hours, before slowly cooling to room temperature.

The density of each bubble-free glass was measured using Archimedes' method with distilled water as the buoyancy liquid. Three samples of each glass were measured and the standard deviation is reported as the experimental uncertainty. The molar volume (MV) was calculated by dividing the density of each glass by the molecular weight, calculated from analyzed glass compositions. The compositions of polished samples were calculated from cation ratios determined using energy dispersive spectroscopy (EDS, Helios NanoLab 600 FIB/FESEM with an Oxford EDS attachment). The compositional uncertainty was determined by analyzing three or more areas of at least three different samples of the same composition and was found to be a maximum of ±0.6 mol% for each oxide [Table 1]. The glasses will be described using their nominal compositions, unless otherwise noted.

Differential thermal analysis (DTA, Perkin-Elmer DTA7) was used to determine the glass transition temperature (T_g) by heating 30–40 mg of glass powder (<75 μm) in an open, alumina crucible at a rate of 10 °C/min in a nitrogen atmosphere; the onset temperatures for the glass transition were determined with the accompanying software and the estimated uncertainty is ±5 °C.

The refractive indices (n) were measured using a prism coupler (Metricon model 2010/M) at 632.8 nm on samples that were ~1 mm thick and polished to a 1 μm finish (diamond paste, Allied High Tech); the uncertainty of these measurements is ±0.0004.

The dilatometric softening temperature (T_d) and the coefficient of thermal expansion (CTE) were determined using an Orton dilatometer (Model 1600D) on cylindrical samples approximately 2.54 cm in length, heated at a rate of 10 °C/min in air. The T_d is established as the maximum of the dilatometric data with a reproducibility of ±5 °C. The CTE is reported as the linear slope of data from 200 to 400 °C and these measurements were reproducible to ±0.2 ppm/°C.

Weight loss measurements from bulk glasses immersed in deionized (DI) water at 21 °C for up to 48 h were made to determine relative chemical durability. Polished disks (10 mm in diameter, 1 mm thick, 5 μm finish) were rinsed with acetone and dried before testing. A constant sample surface area (SA)-to-solution volume ratio of 0.035 cm^{-1} was used for each experiment. Samples were removed periodically from the polypropylene containers used for the corrosion tests, dried and weighed, and then returned to the original solution. Three samples were tested for each condition and the average weight loss and standard deviation are reported. Dissolution rates are reported as the linear slope of the weight loss data over the entire 48 h of each experiment.

Raman spectra were collected from a polished sample of each glass using a Jobin–Yvon micro-Raman spectrometer with a 632.8 nm He–Ne laser (17 mW) as the excitation source.

3. Results

3.1. Glass-forming region

The as-batched and measured compositions of the glasses are given in Table 1 and are shown in Fig. 1 along with other compositions melted to confirm the glass-forming region. Small amounts of alumina (<5 mol%) were dissolved into the glasses because of reactions between the melts and the alumina crucibles (Table 1). The binary magnesium phosphate glass with an intended O/P ratio of 3.25 had the largest alumina content (4.7 mol%) because of the high melting temperature used (1500 °C). P_2O_5-loss from the melts was limited and so compositions are grouped by their nominal O/P ratios. Glasses with an O/P ratio below 2.8, in the ultraphosphate region, were not prepared in this study. Studies of binary compositions prepared by traditional splat-quenching methods produced glasses with up to ~71 mol% ZnO [11,19,21] and ~65 mol% MgO [18,25,27,29]; these compositions coincide with the glass-forming ranges found in this work (Fig. 1).

The binary compositions with 70–80 mol% MgO were melted below 1500 °C, but the melts had very low viscosities and crystallized immediately upon quenching. The use of roller quenching has been shown to push the glass forming region of binary phosphate glasses with both ZnO [17] and MgO [28] up to 80 mol% and these reported roller-quenching limits of glass formation for the respective binaries are also shown in Fig. 1.

3.2. Physical and thermal properties

The densities of ZMP glasses with O/P ratios = 3.0 and 3.25 are shown in Fig. 2a and their molar volumes are shown in Fig. 2b. Also shown are the respective properties of glasses with similar compositions reported in the literature. For glasses with similar O/P ratios, the replacement of ZnO by MgO systematically decreases the density but has no significant effect on molar volume. Glasses with greater P_2O_5 contents (lower O/P ratios) have lower densities and greater molar volumes. Fig. 3a and b shows that the glass transition temperatures (T_g) and dilatometric softening temperatures (T_d), respectively, increase systematically with the replacement of ZnO by MgO, and do not vary significantly with O/P ratio. Fig. 4 shows that there is a small increase in the coefficients of thermal expansion (CTE) as a function of

Table 1
Nomenclature and compositions of the zinc magnesium phosphate glasses.

Designation (mol%)	Batched compositions (mol%)	Measured analyzed compositions [mol%]				
ZMP_mol% MgO_O/P	ZnO–MgO–P_2O_5 [O/P ratio]	ZnO (±0.6)	MgO (±0.5)	P_2O_5 (±0.3)	Al_2O_3 (±0.2)	O/P
ZMP_0_3.0	50–0–50 [3.0]	48.5	0	49.4	2.1	3.05
ZMP_13_3.0	37.5–12.5–50 [3.0]	37.3	12.0	48.9	1.8	3.06
ZMP_25_3.0	25–25–50 [3.0]	25.0	23.4	50.0	1.6	3.03
ZMP_38_3.0	12.5–37.5–50 [3.0]	13.1	35.0	51.1	0.9	3.00
ZMP_50_3.0	0–50–50 [3.0]	0	46.1	53.1	0.8	2.96
ZMP_0_3.25	60–0–40 [3.25]	60.5	0	36.7	2.8	3.44
ZMP_15_3.25	45–15–40 [3.25]	38.7	19.1	41.2	1.0	3.24
ZMP_30_3.25	30–30–40 [3.25]	30.3	27.8	41.3	0.6	3.23
ZMP_45_3.25	15–45–40 [3.25]	15.5	42.0	41.6	0.9	3.22
ZMP_60_3.25	0–60–40 [3.25]	0	55.5	39.8	4.7	3.37