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Structural investigations and calorimetric dissolution of manganese phosphate glasses

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ABSTRACT

Two series of manganese phosphate glasses (50x/2)Na_2O–xMnO–(50 − x/2)P_2O_5 and (50 − x)Na_2O–xMnO–50P_2O_5 ($0 \leq x \leq 33$ mol%), were prepared and investigated by means of density measurements, molar volume evolutions, FTIR and Raman spectroscopy, differential scanning calorimetry and calorimetric dissolution. In both series, density and glass transition temperature increase with composition.

For the first series of glasses ($3 \leq O/P \leq 3.49$), spectroscopic analysis indicates that the addition of MnO content induces an evolution of structural units from Q^2 to Q^1 tetrahedral sites indicating the depolymerization of phosphate chains.

By introducing MnO oxide into the second glass series (O/P = 3), P–O–P linkages are disrupted, suggesting a structural changes in the vitreous network.

Calorimetric dissolution of both series of glasses in 4.5% weight of H_3PO_4 solution shows that the dissolution phenomenon is endothermic for the low MnO content and becomes exothermic as MnO concentration increases. This behavior may be correlated to the structural modification resulted from the depolymerization of the infinite metaphosphate chains.

1. Introduction

Phosphate glasses have been the subject of a large number of applications due to their lower softening and melting temperature and higher thermal expansion coefficients. These properties make them candidates for a variety of applications such as: the manufacturing of glass-polymer composites [1–3], hermetic seals [2–8] optical waveguides [1,2,6,7], rare earth ion hosts for solid state lasers [1,2,6,9], solid state ionic conductors [7] and biomaterials [6,7]. Glasses containing transition metal ions (TMI) have attracted much attention due to their electric, optical and magnetic properties which arise from the presence of TMI in multivalence states. These properties make them suitable for large applications such as memory switching, electronics, catalysis and magnetic information storage [6,10]. Manganese phosphate systems are scientifically and technically interesting materials. The structural role of MnO in many oxide glasses is unique.

Recently, many investigators have been interested in manganese polyphosphate glasses because of their interesting structural properties and their coordination [3,6,10]. It was suggested that the addition of MnO to polyphosphate glasses, results in the formation of P–O–Mn bonds, which leads to the improvement of their chemical durability [11].

Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of glasses. It appears as Mn^{3+} with octahedral coordination in borate glasses and as Mn^{2+} with both tetrahedral and octahedral environments in silicate and germanate glasses [10,12].

In the present work, the structure of glasses with general compositions of (50 − x/2)Na_2O–xMnO–(50 − x/2)P_2O_5 and (50 − x)Na_2O–xMnO–50P_2O_5 ($0 \leq x \leq 33$ mol%) is investigated using FTIR and Raman spectroscopies in order to elucidate the structural evolution as a function of composition. Other properties such as: density, molar volume, glass transition temperature, calorimetric dissolution and ICP analysis are also investigated with the structure changes.

As usual, the conventional notation for phosphate groups adopted in this paper is Q^n, where n (n = 0–3) is the number of bridging oxygen per PO_4 tetrahedron [4,13].

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Table 1
Analyzed and nominal glass compositions for both series of: $(50 - x/2)Na_2O$–$xMnO$–$(50 - x/2)P_2O_5$ and $(50 - x)Na_2O$–$xMnO$–$50P_2O_5$ $(0 \le x \le 33$ mol%) phosphate glasses.

MnO Nominal/analyzed	Na_2O Nominal/analyzed	P_2O_5 Nominal/analyzed	MnO Nominal/analyzed	Na_2O Nominal/analyzed	P_2O_5 Nominal/analyzed
0/0	50/46.7	50/53.3	0/0	50/46.7	50/53.3
5/4.6	47.5/46.0	47.5/49.6	5/4.8	45/44.7	50/49.2
10/9.6	45/43.2	45/47.2	10/9.7	40/39.7	50/50.0
15/14.7	42.5/41.3	42.5/44.1	15/13.2	35/34.8	50/52.0
20/19.5	40/38.1	40/42.5	20/16.8	30/30.1	50/53.2
25/24.8	37.5/35.2	37.5/40.0	25/22.1	25/25.0	50/53.0
30/30.2	35/33.1	35/37.0	30/26.4	20/19.8	50/54.0
33/34	33.5/30.4	33.5/36.0	33/29.4	17/16.9	50/54.0

Table 2
Glass composition, glass transition temperature T_g, density ρ, molar volume V_m, of $(50 - x/2)Na_2O$–$xMnO$–$(50 - x/2)P_2O_5$ and $(50 - x)Na_2O$–$xMnO$–$50P_2O_5$ $(0 \le x \le 33$ mol%) phosphate glasses.

Glass composition (mol%)	Density (g/cm^3)	V_m (cm^3/mol)	T_g(°C)	T_c(°C)
50 Na_2O–50 P_2O_5	2.43	42.00	280	290
47.5 Na_2O–5 MnO–47.5 P_2O_5	2.50	40.20	–	–
45 Na_2O–10 MnO–45 P_2O_5	2.58	38.33	311	395
42.5 Na_2O–15 MnO–42.5 P_2O_5	2.67	36.50	–	–
40 Na_2O–20 MnO–40 P_2O_5	2.63	36.42	345	425
37.5 Na_2O–25 MnO–37.5 P_2O_5	2.65	35.50	355	443
35 Na_2O–30 MnO–35P_2O_5	2.75	33.70	382	487
33.5 Na_2O–33 MnO–33.5 P_2O_5	2.70	34.00	402	485
45 Na_2O–5 MnO–50 P_2O_5	2.52	40.62	–	–
40Na_2O–10 MnO–50 P_2O_5	2.58	40.00	321	–
35 Na_2O–15 MnO–50P_2O_5	2.60	39.72	–	–
30 Na_2O–20 MnO–50P_2O_5	2.67	39.00	361	–
25 Na_2O–25 MnO–50P_2O_5	2.78	37.43	381	–
20 Na_2O–30 MnO–50P_2O_5	2.79	37.50	399	–
17 Na_2O–33 MnO–50P_2O_5	2.85	37.00	400	–

2. Experimental

2.1. Glass preparation

Glasses from $(50 - x/2)Na_2O$–$xMnO$–$(50 - x/2)P_2O_5$ and $(50 - x)$ Na_2O–$xMnO$–$50P_2O_5$ $(0 \le x \le 33$ mol%) were prepared using reagent grade compounds, NaH_2PO_4 (Sigma Aldrich), $(NH_4)_2HPO_4$ (Fluka), MnO (Sigma Aldrich) with a high purity (99% purity) in the suitable proportions.

The mixture having the desired compositions was heated in a platinum crucible at 200 °C for 30 min. The batches were melted at temperatures between 400 and 600 °C in order to eliminate NH_3 and H_2O. The temperature was then progressively increased from 750 °C to 900 °C, depending on glass composition, and held constant for 30 min. The batch was finally quenched to room temperature under air in order to produce vitreous structure which is confirmed by X-ray diffraction. All the products were annealed at 20 °C above their glass transition temperature for 2 h for homogenization. The solids were kept in a desiccator to prevent possible moisture. The nominal and analyzed glass compositions are reported in Table 1.

2.2. ICP analysis

The content of phosphorus, manganese and sodium was analyzed by means of inductively coupled plasma atomic emission spectroscopy (Jobin Yvon Ultra C). The nominal and analytical glass compositions are reported in Table 1 $(50 - x/2)Na_2O$–$xMnO$–$(50 - x/2)P_2O_5$ and $(50 - x)Na_2O$–$xMnO$–$50P_2O_5$ glasses will be labeled by reference to their molar MnO content x ranging from 0 to 33 mol%.

2.3. Density measurements

Density measurements of the glass samples were made using the standard Archimedes method with diethyl orthophthalate as immersion fluid and the relative error of these measurements is ± 0.03 g cm^{-3}. The molar volume (V_m) of glasses has been calculated from the molecular weight (M) and density (ρ) ($V = M/\rho$).

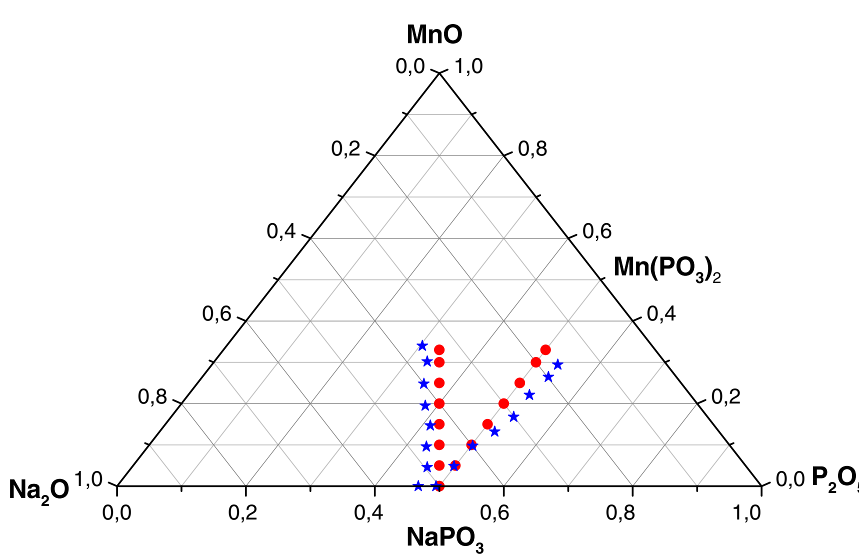

Fig. 1. Analyzed (★) and nominal (●) glass compositions for $(50 - x/2)Na_2O$–$xMnO$–$(50 - x/2)P_2O_5$ and $(50 - x)(Na_2O)$–$xMnO$–$50P_2O_5$ $(0 \le x \le 33$ mol%) phosphate glasses.