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Structural investigation of the pseudo-ternary system AmO_2–Cm_2O_3–ZrO_2 as potential materials for transmutation

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Abstract

The present work describes our investigations of the AmO_2–Cm_2O_3–ZrO_2 system. Selected compositions were prepared using an aqueous route and keeping the Cm/Am ratio constant at 20%. Depending of the compositions, two cubic systems were observed, fluorite- or pyrochlore-type. In the compounds synthesized, curium is present as a trivalent ion but americium may be either in an oxidation state of (IV) or (III), depending of the content of zirconia.

1. Introduction

For the prospect of transmuting actinides, we have studied the phase behavior of different zirconia-based materials, such as AmO_2–ZrO_2–Y_2O_3 [1], and Cm_2O_3–ZrO_2 [2,3]. This work is now being extended to the AmO_2–Cm_2O_3–ZrO_2 system which is discussed in the present paper.

Transmutation of actinides in a uranium-free material has been envisioned for almost a decade [4], and several candidate materials have been investigated. Included are composite materials, metallic alloys or solid solutions of oxides, nitride and carbide compounds. An overview is given in Ref. [5]. Among the possible materials considered the most promising are oxides such as CeO_2, MgO, $MgAl_2O_4$, ZrO_2 as well as different nitride or carbide materials, each having interesting and non-desirable properties. Among the different oxides, cubic zirconia-based materials are considered as pertinent host-material candidates for the long-lived radionuclides. Indeed, various physico-chemical properties of cubic-stabilized zirconia are quite relevant for use in reactors. Some of these are the low neutron cross section of Zr, a stable tetravalent oxidation state, the high resistance of the cubic-stabilized zirconia structure toward damages from neutron irradiation, alpha and fission products [6,7], as well as its chemical inertness with the various reactor cooling fluids (H_2O, Na, He, etc.). However the low thermal conductivity of cubic-stabilized ZrO_2 ($\leqslant 2\ \mathrm{W\,m^{-1}\,K^{-1}}$) and related compounds may be detrimental for this reactor application. This problem may be overcome by the use of a composite ceramic, where the bulk component has a higher thermal conductivity [8,9].

In our initial study of the AmO_2–ZrO_2–Y_2O_3 system [1], Y_2O_3 was selected to stabilize the cubic form of zirconia. The result was the formation of very stable fluorite-type cubic solid solutions. We then replaced yttria with Cm_2O_3. The Cm_2O_3–ZrO_2 system was investigated for selected compositions, with an ultimate goal being to treat Am and Cm in the same transmutation matrix without the use of yttria. We determined that for certain compositions, Cm^{3+} stabilized ZrO_2 in a cubic form, either a fluorite- or a pyrochlore-type structure. For example, the compositions $(Cm_{0.25}Zr_{0.75})O_{1.875}$, and $(Cm_{0.5}Zr_{0.5})O_{1.75}$ were found to exist as a single-phased, fluorite structure and pyrochlore

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structure, respectively. Following the study of each actinide in zirconia, we investigated the Am–Cm–Zr–O system. The first results of these investigations are reported here.

2. Experimental

One of the starting materials was commercial high-purity (99.9%) zirconyl nitrate ($ZrO(NO_3)_2 \cdot nH_2O$), while ^{243}Am oxide (AmO_2) and ^{248}Cm chloride ($CmCl_3$) materials were made available by the US Department of Energy (DOE) through its heavy element research program at the Transuranium Research Laboratory at Oak Ridge National Laboratory (ORNL).

All of the compositions were prepared from aqueous solutions. The starting polycrystalline $^{243}AmO_2$ solid was first calcined at 1273 K to remove moisture, carbonates, etc. Then 18.4 mg of this product were dissolved in 1 ml of 8 M HNO_3. A smaller amount of $CmCl_3$ was available, and it was dissolved in 1 ml of 1M HCl to make the curium starting solution.

The preparation americium–curium–zirconia compounds were obtained by mixing appropriate quantities of the aqueous solutions of each component, using sub-milliliter amounts of solutions and employing in-house developed micro-techniques. Solids were obtained by slowly drying the mixed solutions, and these solids were then calcined in air at 1773 K in Pt crucibles for 10 h. Due to the scarcity of the isotopes employed, all preparations were done with a milligram or less of actinides.

The radioactive products were sealed in quartz capillaries for the X-ray and spectral analyses. Samples were characterized by X-ray diffraction using 114.6 mm Debye-Sherrer cameras ($Mo(K_\alpha)$ radiation = 0.71073 Å). The cell parameters were refined from the observed reflections using a least square method (LAPOD program).

3. Results and discussion

Quantities and isotopic compositions of each long-lived radioisotope produced during irradiation depend on two major factors, which are essentially the type of fuel (UO_2, MOX) and its final burn-up. For example, quantities of the actinides studied in the present studies increase dramatically with the burn-up and the initial plutonium content of the fuel. The Cm/Am ratio found in irradiated fuels also varies significantly, from 6% for a standard UO_2 fuel irradiated at 33 GWd t^{-1} of uranium up to about 20% for a MOX fuel containing initially 5% of Pu and irradiated at 45 GWd t^{-1} of uranium. Details can be found in Ref. [10]. According to the different values expected at the reprocessing stage, the values of the ratio Cm/Am was fixed to be 0.2 in the present studies. This covers a significant composition of each actinide and allows a determination of the influence of the trivalent cation Cm^{3+} on the structure, where the americium is expected to be tetravalent. We then studied various compositions of Am, from 0.10 to 0.83 at.% with curium/americium = 0.2. The experimental points of this work are given Fig. 1. Two extra experimental compositions were added to complement the general trend, and these are marked with cross.

At a low fraction of actinides (An/(An + Zr) = 0.12) a diphasic system was found, which was composed of a monoclinic and a cubic fluorite-type phase. At a higher concentration (An/(An + Zr) = 0.18), a solid solution was formed (single phase, fluorite type). Between the fourth (An/(An + Zr) = 0.36) up to sixth data point, patterns representing pyrochlore structures were observed. These single phased materials showed increasing cell parameters with the actinide content. Above a certain concentration of actinides (An/(An + Zr) $\geqslant$ 0.72), only fluorite structures were observed. These results are summarized in Table 1.

Pyrochlore compounds of the general formula, $A_2B_2O_7$, were found in the present work, where An atoms occupy the A position and Zr atoms the B sites. The structures are isomorphous with the mineral $(Na,Ca)(Nb,Tb)O_6F \cdot nH_2O$. In this type of structure the two cations are long range ordered as shown in Fig. 2. Atomic positions and structural details on the formation of pyrochlore oxides are discussed in [12,13].

These $A_2B_2O_7$ compounds can be considered as having a fluorite structure with a double unit-cell, where

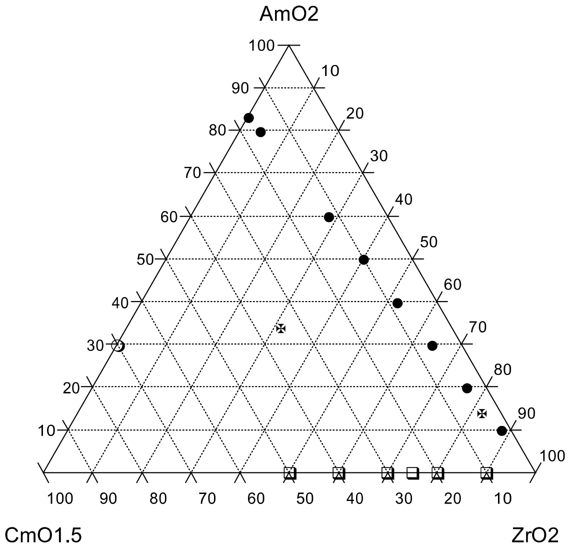

Fig. 1. Experimental studies of the pseudo-ternary system AmO_2–Cm_2O_3–ZrO_2. Our data are represented as dark circle and crosses. Squares represent the data obtained in our previous study on the Cm_2O_3–ZrO_2 system [2], and the open circles represent data obtained from the literature [11].

Table 1
Experimental data for the Am–Cm–Zr–O system

Composition	An/(An + Zr)	Cm/Am	Number of phases	Type of phase	Cell parameter (nm)	
$(Am_{0.1}Cm_{0.02}Zr_{0.88})O_{1.99}$	0.12	0.2	2	Fluorite + monoclinic	$a = 0.5185(4)$	$a = 0.518$ $b = 0.524$ $c = 0.525$ $\beta = 98.9°$
$(Am_{0.14}Cm_{0.04}Zr_{0.82})O_{1.98}$	0.18	0.2	1	Fluorite	$a = 0.5213(5)$	
$(Am_{0.2}Cm_{0.04}Zr_{0.76})O_{1.98}$	0.24	0.2	1	Fluorite	$a = 0.5203(6)$	
$(Am_{0.3}Cm_{0.06}Zr_{0.82})O_{1.98}$	0.36	0.2	1	Pyrochlore	$a = 1.049(1)$	
$(Am_{0.4}Cm_{0.08}Zr_{0.52})O_{1.96}$	0.48	0.2	1	Pyrochlore	$a = 1.0551(6)$	
$(Am_{0.5}Cm_{0.1}Zr_{0.4})O_{1.95}$	0.51	0.2	1	Pyrochlore	$a = 1.0623(6)$	
$(Am_{0.6}Cm_{0.12}Zr_{0.28})O_{1.94}$	0.72	0.2	1	Fluorite	$a = 0.5348(8)$	
$(Am_{0.8}Cm_{0.16}Zr_{0.04})O_{1.92}$	0.96	0.2	1	Fluorite	$a = 0.5381(4)$ and $a = 0.5369(6)$	
$(Am_{0.34}Cm_{0.32}Zr_{0.31})O_{1.99}$	0.66	0.94	1	Fluorite	$a = 0.5349(6)$	
$(Am_{0.833}Cm_{0.167})O_{1.917}$	1	0.2	1	Fluorite	$a = 0.5387(4)$	

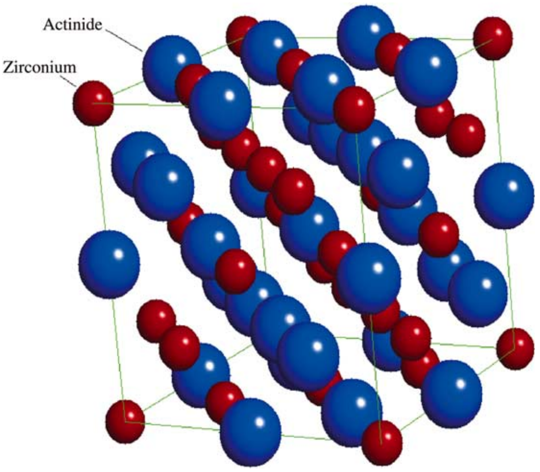

Fig. 2. Cationic long range order in the $A_2B_2O_7$ pyrochlore structure.

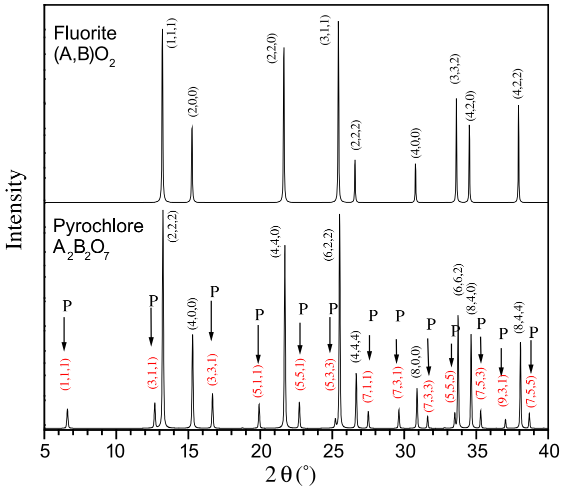

Fig. 3. Evolution of the X-ray diffraction pattern as it progresses from a fluorite solid solution $(A,B)O_2$ to a pyrochlore structure $(A_2B_2O_7)$ (P = pyrochlore Bragg reflections).

1/8 of the oxygen atoms are missing, leading to ordered vacancies. The crystallographic sites, named A in the formula, accommodate the large trivalent cations (here the actinides) and the B sites the smaller cation (here Zr^{4+}). The structure of the pyrochlore oxides can be visualized as a reduced form of a cubic solid solution (e.g., $An_{0.5}Zr_{0.5})O_2$, initially fluorite type, where the actinide (An) has been reduced to its trivalent oxidation state. This gives the final product, $(An_{0.5}Zr_{0.5})O_{1.75}$ where the two cations, An^{3+} and Zr^{4+} order as shown in Fig. 2 to compensate for the change in size and oxidation state. Fig. 3 shows the evolution of this process in the corresponding X-ray diffraction patterns. However, it is also worthwhile to note that one aspect of the pyrochlores is their ability to accommodate, up to a certain degree, different cations with different oxidation states and sizes on both crystallographic sites. The only requirement being that charge neutrality is satisfied. The mineral, pyrochlore, is a good example of this capability. In our case, the A sites are necessarily occupied by a combination of Am^{4+} and Cm^{3+} ions. The cell parameter of the pyrochlore compounds obtained is larger than expected, when both actinides are fully reduced to their trivalent state [13]. Additional oxygen atoms then fill the vacancies to compensate the total charge.

There are two remaining questions regarding oxidation states: (1) is americium fully tetravalent or is it partially reduced; and (2) does it vary with the composition of the material? To understand these questions, the evolution of the cell parameter of the compounds (where Cm/Am = 0.2) was plotted as a function of the total actinide content (Fig. 4). To make a comparison on

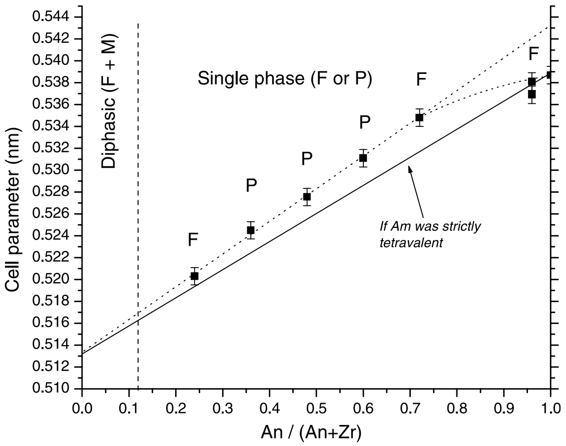

Fig. 4. Evolution of the cell parameter as a function of the actinide content (F = fluorite, P = pyrochlore, and M = monoclinic structure).

basis of the same unit-volume of the different compounds, it was necessary to divide the cell parameters of the pyrochlore structure by two. This is justified as the pyrochlore structure can be considered as a superstructure of the fluorite unit-cell. The unit-volume considered is in essence a fluorite unit-cell, whose dimensions depend only of the radii of the ions constituting the unit.

Based on the profile shown in Fig. 4, one deduces that between $0.24 \leqslant \mathrm{An}/(\mathrm{An}+\mathrm{Zr}) \leqslant 0.72$, the evolution of the cell parameters is linear with respect to the actinide content. It can also be concluded that within the range of compositions considered, the actinides remain in the same oxidation states regardless of the material composition. This is not true for low concentration of zirconium ($\mathrm{An}/(\mathrm{An}+\mathrm{Zr}) > 0.72$), which indicates that Zr could have some influence on the redox behavior of the americium. The trivalent state is stabilized by its $5f^7$ electronic configuration. This latter point is based on the general behavior of the curium oxide systems in which Cm is always trivalent above 675 K, as well as the rather large cell parameter of the zirconium-free compound, $(\mathrm{Am}_{0.833}\mathrm{Cm}_{0.167})\mathrm{O}_{1.917}$, which indicates that curium is trivalent. Thus, Zr appears to influence the partial reduction of Am. If americium was fully tetravalent, the cell parameters of the materials should follow the solid line shown Fig. 4. However, as already mentioned, the reduction to the trivalent state for americium is obviously not complete, as the cell parameters of pyrochlore compounds are smaller than found in earlier studies [13] and diphasic materials would have been be observed such as in the $\mathrm{An_2O_3}$–$\mathrm{ZrO_2}$ or $\mathrm{Ln_2O_3}$–$\mathrm{ZrO_2}$ systems [2–14]. The property of zirconium to enhance the reduction of another cation that exhibits dual oxidation states (III and IV) has already been pointed out by various authors, notably in the system Ce–Zr–O, where it was shown that Zr increases the extent of the Ce reduction [15]. This feature of zirconia may be enhanced in the case of americium, as it can be reduced fairly easily to its trivalent oxidation state [16] (e.g., formation of americium sesquioxide as compared to formation of plutonium sesquioxide).

An analysis of the influence of Zr on the $\mathrm{Am}^{3+}/\mathrm{Am}^{4+}$ redox couple, or that of other actinides having both oxidation states, is out of the scope of the present paper. But this effect, if verified, is quite important with regard to different nuclear materials that involve zirconia. It would mean that the stabilizing element could be the actinide itself. More work is needed in this regard.

From the structural aspect it seems difficult at this stage to define the boundaries between the different phases in the $\mathrm{AmO_2}$–$\mathrm{Cm_2O_3}$–$\mathrm{ZrO_2}$ system. However, it is worthwhile to point out that there are many similarities with the $\mathrm{CeO_2}$–$\mathrm{Nd_2O_3}$–$\mathrm{ZrO_2}$ system [17], which is not surprising as these lanthanides are used frequently as surrogate elements for the actinides, Pu, Am, Cm.

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