Journal of Nuclear Materials 443 (2013) 140–144

Contents lists available at SciVerse ScienceDirect

Journal of Nuclear Materials

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

Structure and properties of calcium iron phosphate glasses

Bin Qian [a], Xiaofeng Liang [b,c,*], Cuiling Wang [c], Shiyuan Yang [c]

[a] School of Science, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China
[c] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China

ARTICLE INFO

Article history:
Received 26 November 2012
Accepted 5 July 2013
Available online 13 July 2013

ABSTRACT

The structural properties of xCaO–(100 – x) (0.4Fe_2O_3–0.6P_2O_5) (x = 0, 10, 20, 30, 40, 50 mol%) glasses have been investigated by XRD, DTA, IR and Raman spectroscopy. XRD analysis has confirmed that the majority of samples are X-ray amorphous, and EDS analysis indicates that the glass matrix can accommodate ≈30 mol% CaO. IR and Raman spectra show that the glass structure consists predominantly of pyrophosphate (Q^1) units. IR spectra indicate that the phosphate network is depolymerized with the addition of CaO content. The density and glass transition temperature (T_g) increase with increasing CaO content for the glasses. This behavior indicates that the addition of CaO improves the strength of the cross-links between the phosphate chains of the glass.

1. Introduction

Iron phosphate glasses have been studied for their potential waste immobilization applications since the mid-1990s [1]. Binary iron phosphate glasses are considered as the candidates for immobilizing certain types of high-level nuclear wastes (HLW), particularly the iron phosphate glass with the 40Fe_2O_3–60P_2O_5 (mol%) composition which was found to have the best chemical durability among several iron phosphate glasses [2–6]. In some instances, iron phosphate glasses may be more technically suitable and less expensive than the borosilicate glasses which have been used to vitrify certain types of HLW [7].

The physical and chemical properties of phosphate glasses can be optimized by controlling the chemical compositions. Due to the complex chemical nature of waste-loaded glasses, it can be useful to simplify their compositions in order to study individual component and its effects on properties and structure. These data can provide useful information for study and application about immobilization and disposal of high-level nuclear wastes of phosphate glasses. In recent years, there are some investigations about the effects of divalent cations on the physical and chemical properties of iron phosphate glasses, these divalent cations including Zn^{2+} [8–10], Pb^{2+} [11,12], Ba^{2+} [13], Ca^{2+} [13]. Some investigations indicate that addition of CaO to iron phosphate glasses improved chemical durability [13,14]. The higher chemical durability is suitable for HLW vitrification. Although, there are many structural information about the binary calcium phosphate glasses [15–18], the structure information about calcium–iron phosphate glasses are less investigated. Knowledge of the structure of calcium–iron phosphate glasses helps in identifying modifications in compositions and processing conditions, which can expand their applications.

In the present study, we have investigated the effects of calcium addition on structure and properties of several iron phosphate glasses in a systematic way by means of X-ray diffraction (XRD), Differential thermal analysis (DTA), Infrared spectroscopy (IR) and Raman spectroscopy.

2. Experimental procedure

2.1. Sample preparation

The starting materials for obtain xCaO–(100 – x) (0.4Fe_2O_3–0.6P_2O_5) glass system with x = 0, 10, 20, 30, 40, 50 mol% were CaO, Fe_2O_3 and $NH_4H_2PO_4$ of analytical reagent grade purity. Batches to produce 30 g of glass were prepared by weighing suitable proportions of the components, powder mixing and heating in alumina crucibles at 250 °C for 2 h to expel the water and ammonia. Then samples were heated to 1200 °C (heating rate was 10 °C/min) and melted at 1200 °C for 3 h. The melts were then poured into preheated steel molds, and moved quickly to an annealing furnace, annealed at 475 °C for 2 h and cooled down to room temperature more than 12 h.

2.2. Structural investigation

Room temperature XRD patterns for all samples were collected with a X'Pert PRO diffractometer (PANalytical, The Netherlands)

* Corresponding author at: Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China. Tel.: +86 13547133875; fax: +86 08166089025.
E-mail address: xfliangswust@gmail.com (X. Liang).

0022-3115/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnucmat.2013.07.014

Table 1
Glass compositions (nominal and measured) and measured properties for xCaO–(100 – x) (0.4Fe_2O_3–0.6P_2O_5) glasses (x = 0, 10, 20, 30, 40, 50).

Sample name	Ca0[a]	Ca10[a]	Ca20[a]	Ca30[a]	Ca40[b]	Ca50[b]
P_2O_5 mol% (analyzed)	60 (59.13)	54 (57.99)	48 (53.44)	42 (48.71)	36 (34.09)	30 (32.58)
Fe_2O_3 mol% (analyzed)	40 (36.43)	36 (28.03)	32 (26.02)	28 (23.93)	24 (36.73)	20 (34.91)
CaO mol% (analyzed)	0 (0)	10 (6.5)	20 (13.2)	30 (21.06)	40 (28.39)	50 (31.26)
Na_2O mol% (analyzed)	0 (0.08)	0 (1.22)	0 (1.17)	0 (1.41)	–	–
TiO_2 mol% (analyzed)	0 (0.26)	0 (0.22)	0 (0.21)	0 (0.18)	–	–
Al_2O_3 mol% (analyzed)	0 (0.65)	0 (0.87)	0 (0.89)	0 (0.54)	0 (0.78)	0 (1.25)
SiO_2 mol% (analyzed)	0 (2.50)	0 (3.57)	0 (3.51)	0 (2.51)	–	–
Others mol% (analyzed)	0 (0.95)	0 (1.06)	0 (1.56)	0 (1.66)	–	–
T_g (°C)	506	528	552	568	–	–
T_r (°C)	621	666	666	667	–	–
T_r–T_g (°C)	115	138	114	99		
T_{x1} (°C)	659	695	680	702	–	–
T_{x2} (°C)	856	None	None	None	–	–
ρ/±0.02 g cm^{-3}	3.00	3.09	3.19	3.28	–	–

[a] Measured by XRF.
[b] Measured by EDS.

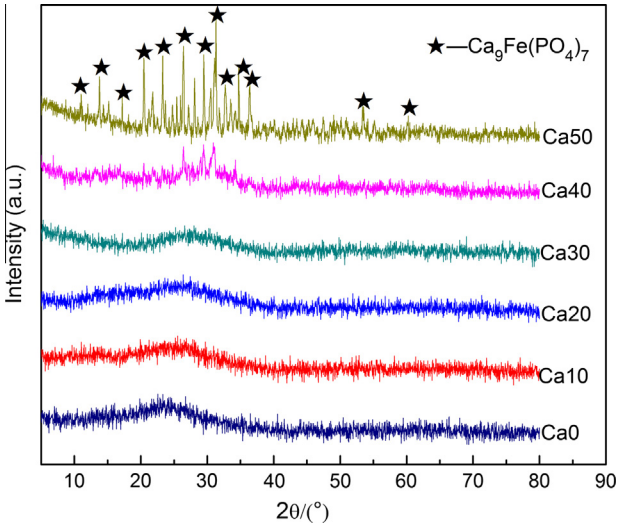

Fig. 1. XRD patterns of xCaO–(100 – x) (0.4Fe_2O_3–0.6P_2O_5) glasses.

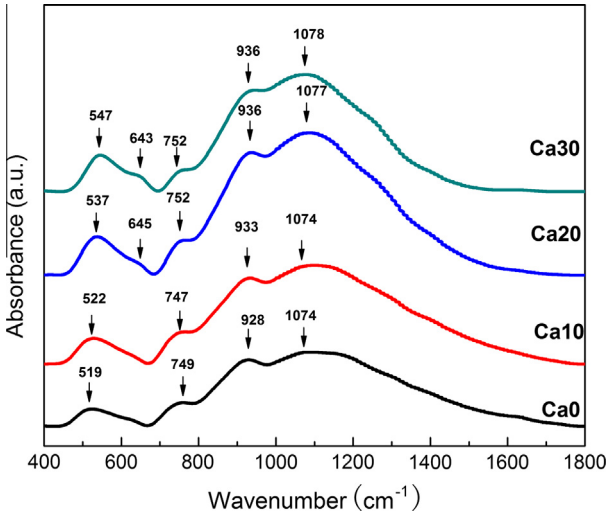

Fig. 2. IR spectra of xCaO–(100 – x) (0.4Fe_2O_3–0.6P_2O_5) glasses (x = 0, 10, 20, 30).

utilizing Cu Kα radiation (λ = 1.5405 Å). The local surface crystallizations were polished off before the powders were prepared for the measurements. The 2θ scans were recorded between 5° and 80° with 0.03° step width.

Bulk chemical composition of samples was analyzed by XRF using powdered samples. A conventional spectrometer PANalytical Axios equipped with a rhodium tube was used. Powdered glasses were pressed in boric acid pellets and methylcellulose as agglomerant.

Infrared spectroscopy (IR) of all glasses were collected in the range of 400–1600 cm^{-1} using a Thermo Nicolet Smart-380 FT-IR spectrometer, the accuracy of this technique is estimated to be ±4 cm^{-1}. The IR spectra absorption measurements were done using the KBr pellet technique.

Raman spectra at 300–1500 cm^{-1} were collected from glass powders using the InVia Raman Microscope (Renishaw, U.K.) at room temperature. The Raman spectra were excited by 514.5 nm light from an argon ion laser.

The glass transition temperature (T_g) was measured on DTA by utilizing a SDT Q600 instrument (TA, USA) in flowing air at a heating rate of 20 °C/min. The temperature scanned over a range from room temperature to 1000 °C and the estimated error in T_g is ±2 °C.

The density (ρ) of the glass was measured at room temperature by the Archimedes method in water as buoyancy liquid. The estimated error is ±0.02 g cm^{-3}.

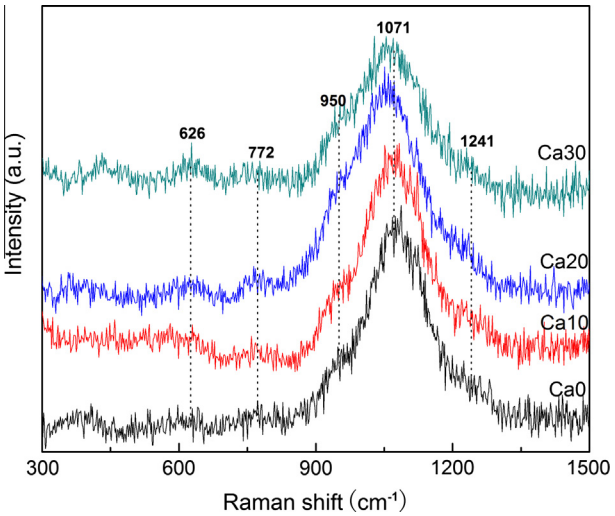

Fig. 3. Raman spectra of xCaO–(100 – x) (0.4Fe_2O_3–0.6P_2O_5) glasses (x = 0, 10, 20, 30).

The chemical durability of glasses was determined according to Product Consistency Test B (PCT–B) in ASTM C1285-02, using 1.5 g of sample glass with size fraction 75–150 μm in 15 ml deionized