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► **To cite this version:**

D. Petit-Maire, J. Petiau, G. Calas, N. Jacquet-Francillon. LOCAL STRUCTURE AROUND ACTINIDES IN BOROSILICATE GLASSES. Journal de Physique Colloques, 1986, 47 (C8), pp.C8-849-C8-852. 10.1051/jphyscol:19868163 . jpa-00226067

HAL Id: jpa-00226067

<https://hal.science/jpa-00226067>

Submitted on 4 Feb 2008

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LOCAL STRUCTURE AROUND ACTINIDES IN BOROSILICATE GLASSES

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RESUME: Nous avons utilisé la spectroscopie d'absorption des rayons X et la spectroscopie d'absorption optique pour étudier la valence et la structure locale de l'uranium et du thorium dans des verres borosilicatés. Des verres de compositions semblables à celles retenues pour le stockage des déchets nucléaires sont comparés à des verres de compositions plus simples. Les atomes de thorium ont une valence (IV) stable et un environnement d'oxygène de 8 atomes. L'uranium est très sensible à la composition du verre. Les valences (IV), (V) et (VI) sont présentes simultanément dans les verres et correspondent à des environnements différents.

ABSTRACT: X-ray absorption and optical absorption spectroscopy have been used to study the valence state and local structure of uranium and thorium in borosilicate glasses. Glasses of composition similar to those studied for the nuclear-waste storage are compared to glasses of simplified composition. Thorium atoms are in the valence state (IV) with an oxygen environment of eight atoms. Uranium is very sensitive to the glass composition. The valence states (IV), (V), and (VI) are simultaneously present and correspond to different local organizations.

INTRODUCTION

Borosilicate glasses are used as matrices for the solidification of high-level nuclear wastes(1). The valence state and the local atomic coordination of long-lived radioelements manage the long-term evolution of the glass. X-Ray absorption spectroscopy has been used together with optical absorption spectroscopy to probe the environment of uranium and thorium which simulate all the actinides in these glasses.

The glasses B have a composition similar to that of glasses prepared for storage (43%SiO₂, 13% B₂O₃, 9%Na₂O and 35% of others elements like 3d and 4d elements and rare earths) but with an increased concentration of uranium or thorium (1, 2 or 5 %). In order to reduce the number of parameters controlling the local organization, we also studied glasses of the same system (61 %SiO₂ - 19 % B₂O₃ - 13%Na₂O) and only containing 7% of uranium or thorium. Oxide melts have been fused in air atmosphere at 1200°C in a platinum crucible. Thorium and uranium have been introduced as ThO₂ and UO_{2.66} oxides. After three hours affining, three types of cooling rates have been used: one by running into water, one onto a sheet of metal and one air-cooling followed by a one-hour annealing at 520°C.

COMPOUNDS STUDIED

A: crystalline ThO₂ oxide

B₁: glasses of technological composition doped with 5% thorium

C₁: " " simplified composition containing 7% thorium

B₂ and C₂: same glasses with uranium instead of thorium

D: crystalline UO_{2.66} oxide

E: " UO₂(NO₃)₂·6H₂O

EXAFS and XANES spectra at the L₃ edges of uranium and thorium have been recorded by the direct transmission method at LURE-DCI (Orsay). The storage ring was running at 1.85GeV with a current of ≈ 200mA. The monochromator was a Si(400) "channel-cut" single crystal for uranium L₃-edge and a Si(311) double crystal for the thorium L₃-edge.

THORIUM ATOMS ENVIRONMENT

The valence (IV) of thorium in glasses, reported by previous works using various spectroscopic methods (2,3), is confirmed by the energy position of the thorium L_3 -edges. Figure 1 compares the Fourier transforms of the EXAFS spectra for crystalline ThO_2 , for glass B_1 and for glass C_1 .

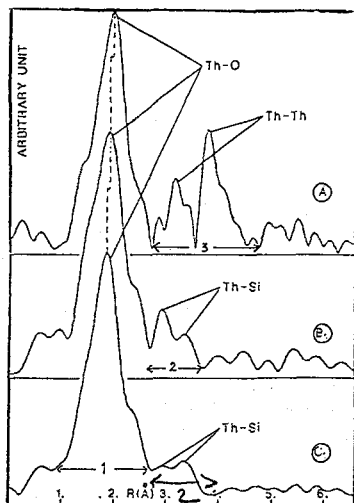


Fig.1 : Fourier transforms of the thorium L_3 -edge spectra of crystalline ThO_2 and of glasses B_1 and C_1

Table 1: Results for the oxygen coordination shell around thorium assuming (a) an unique shell and (b) a double shell

COMPOUND	unique shell			double shell					
	COORD. NBER	DISTANCES	Δr	first subshell			second subshell		
				COORD. NBER	DISTANCES	Δr	COORD. NBER	DISTANCES	Δr
ThO_2 Crystalline	8	2.42	0.0						
B_1	8.7	2.36	0.08	2.4	2.22	.00	6.1	2.39	.00
C_1	7.8	2.34	0.05	5.2	2.31	.00	2.5	2.42	.00

The oxygen coordination shell has been fitted using phases and amplitudes extracted from crystalline ThO_2 . In the range of interatomic distances called "1" in fig.1, the analysis has been made with two different assumptions and the results are reported in the table 1. With the assumption of a unique shell at a unique distance of the thorium atoms, the distance Th-O obtained is smaller than in crystalline ThO_2 and the Debye-Waller factor is larger; that reflects a distance distribution. A double shell modelization has given an improved reliability factor. This is an indication that the Th-O distance distribution is broader than the maximum which can be described by a Debye-Waller factor. Th-O distances are distributed over 0.2 Å at least. In both models the number of oxygen atoms is found nearly equal to eight which is the usual coordination number of thorium in oxides.

In crystalline ThO_2 , the distance range "2" corresponds to the thorium atoms in position of second neighbors. This peak has been used to extract phases and amplitudes relative to the Th-Th atomic pairs. The spectra of glasses do not contain information which could be analyzed by thorium atoms in position of second neighbors whatever the thorium concentration. This indicates that thorium atoms are always dispersed in the glass network. The Fourier transforms contain however a signal of significant amplitude in the distance range "3". For the glass C_1 , this can only be a contribution of silicon atoms, but it was impossible to obtain a satisfactory fit in that hypothesis. In the glass B_1 , the amplitude of the peak "3" is larger. It could result not only from the network formers (silicon and aluminium) but also from the elements of greater atomic number present in the glass (3d and 4d transition elements, rare-earths etc.).

URANIUM ATOMS VALENCE STATE AND ENVIRONMENT

OPTICAL SPECTRA: The various possible valence states of uranium (IV,V,VI) are often present together in the glasses that we have studied. Oxidation state of uranium is very sensitive to the composition and to the conditions of preparation of the glass. Optical absorption spectra in the visible range give directly the repartition of uranium atoms among the different valence states.

A large difference appeared between glasses B_2 and C_2 . The amount of U(IV) and U(V) is significantly larger in the glass C_2 than in the multicomponent glass B_2 (fig.2). The presence of elements in oxidizing state like manganese, chromium or cerium in the glass B_2 explains this difference (4). It has been possible to determine semi-quantitatively the percentages of uranium atoms in each oxidation state by comparison with spectra of known compounds (Table 2).

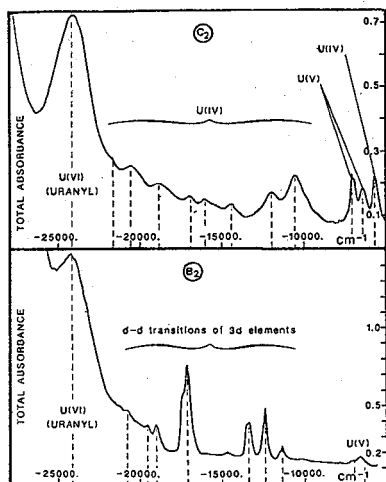


Fig.2: Optical absorption spectra of the glasses B₂ and C₂. Indication is reported of the features characteristic of U(IV), U(V) and U(VI)

Table 2: Valence state distribution of uranium in the oxide UO_{2.66} and in the glasses B₂ and C₂ (as given by optical absorption data)

COMPOUNDS	VALENCE STATES (%)		
	URANYL	U(V)	U(IV)
B ₂	>95	<5	—
C ₂	70	15	15
D	67	33	—

L₃-EDGE SPECTRA: The L₃-edge fine structure confirms and even amplifies the difference between glasses B₂ and C₂ (Fig.3). The feature (a) is characteristic of the uranyl complex which is the usual state for U(VI) (linear or quasi-linear O-U-O group of atoms with a very short U-O distance) (5). It is clearly present in the spectrum of the glass B₂ where nearly all uranium atoms are in the valence state U(VI). On the contrary the feature (a) is far less visible in the spectrum of the glass C₂ which is similar to the spectrum of the oxide UO_{2.66} (D). This oxide contains a mixing of atoms in the formal valence states U(VI)(33%) and U(V) (66%).

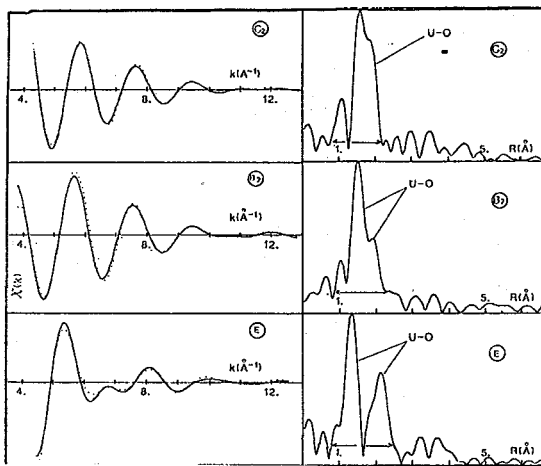
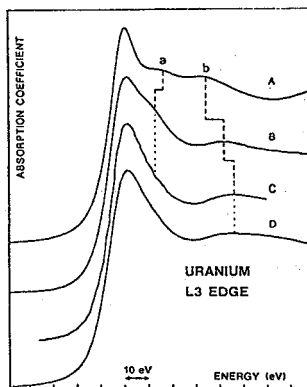


Fig.4: Left side : Fourier transforms of uranium L₃-edge spectra in compounds B₂, C₂ and E
Right side: _____ Inverse Fourier transforms of the peaks selected in left side
----- Calculated spectra

Fig.3: Uranium L₃-edges of crystalline E and D and of glasses B₂ and C₂



EXAFS : Glass B₂: The analysis of the oxygen coordination shell is consistent with a two sub-shells hypothesis. Two atoms are located at a distance corresponding to the small uranium-oxygen distance characteristic of uranyl groups (O-U-O) in uranyl crystalline compounds (1.75-1.80Å) (5). The second oxygen sub-shell is fitted with 4.5-5 atoms at 2.25Å. This is an especially short distance if we compare it to usual ones determined by diffraction or EXAFS (6) (Fig.5). This difference is directly apparent in the comparisons of direct and inverse Fourier transforms of the two glasses and of the crystalline uranyl nitrate (Fig.4). The small contribution of further neighbors cannot be analyzed.

Glass C₂: No fit is convenient with all uranium atoms in uranyl groups. The spectrum analysis with two oxygen sub-shells gives distances similar to those found in the "uranyl" case of glass B₂ but the number of oxygen neighbors found at 1.80Å is too small (0.8 instead of 2). It was also impossible to get a good solution with an environment of all uranium atoms identical to that in UO_{2.66}. A satisfactory solution was obtained by considering the presence of the three uranium valence states, each corresponding to the local environment of uranium atoms which is the most likely:

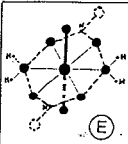
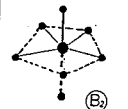

-U(VI) was supposed in the environment determined by EXAFS for the glass B₂.

- we had no a priori indication of the environment of U(IV) and U(V) in the glasses. For U(IV) we supposed 8 oxygen neighbors in a unique shell at an average distance slightly smaller than in crystalline UO₂ (fluorite type structure with first U-O distances equal to 2.38Å). This environment was chosen by reference to the one found for Th(IV) in glasses B₁ and C₁. For U(V) the structure of the L₃-edge suggested an uranium environment similar to that in UO_{2.66} (Fig.5).

VALENCE STATE	% (FROM OPTICAL DATA)	CALCULATED COORDINATION	EXAFS RESULT
(IV)	15	1.4 OXYGENS AT 1.80Å	1.2 OXYGENS AT 1.81Å
(V)	15	0.3 OXYGENS AT 2.05Å	0.3 OXYGENS AT 2.06Å
(VI)	70	5.2 OXYGENS AT 2.25Å	4.6 OXYGENS AT 2.22Å

Table 3: EXAFS result for the first coordination shell of the glass C₂

Fig.5: Oxygen coordination around uranium in crystalline uranyl nitrate and UO_{2.66} oxide and in glass B₂. Corresponding uranium-oxygen distances as given by EXAFS and X-ray diffraction patterns →

STRUCTURES	X-RAY DIFFRACTION DETERMINATIONS	EXAFS DETERMINATIONS
	(DISTANCES Å) URANYL OXYGENS 1.75 1.77 EQUATORIAL OXYGENS 2 X 2.39 2 X 2.50 2 X 2.54	2 X 1.76 2 X 2.36 4 X 2.49
		URANYL OXYGENS 2 X 1.81 OXYGENS OF THE SECOND SHELL 4.5 X 2.25
	U ₁ AXIAL OXYGENS U ₂ 2 X 2.07 2 X 2.07 EQUATORIAL OXYGENS 2 X 2.15 1 X 2.12 2 X 2.20 1 X 2.15 1 X 2.44 2 X 2.20 1 X 2.71	

With that hypothesis the analysis gave the values presented in the table 3. The number of oxygen neighbors so found may be interpreted in term of percentages of uranium atoms in the different states. The result is consistent with the percentages deduced from the optical data. The reason for the wrong number of oxygen atoms obtained with all uranium atoms in uranyl groups is the phase opposition between the contributions of oxygens at 1.80Å and 2.07Å.

For the preceding analysis there is no doubt about the environments of uranium atoms in the valence states (IV) and (VI) because they can be isolated in borosilicate glasses (glass B₂ and ref.3,7). To insure the conclusion, it would be necessary to obtain a glass with all uranium atoms in the formal valence state (V); it seems impossible to obtain such a situation .

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