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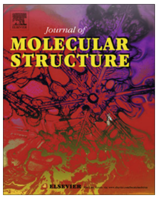

FTIR spectra and properties of iron borophosphate glasses containing simulated nuclear wastes

Qilong Liao [a,*], Fu Wang [a], Kuiru Chen [a], Sheqi Pan [b], Hanzhen Zhu [a], Mingwei Lu [a], Jianfa Qin [a]

[a] *School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China*
[b] *National Key Laboratory for Surface Physics & Chemistry, Chinese Academy of Engineering Physics, Mianyang 621907, PR China*

HIGHLIGHTS

- IBP wasteforms' thermal properties are faintly affected by B_2O_3 doping modes.
- Distributions of PO_4^{3-}, $[P_2O_7]$ and $[BO_4]$ groups are optimal as 10B base glass used.
- $[BO_3]$, PO_3^- and $[PO_2]$ groups are very low in structure of the IBP wasteforms.
- The DR values of IBP wasteforms are about 10^{-8} g cm^{-2} min^{-1}.

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ABSTRACT

30 wt.% simulated nuclear wastes were successfully immobilized by B_2O_3-doped iron phosphate base glasses. The structure and thermal stability of the prepared wasteforms were characterized by Fourier transform infrared spectroscopy and differential thermal analysis, respectively. The subtle structural variations attributed to different B_2O_3 doping modes have been discussed in detail. The results show that the thermal stability and glass forming tendency of the iron borophosphate glass wasteforms are faintly affected by different B_2O_3 doping modes. The main structural networks of iron borophosphate glass wasteforms are PO_4^{3-}, $P_2O_7^{4-}$, $[BO_4]$ groups. Furthermore, for the wasteform prepared by using $10B_2O_3$–$36Fe_2O_3$–$54P_2O_5$ as base glass, the distributions of Fe–O–P bonds, $[BO_4]$, PO_4^{3-} and $P_2O_7^{4-}$ groups are optimal. In general, the dissolution rate (DR) values of the studied iron borophosphate wasteforms are about 10^{-8} g cm^{-2} min^{-1}. The obtained conclusions can offer some useful information for the disposal of high-level radioactive wastes using boron contained phosphate glasses.

Introduction

Vitrification has been one of the primary methods to deal with high-level radioactive wastes (HLWs) over the last half century, and it is, therefore, still of interest to many researchers [1–6]. Borosilicate glasses have been chosen as the first generation HLW host matrix due to their high chemical durability and good thermal stability. However, the constituents of many HLWs awaiting disposal are complex. They usually contain phosphates, sulfates, chlorides and heavy metals. These constituents are easy to produce phase separation or liquid immiscibility problems in the structure of borosilicate glasses [1,2,7–9]. Once a glass undergoes phase separation, its properties will deteriorate greatly. Hence, it is quite essential to search alternative host matrices to immobilize these problematic radioactive wastes [8–10].

Iron phosphate glasses are one of the most potential host materials for above-mentioned problematic radioactive wastes because of their high chemical durability and large compositional flexibility [1,2,7,8,10,11]. However, the irradiation stability and thermal properties of this system glasses are inferior compared with widely used borosilicate system glasses. It is well known that the thermal neutron absorption and mass absorption coefficients of B_2O_3 are two orders of magnitude greater than those of P_2O_5 [12]. Thus, studies on boron-doped iron phosphate glasses have received sufficient attention. It has been proved that doping with B_2O_3 can enhance the thermal stability and crystallization resistance of phosphate system glasses [13–15]. In addition, doping of some phosphate glasses with B_2O_3 also improve their chemical durability [16]. The above-mentioned effects of B_2O_3 on the properties of iron phosphate glasses are all favorable to HLWs immobilization.

The results of the study on the Fe_2O_3–B_2O_3–P_2O_5 glasses [17–19] revealed that doping of $60P_2O_5$–$40Fe_2O_3$ glass with

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* Corresponding author. Tel.: +86 0816 2419201.
E-mail address: liaoqilong@swust.edu.cn (Q. Liao).

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10 mol% B_2O_3 ($10B_2O_3$–$36Fe_2O_3$–$54P_2O_5$, IBP glass) gives superior irradiation stability and thermal stability. Furthermore, it has insignificant effect on its chemical durability. The properties of IBP glass immobilized some metal oxides were also studied by our group [6,20,21]. The acquired results showed that good chemical durability and thermal properties of the IBP glass with 20 mol% Na_2O/K_2O still exist, although mixed alkali effect occurs [6]. Moreover, the glass can immobilize 10–15 mol% CeO_2 which often is simulated nuclide PuO_2 in field of HLWs immobilization research [20]. However, there are not any studies on the structure, thermal properties and chemical durability of iron borophosphate glass wasteforms.

Thus, iron borophosphate glass wasteforms containing 30 wt.% simulated nuclear wastes are prepared by using $40Fe_2O_3$–$60P_2O_5$ glass doped with 10 mol% B_2O_3 in different modes as base glass. There are three modes of B_2O_3 doping. Substituting of 10 mol% B_2O_3 for Fe_2O_3 in $40Fe_2O_3$–$60P_2O_5$ glass (10BFe) is the first mode; directly doping 10 mol% B_2O_3 into $40Fe_2O_3$–$60P_2O_5$ glass (10B) is the second mode, and the third mode is substituting of 10 mol% B_2O_3 for P_2O_5 (10BP). The structure and properties of the prepared glass wasteforms are discussed in detail. The constituents of simulated nuclear wastes are determined according to the features of nuclear wastes from a plant located in China [22]. CeO_2 is used as simulated actinide nuclides [20].

Experimental

Batches to produce 60 g of glass wasteforms were prepared by thorough mixing analysis grade raw material powders according to the designed stoichiometric ratio in Table 1. Then the thoroughly mixed batches were melted in muffle furnace at 1200 °C for 3 h in air. After stirring, the melted liquids were poured into a preheated steel mold to form cubes of about $1 \times 1 \times 1\ \text{cm}^3$. These as-quenched glass wasteforms were annealed at 450 °C for 1 h and slowly cooled in an annealing oven to room temperature for 450 min. The prepared samples are marked by 10BFeW, 10BW and 10BPW. The 10BFeW sample represents the sample prepared by using 10BFe base glass, the 10BW sample represents the sample prepared by using 10B base glass and the 10BPW sample represents the sample prepared by using 10BP base glass. The constituents of simulated nuclear wastes are listed in Table 1.

The densities of samples were measured at room temperature by Archimedes Method using glycerol as immersion liquid, and the estimated error is ±0.01 g cm^{-3}. The glass transition temperature (T_g) and onset temperature of crystallization (T_r) were determined by differential thermal analysis (DTA), with a heating rate of 10 °C min^{-1}, using a Thermal Analyzing Apparatus [Mettler Toledo, TGA/SDTA 851^e, Switzerland]. The DTA measurements were performed in temperature range of 200 and 1000 °C in air flux. Fourier transform infrared spectra (FTIR) of all glass wasteforms were collected in the range of 2000–400 cm^{-1} by using an Infrared Spectrometer (PerkinElmer Instrument Co. U.S.A). The IR absorption measurements were done using KBr pellet technique.

The chemical durability of the bulk glasses was evaluated from the weight loss of samples ($1 \times 1 \times 1\ \text{cm}^3$) immersed in deionized water at 90 °C for 1–56 days. The samples were polished with 600 grit SiC paper, cleaned with acetone and suspended in polyethylene flasks containing 100 mL deionized water at 90 °C. Three duplicate measurements were made for each glass and the average dissolution rate (DR) was calculated from the weigh loss.

$$\text{DR} = \frac{\Delta W(\text{g})}{SA(\text{cm}^2) \times t(\text{min})}$$

where ΔW is the measured weight loss, SA is surface areas of the prepared samples, and t is immersion time.

Results and discussions

Table 2 shows the densities of the studied IBP glass wasteforms. It is shown that the densities of the samples insignificantly vary with the B_2O_3 doping modes changing from 10BFe, 10B to 10BP. Moreover, the densities of the glass wasteforms are about 15% higher than those of many borosilicate glasses or glass wasteforms [8]. Therefore, the volume of the studied glass wasteforms containing a fixed weight of wastes may be about 15% smaller than that of comparable borosilicate wasteforms.

Fig. 1 shows the DTA curves of the as-prepared glass wasteforms. The curves are characterized with an endothermic peak with onset temperature varying from approximately 526, 527 to 529 °C for 10BFeW, 10BW and 10BPW sample, respectively. The endothermic peak represents glass transition phenomenon and the onset temperature corresponds to glass transition temperature (T_g) [19]. It can be concluded from the DTA curves that the variation tendency of T_g is consistent with that of density (Table 2), because the density is directly proportional to the compactability of the prepared wasteforms. According to Hruby method [17,23], the increase of (T_r–T_g) value indicates the enhancement in glass forming tendency and thermal stability [23]. The values of (T_r–T_g) for the studied IBP wasteforms are independent on the B_2O_3 doping modes, as shown in Table 2. This result shows that thermal stability and glass forming tendency of the glass wasteforms is insignificantly affected by the different B_2O_3 doping modes.

The infrared spectra (IR spectra) of the prepared glass wasteforms are shown in Fig. 2(a). The IR spectrum provides information on molecular vibrations associated with specific chemical bonds. As shown in Fig. 2(a), there are insignificant differences among the IR data of the studied glass wasteforms. However, the peak positions of some bands show slight deviations due to the different B_2O_3 doping modes. Moreover, the broadening spectral peak is consistent with the glass structure accommodating many types of bonding states. Thus, in order to acquire quantitative informations about specific structural groups, the recorded IR are deconvoluted using a Gaussian-type function [24], as shown in Fig. 2(b)–(d).

The studied IBP glass wasteforms consist of two glass former oxides, P_2O_5 and B_2O_3, but with P_2O_5 about 30–37 mol%, and B_2O_3 about 6 mol%. Therefore, it is expected that the observed IR data mainly represent the structural networks of phosphate groups, tetrahedral and triangular borate ($[BO_4]$, $[BO_3]$) units [25]. Taking this into consideration, the main assignments of the IR spectra are listed in Table 3.

Table 1
Molar compositions of simulated wastes and iron borophosphate glass wasteforms (mol%).

Samples	P_2O_5	Fe_2O_3	B_2O_3	Al_2O_3	K_2O	Na_2O	NiO	Cr_2O_3	ZrO_2	SO_4^{2-}	CeO_2
Simulated wastes	0	11.9	0	8.2	0.8	66.6	4.9	1.1	0.8	0.8	4.9
10BFeW	37.0	18.6	6.1	3.6	0.3	29.0	2.1	0.5	0.3	0.3	2.1
10BW	33.2	22.2	6.1	3.6	0.3	29.2	2.1	0.5	0.3	0.3	2.1
10BPW	30.7	24.6	6.1	3.6	0.3	29.3	2.1	0.5	0.3	0.3	2.1