On the valency state of americium in $(U_{0.5}Am_{0.5})O_{2-x}$

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Abstract

In the context of nuclear transmutation of minor actinides the compound $(U_{0.5}Am_{0.5})O_{2-x}$ was studied by X-ray diffraction, oxygen potential measurement, X-ray photoelectron spectroscopy and magnetic measurements. According to these results the compound in question should rather be formulated as americium uranate $AmUO_{4-y}$, since Am proved to be in the trivalent oxidation state and not as expected by analogy with $(U_{0.5}Pu_{0.5})O_{2-x}$ with Pu being tetravalent, whereas uranium turned out to be tetra- and pentavalent.

1. Introduction

The concept of nuclear transmutation deals with the idea of irradiating the highly toxic and long-lived α-active minor abundant actinides (Np, Am, Cm) with fast neutrons in order to transmute them into less toxic, short-lived fission products. The compound $(U_{1-z}Am_z)O_{2-x}$ was investigated in this context as a potential nuclear fuel. Sintered pellets of this material should serve for irradiation experiments in fast reactors, and hence a number of parameters needed to be determined before the actual experiment.

2. Preparation of the material

The preparation procedure should be designed such that it results in a homogeneous material, suitable for scientific–technical application. The material was prepared using the gel-supported precipitation (GSP) method [1], resulting in mixed oxide pellets exhibiting the desired properties.

3. Structural aspects

UO_{2+x} and AmO_{2-x} both have a cubic lattice of the CaF_2 type. Since ionic radii of the cations and the lattice parameters of the dioxides of U, Np, Pu and Am are very similar [2], a very good miscibility of UO_2 with the corresponding transuranium compounds re-

TABLE 1. Experimentally determined and calculated lattice constants

	Lattice constants (pm) of the following oxides		
	$(U_{0.5}Np_{0.5})O_{2.0}$	$(U_{0.5}Am_{0.5})O_{2.0}$	$(U_{0.5}Pu_{0.5})O_{2.0}$
Experimental value	545.1 (± 0.1)	545.2 (± 0.1)	543.5 (± 0.1)
Vegard's law	545.05	542.2	543.2

sults. According to Vegard's law, an equimolar mixed oxide of UO_2 and AmO_2 should have a lattice parameter $a' = 542.3$ pm. The experimentally determined value a for $(U_{0.5}Am_{0.5})O_{2.00}$, however, was found to be 545.2 pm [3], a considerable deviation which is not found with mixed dioxides of Np or Pu (Table 1).

The strong deviation from Vegard's law indicates a fundamental difference in the chemistry of the U–Am mixed oxides, as compared with the corresponding U–Np or U–Pu compounds. X-ray diffraction data do not give enough evidence to explain the observed discrepancies; however, they indicate that an analogy with U–Pu or U–Np mixed oxides is unlikely. No second phase was observed for mixed oxides of stoichiometries between $(U_{0.5}Am_{0.5})O_{1.86}$ and $(U_{0.5}Am_{0.5})O_{2.00}$.

4. Oxygen potential

The oxygen potentials ΔG_{O_2} of pseudobinary actinide systems have been investigated by Bartscher and Sari
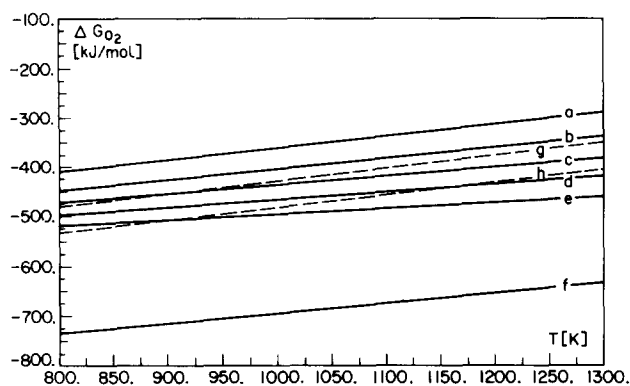
Fig. 1. Oxygen potentials of $(U_{0.5}Am_{0.5})O_{1.99}$ (curve a), $(U_{0.5}Am_{0.5})O_{1.96}$ (curve b), $(U_{0.5}Am_{0.5})O_{1.93}$ (curve c), $(U_{0.5}Am_{0.5})O_{1.90}$ (curve d), $(U_{0.5}Am_{0.5})O_{1.87}$ (curve e), $(U_{0.5}Np_{0.5})O_{1.99}$ (curve f), $(U_{0.78}Ce_{0.3})O_{1.98}$ [6] (curve g) and $(U_{0.73}Gd_{0.27})O_{1.97}$ [7] (curve h).

[4, 5]. Their results are summarized in Fig. 1. Again a clear difference between the values measured for the uranium–americium mixed oxide and those of the corresponding neptunium compound was observed. Figure 1 also shows that the oxygen potentials as observed for uranium lanthanide compounds are close to the values measured for $(U_{0.5}Am_{0.5})O_{2-x}$. The similarity of thermodynamic data indicates an analogy in the chemistry of the elements in question, i.e. Am and the lanthanides.

5. Photoelectron spectroscopy

To investigate more directly the observed deviation from the bonding model as established for U–Pu mixed oxides, X-ray induced photoelectron spectroscopy (XPS) was used in order to determine the valence states of uranium and americium in $(U_{0.5}Am_{0.5})O_{2-x}$ from the chemical shift and the characteristic shape of the U and Am 4f core levels. The experimental results are shown in Figs. 2 and 3, displaying the 4f lines: the shapes are characteristic for tetravalent U as in UO_2 and for trivalent Am as in Am_2O_3.

Tables 2 and 3 summarize the binding energies and compare them with literature data. Some conclusions may be drawn from this comparison.

(1) In pure uranium oxides binding energies of the U 4f shells increase with increasing positive charge (i.e. increasing oxidation state) of the uranium atom (chemical shift).

(2) The binding energies of the U 4f shells are shifted to higher values as compared with $UO_{2.00}$.

(3) Peak shape and peak position of the Am 4f spectrum are very similar to those observed for Am_2O_3.

Consequently, the oxidation state of americium appears to be trivalent whereas uranium exhibits a main
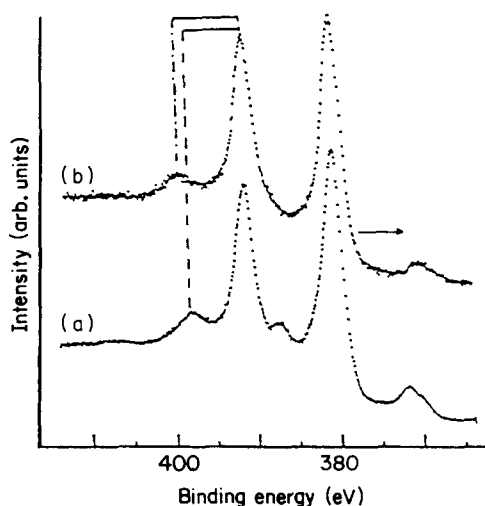

Fig. 2. XPS spectra showing the U 4f peaks: spectrum a, reference spectrum of $UO_{2.00}$; spectrum b, spectrum of $(U_{0.5}Am_{0.5})O_{2-x}$ (shifted by 0.8 eV).
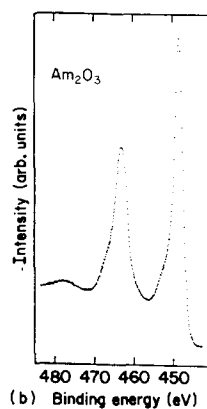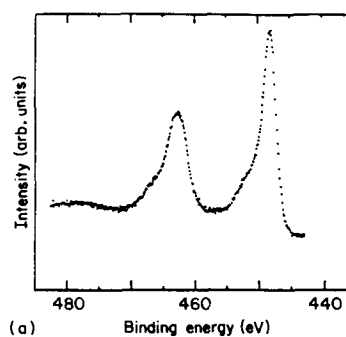

Fig. 3. (a) XPS spectrum of the Am 4f peaks of $(U_{0.5}Am_{0.5})O_{2-x}$. (b) XPS spectrum of the Am 4f peaks of Am_2O_3 [8].

valence state of 4+, with some possible admixture of higher oxidation states. It is, however, worth noting that XPS is a surface analysis technique. Hence, the information obtained results from 5–10 atomic layers on the surface of the sample that may have slightly modified properties compared with the bulk. XPS measurements of the oxidation of Np metal [11, 12] revealed a surface valence modification only for the top atomic

TABLE 2. Binding energies of the U $4f_{5/2}$ and U $4f_{7/2}$ levels as well as the relative positions of the satellites (relative to $4f_{5/2}$)

	U $4f_{5/2}$ (eV)	U $4f_{5/2}$ satellite position (eV)	U $4f_{7/2}$ (eV)
$(U_{0.5}Am_{0.5})O_{2-x}$	391.6[a]	6.2, 8.4[a]	380.9[a]
$UO_{2.000}$ [9]	391.2	6.7	380.3
UO_2 [10]	391.1	5.8, 8.2	380.1
UO_{2+x} [9]	391.6	6.3, 8.2	380.7
UO_3 [10]	391.9		380.9

[a]Uncertainty: ±0.2 eV.

TABLE 3. Binding energies of the Am $4f_{5/2}$ and $4f_{7/2}$ levels

	Am $4f_{5/2}$ (eV)	Am $4f_{7/2}$ (eV)
$(U_{0.5}Am_{0.5})O_{2-x}$	462.7	448.2
Am_2O_3 [8]	462.6	448.2
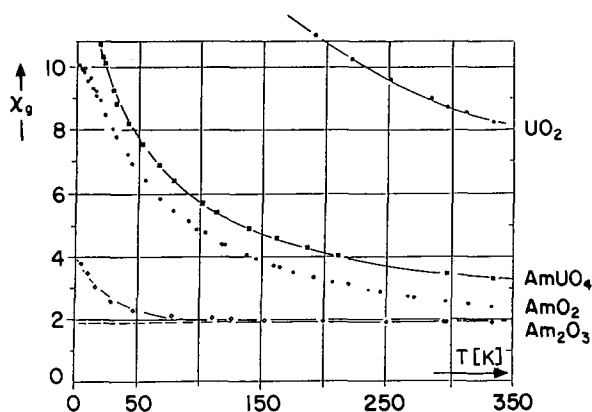
Fig. 4. Magnetic susceptibility per gram (in 10^{-6} c.g.s. units) vs. temperature.

Fig. 5. Squared magnetic moment vs. temperature.

layer. Thus the measurements presented here are considered to represent mainly the bulk properties.

6. Magnetic measurements

Magnetic measurements on polycrystalline samples were performed on a Faraday balance in order to obtain information on the valence states of uranium and americium in the bulk. Figures 4 and 5 show the magnetic susceptibility and the squared magnetic moment of the compound in question as a function of temperature, in comparison with UO_2 and some other compounds.

As can be seen on the μ_{eff}^2 vs. T graph, the compound under investigation behaves more like a ternary uranium(V) oxide with lathanum than a UO_2–AmO_2 mixture. Any contribution from tetravalent uranium should
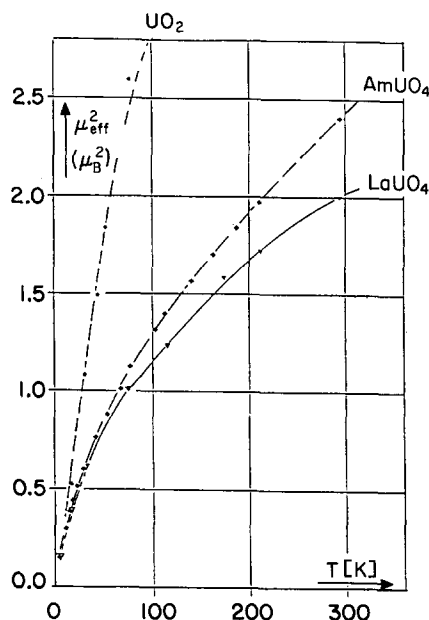
result in much higher μ_{eff}^2 values than observed experimentally.

7. Conclusion

In contrast to the corresponding neptunium and plutonium compounds, $(U_{0.5}Am_{0.5})O_{2-x}$ exhibits high oxygen potentials and deviation from Vegard's law. This already indicates a fundamental difference in the bonding of the latter compound as compared with the former compounds. The first compounds are explained by a bonding model based on a fluorite-type lattice, where the uranium atoms are (statistically) replaced by plutonium (or neptunium) ions. For hypostoichiometric oxides, the plutonium (or neptunium) is of mixed valence, +3 and +4 depending on the stoichiometry, whereas uranium remains tetravalent. This model cannot describe the experimental results obtained for the corresponding americium compound satisfactorily. XPS measurements as well as magnetic data are in contradiction with such a model.

Describing the compound as americium(III) uranate, $AmUO_{4-y}$, in analogy to the well-known lanthanide uranates, allows us to explain the experimental results: the americium is trivalent, while uranium is of mixed valence, +4 and +5, depending on the stoichiometry.

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