

Contents lists available at ScienceDirect

### Journal of Non-Crystalline Solids

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

# Structure and properties of zinc aluminophosphate glasses and those doped with zirconium dioxide



JOURNAL OF NON-CRYSTALLINE SOLIDS

#### Sheng Li<sup>a</sup>, Sanxi Huang<sup>a</sup>, Fengnian Wu<sup>a</sup>, Yunlong Yue<sup>b,\*</sup>

<sup>a</sup> School of Material Science and Engineering, University of Jinan, Jinan 250022, People's Republic of China

<sup>b</sup> Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, People's Republic of China

#### ARTICLE INFO

Article history: Received 21 January 2015 Received in revised form 25 March 2015 Accepted 30 March 2015 Available online 3 April 2015

*Keywords:* Zirconium; Phosphate glasses; Chemical durability

#### ABSTRACT

Structure and properties of two glass systems, group A:  $50P_2O_5-(50 - x)ZnO-xAl_2O_3$  (x = 0, 5, 10, 15, 20 mol%) and group B:  $50P_2O_5-20Al_2O_3-(30 - x)ZnO-xZrO_2$  (x = 1, 2, 3, 4, 5 mol%) were investigated. The density of the first series goes down with introducing more  $Al_2O_3$ , while the density increases as  $ZrO_2$  replaces ZnO in networks. Adding  $Al_2O_3$  or doping more  $ZrO_2$  would raise  $T_g$  as well as  $T_c$  for both series of glasses. Adding  $Al_2O_3$  does improve the chemical durability when comparing A1 with other members in the same group; further, doping  $ZrO_2$  into glasses based on A5 also makes some promotion in chemical properties. Structure analyses all coming from IR tests, it turns out that ion electronegativity does play an essential role in phosphate network when different kinds of ion exchange occur in glasses.

© 2015 Elsevier B.V. All rights reserved.

#### 1. Introduction

The outstanding properties of phosphate glass, such as low melting and transition temperature, high thermal expansion and optical characteristics, have led to its widespread use. Therefore it has been studied for several years in order to apply it to various aspects like the manufacturing of glass–polymer composites [1–3] and nuclear waste immobilization matrices [4,5], besides sealing materials. However, their poor chemical durability makes the phosphate glasses out of reach for a wider application.

Alkali, alkaline earth and some transition metal oxides form glasses when melted with  $P_2O_5$  [6]. Introducing alumina into phosphate glasses improves the chemical durability as well as the glass transition temperature ( $T_g$ ), reducing the thermal expansion coefficient [7].

As for phosphate glasses in solution, the rate of phosphate glass dissolution is dependent on glass compositions. The dissolution process includes acid/base reactions, hydrolysis reactions and hydration reactions [8]. Cacaina and Simon [9] proposed that a surface layer in solution impacts the glass dissolution process, in which the layer would have similar structure as the original glasses; meanwhile, the out layer would transform over time by localized hydrolysis and condensation reactions in the gel layer. All the three processes do have influence on the chemical durability of phosphate glasses. However, there seems to be no report on the chemical properties of zinc aluminophosphate glasses and those doped with zirconium. Thus, the objective of this paper is to study

\* Corresponding author.

the properties and structure of the above glasses, and find out further research work in the future.

#### 2. Experimental

#### 2.1. Sample preparation

The glass samples were divided into two groups according to compositions. Series A is  $50P_2O_5-(50 - x)ZnO-xAl_2O_3$  (x = 0, 5, 10, 15, 20 mol%), made by melting a mixture of reagent grade chemicals ZnO, Al<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub>; while series B is  $50P_2O_5-20Al_2O_3-(30 - x)ZnO-xZrO_2$  (x = 1, 2, 3, 4, 5 mol%), also made by mixing ZnO, Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub>.

All the batches of about 30 g were put in the dense pure alumina crucibles in an electrical furnace in air at 1300–1500 °C, depending on the glass compositions, for 4 h. Besides, samples melt at all temperatures were covered to avoid the volatility of  $P_2O_5$ . Then the melts were poured into the graphite molds and quenched to room temperature in air, moved to the annealing process near the glass transition temperature for 2 h, and then slowly cooled to room temperature with a rate of near 1 °C/min in order to eliminate internal tensions and get more homogenized glasses. One more thing to do is to grind part of the formed glasses into powder for the following tests.

#### 2.2. Sample characterization

The room temperature density ( $\rho$ ) of all the samples was measured by the Archimedes method with distilled water as the immersion medium. For each glass, two samples were measured so that the average density is accurate. The estimated error was  $\pm 0.002$  g/cm<sup>3</sup>.

*E-mail addresses*: biology-che@163.com (S. Li), andygandy@163.com (S. Huang), wfn0922@126.com (F. Wu), yueyl@ujn.edu.cn (Y. Yue).

X-ray powder diffraction (D8 ADVANCE, German) was used to detect the crystalline solid and confirm the vitreous state of samples. Meanwhile, through this test, the results of samples corroded in NaOH were detected to figure out their identification.

DSC investigation by METTLER TGA/DSC1/1600HT was carried to identify the glass transition temperatures on about 10 mg of samples. The first series was measured with a 10 °C/min heating rate from 50 °C to 1000, while the second took 5 °C/min from 50 °C to 1200 °C (accuracy  $\pm$  5 °C). The beginning of the endothermic peak and the onset of the first exothermic peak in the DSC curve were chosen as the glass transition temperature (T<sub>g</sub>) and the onset crystallization temperature (T<sub>c</sub>) respectively.

The infrared (IR) spectrum for each sample was obtained between 450 and 1800 cm<sup>-1</sup> using a Nicolet 380 spectrometer. All the glasses were prepared as tablets with a diameter of 10 mm and 1 mm thick by pressing a mixture that is of approximately 2 mg glass powder and 200 mg anhydrous KBr powder. The spectrometer collected 16 scans for each glass sample and the spectrum was recorded. And then a pure KBr spectrum was subtracted from each glass spectrum to correct the background.

For chemical durability measurements, samples were cut into approximately  $1 \times 1 \times 0.5$  cm<sup>3</sup> and their surface was polished with SiC abrasive papers (800, 1000 and 1200 grit). All edges and corners were also removed to avoid sharp edges. Next came washing all glasses in the anhydrous alcohol. Samples were dried in the oven at 80 °C for nearly 1 h, and then weighed. Strings were adopted to suspend glass samples in plastic containers, which held the volume of 200 ml NaOH solution, at 80 °C for 72 h. During the process, all would be removed from solution, washed with anhydrous alcohol, dried in oven at 80 °C, and finally re-weighed. Each experiment was in duplicate and the average dissolution rate was calculated from the weight loss, which was calculated through normalizing the sample surface area and the corrosion time.

#### 3. Results

Glass compositions of the two series can be seen in Table 1. All the glasses, except for those doped with 4 mol% and 5 mol%  $ZrO_2$  in series B, were transparent, while those two samples turned into totally white, which was probably presumed to be crystalline.

#### 3.1. FTIR

The IR of A series glass samples is shown in Fig. 1. The spectra are similar to other phosphate glasses that have been reported [10–13]. The bands in Fig. 1 are around 510 cm<sup>-1</sup>, 739 cm<sup>-1</sup>, 790 cm<sup>-1</sup>, 926 cm<sup>-1</sup>, 1080 cm<sup>-1</sup> and 1268 cm<sup>-1</sup> [14,15]. The band at 510 cm<sup>-1</sup> could be assigned to bending vibration of P–O bonds,  $\delta$ (P–O), of Q<sup>0</sup> tetrahedra, while bands of 739 cm<sup>-1</sup> and 790 cm<sup>-1</sup> correspond to

#### Table 1

Nominal composition and measured properties of glasses in A  $(50P_2O_5-(50 - x)ZnO-xAl_2O_3)$  and B  $(50P_2O_5-20Al_2O_3-(30 - x)ZnO-xZrO_2)$  series.

Code	$P_2O_5$	ZnO	$Al_2O_3$	$ZrO_2$	O/P	$\rho~(\pm 0.002~{\rm g/cm^3})$	$D_R (g \cdot cm^{-2} \cdot min^{-1})$
A series: $50P_2O_5 - (50 - x)ZnO - xAl_2O_3$							
A1	50	50	0		3.00	2.902	$3.45  imes 10^{-5}$
A2	50	45	5		3.10	2.872	$1.02 \times 10^{-5}$
A3	50	40	10		3.20	2.759	$2.34 \times 10^{-5}$
A4	50	35	15		3.30	2.736	$1.94 \times 10^{-5}$
A5	50	30	20		3.40	2.652	$2.12 \times 10^{-5}$
B series: $50P_2O_5 - 20Al_2O_3 - (30 - x)ZnO - xZrO_2$							
B1	50	29	20	1	3.40	2.645	$1.11 \times 10^{-5}$
B2	50	28	20	2	3.37	2.655	$1.16  imes 10^{-5}$
B3	50	27	20	3	3.34	2.661	$9.56  imes 10^{-6}$
B4	50	26	20	4	3.31	2.660	$7.35  imes 10^{-6}$
B5	50	25	20	5	3.28	2.681	$1.19 \times 10^{-5}$

Treprovision for the second se

Fig. 1. IR spectra of A series:  $50P_2O_5 - (50 - x)ZnO - xAl_2O_3$  (x = 0-20 mol%).

symmetric vibrations of P–O–P bonds of bridging oxygen (OB) in phosphate chains [16]. The  $V_{as}(PO_2)$  and  $V_s(PO_2)$  vibrations of the O–P–O bonds of  $Q^1$  and  $Q^2$  tetrahedra with non-bridging oxygen (ONB) are observed around 1268 cm<sup>-1</sup> and 1080 cm<sup>-1</sup>, respectively [17]. The IR spectra of B series glasses can be seen in Fig. 2, which are similar to those of samples from the A series.

In series A, the intensity of bands at around  $510 \text{ cm}^{-1}$  decreases as  $Al_2O_3$  levels up; At the same time, frequencies at 739 cm<sup>-1</sup> and 790 cm<sup>-1</sup> turn weaker and broader. As for the bands of 1080 cm<sup>-1</sup> and 1268 cm<sup>-1</sup>, both of them become broad and weak. In the second series, with fixed amount of  $Al_2O_3$  and small addition of  $ZrO_2$ , bands change similar to those in Fig. 1.

#### 3.2. Density and XRD

The variants of density of the first series:  $50P_2O_5-(50 - x) ZnO-xAl_2O_3$  (x = 0-20 mol%), whose O/P ranges between 3.00 and 3.40, and the second series:  $50P_2O_5-20Al_2O_3-(30 - x)ZnO-xZrO_2$  (x = 1-5 mol%) with approximately the same O/P range of phosphate glasses versus the mole of  $Al_2O_3$  and  $ZrO_2$  are presented in Fig. 3(a, b).

The density of series A falls smoothly from  $2.902 \text{ g/cm}^3$  to  $2.652 \text{ g/cm}^3$  while ZnO is replaced by Al<sub>2</sub>O<sub>3</sub>. The reason why this phenomenon occurs may be in part due to the greater relative mass of Zn, compared with Al and P. Meanwhile the higher the ZnO, the larger the molar volumes of glasses will be [18]. Therefore, with ZnO replaced, density of the first series drops slightly.



Fig. 2. IR spectra of A series:  $50P_2O_5-20Al_2O_3-(30 - x) ZnO-xZrO_2$  (x = 1-5 mol%).

Download English Version:

## https://daneshyari.com/en/article/1480737

Download Persian Version:

https://daneshyari.com/article/1480737

Daneshyari.com