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Properties and structural features of iron sodium phosphate glasses containing neodymium oxide

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ABSTRACT

Properties and structural features of $x$$Nd_2O_3$-(100-$x$)($20Fe_2O_3$-$60P_2O_5$-$20Na_2O$) ($x$ = 0, 2, 4, 6 and 8 mol%) glasses have been investigated in detail by Differential Thermal Analysis (DTA), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), Raman and Fourier Transform Infrared Spectroscopy (FTIR) respectively. The results show that the samples with x < 8 mol % are completely amorphous. Incorporation of Nd_2O_3 increases the T_g value and thermal stability of the iron sodium phosphate glasses containing less 8 mol% Nd_2O_3. The predominant network structural of the Nd_2O_3-doped iron sodium phosphate glasses is Q^1 units. The content of Q^1 and Q^0 units increases and that of Q^2 decreases with increasing neodymium content. The normalized leaching rates of Nd in Nd_2O_3-doped iron sodium phosphate glasses in 90 °C deionized water for 7 days are below 10^{-6} g m^{-2} d^{-1}. The conclusions show that iron sodium phosphate glass is a potential host for the disposal of high-level nuclear wastes which are rich in trivalent radioactive oxide.

1. Introduction

The main method to deal with high level radioactive wastes (HLWs), over the past 50 years, is vitrification, and it is still attracting interests from researchers in this field [1–5]. Iron phosphate system glasses have been extensively studied in the past decades for potential treatment of "difficult" waste streams that are poorly suited for borosilicate glasses [1, 6–8]. They have higher loading capacity to HLWs containing phosphates, sulfates and chlorides than borosilicate glasses [7]. Moreover, they also possess high chemical durability resulted from Fe^{3+} cations entering in the glass network with four-fold coordination and forming stable P-O-Fe covalent bonds [6–8]. Binary, ternary and quaternary glasses, such as P_2O_5-Fe_2O_3, R_xO_y-P_2O_5-Fe_2O_3 (where R = Na, B, Al, Si) [9–11] and N_xO_y-M_mO_n-P_2O_5-Fe_2O_3 (where M = B, and N=Li, Ce, Zr, Gd, La) [3, 4, 12–14], have been received systematically investigation.

The Na_2O-FeO-Fe_2O_3-P_2O_5 (NFP) system glass is a model of iron phosphate compositions for the vitrification of high alkaline nuclear waste streams [15]. The previous studies [9, 16, 17] of sodium iron phosphate glasses provide glass-forming region, thermal properties and the structural information about distributions of phosphate based glass networks and iron polyhedron. Lina Ma [17] studied glass structure of three series of glasses with compositional ranges of 3.25 < O/P < 3.5 and 0 < Fe/P < 0.67, and the results show that the average chain-length of phosphate anions decreases with increasing O/P ratio and wide distribution of phosphate anions is obtained due to disproportionation reactions in the glass melts with greater Fe/P ratio. Thermal stability, crystallization behavior and the dissolution behavior of several series of Na_2O-FeO-Fe_2O_3-P_2O_5 (NFP) glasses with different O/P (3.0–3.5) and Fe/P (0.13–0.67) ratios were studied by Lina Ma [9, 18]. The results indicated that the glass transition temperature was related to the nature of the P/O_{nb} bonds with the Na and Fe ions. The thermal stability was related to of Fe/(Na + Fe) ratio, O/P ratio, the compositions of the stable crystalline compounds and redox behavior of iron in the glass. The dissolution mechanism and kinetics were determined by the average phosphate chain length corresponding to glass composition. The properties and crystallization tendencies of Na_2O-Fe_2O_3-P_2O_5 glasses with varying Na_2O/Fe_2O_3, Na_2O/P_2O_5, and Fe_2O_3/P_2O_5 ratios were reported. But less is known about the solubility of nuclear surrogates in NFP glass matrix and their influence on structure, thermal stability and chemical stability of the base gasses. Our group investigated the thermal stability and crystallization behaviors of $20Fe_2O_3$-$60P_2O_5$-$20Na_2O$ glass and glass-ceramic in detailed by adding tetravalent zirconium [10].

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Rare earth elements usually improve significantly glass properties if appropriately used, such as hardness, thermal stability and chemical durability [19]. But glass material tends to crystallize spontaneously while adding excessive rare earth elements which may greatly deteriorate the chemical durability of the glass. Nd^{3+} was used to simulate the trivalent minor actinides (such as Am^{3+} and Cm^{3+}) generating from the nuclear fuel reprocessing, which have long term radioactivity and low solubility in glass matrix [20]. The incorporation of neodymium oxide (Nd_2O_3) in borosilicate glasses was investigated, and the result revealed that the solubility of Nd^{3+} was < 3 mol% even if the processing temperature increases up to 1400 °C [21]. In this paper, in order to investigate whether NFP glass is a potential matrix to immobilize trivalent minor actinides, we continue our investigations to the influence of Nd_2O_3 incorporation on the structure, thermal properties and chemical properties of $20Fe_2O_3$-$60P_2O_5$-$20Na_2O$ glasses.

2. Experimental

2.1. Preparation of glass samples

Batches that could produce 50 g of melts were prepared by mixing analysis grade Nd_2O_3 (Sigma Aldrich, 99.99%), Fe_2O_3 (Sigma Aldrich, 99.99%), $(NH_4)H_2PO_4$ (Sigma Aldrich, 99.99%) and Na_2CO_3 (Sigma Aldrich, 99.99%) dry crystalline powders according to the designed stoichiometric ratios in Table 1. The thorough mixed raw materials were preheated in a high temperature furnace (KBF1400, Instrument Co., Ltd. Nanjing Nanda, China) at 450 °C for 1 h. Subsequently, the temperature was progressively increased to 1200 °C with a heating rate of 5 °C·min^{-1} and held at this temperature for 3 h in air to make homogeneous melts. Then, the melted liquids were poured onto a preheated stainless steel plate, annealed at 450 °C for 1 h to eliminate the stress of glasses and slowly cooled in furnace to room temperature for 600 min. The as-prepared samples are marked by Nd_2O_3 content, for instance, Nd8 sample represents $20Fe_2O_3$-$60P_2O_5$-$20Na_2O$ glass containing 8 mol% Nd_2O_3.

2.2. Measurements

X-ray diffraction (XRD) patterns were obtained on a X'Pert PRO diffractometer (PANalytical Company (formerly Philips Analytical), Holland), using Cu K_α radiation, operating at 40 kV and 40 mA in the range of 2θ = 3–80° with an acquisition step of 0.02° and a scan rate of 10° per minute. The collected XRD data were analyzed by using Jade 6 software. The glass transition temperature (T_g) and onset temperature of glass crystallization (T_r) were analyzed by using Differential thermal analysis (DTA). DTA data of the samples were obtained by using a SDT Q600 instrument in flowing N_2 at a heating rate of 10 °C·min^{-1}. The scan temperature over a range from room temperature to 1000 °C, the characteristic temperatures were determined with precision ± 2 °C using the microprocessor of thermal analyzer. The density of each sample was measured on an automatic electronic density meter (MH-300A, Xiamen, China) at room temperature by Archimedes Method using distilled water as immersion liquid and the estimated error is ± 0.001 g cm^{-3}.

Table 1
Chemical composition and molar ratio of O/P with respect to each constituent of the as-prepared samples.

Samples	Composition (mol%)				Molar ratio of O/P
	Na_2O	Fe_2O_3	P_2O_5	Nd_2O_3	
Nd0	20	20	60	0	3.17
Nd2	19.6	19.6	58.8	2	3.22
Nd4	19.2	19.2	57.6	4	3.27
Nd6	18.8	18.8	56.4	6	3.33
Nd8	18.4	18.4	55.2	8	3.38

Glass structure was characterized by Raman and FTIR. Raman spectra were measured in the range of 200–2000 cm^{-1} at room temperature by a Renishaw InVia Raman spectrophotometer with argon ion laser (k = 785 nm) as the excitation light. FTIR spectra were collected in the range of 400–2000 cm^{-1} using a Spectrum One FITR spectrometer (PerkinEImer. USA). The pellets were prepared by mixing and grinding about 1–2 mg of sample powder with 100–200 mg of spectroscopic grade dry KBr powder, then compressing the mixtures to form thin sheets for testing. The accuracy of this technique is estimated to be ± 4 cm^{-1}.

The chemical durability of the studied glass was evaluated with the Product Consistency Test (PCT) [22] at 90 ± 1.0 °C in deionized water (pH = 7) within the polytetrafluoroethylene reactors. The leaching powders between 100 and 200 meshes were washed using alcohol and distilled water by ultrasonic, dried at 90 °C in an oven and weighed (± 0.01 mg), and then put in polyethylene flasks containing the new deionized water for 3 and 7 days at 90 °C. Solution samples analyzing by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700 ×) and inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP6500). The normalized leaching rate LR_i (g·m^{-2} d^{-1}) of element (Nd, Na, P and Fe) was calculated using the formula given below [23]:

$$LR_i = \frac{C_i \cdot V}{f_i \cdot S \cdot \Delta t}$$

Where C_i is the concentration of element (Nd, Na, P and Fe) in the solution (g/L), V is the volume of the leaching solution (L), S is the surface area of the sample (m^2), the value of S/V is about 2000 m^{-1}, f_i is the mass fraction of the element in the glass and Δt is the leaching days (d).

3. Results and discussion

3.1. Glass formation

The molten liquids for all the studied samples have good liquidity at the melting temperature. The quenched and annealed samples show regular and homogeneous surface with shiny, metallic luster on the external surface and no cracks. Fig. 1 shows XRD pattern of the studied samples containing different amounts of Nd_2O_3. It is confirmed that the samples containing Nd_2O_3 up to 8 mol% are fully amorphous and no any crystalline phases are detected.

Glass phase is metastable phase which can spontaneously crystallize to crystalline state. If any crystallite appears in a glassy phase, the crystallite will induce nucleation or provides surface to nucleate,

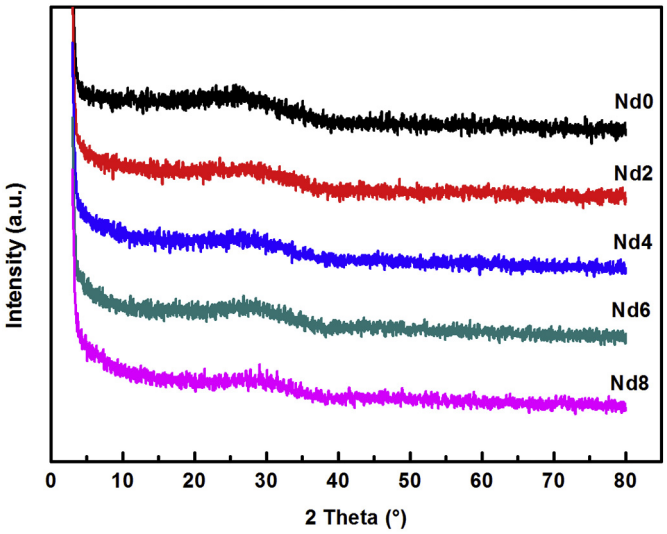

Fig. 1. XRD patterns of the prepared glass samples.