Featured Letter

Vitrification of U_3O_8 in iron aluminium phosphate matrices including Bi_2O_3 as uranium surrogate

J. Ma. Rincón [a,b,*], C. Ramos [c,e], P. Arboleda [d,e], C.J.R. González Oliver [d,e]

[a] Department of Geology, MNCN-CSIC, Madrid, Spain
[b] Department of Agriculture and Environment, Universidad Miguel Hernández (UMH), Elche Alicante, Spain
[c] Centro Atómico Constituyentes, CNEA, GiyA, Buenos Aires, Argentina
[d] Centro Atómico Bariloche, CNEA, Bariloche, Argentina
[e] CONICET, Buenos Aires, Argentina

ABSTRACT

In order to encapsulate nuclear wastes (NW) enriched in Uranium, they have been designed and obtained vitrified matrices of iron aluminum phosphates including substitution of U by Bi. These glasses have been designed and obtained formulating all from the starting binary composition: $60P_2O_5 \cdot 40Fe_2O_3$ where the Fe/P ratio was 0.67. The thermal behavior has been investigated by DTA/TG analysis and thermal expansion, as well as identification of some phases by TEM/EDS. The vitrified structures are difficult to crystallize as is the case of the (Fe + U) contents in the range of 0.50 per P atom. Glasses with Bi-oxide are less resistant to crystallization than those containing U. The glasses here investigated depict a reasonable water chemical stability due to the high percentage of P—O—Fe—O bonds and the presence of U (4+ to 6+). Lately, it has been also investigated the calcination of simulated miniplates of Si_2U_3/Al having additions of these glasses and U_3O_8 to dilute this Uranium enriched in MTR combustible (Material Testing Reactor).

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1. Introduction

Since time it is coming considered the vitrification as an effective way for immobilisation of nuclear wastes (NW) [1]. Much research work has been made in the last decades trying to find the optimal matrices which usually are named as "waste forms" for encapsulation of such wastes in durable and sure compounds or materials [2]. Though, since time also previous authors have considered the iron phosphate matrices as very useful for immobilization of a wide range of NW [3], the use of such type of phosphate glasses for the isolation of uranium compounds has not been considered. Thus, in order to encapsulate nuclear wastes enriched in Uranium oxide (U_3O_8) in the last years they have been designed, obtained and characterized some glasses based on iron aluminum phosphates including uranium oxide [4–6]. Due to difficulties or restrictions for research work with uranium compounds, it is the aim of this research the substitution of U by Bi under surrogate compositions for the obtaining of additional data for the encapsulation of UO_2 and Bi_2O_3 into iron phosphate matrices.

2. Experimental

Several glasses have been designed and obtained formulating them from the starting binary composition: $60P_2O_5 \cdot 40Fe_2O_3$, where the Fe/P = 0.67. Iron phosphate glasses are designed based in de-polymerizing the 3D structure of vitreous P_2O_5 (O/P = 2.5; ultraphosphate) by the addition of other components such as: Fe_2O_3, Al_2O_3, Na_2O, U_3O_8 and Bi_2O_3.

Subsequently, they add oxygen (O/P = 3, metaphosphate); (O/P = 3.5; pyrophosphate); (O/P = 4; orthophosphate) to the network by distributing several cations as modifiers of the vitreous structure. For the formulation of uranium containing glasses, it was used the UO_2 produced as pure quality since 2004 by CNEA in DIOXITEK SA, Cordoba, Argentina. The U_3O_8 incorporated to the original glass compositions was produced by oxidizing the UO_2 at 800 °C. Glass batch compositions have been melted at 1300 °C during one hour in a supekhantal furnace in alumina- magnesia crucibles and then poured over V-shaped grooves steel molds. In all the compositions the final glasses have been opaque and black color (10 mm thickness). Table 1 shows the composition of iron phosphate glasses here investigated including the original with U_3O_8 content and those with Bi_2O_3 substitution.

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* Corresponding author at: Department of Geology, MNCN-CSIC, Madrid, Spain.
E-mail address: rinconjma@mncn.csic.es (J. Ma. Rincón).

Table 1
EDS compositions from the original glasses and corresponding surrogates (symbol t means the theoretical batch compositions and m the measured composition in the final glasses).

Oxide (wt%)	P_2O_5	Fe_2O_3	Na_2O	U_3O_8	MgO	Al_2O_3	Bi_2O_3
RR1t	56.0	28.0	2.0	14.0	–	–	–
RR1m	59.5	15.1	2.0	18.4	–	–	–
AR4t	46.9	44.1	2.0	7.0	–	–	–
AR4m	45.8	42.2	2.3	6.2	1.9	1.6	–
RR6t	58.8	19.6	2.0	19.6	–	–	–
RR6m	59.4	15,5	2.0	18.8	2,1	2.2	–
RB6t	58.8	19.6	2.0	–	–	–	19.6
RB6m	59.0	15.0	3.4	–	2.8	3.2	16.6
RB6Mgm	66.4	13.7	–	–	5.8	2.0	12.1
RR7t	69.6	18.6	2.0	10.2	–	–	–
RR7m	65.2	13,1	4.0	14.1	–	3.4	–
RB7t	69.6	18.6	2.0	–	–	–	10.2
RB7m	65.2	15.7	3.0	–	2.8	5.0	9.0

The X-Ray diffraction (XRD) was used for assessment of the amorphous structure or determination of crystalline phases when they were heated at high temperatures. The thermal behavior has been investigated by thermal analysis (DTA/TG) and differential dilatometry (Theta Inc. USA) and structure previously by Raman and FTIR [7]. The microstructure and identification of some phases such as $Fe(PO)_4$ was followed by XRD and EDS/TEM. Leaching or durability tests carried out in these glasses was followed by the well-known method of Product Consistency Test (PCTB) (ASTM 1285-02,2002) [7]. Though the chemical durability was determined by the PCT-B test [4] for 75 and 150 µm glass powders, the pH of leachates was not measured, but however, it was determined the chemical concentration by the MCC1P test for monolithic samples. Both methods were carried out in hermetic containers into distilled water at 90 °C during 7 days and the leached elements were selectively analyzed by ICP OES Perkin Elmer Optima 3100xl.

3. Results and discussion

The thermal behavior of iron phosphate glasses here investigated is shown in the Fig. 1(a) and (b). It is noted the new glassy series was reproduced/melted based on our previous series RR and AR in [5], with the objective of testing glass melting reproducibility, and making more direct comparisons after re- melting of similar glasses but having replaced U by Bi in the glass batch.

In general, it can be seen that RB6t surrogate glass is less stable than the original RR6, because Tg is reduced from 578° to 511 °C and the expansion coefficient is increased around 70% from 77 to 131×10^{-7} °C^{-1} (Table 2) and also RB6 shows a crystallization peak at around 722 °C (Fig. 1a). For lower level of Bi, RB7, the crystallization peak shifts to lower temperature. It is interesting to note that this weakening effect of the structure, owing to replacement of U by Bi oxides, can be partly suppressed through additions of about 5–6 wt% MgO, to the P—O—Fe—O—Bi glassy network. That is, glass RB6Mgm having lower Tg than RR6, shows a similar expansion coefficient to that for RR6 and a higher temperature crystallization peak (775 °C), than that for RB6.

On the other hand, the higher ratio P/Fe for the RR7 composition, as compared to that for RR6, gives rise to higher values of the expansion coefficient, consistent with those met for compositions AR in [5]. The glass transformation temperature (Tg) for this RR7 glass was not clearly detected both in DTA and expansion experiments, therefore is not given in the Table 2.

Because it was known from previous experiments that RR7 powdered glass sinters since 600 °C [5,6], it was carried out a heating at 660 °C of this glass with the result on microstructure showed in the Fig. 2 depicting a very homogeneous distributed crystalliza-
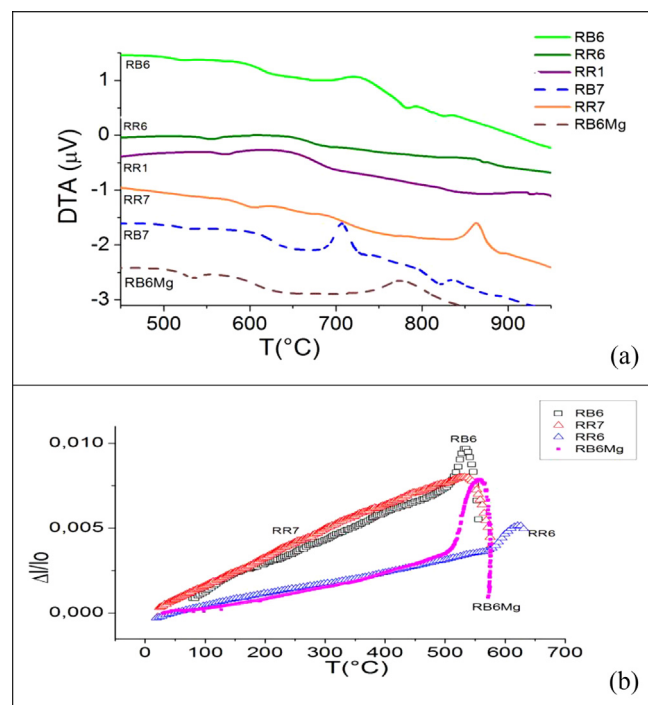
Fig. 1. a) Heating experiments by DTA/TG and b) thermal expansions from original uranium and bismuth surrogate iron phosphate glasses.

Table 2
Thermal properties from DTA and thermal expansion experiments.

Glass sample	Tg (°C)	Tsoft (°C)	$\alpha \cdot 10^{-7}$ (°C^{-1})
RR6	578	650	77
RB6Mgm	514	559	75
RB6	511	538	131
RR7	–	540	159

tion dispersed in the matrix. These crystallizations are "like stars" with small dendritic non-well developed branching of crystallites. At higher magnifications, it can be seen twinned crystals with contrast lines in DF (Fig. 2b) and BF (Fig. 2c) images indicating they are highly stressed due to the growing process. By Selected Area Electron Diffraction it is observed a well- oriented pattern which correspond to a SAD simulated pattern obtained at 200 kV of Fe_2Fe $(P_2O_7)_2$ crystals and oriented in the axis zone [2,3,2] of this iron pyrophosphate compound.

In any case, as was shown in the DTA experiments (Fig. 1) that original and surrogates uranium phosphate glasses containing iron
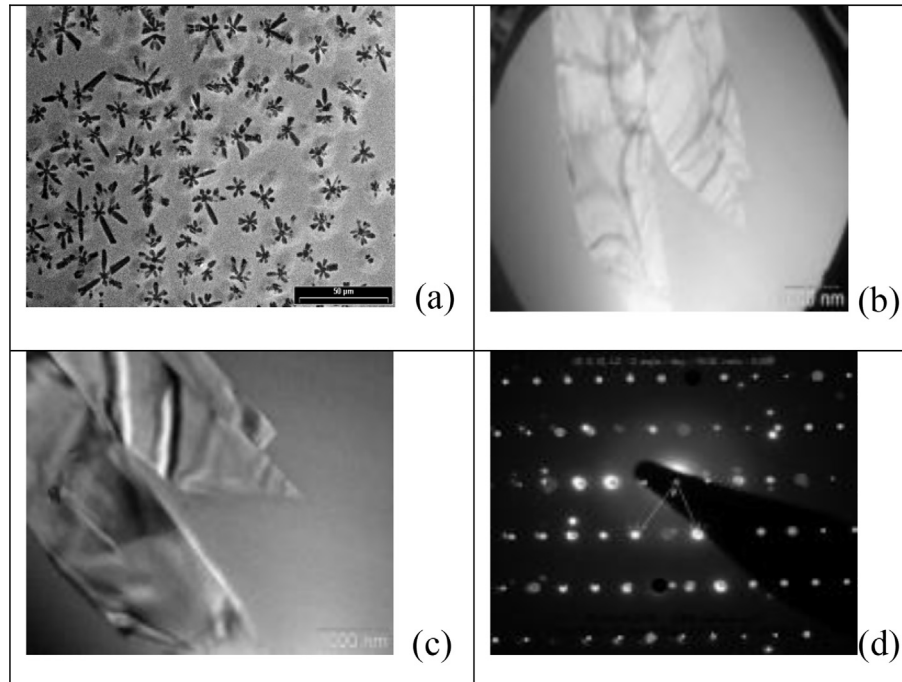
Fig. 2. TEM observation from thin foil of the RR7 glass heat treated at 660 °C for 4 h in air: a) lower magnification, b) and c) higher magnifications in BF and DF images and d) the corresponding electron diffraction pattern from the crystallization edges.

are very stable making difficult to crystallize in special as is the case of (Fe + U) contents in the range of 0.5 per P atom. From the infrared spectroscopy results (not shown), there are bonding of P—O—P vibracional modes at 914 and 923 cm^{-1} and P—O groups at 1065 and 1122 cm^{-1} for the RB6 and RB7 glasses. Equally, symmetric elongations and anti- symmetric of P=O bands have been detected in these glasses as was observed in [7].

In order to evaluate their chemical durability the water leaching was measured for these glasses. The leaching test results are shown in the following Fig. 3, depicting a reasonable chemical stability and corrosion resistance to the water attack due to the high percentage of P—O—Fe—O bonds, as was reported also for the only binary glasses by Reis et al [8]. This bonding jointly with the presence of U (4+ to 6+) giving rise to a strong bonding between PO$_4$ chains and the Fe^{3+} tetra or octahedral coordinated with the oxygen and the uranium included in the composition of these special glasses. Not enough chemical durability data are available for Bi-containing glasses. However, although the high extractions for RB6, RR6 and RR7, as well as the high expansion coefficient measured for RB6 could suggest poor chemical durability. However, it has been preferred to collect first leaching-data for the considerably RB6Mg more stable (thermally and towards crystallization trend) than RB6, before making a more accurate comparison with surrogates U-containing glasses.

As a complementary experiment in this research it was carried out a sintering of calcined at 800 °C spent fuel plates with natural uranium oxide (UO$_{2.67}$). For sintering it was added a small fraction of borosilicate VG98 glass or RR6 iron phosphate glass [9]. These sintered pellets were tested in simulated mini-plates of Si$_2$U$_3$/Al and adding the MTR (Material Testing Reactor from Bariloche Atomic Center). After testing they showed low enrichment, structural integrity, good mechanical properties and water corrosion resistance.

4. Conclusion

Iron phosphate glasses containing uranium have shown adequate thermal stability and durability in water. It has been demonstrated that iron phosphate glasses here investigated are thermally stable under DTA and thermal expansion experiments and also they depict good resistance to the water corrosion by following the PCTB standard test. However, the respective surrogates with Bi$_2$O$_3$, and without additions of MgO, appear less chemically durable than glasses with U. Further research is needed to clarify this point. Finally, it is point out that glass compositions here investigated contain also alkali and alkaline- earth modifiers (Na$_2$O, MgO), as well as intermediate oxides such as Al$_2$O$_3$ which, in any case, can afford more chemical corrosion stability to these glasses.
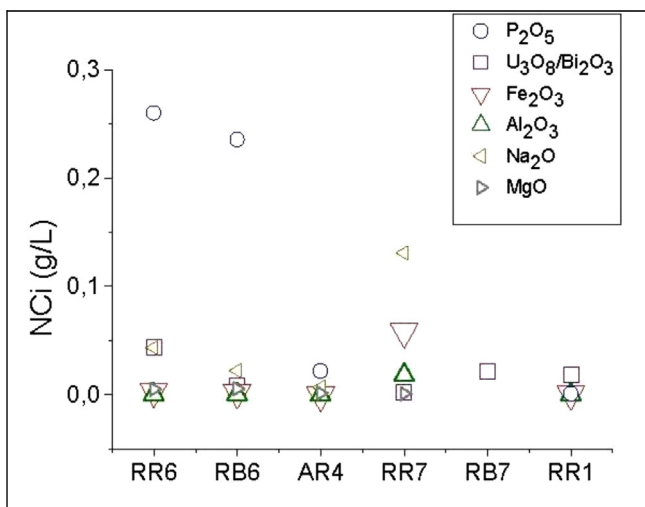
Fig. 3. Elements leached (according to the PCTB test) from the uranium phosphate glasses and bismuth surrogates.

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