Journal of Non-Crystalline Solids 450 (2016) 87–94

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Effects of barium oxide on structure and properties of calcium iron phosphate glasses

Sheng Li [a], Hongting Liu [a], Yadong Lu [a], Ya Qu [a], Yunlong Yue [a,b,*]

[a] School of Materials Science and Engineering, University of Jinan, Jinan, China
[b] Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan, China

ARTICLE INFO

Article history:
Received 22 March 2016
Received in revised form 16 June 2016
Accepted 2 August 2016
Available online xxxx

Keywords:
Barium oxide
Calcium iron phosphate glass
Chemical durability

ABSTRACT

In order to study the effects of barium oxide on the structure and properties of glasses from the glass system of xBaO-(20-x)CaO-32Fe_2O_3-48P_2O_5 (x = 2,4,6,8,10,12,14,16,18 mol%), several methods are applied to the investigation, including XRD, FTIR, DSC and chemical durability tests. Results from FTIR spectra shows that BaO loosens the glass network, with some sorts of crystals forming in the two glass groups depicted in the XRD spectra. However, the glass transition temperature (T_g) and glass crystalline temperature (T_c), as well as the difference between the two($\Delta T = T_c$-T_g), rise with the addition of BaO. All densities of glasses level up with larger concentration of barium oxide; fluctuations occur in the glass system with the formation of different crystals. When CaO is replaced by BaO, the dissolution rate moves to high level in alkali solution when compared with the basic glass (20CaO-32Fe_2O_3-48P_2O_5), while glasses in acid solution possess the inferior resistance than glasses in alkaline solution. It turns out that crystals in these glasses did improve resistance to acid and alkaline ions when they are compared with their base glasses.

1. Introduction

Phosphate glasses have been used in a large number of fields [1–5]because of their advantages such as low melting temperature, high refractive indices, high thermal expansion coefficient and so forth. However, their poor chemical durability does prohibit them from widespread application [6]. The iron phosphate glasses are first proposed to dispose nuclear waste in 1984 for the excellent stability among many phosphate glasses [7]. Therefore, there are also a host of studies on improving chemical durability with different oxides: alkali oxides [8–11], alkali-earth metal oxides [8,12–15], transition metal oxides [7,8], rare earth oxides [16] and other oxides [17].

Calcium oxide and barium oxide are two effective modifiers in modifying the phosphate properties. Richard K. Brow [18] has reported the influence of calcium oxide on iron phosphate, which proposed that CaO could improve glass chemical durability, especially the alkaline-resistance for Glass Fiber Reinforced Concrete (GFRC). On the other hand, Mingwei Lu [19]studied how the doped BaO affects iron phosphate glass in which we can know that BaO works as the modifier that could strengthen the glass network, restraining glass from crystallization, leading to P-O-Ba bands and improving the glass thermal stability.

In our previous paper [12], we studied the influences from three different alkali-earth metal oxides (MgO, CaO, SrO) on the structure and properties of iron phosphate glasses. Results indicate that CaO could improve the glass chemical stability, especially the resistance to alkali solution. Even though the former glass with 10 mol% CaO possess the best in alkaline-resistance, another glass sample with 20 mol% CaO is the best in thermal stability, which was chosen as the basic glass in this investigation. Another aspect that should be in notice is that Ba^{2+} has the largest ionic radius of the alkali-earth metal oxides, which would have positive effects on the structure and chemical properties of iron phosphate glasses [19]. However, there is not much research on how the barium oxide impacts the calcium iron phosphate glasses to our knowledge, especially the alkaline resistance of calcium phosphate glass with barium. Thus, we are going to study the effects of BaO on glass structure and properties of calcium phosphate glasses with XRD, FTIR, DSC and chemical tests.

2. Experimental procedure

2.1. Preparation of samples

Glasses from the glass system of xBaO-(20-x)CaO-32Fe_2O_3-48P_2O_5 (x = 2,4,6,8,10,12,14,16,18 mol%), have been prepared with P_2O_5, Fe_2O_3, CaO and $BaCO_3$(analytical grade purity). All mixed batches (about 40 g) were transferred into alumina crucibles and heated at 1350 °C in the air for 3 h. During the heating process, samples were

* Corresponding author at: School of Materials Science and Engineering, University of Jinan, Jinan, China.
E-mail address: yueyl@ujn.edu.cn (Y. Yue).

http://dx.doi.org/10.1016/j.jnoncrysol.2016.08.003
0022-3093/

covered to avoid the volatility of P_2O_5. Then, all melts were removed into the preheated graphite molds and quenched quickly to the room temperate in the air; all samples were annealed near the glass transition temperature for 1 h, samples labeled as BCFP2,4,6,8 being treated at 680 °C to get crystals. After the former procedure, glasses cooled slowly to room temperature. A small proportion of samples ware ground into powder with the Retsch RM-200 agate mortar, while the rest would be cut into standard bulks (10 mm × 5 mm × 5 mm) for chemical stability tests. Table 1 shows the nominal compositions and accurately analyzed compositions by XRF, as well as their properties.

2.2. Characterization of samples

The XRD analyses were carried on samples with the Bruker D8 ADVANCE diffract meter (German). The scanning degree (2θ) spanned from 10 to 80° with patterns from Cu-K_α radiation at a step of 0.02°.

The differential scanning calorimetry (DSC) was carried out on a METTLER TGA/DSC1/1600HT simultaneous thermal analyzer (Switzerland) with an empty alumina crucible as the reference at a 10 °C/min heating rate from 50 °C to 1300 °C. The weight of samples was about 10 mg. The machine was calibrated by standardized pure indium, copper and gold, before carrying out experiments. The middle of the first endothermic peak would be determined as the glass transition temperatures (T_g), the middle of the first exothermic peaks being treated as the crystallization temperatures (T_c), and the difference between T_g and T_c would be the rough measurement of glass thermal stability ($\Delta T = T_c - T_g$). The estimated error in the measurements was about 5 °C.

Densities (ρ) of all samples have been measured by the Archimedes methods using the distilled water as the suspension medium. Three samples were put into the measure process in order to get the average density for accuracy. The estimated error was ± 0.002 g/cm^3.

The researchers polished all well-cut bulks with SiC abrasive papers (800,100 and 1200 grit) to remove all edges and corners to avoid sharp edges. And then all samples were washed with the anhydrous alcohol and dried in the oven at 80 °C for about 24 h, and finally weighed. At last, plastic tubes with holes were used to hold glass samples that would be immersed in 5 wt% NaOH solution or 5 wt.% H_2SO_4 solution. All the above materials were put into the PE containers at 80 °C with about 200 ml. All samples, each group repeating three times for the accurate results, would be removed from solution, washed by anhydrous alcohol, dried in oven at 80 °C, and finally re-weighed for every 24 h. The whole process contained around five corrosion-weight cycles. Last but not least, the last weight test would be carried one week after the fifth round of corrosion. The average dissolution rate would be obtained by calculation by dividing the weight loss with sample surface area and corrosion time through following equation

$$D_R = \frac{m_2 - m_1}{2(ab + ac + bc) \cdot t} \quad (1)$$

In this equation: D_R-the dissolution rate; m_1-the weight of each glass sample with the plastic tube before corrosion for each cycle; m_2-the weight of each glass sample with the plastic tube after corrosion for each cycle; a-the length of each bulk; b-the width of each bulk; c-the height of each bulk; t-the corrosion time, namely 24 h for each cycle.

Fourier transform infrared (FTIR) spectra of the as-received glasses were recorded from 400 to 2000 cm^{-1} on a Thermo Nicolet 380 FT-IR spectrometer (U.S.). The IR measurements were carried through KBr pellet method, with all samples being ground to powder and weighed about 2 mg. The mixture of glass powder and KBr powder, at the ratio of 1:100, would be made into tablets for measurement. The testing machine firstly got spectra of samples with 32 times scanning, and then, it would scan the pure KBr to eliminate potential effects from the background.

3. Results and discussion

3.1. Glass structure

Fig. 1 shows the XRD spectra of glasses from xBaO-(20-x)CaO-32Fe_2O_3-48P_2O_5 (x = 2,4,6,8,10,12,14,16,18 mol%) glasses system, with Fig. 1(a) illustrating glasses doped with 2,6,10,14,18 mol% BaO and the rest in Fig. 1(b). As we can see from Fig. 1(a), glasses with 2 mol% (BCFP1) has few crystal peaks containing $Ca_3(PO_4)_2$ (PDF#09-0169), $Ca_4P_6O_{19}$(PDF#15-0177) and $Ca_4O(PO_4)_2$·While when doped with 6 mol% BaO, the BCFP3 glass demonstrates more crystal peaks in the XRD spectra, sharper and clearer, which contain only one more kind of crystal than the former one – $BaCa(PO_3)_4$(PDF#29-0155). When more barium are introduced into glasses, there are no crystalline peaks showing up in Fig. 1(a), which indicates the crystallization of glasses are restrained by the introduction of BaO. In the previous paper [19] that studied the effects of BaO when doped into glasses from xBaO-(90×)(60P_2O_5–40Fe_2O_3)-10CaF_2 (x = 0, 5,10, 15 and 20 mol%), they contribute the less and weaker XRD peaks in glass samples with more BaO to the restraining effect from BaO. This might be due to the larger ionic radius of Ba^{2+}, when compared with that of Ca^{2+}, which prevents other ions from moving casually in glass network.

Fig. 1(b) depicts XRD spectra of samples heated at 680 °C and labeled with BCFP2, 4, 6, 8. There are more crystals than glasses in the first part of this figure. Glass marked with BCFP4 has the least sorts of crystals than the other three glasses, the main phases being

Table 1
the nominal and analyzed compositions and the measured properties of all samples.

Sample	BCFP1	BCFP3	BCFP5	BCFP7	BCFP9	BCFP2	BCFP4	BCFP6	BCFP8
P_2O_5(analyzed)	48(40.87)	48(41.45)	48(41.78)	48(41.95)	48(41.07)	48(41.91)	48(41.47)	48(41.71)	48(41.98)
Fe_2O_3(analyzed)	32(30.90)	32(30.70)	32(30.35)	32(30.26)	32(30.24)	32(30.30)	32(30.67)	32(30.44)	32(30.25)
CaO(analyzed)	18(17.01)	14(13.57)	10(8.94)	6(5.22)	2(1.85)	16(15.52)	12(11.25)	8(7.36)	4(2.16)
BaO(analyzed)	2(2.61)	6(6.34)	10(10.76)	14(14.27)	18(18.32)	4(4.14)	8(8.30)	12(12.56)	16(16.91)
Na_2O(analyzed)	0(0.39)	0(0.41)	0(0.43)	0(0.43)	0(0.46)	0(0.42)	0(0.37)	0(0.41)	0(0.37)
K_2O(analyzed)	0(0.66)	0(0.46)	0(0.45)	0(0.49)	0(0.45)	0(0.45)	0(0.43)	0(0.46)	0(0.46)
Al_2O_3(analyzed)	0(2.57)	0(2.16)	0(2.43)	0(2.43)	0(2.59)	0(2.84)	0(2.91)	0(2.55)	0(2.97)
SiO_2(analyzed)	0(3.24)	0(3.32)	0(3.23)	0(3.53)	0(3.53)	0(2.90)	0(3.03)	0(2.93)	0(3.25)
Other oxides (analyzed)[a]	0(1.75)	0(1.59)	0(1.63)	0(1.42)	0(1.49)	0(1.52)	0(1.57)	0(1.58)	0(1.65)
Phase	Crystal	Crystal	Amorphous	Amorphous	Amorphous	Crystal	Crystal	Crystal	Crystal
O/P	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71
ρ[g/cm^3]	2.980	3.035	2.981	3.126	3.314	3.206	3.235	3.140	3.504
Tg[°C]	553	558	566	570	572	539	550	556	567
Tc[°C]	820	825	884	897	916	656	685	681	713
ΔT[°C]	267	266	318	327	344	117	136	125	186

[a] Other oxides: PbO, ZnO, MgO and TiO_2.