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Local structure characterization and thermal properties of P₂O₅–MgO–Na₂O–Li₂O glasses doped with SiO₂



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ABSTRACT

Pure and SiO₂ doped P₂O₅–MgO–Na₂O–Li₂O glass has been prepared by the traditional melt quenching and heat treatment techniques. Via X-ray diffraction (XRD) patterns, all the samples are proved to be amorphous. Field emission scanning electron microscopy (FESEM) and macroscopic observation show that all the samples are homogeneous glasses and no phase splitting phenomenon. Fourier transform infrared (FTIR) spectrum shows that the amount of non-bridging oxygen decreases and the polymerization degree of the glass network structure increases after introducing SiO₂ into glasses. Meanwhile, density and molar volume gradually decline with the increasing of SiO₂. The glass transition (T_g) and the first crystallization temperature (T_c) indicates thermal stability increases in SiO₂ added glasses.

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1. Introduction

Phosphate glasses have more advantages than borate and silicate glasses because of their lower melting temperatures, higher ultraviolet transmission, higher thermal expansion coefficients [1] and biocompatibility [2–5]. However, their utilization is often limited by their poor chemical durability [6,7]. The structure of amorphous P_2O_5 consists of three-dimensional corner sharing [PO₄] tetrahedra, which is decorated with the center asymmetric structure of phosphorus oxygen double bond (P=O). Many studies have shown that the chemical durability of phosphate glasses could be improved by adding network modifiers like CuO [8], MgO [9,10], Ag₂O [11], etc. The addition of network-modifying oxides could lead to depolymerising of long phosphate chains, as well as replacing of P=O-P bonds by more chemically durable bonds, and then the three-dimensional network of metaphosphate chain generates along with the generation of non-bridging oxygen ions [12].

It is well known that, SiO_2 is a sort of conventional glass network former, and has received a remarkable attention due to wide application in electronic glass fabrics, glass fiber-reinforced polymer matrix composites [13] and optical lenses. Meanwhile, Aluminoborosilicate glasses also have attracted considerable attention in recent decades. R. K. Brow et al. [14] reported the effects of P_2O_5 on the chemical durability for aluminoborate and aluminoborosilicate glasses.

However, researches related to the effects of network former SiO₂ on the structural and thermal properties in phosphate glasses are rare and incomplete. Our group has been committed to research low dielectric and corrosion resistant fiberglass many years our group has been committed to research low dielectric and corrosion resistant fiberglass many years. This paper intends to discuss the structural and thermal properties of pure and SiO₂ doped P₂O₅–MgO–Na₂O–Li₂O glasses via XRD, density and molar volume, FTIR spectra and DTA. The purpose is to explore the local structure characterization and thermal properties of SiO₂ doped phosphate system glasses, in order to further develop a good fiberglass that combines the advantages of silicate and phosphate. At the same time, we hope our work could provide some reference for the future research of related field.

2. Experimental

In this work, a particular glass system $(60P_2O_5-10MgO-15-Na_2O-15Li_2O)$ was chosen as basic formula. Detailed samples composition was shown in Table 1. Glass samples were all prepared by the normal melt quenching technique. Appropriate amount of



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analytical grade reagents of P₂O₅, MgO, Na₂O, Li₂O and SiO₂ were thoroughly mixed and melted in platinum crucible at 1450 °C for about 2h until the bubble-free liquid was obtained. Besides, samples were covered to avoid the volatility of P₂O₅. Then the resultant melts was poured into a brass mold and annealed at 400 °C for about 3h subsequently, after which they cooled slowly to the room temperature with a rate of about 1 °C/min. After that, a part of samples was ground into powder, while the rest was processed into several rectangular bulks(about 10 mm × 10 mm × 5 mm).

Density(ρ) measurements were carried out at room temperature(23.5 °C, the density of distilled water is 0.99744 g/cm³ under this temperature) using the Archimedes method with distilled water as the immersion fluid. For each glass, three samples were measured to get the average density for accuracy. The relative deviation in these measurements were±0.002 g/cm³.

X-ray diffraction (XRD) was carried out with the Bruker D8 ADVANCE diffractometer. The spectra was recorded from 10° to 80° at scanning rate of $0.2^{\circ} 2\theta$ /min.

Field emission scanning electron microscopy (FESEM) images was obtained from bright and clean raw surface of samples by the FEI QUANTA FEG250 field emission scanning electron microscope from America with a magnification of 8000 times.

Fourier transform infrared (FTIR) spectra for the glasses was obtained by using a Nicolet 380 FTIR spectrometer in the frequency range of $2000-400 \text{ cm}^{-1}$ and potassium bromide (KBr) pellet method. All the glasses were prepared as tablets by pressing a mixture of approximate 2 mg glasses powder and 200 mg anhydrous KBr powder. The resolution is better than 0.5 cm⁻¹ and the spectrometer collected 32 scans for each glass sample.

Differential Thermal Analysis(DTA) was carried out using a Netzsch DTA-200 differential thermal analyzer in the temperature range $100-1000^{\circ}$ Cwith a 10° C/min heating rate to determine the glass transition temperature(T_g) and the first crystallization temperature(T_c).

3. Results

Transparent glass samples whose components were illustrated above were obtained. FESEM images and macroscopic observation images of S1 and S5 glasses were shown in Fig. 1. The images marked with "a" and "c" are macro photo and FESEM images of S1 glass, respectively. In the same way, the images marked with "b" and "d" are macro photo and FESEM images of S5 glass. We can learn from Fig. 1 that the samples are homogeneous glasses and no phase splitting phenomenon and the micro surface of S5 glass (SiO₂ doping glass) is smoother and cleaner.

X-ray diffraction (XRD) patterns in Fig. 2 did not reveal the presence of crystalline phases in all samples, so it was concluded that the samples were homogeneous amorphous.

Infrared spectroscopy is one of the most effective experimental methods for clarifying structural research of glasses [15–17]. The effect of adding SiO₂ gradually on the structural properties of phosphate-based glasses is investigated by recording their FTIR

spectrum in the range of $400-1400 \text{ cm}^{-1}$, as shown in Fig. 3. The spectrum of the glass sample S2, S3, S4 and S5 is similar, but the differences between the SiO₂-free glass sample S1 and the SiO₂addition phosphate glass samples S2~S5 are quite obvious. The infrared spectra of pure P2O5-MgO-Na2O-Li2O glass(S1) containing five main characteristic peaks (distribute in the frequency 494 cm⁻¹, 735 cm⁻¹, 937 cm⁻¹, 1160 cm⁻¹, 1250 cm⁻¹ respectively) as shown in Fig. 3. As SiO₂ doped and increases, some variation of infrared spectra appeared in S2-S3 glasses. The five main characteristic peaks observed in the S1 glass became more and more weak or shift to lower wave number slightly in S2-S3 glasses. Meanwhile, some new characteristic peaks developed, such as peaks in frequency range 476–467 cm⁻¹, 1130 and 1137 cm⁻¹. Tasi and Greenblatt [18] have assigned the bands in the region 450–550 cm⁻¹ to the possible modes of P–O–P linkage. Dayanande et al. [19] attributed harmonics of bending P–O–P and O= P–O vibrations for weak shoulder at 530 cm^{-1} in the P₂O₅ glass. However, Higazy and Bridge [20] have attributed these bands at 500 cm^{-1} to the harmonics of P–O–P bending. Based on the above observation the bands obtained at 484, 494 and 503 cm^{-1} can be assigned to P–O–P bending vibration frequency. Meanwhile, Higazy and Bridge [20] observed stretching frequency of P–O–P unit in the vitreous $C_{03}O_4 - P_2O_5$ system in the 780-730 cm⁻¹ range. So the bands at 735 and 754 cm⁻¹ can be assigned to P–O symmetric stretching vibration. M.R. Ahsan and M.G. Mortuza [1] have attributed the bands in the region 917–1037 cm^{-1} to PO_{4}^{3-} stretching mode. So the bands at 928, 937, 947 and 965 cm^{-1} can be assigned to PO_{4}^{3-} stretching vibration. Several authors have observed groups P=O and P-O⁻ [1.20.21]. M.R. Ahsan and M.G. Mortuza [1] have attributed the bands in the region 1150 and 1200 cm⁻¹ to P–O⁻ stretching mode. Miller [21] argued that P=O lies in the range 1282–1205 cm⁻¹ in poly-phosphate chain and the $P-O^{-}$ group is characterized by the stretching frequency 1110 cm⁻¹. Higazy and Bridge [20] observed stretching vibration of P=O and $P-O^{-}$ unit within the range 1340–1235 and 1170–1070 cm⁻¹, respectively. Hence, the bands obtained at 1250, 1270 and 1280 cm^{-1} can be assigned to P=O stretching frequency. At the same time, the bands obtained at 1090, 1095, 1100 and 1160 cm^{-1} can be assigned to $P-O^-$ stretching frequency. P=O and $P-O^-$ unit. From the spectrum of the glass sample S1–S5, we can see that the intensity of characteristic peaks of P-O-P bending vibration, P-O symmetric stretching vibration, PO₄³⁻ stretching vibration and P=O stretching vibration became more and more weak and the frequency of those bands shift slightly to higher wave numbers as SiO₂ doped and increases. The bands of P-O⁻ stretching vibration shift to lower wave number with the addition of SiO₂. The above description illustrates that symmetric P-O-P bands and smaller ion unit (such as PO_4^{3-} and $P-O^{-}$ units) reduce together. This means that phosphate framework is open in the glass network, but the polymerization degree did not reduce, increase instead.

In the rare earth aluminosilicate glasses containing 10–20 mol% samaria the bands within the 451–480 cm⁻¹ range are assigned to Si–O–Si bending vibrations as observed by Kholi et al. [22]. The

The chemical composition an	d some parameters	of the studied glasses.
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Sample	Composition (g)					Si/P	Density (g/cm ³)	Vm (cm ³ /mol)	O/(P+Si) ratio	Y parameter
	P_2O_5	MgO	Na ₂ O	Li ₂ O	SiO ₂					
S1	20.6	4.4	3.39	1.62	0	0	2.59	31.96	3.26	148
S2	20.6	4.4	3.39	1.62	5	0.57	2.48	31.21	2.98	2.04
S3	20.6	4.4	3.39	1.62	10	1.15	2.44	30.54	2.80	2.40
S4	20.6	4.4	3.39	1.62	15	1.72	2.42	30.48	2.68	2.64
S5	20.6	4.4	3.39	1.62	20	2.30	2.39	30.32	2.59	2.82

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