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Structural and Thermal Properties of Li_2O-Na_2O-P_2O_5 Glasses Doped with La_2O_3

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Glasses of general formula (1-x)(0.5P_2O_5-0.25Na_2O-0.25Li_2O)-xLa_2O_3 with x = 0, 0.5, 1.0, 1.5 and 2.0 mol % were prepared by the traditional melting-quenching method. Fourier transform infrared spectrum and differential thermal analysis have been investigated, meanwhile density and molar volume (V_m) have been analyzed. The FTIR spectra show that the structure of glass has little changes after doping with lanthanum ions for all glass samples. The results of density show minimum and the values of V_m observe maximum when doping 1 mol % La_2O_3. The glass transition, T_g and T_c-T_g indicate that the glass doping 1 mol % La_2O_3 had better glass-forming ability than other samples.

Keywords: Phosphate glasses, Lanthanum oxide, Infrared spectroscopy, Differential thermal analysis.

INTRODUCTION

Phosphate glasses are scientifically important materials for they offer many excellent physical and chemical properties better than other glasses, such as softening temperature, high thermal expansion coefficients[1] and high electrical conductivity. However, their relatively poor chemical durability often limits their use in many applications[1-3], which results from the center asymmetric structure of phosphorus oxygen double bond (P=O). This is due to the hybrid orbital of sp^3d. Several studies have shown that the chemical durability of phosphate-based glasses can be improved by the addition of various oxides[4-6]. It is found that, the chemical durability of phosphate glasses increases dramatically with addition of Al_2O_3, Fe_2O_3, MnO/MnO_2, MgO, CuO and ZnO. With the addition of these oxides, the P-O-P bond are replaced by more chemically durable P-O-Al[7,8], P-O-Fe[6], P-O-Mn, P-O-Mg[9], P-O-Cu[10] and P-O-Zn[11] bonds, respectively.

Recently, the study of structural property of phosphate-based glasses has gained important attention[12]. It was found that structural property of P_2O_5-Na_2O-Li_2O glasses strongly depends on Na_2O and Li_2O contents and the mixed alkali effect (MAE) was very significant in the glass matrices[13].

On the other hand, the influence of rare earth oxides on the structural and thermal property of ceramics and films has been extensively investigated in recent years[14,15]. However, data that the effects of rare earth oxides on the structural and thermal property of these glasses is comparatively less.

Therefore, the aim of this work is to investigate the effect of rare earth ions, introduced by doping with lanthanum ions on the phosphate-based glasses. (1-x)(0.5P_2O_5-0.25Na_2O-0.25Li_2O)-xLa_2O_3 glasses were prepared by melting-quenching method. The structural and thermal properties of the glasses were investigated with the aid of the data on the Fourier transform infrared spectra (FTIR) and the differential thermal analysis (DTA).

EXPERIMENTAL

Phosphate-based glasses with the composition (1-x)(0.5P_2O_5-0.25Na_2O-0.25Li_2O)-xLa_2O_3, were prepared by analytically pure grade La_2O_3, Li_2CO_3, Na_2CO_3 and $NH_4H_2PO_4$ and were listed in Table-1. The oxidation and reduction reactions in a phosphate glass melt are known to depend on the sample geometry, thermal history, quenching rate and the size of the melt[16], so all phosphate glasses samples were prepared under the same conditions. The batch materials were homogeneous mixtures for about 0.5 h in an agate mortar and melted in alumina crucible using an electric furnace (Deltech DT-33-CVT-912) in air, at 900 °C for 2 h. The liquid was then cast in a brass mold and subsequently annealed at 430 °C for 2 h (near the glass transition temperature T_g). After annealing, the glass samples were stored in a desiccator until use. Density measurements were carried out at room temperature using the Archimedes method with distilled water as the immersion fluid. The relative error in these measurements was about 0.01 g/cm^3.

TABLE-1
GLASS COMPOSITIONS, O/P RATIO, DENSITY AND MOLAR VOLUME V_m of (1-x)(0.5P_2O_5-0.25Na_2O-0.25Li_2O)-xLa_2O_3 GLASSES

Sample	Mole fraction (%)				O/P ratio	Density (g/cm^3)	V_m (cm^3/mol)
	P_2O_5	Na_2O	Li_2O	La_2O_3			
P1	50	25	25	0	3.00	2.4541	38.28
P2	49.75	24.875	24.875	0.5	3.16	2.4338	39.07
P3	49.5	24.75	24.75	1	3.33	2.4336	39.55
P4	49.25	24.625	24.625	1.5	3.50	2.5064	38.87
P5	49	24.5	24.5	2	3.75	2.5698	38.36

FTIR spectra for the glasses were presented using a Perkin-Elmer 577 infrared spectrophotometer in the frequency range 400-2000 cm^{-1} by potassium bromide (KBr) pellet method. DTA was carried out in the temperature range 100-1000 °C using a Netzsch DTA-200 differential thermal analyzer, to determine T_g and other glass forming ability parameters.

RESULTS AND DISCUSSION

FTIR spectroscopy: It is well known that PO_4 tetrahedron is the fundamental structural unit in phosphate glasses[17]. The structural units are classified by the Q^n notation where "n" (n = 0, 1, 2, 3) is the number of bridging oxygen in a PO_4 tetrahedron[18]. A Q^0 group represent isolated PO^4 tetrahedron with four non-bridging oxygens, is called orthophosphate glasses. Pyrophosphate glasses have Q^1 P-tetrahedral with one bridging and three non-bridging oxygens. Metaphosphate glasses have Q^2 groups with two terminal oxygens that are participated in the modifying cation polyhedron. A Q^3 P-tetrahedron represents a PO_4 tetrahedron with three bridging oxygens and a terminal oxygen, it is known to structure of crystalline P_2O_5.

The local structure of the glass samples was evidenced by FTIR. The FTIR of P_2O_5-Na_2O-Li_2O glasses were shown in Fig. 1. The figure showed similar IR spectra for all the samples, indicated that the structure of glass had little changes after doping with lanthanum ions. The IR spectra for all the samples exhibited vibration bands around 1275, 1100, 899, 783, 552 and 494 cm^{-1}. The important bands and their assignments are given in Table-2. The vibration band observed at about 1275 cm^{-1} was corresponded well to the asymmetric stretching vibration of P=O bond[19,20]. The band at about 1100 cm^{-1} was assigned to asymmetric stretching vibration of P-O- mode in Q^2 units[21]. The band at about 899 cm^{-1} was attributed to the asymmetric stretching vibrations of P-O-P[22]. The bands due to the symmetric stretching vibrations of P-O-P were expected[23] at about 726 cm^{-1}. The vibration band at about

TABLE-2
IR BANDS AND BAND ASSIGNMENT FOR (1-x)(0.5P_2O_5-0.25Na_2O-0.25Li_2O)-xLa_2O_3 GLASSES

Wavenumber (cm^{-1})	FTIR band assignment
494	Bending vibration of P-O$^-$
552	Bending modes of O-P-O in the Q^1 units
726	Symmetric stretching vibrations of P-O-P ring in Q^2 units
899	The asymmetric stretching vibrations of P-O-P in Q^1 units
1100	Asymmetric stretching vibration of P-O$^-$ mode in Q^2 units
1275	Asymmetric stretching vibration of P=O bond

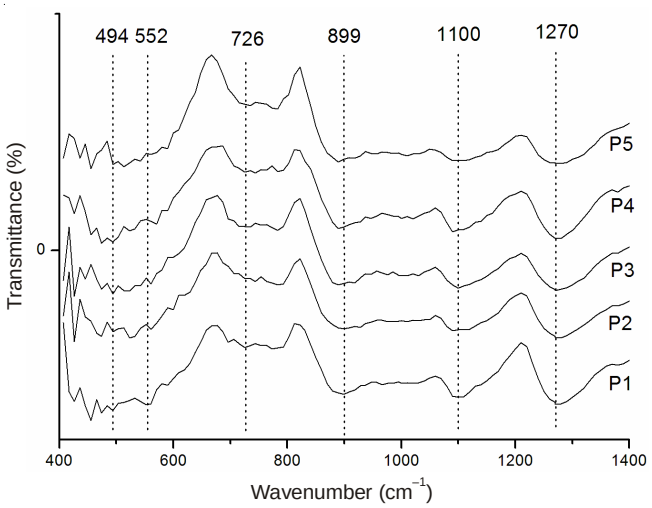

Fig. 1. FTIR spectra of (1-x)(0.5P_2O_5-0.25Na_2O-0.25Li_2O)-xLa_2O_3 glasses

552 cm^{-1} corresponded to the bending modes of O-P-O in the Q^1 P-tetrahedron[24]. The band at about 494 cm^{-1} was assigned to bending vibration[25] of P-O$^-$.

Glasses with a nominal O/P molar ratio of 3.0, 3.5 and 4. predicts that Q^2, Q^1 and Q^0, respectively[26]. The present studied glasses had O/P molar ratio of 3 in P1 samples, 3.16 in P2 samples, 3.33 in P3 samples, 3.5 in P4 samples, 3.75 in P5 samples is shown in Table-1. The glass sample is mainly constituted by pyrophosphate, with a small proportion of metaphospahte and orthophosphate glass based structural units is confirmed by FTIR[27] (Fig. 1). With increasing La_2O_3 the intensity of the 726 cm^{-1} band increased, whereas, the bands at 1100 and 1275 cm^{-1} decreased. This suggested an increase of the structural symmetry, resulting to the improvement of the chemical durability of the present glass samples. Moreover, the radius of lanthanum ions (1.06 Å) is larger than the radius of sodium ions (1.02 Å) or lithium ions (0.76 Å), the band at 899 cm^{-1} shifted to lower wavenumber, indicated that the P-O-La bond is stronger compared to P-O-Na and Li-O-P bonds[5-11]. The number of P-O-M (M=Na, Li, La) is believed to improve the chemical durability of the present studied glass.

According to the changes between lanthanum-free glasses and lanthanum-doped glasses in the infrared spectra, it was concluded that there was no significant difference in structure network in the studied samples. Thus, the structure of the phosphate chains is not evidently affected by lanthanum ions in the glass samples[28]. Also, these observations are consistent with the analyzed compositions which yield O/P ratio of the present studied glasses. Therefore, it is expected that La_2O_3 acts as glass modifiers[29], which will occupy the positions between P-O-P layers creating non-bridging oxygen ions.

Density and molar volume: Density of the studied glass samples was determined at room temperature using Archimedes method with distilled water as an immersing liquid. The molar volume (V_m) of the samples were calculated from density, ρ and molecular weight, M, using the formula $V_m = M/\rho$. The effect of La_2O_3 on the density and molar volume of the studied glasses was shown in Fig. 2, as a function of composition. It can be noticed that the values of density showed a decreasing trend initially, afterwards followed by a gradual increase as the addition of La_2O_3, was given in Table-1. The density decreased

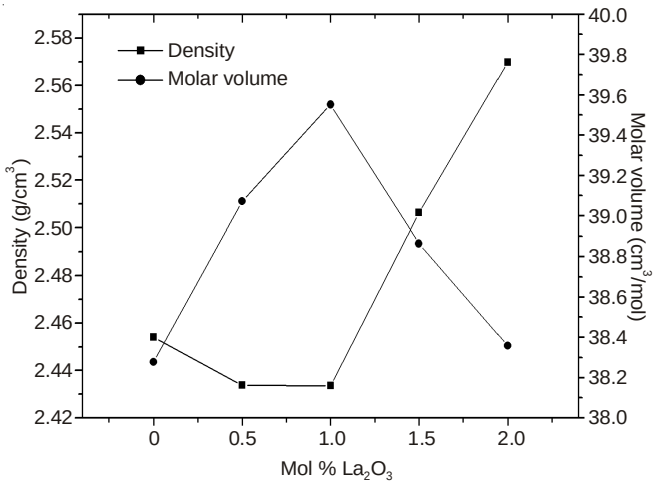

Fig. 2. Composition dependence of density and molar volume for (1-x) $(0.5P_2O_5$-$0.25Na_2O$-$0.25Li_2O)$-xLa_2O_3 glasses

from 2.4541 g/cm^3 (glass P1) to 2.4338 g/cm^3 (glass P2), followed increased from 2.4336 g/cm^3 (glass P3) to 2.5064 g/cm^3 (glass P4), then increased to 2.5698 g/cm^3 (glass P5). These data were corresponding to the values of the molar volume (V_m) in Table-1, where they increased from 38.28 cm^3/mol (glass P1) to 39.07 cm^3/mol (glass P2), after that increased to maximum 39.55 cm^3/mol (glass P3), then decreased from 38.87 cm^3/mol (glass P4) to 38.36 cm^3/mol (glass P5).

The density is an additive property[17,30]. It can be proposed that each oxide in glass would have its contribution. Thus, the density should increase because of the higher molecular weight of La_2O_3 than that of Na_2O and Li_2O (MLa_2O_3 = 325.81 g/mol; MNa_2O = 61.98 g/mol; MLi_2O = 29.88 g/mol). However, density was found to decrease with the addition of La_2O_3 in glass P2 and glass P3. This behaviour is related to atom coordination number[31,32]. The lanthanum atom coordination number is more than six, which is greater than sodium atom and lithium atom[33]. As a result, the number of non-bridging oxygen would increase in lanthanum-doped glasses compared with in lanthanum-free ones, resulting in the glass structure becomes more randomized. Therefore, the density abnormally decreases in glass P2 and glass P3 samples.

In order to confirm the change of structural network in the studied glasses, V_m was investigated on the same term. As the relative molecular mass of La_2O_3 was higher than that for Na_2O and Li_2O, trended to decrease in V_m was an expected result. The abnormally increase in V_m may indicated that the volume of non-bridging oxygen ions produced by modifier La_2O_3 was greater than that produced by equivalent quantity of Na_2O or Li_2O. Thus the content of network modifier did not contribute in glass formation but cleaves the structure of glass samples and resulted to increase in V_m of the studied glasses. This result is in agreement with those reported for semiconductor glasses[34].

Differential thermal analysis: Differential thermal analysis traces of P_2O_5-Na_2O-Li_2O glasses doped with different concentrations of La_2O_3 were shown in Fig. 3. Differential thermal curves indicated an inflection due to the glass transition temperature, T_g, in the temperature ranged from 450 to 500 °C, followed by a low degree of resolution of exothermic effect resulted from crystallization temperature, T_c, between 760 and 850 °C. The values of T_g, T_c and T_c-T_g (a parameter which measures the thermal stability of glass[35]) obtained for all the samples were furnished in Table-3. The appearance of single peak due to the glass transition temperature in DTA pattern of all the glass samples indicated the homogeneity of the samples prepared[36]. With the increase in the concentration of La_2O_3 up to 1 mol % in the glass matrix, the glass transition temperature, T_g and the parameter T_c-T_g were observed to maximum value, indicated that the glass P3 had better glass-forming ability than other samples. This result was corresponding to O/P molar ratio of 3.33, which was mainly constituted by pyrophosphate and metaphospahte.

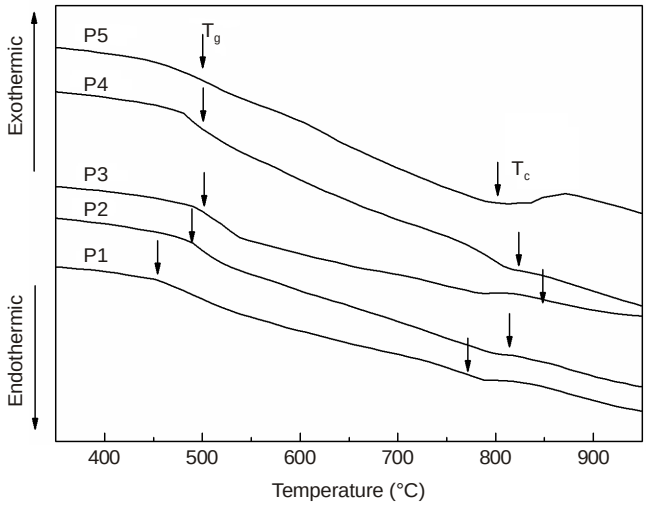

Fig. 3. DTA traces of (1-x)$(0.5P_2O_5$-$0.25Na_2O$-$0.25Li_2O)$-xLa_2O_3 glasses

TABLE-3
DATA ON DIFFERENTIAL THERMAL ANALYSIS
OF (1-x)$(0.5P_2O_5$-$0.25Na_2O$-$0.25Li_2O)$-xLa_2O_3 GLASSES

Sample	T_g (°C)	T_c (°C)	T_c-T_g (°C)
P1	451	769	312
P2	490	816	326
P3	500	847	347
P4	499	826	327
P5	498	812	314

Conclusions

The structural properties of (1-x)$(0.5P_2O_5$-$0.25Na_2O$-$0.25Li_2O)$-xLa_2O_3 with x = 0, 0.5, 1.0, 1.5 and 2 mol % have been investigated by FTIR, density, V_m and DTA. The obtained results can be concluded as follows:

• The FTIR of P_2O_5-Na_2O-Li_2O glasses showed similar IR spectra for all the samples, indicated that the structure of glass had little changes after doping with lanthanum ions which was expected act as glass modifiers. The chemical durability of the present studied glass improved due to the P-O-La bond is stronger compared to P-O-Na and Li-O-P bonds, especially glass doped 1 mol % La_2O_3.

• The values of density and V_m show extremum. This behaviour is related to atom coordination number, resulting in the structure becomes more randomized in glass when doping 1 mol % La_2O_3.

• The glass transition temperature, T_g and the parameter T_c-T_g were observed to maximum values, indicated that the glass doped 1 mol % La_2O_3 had better glass-forming ability than other samples, which was mainly constituted by pyrophosphate and metaphospahte.

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