



Structural aspects of calcium iron phosphate glass containing neodymium oxide



Haijian Li ^{a,b}, Xiaofeng Liang ^{a,b,*}, Cuiling Wang ^{a,b}, Huijun Yu ^{a,b}, Zhen Li ^{a,b}, Shiyuan Yang ^b

^a Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China

^b State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, PR China

HIGHLIGHTS

- $\text{Nd}_2\text{O}_3\text{—CaO—Fe}_2\text{O}_3\text{—P}_2\text{O}_5$ glass was investigated by hardness, infrared and Raman spectra.
- Homogeneous glasses were obtained within 10 mol% Nd_2O_3 additions.
- Hardness showed that Nd_2O_3 strengthened the crosslinking of the glass network.
- P—O—Nd bonds enter the pyrophosphate structure by replacing Q^1 terminal oxygen.

ARTICLE INFO

Article history:

Received 23 January 2014

Received in revised form 5 March 2014

Accepted 12 March 2014

Available online 24 March 2014

Keywords:

Neodymium oxide

Vickers-hardness

Infrared spectra

Raman spectra

ABSTRACT

Homogeneous glasses of the $x\text{Nd}_2\text{O}_3\text{—}(100-x)(12\text{CaO—}20\text{Fe}_2\text{O}_3\text{—}68\text{P}_2\text{O}_5)$ system were obtained within the $0 \leq x \leq 10$ mol% composition range. The density and molar volume measurements helped to understand the structural changes occurring in these glasses. Vickers-hardness results showed that addition of Nd_2O_3 strengthened the crosslinking of the glass network. Spectra analysis indicated that Nd_2O_3 enters in the structure of the phosphate glasses as a network modifier. The depolymerization of the glass network by the addition of Nd_2O_3 is characterized by the increase in the concentration of pyrophosphate. The decrease of the Q^1 terminal oxygen with increasing Nd_2O_3 content indicated that P—O—Nd bonds participated in the pyrophosphate glass structure, determined from the Raman spectra.

© 2014 Elsevier B.V. All rights reserved.

Introduction

In the nuclear field, vitrification is a worldwide recognized method to confine the highly radioactive nuclear liquid wastes arising from spent nuclear fuel reprocessing, which includes fission products and minor actinides [1,2]. Iron phosphate glasses with the $40\text{Fe}_2\text{O}_3\text{—}60\text{P}_2\text{O}_5$ (mol%) composition, alternative host matrices to be used as radioactive waste immobilization, were found to have the better chemical durability, compositional flexibility, higher waste loading and lower melting temperatures than borosilicate glasses [3–5]. Calcium phosphate glasses have distinct advantages over the borosilicates for nuclear wastes disposal, which is due to their low melting temperature and melting time, and low viscosity in the temperature range of 800–1000 °C [5,6].

Recently, the $\text{CaO—Fe}_2\text{O}_3\text{—P}_2\text{O}_5$ system, called base glass, has been known and studied for vitrifying certain high-level nuclear wastes [7,8]. Spectroscopic studies have shown that iron ions in the calcium iron phosphate glasses can form stable P—O—Fe covalent bonds, and calcium ions can form P—O—Ca covalent bonds and the non-bridging oxygen (P—O[−]Ca²⁺—O—P) ionic cross-links, and accordingly increase chemical durability [4,8,9].

In radioactive waste forms, trivalent lanthanide ions (such as Nd^{3+} ions) are good surrogates only for the heaviest transuranic elements occurring in high level waste (HLW) such as Cm and Am [10,11]. Indeed, these two actinide elements have cation radii r similar to the one of Nd^{3+} ion (for instance, in sixfold coordination: $r(\text{Am}^{3+}) = 1.09 \text{ \AA}$ and $r(\text{Nd}^{3+}) = 1.109 \text{ \AA}$ [12]). On the other hand, rare earth glasses are well known for their superior properties, such as hardness, thermal characterization, especially, chemical durability, owing to higher field strength than traditional network modifier cation [13,14].

Chouard et al. [15] investigated the effect of neodymium addition (from 0 to 3.54 mol% Nd_2O_3) on the structure of $\text{SiO}_2\text{—B}_2\text{O}_3\text{—Al}_2\text{O}_3\text{—Na}_2\text{O—CaO—MoO}_3$ system for the vitrification of

* Corresponding author at: Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China. Tel.: +86 0816 6089507.

E-mail address: XFLiang@swust.edu.cn (X. Liang).

¹ Co-first author.

high-level radioactive wastes, the results showed that neodymium acted as a network modifier and generated a depolymerization of the glassy network. Quintas et al. [16] found that the neodymium ion in aluminoborosilicate glass was surrounded by 7–8 non-bridging oxygens (NBO), and every NBO was charge compensated by 2–3 alkalis and alkaline-earths (Ca^{2+}). However, little work has been done to identify the effects of neodymium oxide addition on the structure of calcium iron phosphate glasses. In the present work, to investigate the effect of the Nd_2O_3 content on the structure of calcium iron phosphate glasses in detail using X-ray powder diffraction (XRD), density, Vickers-hardness, Fourier transformed infrared spectra (FT-IR) and Raman spectra.

Experimental procedure

Preparation of glass samples

Glasses with molar composition $x\text{Nd}_2\text{O}_3-(100-x)(12\text{CaO}-20\text{Fe}_2\text{O}_3-68\text{P}_2\text{O}_5)$, $x=0, 2, 4, 6, 8, 10, 12$ mol%, were prepared by reacting neodymium oxide (99.9%), calcium oxide, ferric oxide and ammonium phosphate monobasic. After thorough mixing the powders were introduced in corundum crucibles, in order to prevent the excess boiling and consequent spillage, water and ammonia in ammonium phosphate monobasic were removed initially by preheating it at 220°C for about 2 h and then the electric furnace was raised to 1250°C (heating rate was $10^\circ\text{C min}^{-1}$), and samples were melted at 1250°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. Samples for property measurements were cut from the ground.

Structural investigation

XRD analysis was performed on samples employing a X-ray diffractometer (PANalytical X'Pert PRO, The Netherlands). The 2θ scans were made between 5° and 80° with step width of 0.03° and utilized Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Preparation of the samples used a simple top pack loading method for an acquired smooth surface.

The density, D , of each glass was measured at room temperature using the Archimedes method with water as an immersing liquid. The sample weights varied between 3 and 4 g, and the measured densities were reproducible within 0.03 g cm^{-3} . The molar volume (V_m) was calculated using the relation $V_m = \sum(X_i M_i)/D$, where x_i is the molar fraction and M_i is the total molecular weight of the component. The composition of the prepared glass were used for the calculation of V_m .

The Vickers-hardness was measured using a Hv-1000A hardness tester equipped with a conical Vickers indenter at a load of 0.3 kgf for 13 s. The absolute hardness values were calculated automatically according to the well known formula and expressed in conventional units HV, $\text{HV} = 2F \sin(\alpha/2)/d^2 = 1.8544F/d^2$, where d is the average of two indentation diagonals in mm, F is the loading force in kgf and α is the diamond pyramid edge angle in 136° . The hardness was determined from the mean value of 8 indentations. Hence the errors on the measured values correspond to the standard deviation is about 3%.

The infrared spectra of the samples were measured from 400 to 2400 cm^{-1} using a Spectrum One FT-IR spectrometer (Perkin-Elmer, USA) and the KBr standard pellet method. Glass pellets were prepared by mixing about 2 mg powder with 200 mg dried KBr powder and compressing the resulting mixture in an evacuated die. The accuracy of this technique is estimated to be $\pm 4 \text{ cm}^{-1}$.

Raman spectra at $300\text{--}1600 \text{ cm}^{-1}$ were collected from glass powders using the InVia Raman Microscope (Renishaw, UK) at room temperature. The Raman spectra were excited by 514.5 nm light from an argon ion laser. The spectral resolution was about $1\text{--}2 \text{ cm}^{-1}$ and the wavenumber accuracy was 0.2 cm^{-1} . Six multiple measurements per sample were done to check for the potential micron-range heterogeneity and for the effects of sample orientation; both have not been found, as it would be expected for a nearly homogeneous glass sample.

Because the majority of the bands are large and asymmetric, presenting also some shoulders, a deconvolution of the experimental spectra was necessary. This fact was made with ORIGIN 7.5

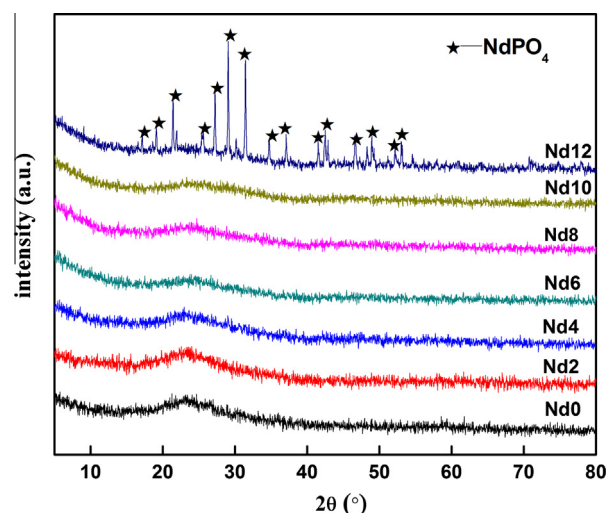


Fig. 1. XRD patterns of $x\text{Nd}_2\text{O}_3-(100-x)(12\text{CaO}-20\text{Fe}_2\text{O}_3-68\text{P}_2\text{O}_5)$ glasses.

Table 1

The density, mole volume and Vickers-hardness of the studied glasses.

Physical parameters	Nd0	Nd2	Nd4	Nd6	Nd8	Nd10
D (g/cm^3)	2.82	2.91	2.99	3.07	3.21	3.23
V_m (cm^3/mol)	47.94	47.92	47.90	47.81	47.13	47.92
Vickers-hardness (kgf/ mm^2)	470	486	511	523	533	540

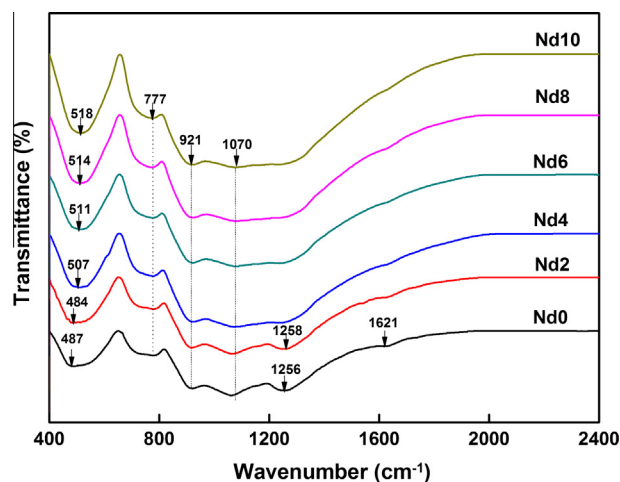


Fig. 2. IR spectra of $x\text{Nd}_2\text{O}_3-(100-x)(12\text{CaO}-20\text{Fe}_2\text{O}_3-68\text{P}_2\text{O}_5)$ glasses.

Download English Version:

<https://daneshyari.com/en/article/1405214>

Download Persian Version:

<https://daneshyari.com/article/1405214>

[Daneshyari.com](https://daneshyari.com)