



Iron phosphate glass containing simulated fast reactor waste: Characterization and comparison with pristine iron phosphate glass



Kitheri Joseph^{a,*}, R. Asuvathraman^a, R. Venkata Krishnan^a, T.R. Ravindran^b, R. Govindaraj^b, K.V. Govindan Kutty^a, P.R. Vasudeva Rao^a

^a Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

^b Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

ARTICLE INFO

Article history:

Received 17 January 2014

Accepted 17 May 2014

Available online 24 May 2014

ABSTRACT

Detailed characterization was carried out on an iron phosphate glass waste form containing 20 wt.% of a simulated nuclear waste. High temperature viscosity measurement was carried out by the rotating spindle method. The Fe³⁺/Fe ratio and structure of this waste loaded iron phosphate glass was investigated using Mössbauer and Raman spectroscopy respectively. Specific heat measurement was carried out in the temperature range of 300–700 K using differential scanning calorimeter. Isoconversional kinetic analysis was employed to understand the crystallization behavior of the waste loaded iron phosphate glass. The glass forming ability and glass stability of the waste loaded glass were also evaluated. All the measured properties of the waste loaded glass were compared with the characteristics of pristine iron phosphate glass.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Borosilicate glass (BSG) [1] is the most acceptable matrix for the immobilization of aqueous high level waste (HLW) arising after reprocessing spent thermal reactor fuel. The HLW originating from fast reactor fuel reprocessing differs significantly from that of thermal reactor. The fast reactor waste consists of fission products, minor actinides, noble metals and volatile fission products in higher concentration when compared to the HLW of thermal reactor. It is also well known that the noble metals are less compatible with BSG. The maximum amount of loading of molybdenum oxide in BSG in the presence of cesium is only 2.5 wt.% [2] and this can also limit the percentage of fast reactor waste loading in BSG. Hence it is essential to investigate alternate matrices suitable for the HLW of fast reactor.

Iron phosphate glass (IPG) is considered as a suitable matrix for the immobilization of nuclear waste containing higher concentration of Mo and Cr [3,4] compared to BSG. In our earlier study [5], 20 wt.% of simulated fast reactor waste was successfully loaded in IPG without phase separation or crystallization. Besides the immobilization of simulated waste in IPG, this waste form was characterized for its amorphous nature, density, glass transition temperature, thermal expansion behavior, surface morphology and thermal stability. The 20 wt.% simulated fast reactor waste

loaded IPG is henceforth referred as IP20FRW. The present study involves determination of high temperature viscosity of molten IP20FRW, specific heat of solid IP20FRW, Fe³⁺/Fe ratio by Mössbauer spectroscopy and structure by Raman spectroscopy. Thermogravimetric-differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC) were employed to understand the glass characteristics (glass forming ability (GFA) and glass stability (GS)) and crystallization behavior respectively.

2. Experimental

2.1. Preparation

IP20FRW and IPG waste form were prepared as explained in detail elsewhere [5,6]. In short, IPG was prepared by mixing Fe₂O₃ (Alfa Aesar, 99.5% purity) and ADP (NH₄H₂PO₄) (Merck, 99% purity) maintaining Fe/P atomic ratio as 0.67. The homogenized mixture was calcined at 673 K in a Pt crucible for 1½ h for facilitating the decomposition of ADP. The calcined mixture was heated and the molten material was air quenched at 1423 K. IP20FRW was prepared similarly by mixing 80 wt.% of Fe₂O₃ and P₂O₅ (as ADP) with 20 wt.% of waste components listed in Table 1. IP20FRW was also prepared by maintaining Fe/P ratio as 0.67. The molten material was air quenched at 1323 K.

During the preparation of IP20FRW glass, the batch composition was such that the final amount of glass aimed was 50 g. The actual

* Corresponding author. Fax: +91 44 2748 0065.

E-mail address: joskit@igcar.gov.in (K. Joseph).

Table 1
Composition of IP20FRW and IPG.

IP20FRW		IPG	
Oxide	wt.%	Oxide	wt.%
Ag ₂ O	0.15	Fe ₂ O ₃	42.86
BaO	0.75	P ₂ O ₅	57.14
CdO	0.07		
Ce ₂ O ₃	1.25		
Cr ₂ O ₃	0.08		
Cs ₂ O	2.08		
Eu ₂ O ₃	0.31		
Gd ₂ O ₃	0.17		
La ₂ O ₃	0.68		
MnO ₂	0.03		
MoO ₃	2.95		
Nd ₂ O ₃	1.93		
NiO	0.15		
PdO	1.37		
Pr ₆ O ₁₁	0.69		
Rb ₂ O	0.10		
Rh ₂ O ₃	0.60		
RuO ₂	1.99		
Sm ₂ O ₃	0.55		
SnO ₂	0.08		
SrO	0.24		
TeO ₂	0.28		
TiO ₂	0.02		
U ₃ O ₈	1.09		
Y ₂ O ₃	0.15		
ZrO ₂	1.70		
Fe ₂ O ₃	34.83		
P ₂ O ₅	45.71		

weight obtained was 49.6228 g. The weight loss was 0.75% and it is well within the experimental uncertainty.

2.2. Characterization

2.2.1. Thermal stability

The air quenched glass sample was ball milled and the resultant glass powder (10 mg) was used for the determination of characteristic temperatures using TG/DTA. The TG/DTA (Setsys Evolution 16/18, M/s. Setaram, France) was calibrated for temperature by fixed melting point method by using ICTAC (International Confederation for Thermal Analysis and Calorimetry) recommended standards such as In, Sn, Zn, Al, Ag and Au. The error in the temperature measurement was ± 1 K. The characteristic temperatures include glass transition temperature (T_g), onset temperature of crystallization (T_x) and liquidus temperature (T_L). Since the values of these characteristic temperatures strongly depend on the heating rate employed during TG/DTA experiment, their values need to be obtained at a fixed heating rate, i.e., 10 K/min. The characteristic temperatures were determined in flowing argon (rate: 20 ml/min) using Pt crucibles. Blank runs were carried out under similar conditions and the data presented are the blank corrected ones.

2.2.2. Crystallization studies and specific heat measurements

Crystallization kinetics [7,8] of the glass powder was carried out using DSC (model DSC 821e/700 of Mettler Toledo GmbH, Switzerland) at various heating rates such as 0.5, 1, 2 and 3 K/min. in the temperature range of 850–970 K. The variations in the quantity of the sample used in the DSC measurements were within ± 2 μ g and experiments were carried out in flowing Ar atmosphere (flow rate: 50 ml/min.). The DSC was also used for the measurement of specific heat (at constant pressure). The temperature, heat flow rate calibration and specific heat measurements were carried out as explained elsewhere [9].

2.2.3. X-ray diffraction studies

The products of crystallization were characterized by XRD technique (Siemens D500 X-ray diffractometer employing Cu K α radiation). The IP20FRW glass was heated (for crystallization) at 900 K (for 80 h) and at 1100 K (for 24 h) in flowing Ar atmosphere. The crystallization temperature was chosen based on the DSC/DTA results.

2.2.4. High temperature viscosity measurements

Viscosity of IP20FRW and IPG were measured using a Brookfield viscometer (Model DV-III+) using an alumina spindle rotating at 10 rpm. Standard borosilicate glass (SRM No. 717) was used for the calibration of the viscometer. The viscosity measurements of IP20FRW and IPG were carried out in the temperature range of 1210–1425 K. Measurements were repeated thrice and the error in the viscosity measurement was $\pm 1\%$.

2.2.5. Mössbauer spectroscopy

Mössbauer spectrum of the sample was measured by employing a Wissel made spectrometer. Mössbauer spectrum was recorded under constant acceleration mode using ⁵⁷Co source in Rh matrix with a maximum velocity of ± 12 mm/s and the instrument was calibrated using standard alpha-Fe foil. WinNormos least square fitting program was used for fitting the Mossbauer data.

2.2.6. Raman spectroscopy

Raman spectra of the IP20FRW and its crystallization products were recorded using a micro-Raman spectrometer (Renishaw, UK, model InVia). The spectra were recorded at room temperature using powder samples with 514 nm laser excitation beam focused to a spot size of ~ 1 μ m with a 50 \times microscope objective.

3. Results and discussion

3.1. Thermal stability

The thermogravimetric – differential thermal analysis curves of IPG and IP20FRW were already presented elsewhere [5]. In order to evaluate the glass characteristics (glass forming ability and glass stability), it is essential to know the characteristic temperatures of these glasses. The characteristic temperatures (T_g , T_x and T_L) were determined from DTA curves. Glass characteristics were evaluated for IP20FRW and compared with that of IPG to understand the effect of waste loading during the formation of glass waste form.

3.1.1. Glass stability (GS)

GS is defined as the resistance to crystallization of glass during re-heating [10]. GS can be estimated by knowing the values of T_g , T_x and T_L (Table 2). Though IPG showed two crystallization peaks, the onset of first crystallization peak was considered as T_x to evaluate the stability of glass. Hruby ($K_H = (T_x - T_g)/(T_L - T_x)$), Weinberg ($K_W = (T_x - T_g)/T_L$) and Lu/Liu ($K_{LL} = T_x/(T_g + T_L)$) criteria were used for the evaluation of GS and their values were also presented in Table 2. The values of GS parameter of IPG [6] are also given in Table 2 for comparison. The larger the value of K_H , K_W and K_{LL} , greater would be the glass stability against crystallization. The values obtained for certain silicate glasses [11,12] reported in the literature are 0.14–0.69. However, these authors [11,12] used melting temperature (T_m) during the estimation of GS instead of liquidus temperature. For the estimation of GS of multi component glasses, it would be correct to use liquidus temperature rather than melting temperature. The GS values of glasses under present study would still increase if melting temperatures (Table 2) are used instead of liquidus temperature, since the melting temperatures

Download English Version:

<https://daneshyari.com/en/article/1565109>

Download Persian Version:

<https://daneshyari.com/article/1565109>

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