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The incorporation of plutonium and neptunium in zirconolite and perovskite

B.D. Begg[a,*], E.R. Vance[a], S.D. Conradson[b]

[a]Materials Division, ANSTO, PMB 1, Menai, NSW 2234, Australia
[b]Los Alamos National Laboratory, New Mexico, USA

Abstract

The incorporation of Pu and Np in one zirconolite and a number of perovskite formulations has been investigated under oxidising and reducing conditions. The Pu valence in both perovskite and zirconolite was found to vary independently of the crystal chemical design by altering the annealing atmosphere, from Pu^{4+} in air to Pu^{3+} in 3.5% H_2/N_2. For both atmospheres, only tetravalent Np was found in the zirconolite. Tetravalent Np was observed in perovskites fired in air, but trivalent Np was stabilised in suitable perovskite formulations annealed under a reducing atmosphere. A trivalent Np phosphate, $NpPO_4$ was also prepared under reducing conditions. © 1998 Elsevier Science S.A.

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1. Introduction

The long-term immobilisation of Pu and Np along with the other transuranic elements is an issue of international interest, arising primarily from the partitioning of reprocessed high-level nuclear waste (HLW) and the current focus on the disposition of excess weapons Pu. One of the options available for these tasks is to use a ceramic matrix such as Synroc. Synroc is a mineral analogue based ceramic designed to immobilise HLW in a series of highly durable titanate phases [1]. Waste elements are incorporated into each of the Synroc phases by a substitutional solid solution mechanism. The two Synroc phases capable of incorporating transuranic elements are zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$).

Previously we have reported the incorporation of Pu and Np in zirconolite [2]. We set out to investigate the incorporation of tri- and tetravalent Pu and Np on both the Ca and Zr sites of zirconolite by only providing sufficient charge compensation for the desired Pu/Np valence on the selected site. The relative influence of crystal chemical design and sintering atmosphere on the Pu and Np valence state was then determined by annealing the samples in oxidising and reducing atmospheres at temperatures of 1200–1400°C. The Pu valence in each of the zirconolite series, irrespective of the chemical design, was found to vary with the firing atmosphere, from trivalent after heating at 1200°C in 3.5% H_2/N_2, to tetravalent after sintering in air at 1400°C. The compositions of the individual zirconolites however were essentially unchanged as found from the microanalytical SEM studies. In contrast, the Np in the parallel Np-doped zirconolites remained tetravalent in all samples irrespective of both the crystal chemical design and the annealing atmosphere using the same temperatures as used in the Pu series. Again, no observable compositional change was seen between firing atmospheres. The ability of the Pu valence to change, and the Np valence to remain tetravalent, independently of the crystal chemical design of the zirconolite, raised questions as to how electroneutrality was being preserved in many of these samples. Therefore a further series of zirconolite samples has now been prepared to determine whether or not Pu and Np could be incorporated into zirconolite in the absence of any specific charge compensating additives.

This investigation has also been extended to examine the influence of crystal chemical design and annealing atmosphere on the incorporation of Pu and Np in perovskite. Samples were prepared targeting tri- and tetravalent Pu and Np on the Ca site of perovskite by only providing an appropriate amount of Al substituted on the Ti site to ensure electroneutrality for the selected Pu/Np valence

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*Corresponding author. Tel.: 61 2 97173747; fax: 61 2 95437179; e-mail b.begg@ansto.gov.au

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state. Based on experiments with Ce, Pu and Np would not be expected to have any solubility on the Ti site in perovskite [3]. Once prepared, the perovskites were annealed in an oxidising and reducing atmosphere. Pu- and Np-perovskites were also fabricated without any charge compensating additives.

As part of our investigation into the viability of various Pu and Np valence states in Synroc we have looked at the general stability of Np^{3+} by attempting to fabricate $NpPO_4$. Pu can form a trivalent metal monazite-structured phosphate, $PuPO_4$, when heated in air. However, the known Np phosphate is NpP_2O_7, in which Np is formally present as Np^{4+}.

2. Experimental

The preparation of the zirconolite samples used in this study has been described previously [2]. The perovskite samples were prepared via a sol–gel route, from a liquid mix of alkoxides and nitrates. The solution was stir-dried prior to calcination in air at 750°C for 1 h. The calcined powder was then pressed into pellets and sintered at 1500°C for 10 h in air. Each sample was then divided into two; one part was set aside and the other sintered at 1200°C for 10 h in flowing 3.5% H_2/N_2. The $NpPO_4$ sample was prepared by mixing NpO_2 dissolved in ~6 mol l^{-1} nitric acid with 85% H_3PO_4. This solution was then brought to a pH of 9 by NH_3 addition and stir dried. The powder was calcined for 1 h at 750°C in 3.5% H_2/N_2, and then hot-pressed in a graphite die at ~1350°C and 20 MPa for 2 h.

Samples were prepared for microstructural analysis by polishing to a one micron diamond finish. Scanning electron microscopy (SEM) and microanalysis were carried out using a JEOL JSM-6400 scanning electron microscope fitted with a Tracor Northern MICRO-ZII X-ray detector and a Series II TN5502 analysis system. X-Ray diffraction was carried out with a Scintag X-1 instrument. X-Ray absorption spectroscopy (XAS) was performed at the Stanford Synchrotron Radiation Laboratory (SSRL) in fluorescence mode on the Pu L_{III}-edge and the Np L_{III}-edge at 80 K. The samples were powdered and triply contained in certified sample holders.

3. Results and discussion

3.1. Uncompensated Pu and Np-bearing zirconolite

Zirconolites were prepared with the Pu and Np nominally substituted on the Ca site without any charge compensation to offset the associated charge imbalance, giving a $Ca_{0.9}(Pu/Np)_{0.1}HfTi_2O_7$ composition. The zirconolites were prepared with Hf completely replacing Zr on a molar basis to avoid overlap between the Pu L_{III}-edge and the Zr K-absorption edges. Hf has complete solid solubility for Zr in zirconolite [4]. Unfortunately, however, both these zirconolites were prepared with an excess of Pu and Np, respectively, over and above the nominal value of 0.1 formula units.

The Pu-doped zirconolite that formed after the initial air sinter at 1400°C had the following composition, $Ca_{0.95}Pu_{0.12}Hf_{1.11}Ti_{1.81}O_7$, where, contrary to the design, the Pu appears to be evenly distributed between the Ca and Hf sites. The Pu is too large to substitute directly for Ti; however, a degree of solid solubility exists between Hf and Ti which enables the Pu to substitute on the Hf site. In addition to the zirconolite, a small quantity (~5%) of pyrochlore $Ca_{0.92}Pu_{0.56}Hf_{0.75}Ti_{1.74}O_7$, as well as rutile and hafnium titanate had formed. Annealing this sample at 1200°C for 10 h in 3.5% H_2/N_2 did not lead to a detectable change in either the phase assemblage or composition of the individual phases. The Pu L_{III}-edge XANES spectra from these two samples indicated that the Pu was completely tetravalent after the initial air sinter, and approximately 80% of this was reduced to Pu^{3+} as a result of the reducing atmosphere heat treatment.

Based on the measured composition of the zirconolite, where the Pu was equally divided between the Ca and Hf sites, electroneutrality could only be achieved when the Pu is trivalent. The Pu^{4+}-bearing zirconolite would, therefore, appear to contain an excess of positive charge. Parallel studies on charge compensation in air-fired Ce-doped zirconolites suggest that the most likely means of compensating for an excess of positive charge in zirconolite is via the introduction of Hf or Ti vacancies [3]. In this instance ~0.03 formula units of Hf or Ti vacancies would be required, which is just beyond the ~0.02 atoms per formula unit detection limit of the SEM microanalysis.

The Np-doped zirconolite formulation, inadvertently prepared with an excess of Np, resulted in the formation of a similar group of phases. The composition of the zirconolite was $Ca_{0.93}Np_{0.17}Hf_{1.01}Ti_{1.87}O_7$, in which the Np appears to be predominantly located on the Hf site. A small amount (~5%) of pyrochlore $Ca_{0.91}Np_{0.59}Hf_{0.74}Ti_{1.73}O_7$ was also formed. Once again, the compositions of the phases were unchanged by the reducing atmosphere anneal. Np L_{III}-edge XANES indicated that the Np was tetravalent after the initial air sinter whilst the reducing anneal stabilised about 20% of the Np as Np^{3+}. This was slightly more than the maximum of 10% Np^{3+} observed for the other Np-doped zirconolites subject to an identical reducing atmosphere heat treatment, although the Np^{3+} in the present sample may well be located in the pyrochlore, which contains just under 20% of the Np in the sample [2]. The Np^{4+}-bearing zirconolites both appear to contain an excess of positive charge, which would most likely be compensated for by ~0.03 formula units of Hf/Ti vacancies.

3.2. Perovskite

3.2.1. Plutonium

3.2.1.1. Design: Pu^{3+} on Ca site with Al compensation on Ti site – $Ca_{0.9}Pu_{0.1}Ti_{0.9}Al_{0.1}O_3$

As shown in Table 1 the perovskite composition determined after both the air sinter and 3.5% H_2/N_2 anneal closely approximated the design. Despite the presence of excess Pu, each perovskite only contained ~0.1 formula unit of Pu, with the remaining being present as PuO_2. The reduced sample also contained a minor amount of pyrochlore. The Pu L_{III}-edge XANES indicated that the Pu was tetravalent after the initial air sinter, whilst the 3.5% H_2/N_2 heat-treatment was sufficient to reduce ~80% to Pu^{3+}. However, the ~2% PuO_2 present in the reduced sample actually contains about ~20% of the total Pu, therefore the Pu in the perovskite and pyrochlore would be expected to be completely trivalent.

The composition of both these perovskites is consistent with electroneutrality only being preserved for trivalent Pu. Yet in the sample sintered in air all the Pu was tetravalent, giving the perovskite an apparent excess of positive charge. Based on parallel studies looking at the incorporation of Ce in perovskite [3], it would appear that the most likely means of compensation for this excess positive charge would be via Ti vacancies. In this instance approximately 0.02 formula units of Ti vacancies would be required.

3.2.1.2. Design: Pu^{4+} on Ca site with Al compensation on Ti site – $Ca_{0.9}Pu_{0.1}Ti_{0.8}Al_{0.2}O_3$

The perovskites formed after the air sinter and reducing anneal both contained a slight excess of Pu compared with the design (see Table 1). Both samples also contained ~1% PuO_2, whilst an equivalent amount of pyrochlore was observed in the reduced sample. Pu L_{III}-edge XANES found the Pu to be tetravalent after the air sinter, with only ~10% of the Pu being present as Pu^{4+} in the reduced sample, in approximate agreement with the amount of PuO_2 present in this sample: the rest of the Pu in this sample was trivalent.

The composition of the perovskite annealed in air contained enough Al on the Ti site to compensate for the tetravalent state of the Pu; however the reduced perovskite contained an excess of Al on the Ti site for the 0.14 formula units of Pu^{3+} present. The only means of compensating for such an excess of negative charge is through the introduction of oxygen vacancies [3].

3.2.1.3. Design: Pu^{3+} on Ca site with no charge compensation – $Ca_{0.9}Pu_{0.1}TiO_3$

Despite the absence of any charge compensating Al on the Ti site, Pu-bearing perovskites were formed after both the oxidising and reducing heat treatments in close approximation to the design. The proportion of perovskite in both samples was, however, less than for the previous two series, with a considerable amount of pyrochlore and a lesser amount of PuO_2 present after both heat-treatments (see Table 1). Pu L_{III}-edge XANES indicated that the Pu was tetravalent after the air sinter, with ~15% Pu^{4+} present after the reducing anneal (the rest being trivalent).

Table 1
Summary of Pu-doped perovskite results

Design	Firing atmosphere	Composition of Pu-phases	Overall Pu-valence
$Ca_{0.9}Pu_{0.1}Ti_{0.9}Al_{0.1}O_3$	Air	$Ca_{0.90}Pu_{0.09}Ti_{0.87}Al_{0.10}O_3$ (98%) PuO_2 (2%)	100% Pu (IV)
	3.5% H_2/N_2	$Ca_{0.91}Pu_{0.09}Ti_{0.89}Al_{0.09}O_3$ (96%) PuO_2 (2%) $Ca_{0.96}Pu_{1.28}Ti_{1.13}Al_{0.74}O_7$ (2%)[a]	20% Pu (IV) 80% Pu (III)
$Ca_{0.9}Pu_{0.1}Ti_{0.8}Al_{0.2}O_3$	Air	$Ca_{0.89}Pu_{0.12}Ti_{0.78}Al_{0.21}O_3$ (99%) PuO_2 (1%)	100% Pu (IV)
	3.5% H_2/N_2	$Ca_{0.89}Pu_{0.14}Ti_{0.77}Al_{0.19}O_3$ (98%) PuO_2 (1%) $Ca_{1.49}Pu_{0.80}Ti_{1.37}Al_{0.60}O_7$ (1%)[a]	10% Pu (IV) 90% Pu (III)
$Ca_{0.9}Pu_{0.1}TiO_3$	Air	$Ca_{0.91}Pu_{0.09}Ti_{0.97}O_3$ (93%) PuO_2 (1%) $Ca_{1.08}Pu_{1.06}Ti_{1.89}O_7$ (6%)[a]	100% Pu (IV)
	3.5% H_2/N_2	$Ca_{0.93}Pu_{0.07}Ti_{0.97}O_3$ (89%) PuO_2 (1%) $Ca_{1.33}Pu_{0.68}Ti_{2.10}O_7$ (10%)[a]	15% Pu (IV) 85% Pu (III)

[a] Pyrochlore.

Clearly both perovskites contain an apparent excess of positive charge, since no Al was present on the Ti to assist with charge compensation. In accordance with the results obtained from the Ce-doped perovskites [3], the air fired Pu^{4+} perovskite would require ~0.04 formula units of Ti vacancies, in good agreement with the measured stoichiometry, which is twice the amount needed for the Pu^{3+} perovskite.

3.2.1.4. Summary

The incorporation of Pu in perovskite mirrors that of Pu in zirconolite, with the Pu valence being clearly dependent on the prevailing firing atmosphere and independent of the crystal chemical design. In each of the perovskite formulations annealed in a reducing atmosphere a small amount of pyrochlore was observed, which appears to have been stabilised by the presence of Pu^{3+}. Pyrochlore is known to readily accept cation vacancies, which may explain why a greater proportion of pyrochlore was observed in both samples in the uncompensated series.

3.2.2. Neptunium

3.2.2.1. Design: Np^{3+} on Ca site with Al compensation on Ti site – $Ca_{0.9}Np_{0.1}Ti_{0.9}Al_{0.1}O_3$

The composition of the perovskite present in both the air sintered and 3.5% H_2/N_2 annealed samples closely approximated the design, with approximately 0.1 formula units of Np and Al located on the Ca and Ti sites, respectively (see Table 2). In addition to perovskite, both samples contained a small quantity (~2%) of NpO_2 and pyrochlore. Np L_{III}-edge XANES revealed that the Np was tetravalent after the initial air sinter, whilst the reducing atmosphere anneal stabilised ~80% of the Np as Np^{3+}. The presence of such a significant proportion of Np^{3+} was unexpected, given the consistent tetravalent state of Np incorporated in zirconolite. The 2% NpO_2 in the reduced sample would account for the ~20% of Np as Np^{4+}, suggesting the Np in the perovskite and pyrochlore was completely trivalent.

Since this perovskite formulation was designed to incorporate Np^{3+}, the air sintered Np^{4+} perovskite contains an apparent excess of positive charge. Charge compensation has most likely been effected in this perovskite by the introduction of 0.02 formula units of Ti vacancies. The reduced perovskite contains enough Al on the Ti site to compensate for the trivalent Np.

3.2.2.2. Design: Np^{4+} on Ca site with Al compensation on Ti site – $Ca_{0.9}Np_{0.1}Ti_{0.8}Al_{0.2}O_3$

The air-fired and reduced perovskites from this series both contained an excess of Np relative to the design, as shown in Table 2. Significantly, neither sample contained any pyrochlore although each had a small amount (~1%) of NpO_2. Np L_{III}-edge XANES confirmed the tetravalent state of Np in the air sintered sample; however, in contrast to the previous Np-doped perovskite, the Np remained tetravalent after the reducing anneal in accordance with its crystal chemical design. Since both these perovskites had an excess of Np relative to the design, neither contained sufficient Al on the Ti site to completely compensate for the amount of Np^{4+}. Based on the microanalysis results,

Table 2
Summary of results from the Np-doped perovskites

Design	Firing atmosphere	Composition of Np-phases	Overall Np-valence
$Ca_{0.9}Np_{0.1}Ti_{0.9}Al_{0.1}O_3$	Air	$Ca_{0.89}Np_{0.09}Ti_{0.91}Al_{0.09}O_3$ (96%) NpO_2 (2%) $Ca_{0.96}Np_{0.97}Ti_{2.06}O_7$ (2%)[a]	100% Np (IV)
	3.5% H_2/N_2	$Ca_{0.89}Np_{0.11}Ti_{0.90}Al_{0.07}O_3$ (96%) NpO_2 (2%) Pyrochlore (1%)	20% Np (IV) 80% Np (III)
$Ca_{0.9}Np_{0.1}Ti_{0.8}Al_{0.2}O_3$	Air	$Ca_{0.86}Np_{0.16}Ti_{0.77}Al_{0.20}O_3$ (99%) NpO_2 (1%)	100% Np (IV)
	3.5% H_2/N_2	$Ca_{0.87}Np_{0.15}Ti_{0.77}Al_{0.20}O_3$ (99%) NpO_2 (1%)	100% Np (IV)
$Ca_{0.9}Np_{0.1}TiO_3$	Air	$Ca_{0.91}Np_{0.09}Ti_{0.97}O_3$ (95%) NpO_2 (3%) $Ca_{0.83}Np_{1.45}Ti_{1.66}O_7$ (2%)[a]	100% Np (IV)
	3.5% H_2/N_2	$Ca_{0.92}Np_{0.08}Ti_{0.97}O_3$ (95%) NpO_2 (2%) $Ca_{0.82}Np_{1.29}Ti_{1.83}O_7$ (3%)[a]	20% Np (IV) 80% Np (III)

[a] Pyrochlore.

the perovskites would each require ~0.03 formula units of Ti vacancies.

3.2.2.3. Design: Np^{3+} on Ca site with no charge compensation – $Ca_{0.9}Np_{0.1}TiO_3$

In a similar manner to the Pu-doped perovskites, the lack of any charge compensating additives did not hinder the formation of a perovskite in agreement with the design. In addition to the perovskite, both the oxidised and reduced samples contained small quantities (~2–3%) of both NpO_2 and pyrochlore. Np L_{III}-edge XANES indicated that even in the absence of any charge compensating additives the Np was tetravalent after the initial air sinter, whilst the majority of Np^{4+} (~80%) was reduced to Np^{3+} after the reducing atmosphere anneal. Clearly both Np-bearing perovskites contain an excess of positive charge, which would need to be compensated by a maximum of ~0.04 formula units of cation vacancies in the sample sintered in air.

3.2.2.4. Summary

In contrast to the Np-bearing zirconolites, trivalent Np may be stabilised in favourable perovskite formulations under reducing conditions. Crystal chemical forces however are still able to stabilise Np^{4+} under reducing conditions when charge compensation is available.

3.2.3. $NpPO_4$

Hot-pressing the $NpPO_4$ precursor at 1350°C in a graphite die yielded a mixture of a monazite-structured phase and NpO_2. SEM revealed an extensive porous reaction layer, ~1 mm thick, around the outer edge of the pellet where it had been in contact with the graphite die. Analysis from the porous outer region found only Np with trace amounts of P, whilst the dense core had a composition close to the design, $Np_{1.05}P_{0.81}O_{3.6}$. Clearly the graphite had completely reduced the P in the outer region of the pellet to an elemental state which had subsequently volatilised leaving a porous rim of NpO_2. In the core of the pellet however a monazite-structured $NpPO_4$-type phase had been stabilised as found from XRD, although it was slightly deficient in P due to volatilisation and diffusion of the P. A comparison of the Np L_{III}-edge XANES spectra from this $NpPO_4$ sample and a tetravalent NpO_2 standard revealed a shift of ~-2.5 eV. This is less than the -3.5 eV shift expected based on the shift between Pu^{3+} and Pu^{4+} and would correspond to the presence of ~70% Np^{3+}. Given that the powdered XANES sample would have contained a proportion of NpO_2 and the phosphate that formed had a monazite-structure, the valence of the Np in the $Np_{1.05}P_{0.81}O_{3.6}$ phase would be expected to be trivalent.

The role of crystal chemical forces in determining valency in an oxide system may be seen in this sample. The highly reducing conditions adjacent to the graphite die were clearly unable to reduce the Np beyond Np^{4+}, for that was where the NpO_2 was stabilised, and yet further away from the reducing graphite die in the core of the sample where ionic P was present, trivalent Np was stabilised in the monazite-structured phosphate. The formation of Np^{3+} was therefore predominantly effected by the presence of ionic P and not just the external reducing atmosphere applied by the graphite die, though this was certainly necessary. If anything, the hot-pressing conditions used in the formation of this sample were too reducing to completely stabilise $NpPO_4$ since the preferential reduction and volatilisation of the P facilitated the formation of NpO_2.

4. Conclusions

The flexibility of zirconolite as a host for multivalent actinides has been clearly demonstrated by its ability to incorporate ~0.1 formula unit of Pu and Np in the absence of any specific charge compensating additives. The valence of the Pu in the zirconolite was once again found to vary with firing atmosphere, whilst the Np remained predominantly tetravalent. The behaviour of Pu in perovskite and zirconolite was very similar, with the Pu valence being dependent on the firing atmosphere and independent of the crystal chemical design. In contrast, trivalent Np was stabilised in suitable perovskite formulations under reducing conditions where only tetravalent Np was found in zirconolite. Tetravalent Np was also observed after a reducing anneal in a perovskite formulation designed to stabilise Np^{4+}, highlighting the role of crystal chemical stabilisation. By analogy with Ce-doped materials [3], the presence of cation vacancies have been inferred to provide charge compensation in the zirconolite and perovskite samples displaying an apparent excess of positive charge, whilst oxygen vacancies are thought to be present in samples with an excess of negative charge. The monazite-structured trivalent Np phosphate, $NpPO_4$, was also successfully synthesised.

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