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Alpha self-irradiation effects in ternary oxides of actinides elements: The zircon-like phases $A\mathrm{m}^{\mathrm{III}}\mathrm{VO}_4$ and $A^{\mathrm{II}}\mathrm{Np}^{\mathrm{IV}}(\mathrm{VO}_4)_2$ (A = Sr, Pb)

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Abstract

We report the experimental studies of irradiation damage from alpha decay in neptunium and americium vanadates versus cumulative dose. The isotopes used were the transuranium α-emitter ^{237}Np and the α,γ-emitter ^{241}Am. Neptunium and americium vanadates self-irradiation was studied by X-ray diffraction method (XRD). The comparison of the powder diffraction patterns reveal that the irradiation has no apparent effect on the neptunium phases while the americium vanadate swells and becomes metamict as a function of cumulative dose.

Keywords: Americium; Auto irradiation; Damage; Neptunium; Zircon

1. Introduction

In France, spent nuclear fuels are processed and the high-level nuclear wastes (HLNW) are vitrified to form borosilicate glasses. The vitrification process is part of the multibarrier concept to prevent radionuclides from reaching the biosphere when stored in a geologic repository [1]. At present, glasses are the most preferred waste form because they can easily accommodate a large number of heavy ions [2]. However, glasses inevitably corrode when in contact with water and atmospheric conditions. The management of HLNW requires the use of host matrices exhibiting high resistance to ionizing radiations. One has to consider the stability of this type of material under radiation as the main parameter in the selection of acceptable host matrices. Radiations can affect the release rate of radionuclides from these wastes by increasing the surface area (microfracturing) and thus by changing the leaching rate of the matrix. Presently, there are insufficient data and understanding currently available to predict the long-term behavior of nuclear waste forms. The physical and chemical durability of the waste matrices can contribute greatly to successful isolation of the HLNW.

Due to the emergence of various sources of wastes there is an interest in the development of alternatives to glass forms [3–6]. Several crystalline ternary phases have been proposed to produce specific hosts for the different radionuclides. When considering this option, a new parameter appears: radiations which affect the chemical durability when a crystalline to amorphous transformation occurs. Alpha decay of actinide elements is the primary source of radiation defects in nuclear waste forms [7–9]; thus, the study of these effects in solid matrices is important for the possible development of radiation-resistant materials. Obviously, materials that are chemically and thermally stable over geologic periods are good candidates. In this instance, actinide-containing minerals studies suggest that zircon,

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scheelite, monazite or apatite-phases will be potential nuclear waste disposal materials [10,11]. Moreover, such minerals are amorphous (metamict) resulting from radiation damages. One challenge is to create these damages at relatively low flux over long periods of time to relatively high total doses; thus, self-irradiation experiments in ternary phases containing transuranium elements were performed. This technique has been used to simulate, at accelerated dose rates, the simultaneous α-particle and α-recoil nucleus effects that are expected over extremely long times in ceramics for HLNW immobilization [12,13].

To our knowledge the studies of long term effects of α-decay events were simulated essentially by incorporating short-lived actinides—such as ^{238}Pu [7,14–17] with half-life of 87.7 years or ^{244}Cm [16,18,19] with half-life of 18.1 years—into the phases in concentrations large enough so that the total α-decay dose reaches values of 10^{18}–10^{19} α-decay events g^{-1} in reasonable amounts of time.

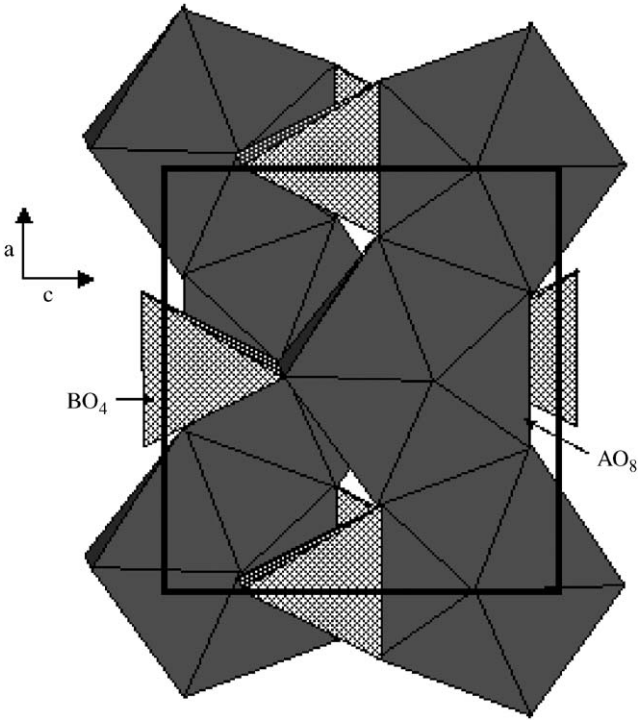

Fig. 1. ABO_4 Zircon structure.

In this regard, studies of naturally occurring U and Th bearing phases that are structurally and chemically analogous to waste form phases provide important data for these long term effects. Zircon occurs in nature with thorium and uranium concentrations typically reaching 10 wt%. The actinide zircon-type minerals, like $ThSiO_4$ (thorite) or $USiO_4$ (coffinite), represent a class of minerals which can exist in partially or totally non-crystalline forms; the metamictization of these alpha emitting radioactive minerals was brought about by self-irradiation damage. The propensity to incorporate actinides, its durability and its resistance to chemical and physical degradation has made zircon one of the most useful accessory mineral in geologic studies and has lead to suggest that zircon could be used to immobilize artificial actinide isotopes [20,21].

2. Experimental section

Zircon is a common structural form of ABO_4-type materials. The structure is tetragonal (space group $I4_1/amd$; $Z = 4$) and consists of alternating AO_8 polyhedra and BO_4 tetrahedra forming chains that are parallel to the c axis (Fig. 1). This structure is also encountered with trivalent and tetravalent transuranium ions located in the A site [22]; e.g., plutonium can readily substitute for A ions in the zircon structure. The effects of alpha decay in both Pu-containing and natural zircons have been studied [12,23]. Moreover, unit cell expansion due to irradiation has been determined for a number of ceramics [18,24] and also in natural zircons [25,26].

The purpose of our work was to perform experiments on real materials rather than simulations by heavy ion bombardments. We have tried to investigate the effects of alpha self-irradiation effects on the crystal-structure of the transuranium orthovanadates $AmVO_4$ and $ANp(VO_4)_2$ (A = Sr, Pb). The sources of radiation are the long half-life ^{237}Np and ^{241}Am isotopes. Alpha decay produces energetic α-particle and energetic recoil nuclei (Table 1).

The average number of atomic displacements generated by an α-decay event in a ceramic was estimated to be about 1400 (220 due to the α particle plus 1180 due to

Table 1
Nuclear characteristics of the isotopes

Isotope	$T_{1/2}$ (years)	E_α (MeV)	Recoil nucleus and E_{RN} (keV)	Major E_γ (keV)
^{237}Np	2.14×10^6[27]	4.78 (75%) 4.65 (12%)	^{233}Pa; ≈80	—
^{241}Am	426.3 [28]	5486 (86%) 5443 (13%)	^{237}Np; ≈92	59

E_{RN} = energy of the recoil nucleus

the recoil atom). The processes of the damages are elastic collisions between α particles, and α-recoil nuclei, and atoms which cause atomic displacements as well as the creation of Frenkel defects [29].

The americium isotope ^{241}Am was chosen as the α-emitter because its half-life allowed the damages to accumulate at a rate compatible with a possible experimental time of a few years and larger than in other studies of about an order of magnitude. Phases containing the ^{237}Np isotope, due to its very long half-life, were studied in the same way essentially as a control over an extended period of time (5 years).

All the experiments were carried out in depressurized glove boxes using very small amounts, from one (^{241}Am) to ten (^{237}Np) milligrams, of oxides; moreover, sheets of glass (Pb-doped) were used to protect the experimentalist from the ^{241}Am γ-rays.

$AmVO_4$ was prepared by the appropriate molar amounts of AmO_2 and V_2O_5 powders annealed in air at 600 °C for 2 days. Compensated substitution of Am^{III} by bivalent (Sr^{II} and Pb^{II}) and tetravalent (Np^{IV}) cations also stabilizes the zircon structure. The double orthovanadates $ANp(VO_4)_2$ ($A = Sr$, Pb) were obtained at 700 °C. The substitution corresponds to the equivalent scheme: $2\ Am^{III} = A^{II} + Np^{IV}$.

X-ray diffraction (XRD) measurements, ideally suited to small quantities of materials, were obtained with Cu$K\alpha$ radiation using a modified Philips powder diffractometer partially housed within a glove box; the X-ray beam passes throughout a beryllium window to enforce the complete separation between radioactive and inactive areas [30]. The powder diffraction profiles were collected, at 25 °C, over the angular range $17 < 2\theta < 77^\circ$ using a 2θ step size of 0.01° at a rate 0.02 ° min^{-1}.

3. Results and discussion

$Am^{III}VO_4$, identified by Keller and Walter [31], was the first transuranium zircon-like phase containing a transition element ($a = 7.31$ and $c = 6.42$ Å). Our X-ray diffraction analysis unambiguously confirmed the zircon structure (systematic extinctions hkl: $h+k+l = 2n+1$; $hk0 : h = 2n+1$) and our refined cell parameters are in excellent agreement with Keller's values.

The tetragonal lattice parameters of the neptunium and americium phases are listed in Table 2. No superstructure line was detected by XRD for the neptunium double vanadates. Therefore the zircon structure results in a disordered distribution of the A^{II} and Np^{IV} cations over the eight-fold sites; thus, it would be better to write these ternary oxides as $A_{1/2}Np_{1/2}VO_4$.

The changes in lattice parameters were determined during damage ingrowth every month over 5 years. Between the measurements the products were stored in a safe box at room temperature. Time $t = 0$ was defined as the samples removal from the furnace after annealing.

Table 2
Experimental lattice parameters for $t = 0$.

Phase	a_0 (Å)	c_0 (Å)	V_0 (Å^3)
$PbNp(VO_4)_2$	7.334(3)	6.520(3)	350.7(4)
$SrNp(VO_4)_2$	7.315(2)	6.485(2)	347.0(3)
$AmVO_4$	7.311(2)	6.422(2)	343.3(2)

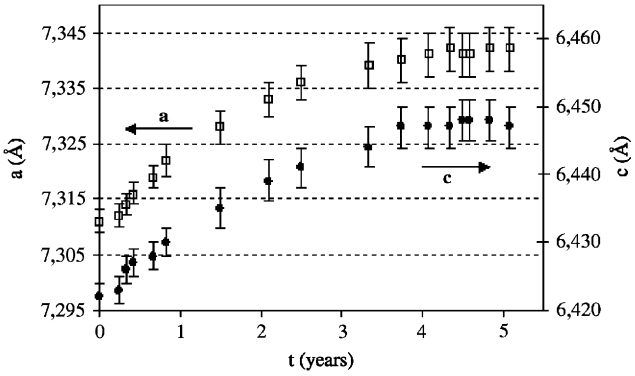

Fig. 2. Changes in lattice parameters as a function of time in alpha self-irradiated $AmVO_4$.

XRD patterns with ^{237}Np-containing vanadates remained unchanged during the experimental time. The calculated cell parameters showed identical values (within the limits of error) for all the time periods. Furthermore, the ^{237}Np Mössbauer experiments showed no observable isomer shift variation or broadening of the resonance spectra [32].

The XRD results of americium vanadate self-irradiated at various doses showed no considerable difference compared with the start of the experiment. All (hkl) reflections were found to be characteristic of $AmVO_4$ in each case if we accept the very slow cell parameter evolution and amorphization process. The measured changes in unit cell parameters (a and c) as a function of time are shown in Fig. 2. The phase has become predominantly amorphous after 5 years and thus it was impossible to do significant measurements past this irradiation time. The changes in unit-cell volume, $\Delta V/V_0$, as a function of the cumulative dose, D_C, are shown in Fig. 3 and Table 3.

The amorphization process is consistent with models based on the multiple overlap which suggests that amorphization occurs as a result of a critical defect concentration. The energy of the recoil nucleus is lost through elastic collisions with atoms in the structure, producing highly localized damages. The alpha particle, on the other hand, dissipates most of its energy by

ionization processes but still undergoes enough elastic collisions near the end of its path to produce several hundred atomic displacements.

Usually, the unit-cell volume expansion $\Delta V/V_0$ follows the exponential behavior predicted by models [21,33–36]. It is given by

$$\frac{\Delta V}{V_0} = A[1 - \exp(-BD_C)] \quad \text{(model I)}$$

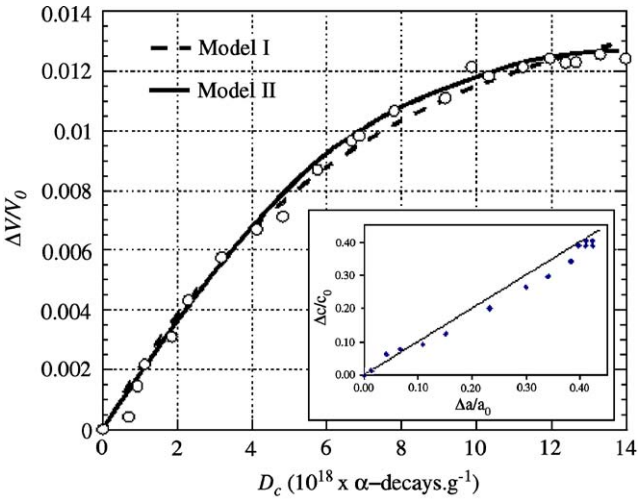

Fig. 3. Unit-cell volume expansion as a function of cumulative dose. Inset: relationship between $\Delta a/a_0$ and $\Delta c/c_0$.

with A the relative unit-cell volume expansion at saturation; B the rate constant (per unit dose) and D_C the cumulative dose (α-decay events g^{-1}).

Different types of amorphous accumulation behaviors have been reported in the literature. E.g. when amorphization occurs by cascade overlap [16] another evolution is proposed:

$$\frac{\Delta V}{V_0} = A[1 - \exp(-BD_C)^n]. \quad \text{(model II)}$$

This model assumes that the curvature at the beginning (“reflected” by the n factor value different from 1) would be caused by the necessity to create damage zones and so that cascade superposition would become more probable. A least-squares fit of the two above-mentioned equations with the data in Fig. 3 yields values given in Table 4.

Inset in Fig. 3 shows the evolution $\Delta a/a_0 = f(\Delta c/c_0)$; no anisotropic unit cell expansion is apparent. As observed in Figs. 2 and 3, the radiation-induced

Table 4
Empirical fit parameters for structural changes as given by the models I and II.

		A	B	n
$\Delta V/V_0$	Model I	0.0148(5)	$0.15(1) \times 10^{18}$	1
	Model II	0.0131(3)	$0.188(8) \times 10^{18}$	1.24(5)

Table 3
Experimental lattice parameter evolutions and unit-cell volume for $AmVO_4$ versus time

t (years)	Dose ($\alpha\, g^{-1}$) ($D_C \times 10^{-18}$)	$\Delta a/a_0$ (%)	$\Delta c/c_0$ (%)	V (Å^3)	$\Delta V/V_0$ (%)
0	0	0.000	0.000	343.3(2)	0.000
0.250	0.687741	0.01368	0.01557	343.4(3)	0.0291
0.333	0.916988	0.04103	0.06229	343.8(3)	0.1456
0.417	1.147152	0.06839	0.07786	344.0(2)	0.2039
0.667	1.833977	0.10942	0.09343	344.3(3)	0.2913
0.833	2.292471	0.15046	0.12457	344.7(3)	0.4078
1.167	3.209460	0.20517	0.15571	345.2(4)	0.5535
1.500	4.126447	0.23253	0.20243	345.6(4)	0.6700
1.750	4.814188	0.24620	0.21800	345.7(4)	0.6991
2.083	5.731177	0.30092	0.26472	346.2(4)	0.8447
2.417	6.648165	0.34195	0.28029	346.6(4)	0.9613
2.500	6.877412	0.34195	0.29586	346.6(4)	0.9613
2.833	7.794400	0.36931	0.32700	346.9(4)	1.0486
3.333	9.169883	0.38298	0.34257	347.1(5)	1.1069
3.583	9.857624	0.41034	0.38929	347.4(5)	1.1943
3.750	10.316118	0.39666	0.38929	347.3(5)	1.1652
4.083	11.233106	0.41034	0.38929	347.4(5)	1.1943
4.333	11.920848	0.42402	0.38929	347.5(5)	1.2234
4.500	12.379342	0.41034	0.40486	347.5(5)	1.2234
4.583	12.608589	0.41034	0.40486	347.5(5)	1.2234
4.833	13.296330	0.42402	0.40486	347.6(5)	1.2525
5.083	13.984071	0.42402	0.38929	347.5(5)	1.2234

D_C = cumulative dose $\alpha \times 10^{18}\, g^{-1}$; V_0 = cell volume at $t = 0$.

amorphization is predicted to be predominant at a dose of about 15×10^{18} α-decays g^{-1}.

4. Conclusion

To our knowledge, this is the first investigation of alpha self-irradiation damage using the relatively long-life isotope ^{241}Am. The effects of damages accumulated over 5 years from alpha decay in an Am–zircon phase have been studied by XRD. The main conclusions of this work are as follows:

(1) The accelerated decay (damage) rates determined in these americium-doped material studies were initiated to evaluate long-term behavior of nuclear waste materials. Our experimental objective was to show the simultaneous α-particle and α-recoil nucleus effects with doses that one expects over long periods of time (10^3–10^6 years for nuclear waste forms).
(2) Ceramic waste forms may incorporate specific radionuclides, such as the tri- and tetravalent transuranium ions, which occupy specific atomic positions in periodic structures. The coordination polyhedron in each phase imposes specific size, charge and bonding constraints on the nuclides.
(3) The zircon vanadates have a compact structure which remains in its original form during the irradiation, even at a high dose rate such as in the americium phase. The cumulative alpha decay doses per gram reach values of about 14×10^{18} α-decay events g^{-1} during the 5 year experiment; the americium phase becomes aperiodic (metamict): the XRD lines are attenuated but not broadened.
(4) Alpha-self irradiation causes an isotropic expansion of the unit cell of the $AmVO_4$ unit cell and the volume expansion obeys an exponential relation.

Radiation-induced changes in $AmVO_4$ result from the accumulation of defects, which increases with the cumulative dose. Although the exact nature of the amorphization process is not well defined, the mechanism would be direct recoil of alpha, direct recoil of heavy nuclei and accumulation of local defects.

All the experiments were performed at the "Institut du Radium", Paris, France.

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