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Studies on the synthesis and characterization of cesium-containing iron phosphate glasses

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ABSTRACT

Isotopes of cesium and strontium can be utilized as radiation source for various industrial and medical applications after their separation from high level nuclear waste. However, these elements need to be immobilized in a suitable matrix. In the present work, a systematic approach has been made to immobilize inactive cesium into iron phosphate glass. Up to 36 mol% of Cs_2O has been loaded successfully without crystallization. The glass transition temperature of the cesium loaded glass was found to increase initially and then decrease as a function of Cs_2O content. Mössbauer studies show that the concentration of Fe^{3+} ions in the cesium loaded glasses is >95%. Volatilization experiments at 1263 K show that the weight loss is >0.5% for a period of 4 h. The 36 mol% of Cs_2O loaded iron phosphate glass with high Fe^{3+} content described in this paper is reported for the first time.

1. Introduction

Immobilization of nuclear waste with complex and diverse composition in a suitable matrix is highly challenging. Among the various methods of immobilization, vitrification is considered as the best for radioactive and nuclear waste materials. As on today, borosilicate (BS) types of glasses are the most widely used form of the vitreous matrix. However, nuclear wastes rich in phosphates, sulphates, chrome oxide and heavy metals are poorly soluble in BS glasses [1–3]. These wastes need to be diluted before immobilizing in BS glasses. Hence, it is necessary to look for an alternate vitrification matrix. The next choice of glasses would be phosphate glasses. According to Donald et al. [4], in spite of lower glass forming temperature and better solubility for sulphates, the phosphate glasses like sodium aluminophosphates, iron-aluminophosphate, zinc phosphate etc., are not attractive due to their poor chemical durability. Until 1995, phosphate glasses were not considered as a potential vitreous matrix.

A new group of phosphate glasses, iron phosphate glasses [5–17], known as IPG has been found to be suitable for vitrification of high level nuclear waste (HLW) rich in alkali oxides, sulphates and chrome oxides. For the same amount of waste immobilization, the density of iron phosphate vitreous waste form (3.2 g/cc) is ~25% higher than that of BS waste form; consequently its volume is 25% lower than that of borosilicate waste form [9].

1.1. Literature data and salient features of iron phosphate glass waste form

Iron phosphate glasses are known for their excellent chemical durability [1,3,7]. The melts are produced at lower temperatures (<1273 K) than in the case of the borosilicate glass (1423 K) [9]. Because of their high fluidity, IP melts homogenize in shorter durations (1.5–3 h) than do the BS glasses (>24 h) [9,10]. Among the various compositions of IPG, the one with the composition 40 mol% Fe_2O_3–60 mol% P_2O_5 is found to be chemically more durable [5].

1.2. Present study

In view of the excellent properties of IP melts, a systematic approach has been made in this study to immobilize cesium into IP glass. Presently, ^{137}Cs (12 wt% Cs_2O) separated from HLW is loaded into borosilicate glass for the clinical applications such as the treatment of cervical cancer [18]. Nearly 10–15 wt% of cesium has been reported [18] to volatilize during vitrification of cesium loaded borosilicate glass. So far, iron phosphate glass with 29 mol% Cs_2O had been reported in the literature [19]. Cs_2O of 55 mol% containing cesium phosphate glass has been prepared successfully [20]. But this glass cannot be handled in air because of its moisture sensitive nature. The glass transition temperature of this glass is 500 K, showing its poor thermal stability. The present work aims to investigate the maximum amount of cesium loading that can be achieved in iron phosphate glasses, which could be handled in air. Experiments have been carried out with inactive cesium (which would stimulate ^{137}Cs) in understanding

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the formation and volatilization of the glass. ^{137}Cs (separated from HLW), when loaded in IPG, can be used as radiation source.

2. Experimental

2.1. Batch preparation

Batches of IPG were prepared by mixing different amounts of Cs_2CO_3 (99.9%, Aldrich) (source of Cs), Fe_2O_3 (99.5%, Fisher Scientific) (source of Fe), $NH_4H_2PO_4$ (ADP) (99%, Ranbaxy) (source of P). The mixture was homogenized by grinding in a mortar and pestle in an inert argon glove box. Table 1 shows the batch composition of the materials used for the synthesis of glasses. The sample code IP stands for iron phosphate and C stands for cesium. The percentage of each constituent is as shown in Table 1.

2.2. Precursor studies

Thermogravimetric Analysis (TGA) was carried out to understand the thermal stability of Cs_2CO_3, $NH_4H_2PO_4$ and the mixture of precursors giving 40 mol% Fe_2O_3–60 mol% P_2O_5. The TGA experiments were also carried out on batch compositions of IP9C1 and IP5C5 to evaluate the percentage of weight loss. These data would help to fix the calcination temperature during the formation of glass. The TGA system (M/s. Setaram) 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 and Au. The error in the temperature measurement would be ±1 K. Experiments were carried out at the heating rate of 10 K/min. Pt crucibles were used as the container and experiments were carried out in flowing argon atmosphere at the flow rate of 50 ml/min. Blank runs were carried out under identical experimental conditions and the data presented are the blank corrected ones.

2.3. Glass preparation

Based on the TGA results, each batch was maintained at 873 K for 1½ h for facilitating decomposition of ADP and Cs_2CO_3 before taking it to higher temperature. Each calcined sample was melted in platinum crucible inside an electric furnace. The pouring temperature (temperature at which the molten glass poured onto stainless steel plate) varied from 1263 to 1403 K depending on the composition as shown in Table 1. The melts were maintained at pouring temperature in air for 1 h for homogenization. The melts were then air quenched on stainless steel plates. The air quenched bulk materials were ball milled and powder samples were used for all the characterization studies except for density measurements. As-quenched granules were used for the density measurements.

2.4. Characterization

2.4.1. X-ray diffraction

Samples were characterized by XRD (X-ray diffraction) by using a Siemens D500 X-ray diffractometer employing Cu Kα radiation. Scans were performed with the step size of 0.05° over an angular range of $2\theta = 5°–80°$ with one second as counting time per step.

Table 1
Batch composition.

Sample code	Glass composition (mol%)			Pouring temperature/K
	Fe_2O_3	P_2O_5	Cs_2O	
IP9C1	38	57	5	1403
IP8C2	35	53	12	1373
IP7C3	33	49	18	1353
IP6C4	30	44	26	1323
IP5C5	26	39	35	1263

2.4.2. Chemical composition

The chemical compositions of the glasses were analysed by XRF (X-ray fluorescence) technique. XRF spectrometry was performed in EX JV 3600 instrument with Rh as anode. XRF measurements were performed on chloride solutions of glasses. The XRF system was previously calibrated using standards of known compositions containing Cs, Fe and P. The references were solutions of mixture of Cs_2CO_3, Fe_2O_3 and $NH_4H_2PO_4$. Solutions were made by dissolving the mixture or glass in warm Conc. HCl. The maximum error in the measurement would be ±2%.

2.4.3. Density

The density of each glass was determined by using Archimedes principle. Dibutyl phthalate was used as the liquid medium. Randomly chosen pieces of glasses were subjected to density measurements. The error in the density measurements would be ±0.005 g/cc.

2.4.4. DSC experiments

Glass transition temperature of each Cs loaded glass was determined by differential scanning calorimetry (DSC) (M/s. Mettler Toledo model DSC 821e/700) in flowing Ar atmosphere (flow rate 50 ml/min). Nearly 30 mg of each sample was taken in a Pt crucible and heated at the rate of 10 K/min. The DSC experiments were carried out in duplicate and the agreement between them was very good. The DSC was calibrated for temperature and the error in the measured temperature would be ±0.5 K.

2.4.5. Mössbauer measurements

Mössbauer spectra of the samples were measured by employing a Wissel instrument, Germany. Mössbauer spectra were recorded under constant acceleration mode using ^{57}Co source in rhodium matrix with a maximum velocity (±10.2 mm/s) and the instrument was calibrated using standard α-iron. "NORMOS" least square fitting program was used for fitting the data.

2.4.6. Volatilization studies

The volatilization measurements were made on the glass with the highest Cs content (IP5C5). IP5C5 glass of 9 g was taken in a Pt crucible and heated to 1263 K (pouring temperature) and maintained at that temperature for 15, 80 and 260 min. The air quenched glass samples were cooled and weighed.

3. Results and discussion

3.1. Precursor studies

The TGA curves of pure $NH_4H_2PO_4$ and Cs_2CO_3 are shown in Fig. 1. Weight loss due to decomposition of $NH_4H_2PO_4$ (ADP) is observed to be similar to that reported in literature [21,22]. From the figure it is seen that the weight loss due to the decomposition of ADP commences at ~473 K, whereas the decomposition of Cs_2CO_3 starts around 1060 K. It has been reported in the literature that Cs_2CO_3 decomposes above 873 K [23,24]. As per the Ref. [25], Cs_2CO_3 is stable up to its melting point 1066 K. Our data are in agreement with this report. The TGA runs were carried out only up to 1473 K. The initial weight loss observed below 473 K is due to loss of absorbed moisture in Cs_2CO_3. Cs_2CO_3 decomposes to Cs_2O with evolution of CO_2. The weight loss expected for the loss of CO_2 from Cs_2CO_3 would be 13.5%. But the weight loss observed up to 1473 K was found to be more than 13.5%. This clearly shows the loss of cesium (may be as Cs or Cs_2O) during heating.

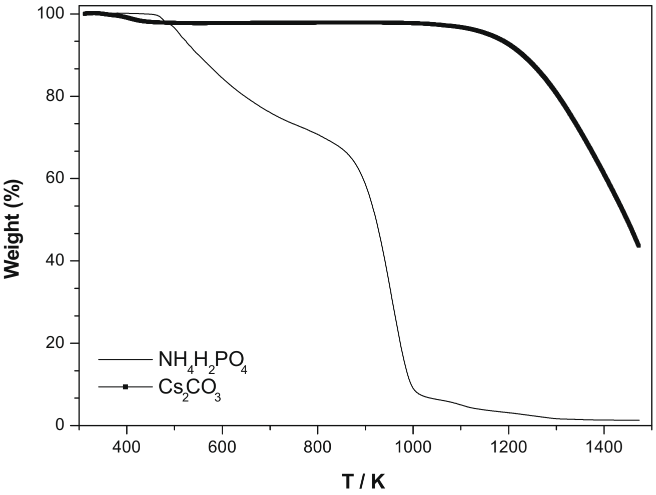

Fig. 1. Thermogravimetric patterns of $NH_4H_2PO_4$ and Cs_2CO_3 at 10 K/min in Ar atmosphere (50 ml/min).

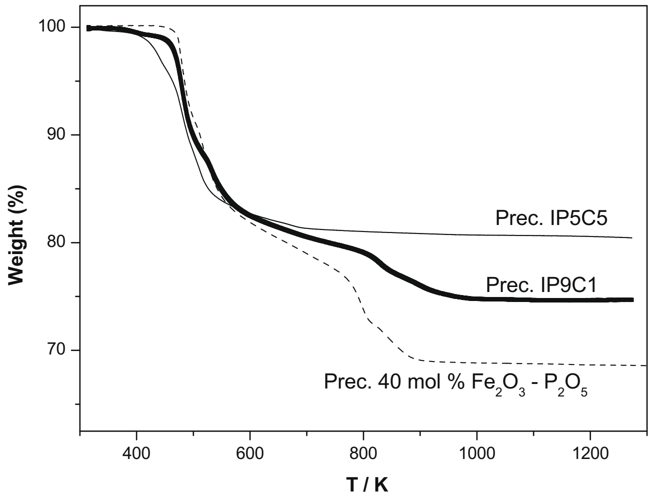

Fig. 2. TGA patterns of the precursors of IP5C5, IP9C1 and 40 mol% Fe_2O_3–60 mol% P_2O_5.

The thermogravimetric curves of the precursors of: (i) 40 mol% Fe_2O_3–60 mol% P_2O_5 ($NH_4H_2PO_4$ as source of P_2O_5); (ii) IP9C1; and (iii) IP5C5 are shown in Fig. 2. The TGA pattern of binary precursor clearly shows that, the total weight loss is complete well below 973 K. The observed weight loss corresponds to 31.5% at 973 K, but the expected weight loss (due to conversion of $NH_4H_2PO_4$ to P_2O_5) was only 27.9%. Similar loss is also observed in binary iron phosphate glass which may be due to the loss of P_2O_5 [2,26].

From the TGA patterns of the precursors of IP9C1 and IP5C5, the weight loss of cesium loaded samples were measured. The observed weight loss (due to conversion of $NH_4H_2PO_4$ to P_2O_5 and Cs_2CO_3 to Cs_2O) matches with expected weight loss within the experimental uncertainty (±1%) and it occurs well below the normal decomposition temperature of Cs_2CO_3. This clearly indicates that the decomposition of Cs_2CO_3 is also facilitated at low temperature in the presence of ADP and Fe_2O_3. Hence all the precursors were calcined at 873 K for 1½ h before converting them into glass. It is observed that the pouring temperature decreases with increasing cesium content (Table 1).

3.2. X-ray diffraction

Bulk glass samples were characterized by XRD. All the glass samples were found to be amorphous as shown in Fig. 3.

3.3. Chemical composition

The cesium loaded glass samples were analysed for P, Cs and Fe by XRF and the actual composition of the glass is shown in Table 2. The analysed compositions are very close to the nominal batch values.

3.4. Density

The glass density was found to increase with increase in cesium oxide content. Generally, density increases with cesium content [27,28]. The average measured density of each glass is shown in Table 2. The linear variation of measured density with Cs is shown in Fig. 4.

3.5. DSC studies

The DSC patterns of the cesium loaded glasses in the temperature range of 620–835 K are presented in Fig. 5. From the DSC runs, the glass transition temperature, T_g was determined and plotted as a function of mol% of Cs_2O. The effect of cesium addition on T_g is shown in Fig. 6. The networking in phosphate glasses depends on the O/P ratio as set by the composition of the glass. Based on the O/P ratio, all the present cesium loaded glasses (IP9C1 to IP5C5) are classified as polyphosphate glasses [29], where the ratio is >3.0. The P–O linkage is modified by the presence of both Fe and Cs ions. The less stable P–O–P linkage in normal phosphate glasses is replaced by the stronger Fe–O–P linkage in iron phosphate glasses. This Fe–O–P linkage is more hydration resistant than P–O–P bonded phosphates [6–8,14–17]. O/P ratio of the present glasses increases from 3.5 to 4.0 with the addition of cesium. Generally, an increase in the number of orthophosphate units [30] could be the reason for increase in O/P ratio in iron phosphate glasses. When alkali ions are further added to these glasses, cation cross linking can either increase or decrease the strength of the glass depending on the percentage of alkali ion [31]. As seen from the Fig. 6, the glass transition temperature increases with addition of Cs_2O up to 20 mol%, beyond which it decreases. Generally, the cause for rise in T_g is the increasing cation mediated cross link in the glasses. Beyond a certain concentration, the break down of phosphate network by the presence of non-bridging oxygen could be the reason for decrease in T_g [31]. This would be further explored with other structural characterization techniques like Raman, IR and ^{31}P NMR spectroscopy. Cs_2O of 55 mol% loaded binary phosphate glass [20] has the T_g of only 500 K, whereas the 36 mol% Cs_2O loaded IP glass prepared in the present studies has a T_g of 743 K. The minimum crystallization temperature specified by the Department of Energy (DOE, USA) is 673 K [9]. Since the glass transition temperature of the IP5C5 glass (36 mol% cesium oxide loaded iron phosphate glass) is >673 K, the crystallization temperature would be still higher. This shows the superior thermal stability of the cesium loaded IPG.

3.6. Mössbauer measurements

Mössbauer spectra of all the glass samples (typical spectrum of IP5C5 is shown in Fig. 7) was found to consist of two kinds of quadrupole doublets. This is caused by the presence of Fe^{2+} and Fe^{3+} ions in the glass. Normally, ferrous ions have larger isomer shifts (IS) and quadrupole splittings (QS) compared to ferric ion. The IS values range from 0.35 to 0.55 mm/s relative to metallic iron

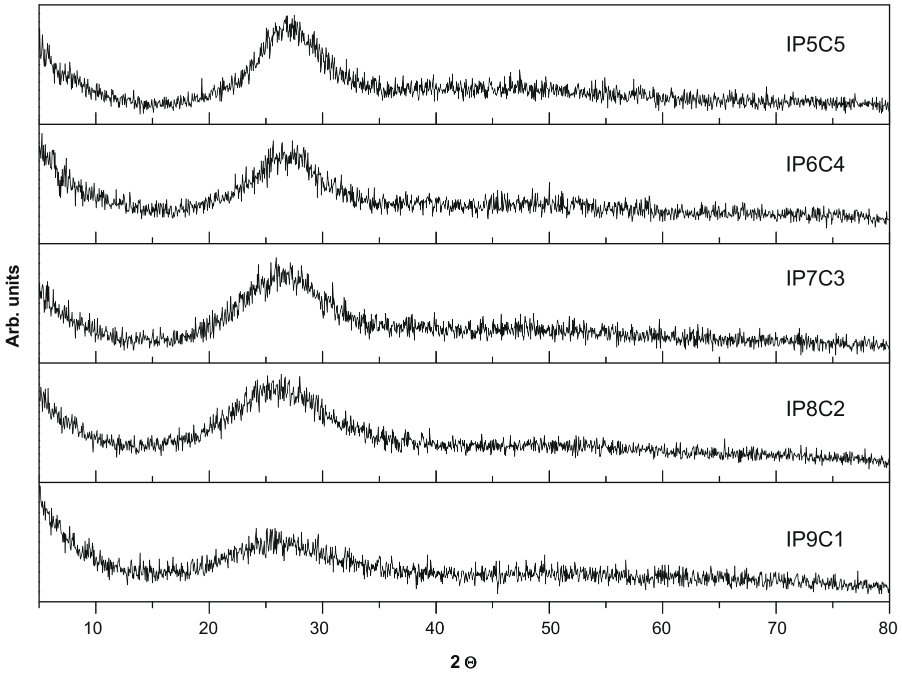

Fig. 3. XRD patterns of the cesium loaded glasses.

Table 2
Composition of the glasses as determined by XRF technique and the average density.

Sample code	Glass composition (mol%)			Density (g/cc)
	Fe_2O_3	P_2O_5	Cs_2O	
IP9C1	37	57.5	5.5	3.119
IP8C2	34.5	53	12.5	3.278
IP7C3	33	46	21	3.448
IP6C4	29	44	27	3.597
IP5C5	26	38	36	3.691

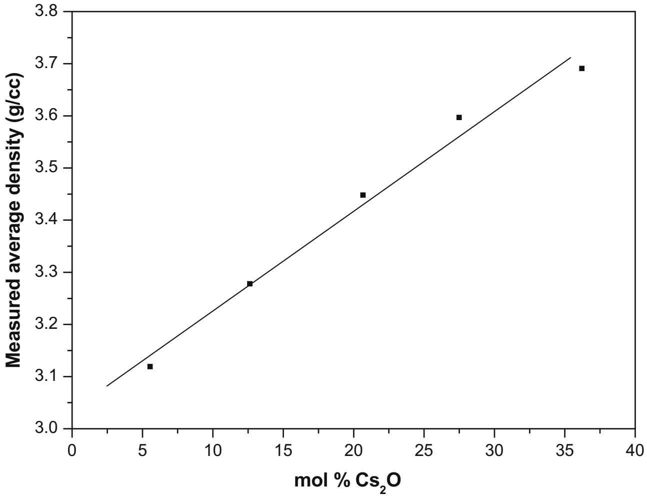

Fig. 4. Variation of density with mol% of Cs_2O. The solid line is the linear least square fit.

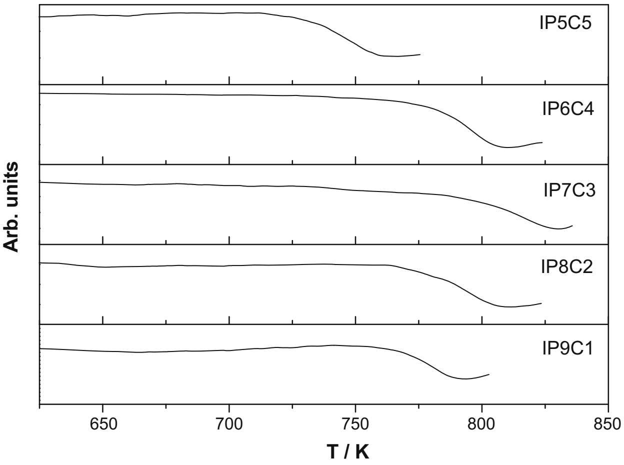

Fig. 5. DSC curves of the cesium loaded glasses at 10 K/min in Ar atmosphere (50 ml/min).

corresponds to Fe^{3+} ions. Similarly, IS values above 1.0 mm/s are associated with Fe^{2+} occupancy [32]. The Mössbauer parameters and fraction of iron ions present in the cesium loaded glass is presented in Table 3. These hyperfine parameters are typical of the eight-coordinated Fe^{2+} and six-coordinated Fe^{3+} [33].

The concentration of Fe^{3+} is found to be always >95% in all these glasses. The fraction of Fe^{2+} reported in literature [5,34] is much higher than the values observed in this study. It is well known that the presence of Fe^{3+} helps the formation of IP glasses and also strengthens the networking in IP glasses [16]. Melting temperature has greater effect on the concentration of Fe^{2+} ions than the time of homogenization. As the melting temperature increases beyond 1473 K, the Fe^{2+} content also increases [5,8,34]. In the present work, cesium loaded glasses were melted and poured below 1473 K and this could be the reason for the low concentration of Fe^{2+} in the present cesium loaded glasses.

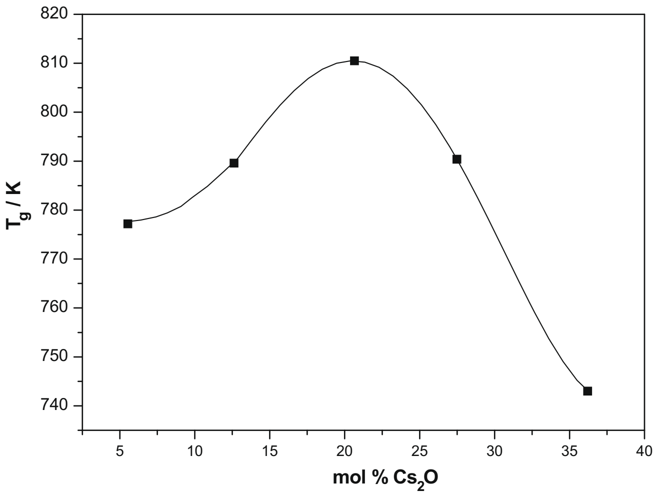

Fig. 6. Change in glass transition temperature as a function of mol% Cs_2O. The solid line is only to guide the eye.

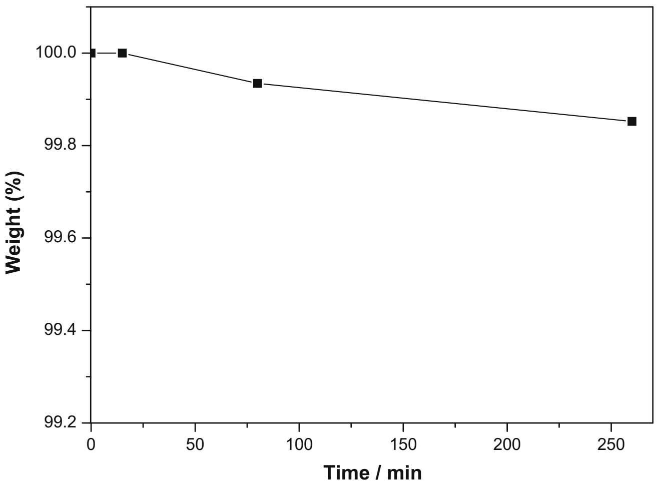

Fig. 8. Weight percentage of the IP5C5 glass as a function of time (min).

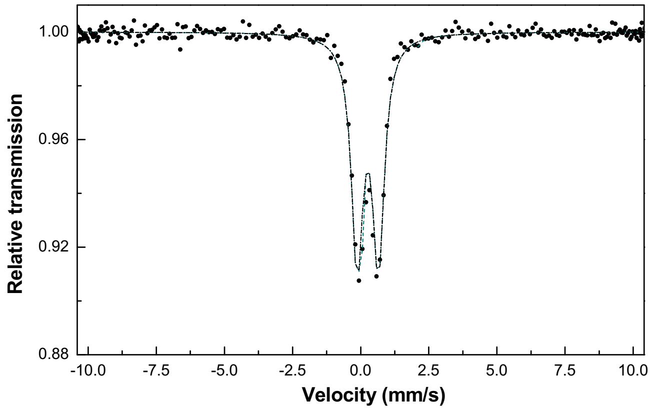

Fig. 7. Mössbauer spectrum of IP5C5 glass.

Table 3
Results of Mössbauer spectral parameters of cesium loaded IPG.

Sample	Fe^{3+}/(mm/s)		Fe^{2+}/(mm/s)		Relative (%)	
	IS	QS	IS	QS	Fe^{3+}	Fe^{2+}
IP9C1	0.36	0.85	1.22	2.14	98.01	1.99
IP8C2	0.37	0.86	1.23	2.13	94.9	5.1
IP7C3	0.37	0.83	1.25	2.09	96.9	3.1
IP6C4	0.38	0.78	1.23	2.09	98.7	1.3
IP5C5	0.37	0.78	1.21	2.10	98.8	1.2

IS, isomer shifts; QS, quadrupole splittings.

3.7. Volatilization studies

In order to understand the Cs loss in IP5C5 (which is loaded with maximum Cs) glass, static weight loss was measured as a function of time at 1263 K. As seen from Fig. 8, the weight loss was found to be less than 0.5% till 4 h. These volatilization experiments clearly indicate that the material loss during the normal homogenization time (1–3 h) for the present glass is very less compared to the glass used for preparing pencil source as given in the Ref. [18].

The above studies bring out the positive features of cesium containing IPG. Ease of fabrication of cesium loaded glass at low temperature along with short homogenization time, makes the iron phosphate glass matrix as a potential medium of immobilization of cesium. Negligible loss of material during calcination and melting of these glasses would be advantageous while immobilizing ^{137}Cs. Since the chemical nature of inactive cesium is same as that of ^{137}Cs, iron phosphate glass matrix can be effectively used for immobilization of ^{137}Cs, which could be used as radiation source for medical purposes [18].

4. Conclusion

Cs_2O of 36 mol% was loaded successfully for the first time in iron phosphate glass. Volatilization loss was <0.5 wt% of glass even at 1263 K. The density of cesium loaded glass monotonically increases with cesium content and the density of 36 mol% Cs_2O loaded glass is 3.7 g/cc. The Mössbauer studies on 36 mol% Cs_2O loaded IP glass showed the concentration of Fe^{3+} to be >98%. The glass transition temperature of this glass is 743 K. Glass transition temperature increases and then decreases as a function of mol% of Cs_2O, indicating perhaps a change in the nature of the glass network. This needs to be explored with other characterization techniques like Raman, IR and ^{31}P NMR spectroscopy.

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