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Letter to the Editors

Radioactive behavior of UO_3 immobilized in borate glasses

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The study of glasses containing radionuclides is important since glass is used to immobilize nuclear waste [1]. Uranium is one of the radionuclides contained within the nuclear waste that requires secure immobilization from the environment through its storage in appropriate glass matrices. Previous studies investigated the influence of the glass composition and the parameters of glass processing on the spectroscopic behavior of uranium ions incorporated in some borate and borosilicate glasses [2,3].

The aim of this study was to investigate the radioactive behavior of uranium ions immobilized in some simple borate glasses.

Samples were prepared using reagent grade $Na_2B_4O_7 \cdot 10H_2O$, Al_2O_3 and TiO_2 (Reactivul, Romania), and uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (Chemapol, Czechoslovakia). First the $Na_2B_4O_7$ glass was prepared by melting dehydrated borax at 1000°C for 1 h. Then the glass samples were prepared by melting adequate mixtures of powdered $Na_2B_4O_7$ glass, Al_2O_3, TiO_2 and UO_3 at 1200°C for 30 min. Two series of samples were prepared: (a) samples of $(1-x)$ $(0.96Na_2B_4O_7–0.05Al_2O_3) \cdot xUO_3$ molar compositions, with $x = 0.005$, 0.02, 0.05, 0.10, 0.20 and 0.30, where the UO_3 content was varied; and (b) samples of $0.98Na_2B_4O_7–0.02UO_3$, $0.93Na_2B_4O_7–0.05Al_2O_3–0.02UO_3$ and $0.93Na_2B_4O_7–0.05TiO_2–0.02UO_3$ molar compositions where the UO_3 content was maintained constant, but the glass matrix composition was slightly changed. All the mixtures were molten in alumina crucibles. The glass charges were obtained as slabs (about 20 × 8 × 3 mm) by pouring the melts in stainless steel having an appropriate groove.

Chemical analysis indicated that the obtained glasses had the same compositions as the raw material mixtures introduced in the crucibles. X-ray powder diffraction ascertained the vitreous state of all the samples.

The obtained samples were yellow for low UO_3 contents and brown for high contents ($x \geq 0.05$). This observation suggests the presence of uranium ions mainly as U^{6+}. Spectroscopic investigations proved the presence of a major fraction of U^{6+} ions (as UO_2^{2+} ions), but also of a small fraction of U^{4+} ions [3].

The β radioactivity of the glass slabs and of the UO_3 powder was measured. Counting rate measurements were made using a 70020 VAZ-520 proportional detector (Robotron Messelektronik, Germany) and a Strahlungsmessgerät 20026 RFT counter (Germany). Glass slabs were measured exposing their 20 × 8 mm surface to the detector. The UO_3 powder was placed for the measurement in a circular plastic box with a diameter of 20 mm, being uniformly spreaded on the available surface. The sample–detector distance was 5 mm in all cases.

The specific activity was computed using the following equation [4]:

$$A_s = \frac{4\pi n}{60\Omega m}, \tag{1}$$

Table 1
Specific activity A_s of $(1-x)(0.95Na_2B_4O_7–0.05Al_2O_3) \cdot xUO_3$ glasses

Composition x	mass (g)	Counting rate (pulses/min)	A_s (Bq/g)	ΔA_s (Bq/g)
0.005	1.423	277	10	0.3
0.02	2.433	1436	31	0.9
0.05	1.500	1875	67	2.0
0.10	1.130	2886	138	4.1
0.20	1.132	6673	317	9.5
0.30	1.061	9178	466	14.0
UO_3 powder	0.750 [a]	42971	2958	88.7

[a] Close to 0.80 g that represents the UO_3 content of sample $x = 0.30$.

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Table 2
Dependence of the specific activity Λ_s on the glass matrix composition

Composition	Mass (g)	Counting rate (pulses/min)	Λ_s (Bq/g)	$\Delta\Lambda_s$ (Bq/g)
$0.98Na_2B_4O_7$–$0.02UO_3$	2.425	1079	24	0.7
$0.93Na_2B_4O_7$–$0.05Al_2O_3$–$0.02UO_3$	2.433	1436	31	0.9
$0.93Na_2B_4O_7$–$0.05TiO_2$–$0.02UO_3$	2.496	877	19	0.6

where n is the counting rate of β particles (pulses/min), Ω is the solid angle (sr), and m is the mass of the samples (g). The values for the solid angle were computed according to the shape of the samples using a standard computer program. We obtained $\Omega = 3.89$ for the glass slabs and $\Omega = 4.06$ for the UO_3 powder.

Specific activity values as a function of the UO_3 content of the samples are tabulated in Table 1. The estimated relative error of the specific activity $\Delta\Lambda_s/\Lambda_s$ is less than 3%. Note that the amount of 0.75 g of UO_3 powder for which data are presented in the last row of Table 1 is close to the UO_3 content of the sample $x = 0.30$, namely 0.80 g. Comparing the specific activity of the UO_3 powder and of the sample with $x = 0.30$, a ratio higher than 6 was observed. This evidences an efficient radioprotective effect of the glass matrix.

Specific activity values obtained for some glasses having the same UO_3 content, but slightly different matrix composition, are given in Table 2. The presented data show the dependence of the radioprotective effect of glass matrices on their composition. We note important changes of the specific activity due to the addition of small amounts of Al_2O_3 or TiO_2. More studies are necessary in order to clarify the mechanism which determines this important influence of the mentioned additives. The higher absorption of β radiation in the case of the $0.93Na_2B_4O_7$–$0.05TiO_2$–$0.02UO_3$ glass may be related (a) to the presence of titanium atoms (having a higher atomic radius than the other atoms present in this glass matrix), or/and (b) to the structural changes produced by addition of TiO_2 to the $Na_2B_4O_7$ glass (having as a result a more compact structure of the glass matrix) [5].

These results suggest that an appropriate glass matrix could ensure note only an efficient immobilization of nuclear waste but also an important radioprotection.

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