Viscosity and crystallization mechanism of cesium loaded iron phosphate glasses

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ABSTRACT

This paper describes the melt viscosity behaviour and the crystallization mechanism of a series of iron phosphate glasses. High temperature viscosity measurements were carried out on pristine iron phosphate glass and a series of cesium loaded iron phosphate glasses in order to understand the effect of addition of Cs_2O on viscosity of iron phosphate glasses. Activation energy of viscous flow was estimated from the experimental data by applying Arrhenius model of viscosity–temperature relationship. Activation energy of viscous flow is observed to be strongly correlated to glass transition temperature of these glasses. Fragility of iron phosphate and cesium loaded iron phosphate glass systems were also evaluated in region of high temperature. Crystallization of these glasses was studied using thermal analysis techniques. Temperature integral approximation free method was utilized to evaluate the kinetic parameters such as activation energy of crystallization (E_c) and Avrami exponent (n). The value of Avrami exponent 'n' obtained showed that the glasses under present study crystallize via bulk crystallization mechanism, i.e., nucleation and three dimensional growth.

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1. Introduction

Presently, vitrification is considered as the method of immobilization of nuclear waste arising after reprocessing spent nuclear fuel [1–3]. As on today, borosilicate glass (BSG) is used for the immobilization of nuclear waste. However, nuclear wastes containing significant amounts of chrome oxides, heavy metal oxides and rare earth oxides are not very compatible [4] with BSG. Nuclear wastes rich in these oxides need to be diluted before immobilizing in BSG, which in turn increases the waste volume. Hence an alternate matrix is required for the vitrification of nuclear waste rich in these substances.

Iron phosphate glasses (IPG) are considered as a suitable matrix for the immobilization of high level nuclear waste containing alkali oxides, sulphates, and chrome oxides [5–7]. The synthesis and characterization of IPG containing simulated fast reactor waste (rich in Cs_2O, noble metals and rare earths) was reported by us earlier [8]. Iron phosphate glass can also be used for the immobilization of specific oxides like MoO_3, UO_2, Bi_2O_3 and Cs_2O [9–11]. Among the various oxides, the incorporation of Cs_2O is of interest because $^{137}Cs_2O$ loaded glass can be used as a γ-radiation source for medical applications [12]. In our earlier studies, 36 mol % inactive Cs_2O was successfully loaded in IPG without crystallization or phase separation [13]. It was also demonstrated that IPG is a better matrix for loading cesium in terms of volatilization loss [13]. Besides the incorporation of various amounts of Cs_2O in IPG, detailed characterization of these glasses was also reported by us [13–18]. During the preparation of IPG and cesium loaded IPG, the pouring temperature (temperature at which the molten glass is poured on stainless steel plate) was determined by physically checking the fluidity of molten glass at every 25 K beyond 1200 K by tilting the crucible. It is well known that the melting behaviour of glasses depends on their viscosity – temperature relationship and the knowledge of molten glass viscosity as a function of temperature is essential for efficient glass making. The first part of the present study is aimed to determine the viscosity of the iron phosphate glass melt and the change in viscosity of the melt with the addition of Cs_2O.

It is also known that, viscosity of the melt can be changed depending on the Fe^{2+}/Fe^{3+} ratio in IPG [19]. However, it was well established by Mössbauer spectroscopy that the Fe^{3+} content for the glasses under the present study was high (>95%) and almost constant (ranging from 95% to 98.8%) [13,17] compared to IPG systems reported in literature [19]. Thus, in the first part of the present study, understanding the viscosity of IPG melts was explored as a function of only the cesium oxide content.

Table 1
Composition of glass along with pouring temperature and the temperature range of viscosity measurements.

Sample	Composition of glass (mol %)			Pouring temperature/K	Temperature range of viscosity measurements/K
	Fe_2O_3	P_2O_5	Cs_2O		
IPG	40	60	–	1423	1215–1450
IP9C1	37	57.5	5.5	1403	1200–1425
IP8C2	34.5	53	12.5	1373	1220–1450
IP7C3	33	46	21	1353	1300–1450
IP6C4	29	44	27	1323	1300–1425
IP5C5	26	38	36	1263	1150–1275

The isoconversional kinetic analysis of the crystallization of these glasses [14,15,17] clearly indicated that the activation energy of the process depends strongly on the fraction of crystallization. However, the isoconversional analysis does not provide any information about the mechanism of crystallization. Thus, the second part of the present study explores the mechanism of the crystallization process of IPG and cesium loaded IPG.

2. Experimental

IPG was prepared by mixing Fe_2O_3 (99.5, Fisher Scientific) and $NH_4H_2PO_4$ (ADP) (99% Ranbaxy) maintaining Fe/P ratio as 0.67. The mixture was homogenized by grinding in a mortar and pestle and the mixture was calcined at 673 K in a platinum crucible for 1 h for facilitating the decomposition of ADP. The calcined mixture was heated to 1423 K and air-quenched by pouring it on a stainless steel plate. Cesium loaded IPG was prepared by mixing various amounts of Cs_2CO_3 (99.9% Aldrich), Fe_2O_3 and ADP. The Fe/P ratio was maintained as 0.67. The mixture was homogenized by grinding in a mortar and pestle in an argon glove box and calcined at 873 K in a similar platinum crucible. The calcined mixture was heated to the pouring temperature for about ½ h and air-quenched as mentioned earlier. The data on pouring temperature and details of analysis of composition were presented elsewhere [13,17]. The chemical composition and pouring temperature of the glasses under present study are shown in Table 1.

Viscosity of cesium loaded IPG was measured using a Brookfield viscometer (Model DV-III+) using an alumina spindle rotating at 10 rpm. The viscometer was calibrated using borosilicate glass (SRM No. 717). The temperature of viscosity measurements of iron phosphate glasses varied depending on the pouring temperature as indicated in Table 1. The viscosity measurements were repeated thrice and the error in the measurement was ± 1%.

DSC (M/s. Mettler Toledo model DSC 821e/700) was employed to understand the crystallization behaviour of cesium loaded iron phosphate glasses (IP8C2–IP6C4). The details of experimental conditions are presented in Table 2. Crystallization study of IPG and IP9C1 was carried out using a TG-DTA (Setsys Evolution 16/18, M/s. Setaram, France) system, owing to its higher temperature of crystallization (>973 K). Experiments were carried out at various heating rates (Table 2) except that 50 mg of glass powder of IP9C1 was used for DTA measurements. The DSC and TG-DTA equipments
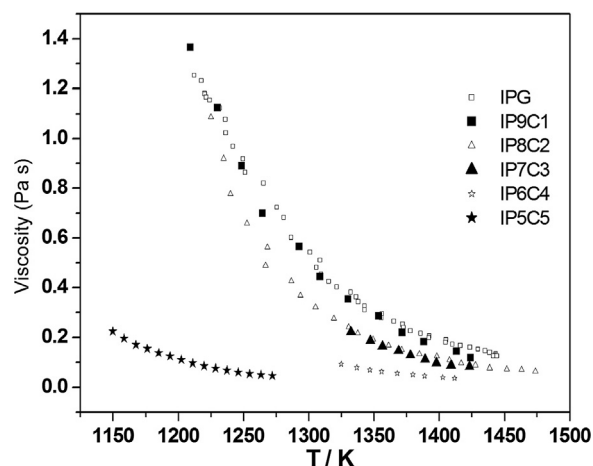
were calibrated for temperature and the accuracy of temperature measurement was ± 1 K. Pt was used as the sample holder and crystallization studies were carried out under flowing Ar (50 ml/min.) atmosphere.

3. Results and discussion

3.1. High temperature viscosity

The measured viscosity of cesium loaded IPG melt as a function of temperature is shown in Fig. 1. The viscosity of IPG [20] is also plotted along with that of cesium loaded glasses for comparison. The measured viscosity shows no discontinuity and decreases with increasing temperature. It is clearly seen from the figure that the viscosity of glass melt decreases with addition of Cs_2O and shifts the working range of the melt. This is in agreement with the observation of Kim and Day [21] that viscosity generally decreases with increasing alkali oxide content. Higher the viscosity within a reasonable range of temperature, better would be the glass forming ability of the melt. Of all the glasses under present study, plain IPG possesses higher viscosity and is thus expected to show the highest glass forming ability. This is indeed true as explained in our earlier work [17].

The variation of viscosity with temperature can be analyzed using various theoretical models [22] such as Vogel-Tamman-Fulcher (VTF) model, two-exponential equation model given by Douglas, Adam–Gibbs model, Avramov–Milchev model and Arrhenius model. Among the above mentioned models, VTF equation is the most commonly used to describe viscosity–temperature relationship covering a wide range of viscosity (10^{13}–10 Pa s). However during melting process, generally, the change in viscosity ranges

Table 2
Experimental conditions of crystallization of IPG and cesium loaded IPG.

Sample	Technique employed	Heating rate/(K/min)	Weight of sample/mg
IPG	DTA	4, 6, 8, 10 and 12	10 ± 0.1
IP9C1	DTA	4, 6, 8, 10 and 12	50 ± 1
IP8C2	DSC	2, 5, 7, 10 and 15	7 ± 0.05
IP7C3	DSC	2, 5, 7 and 10	7 ± 0.05
IP6C4	DSC	5, 7, 10 and 15	7 ± 0.05
IP5C5	DSC	5, 7, 10 and 15	7 ± 0.05

Fig. 1. Viscosity curves of IPG and cesium loaded IPG as a function of temperature.