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Actinide and rare earth incorporation into zirconolite

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Abstract

Nd^{3+} and Ce^{3+} can substitute for about 65% of the Ca in monoclinic zirconolite, using Al as a charge compensator in a Ti site. Further substitution up to 85% of Nd^{3+} and Ce^{3+} produces an orthorhombic structure, while more than 85% substitution produces additional phases. Substitution of Ce^{4+} in the Zr site appeared to be quite limited. Incorporation of U^{4+} into the Ca and Zr sites in zirconolite gave results which were similar to those observed by others. Both trivalent and tetravalent Np and Pu can be substituted in the Ca and Zr sites, respectively, under oxygen partial pressures of $0.2–1\times10^{-5}$ atm, provided appropriate charge compensators are present. The implications of these results for formulating actinide-bearing zirconolite-rich ceramics are discussed briefly.

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1. Introduction

Zirconolite is a substantial (about 20 wt.%) component of synroc, a titanate-based ceramic designed for immobilizing high level waste (HLW) from nuclear fuel reprocessing [1]. Recently, we have been developing a titanate ceramic with as much as 85% zirconolite for incorporating actinide wastes – mainly U, Np, Pu, Am and Cm. Such wastes are isolated by advanced reprocessing schemes under intense development in Japan and France, which partition waste elements into chemically similar groups. To design a zirconolite-rich ceramic incorporating several tens of per cent of actinides, it is necessary to know the valences of the actinides and the ions for which they substitute, under the conditions prevailing in hot consolidation. This is also useful information to have for synroc-C, which is designed for unpartitioned Purex waste.

Zirconolite is readily formed on heating a reactive $CaO–ZrO_2–TiO_2$ precursor at 1200–1400 °C under oxidizing conditions [2]. However, in this case, any actinides mixed with the precursor may assume pentavalent or hexavalent states, in which they are relatively leachable by water. Under severely reducing conditions, the actinides will be reduced to trivalent or tetravalent states which are leach resistant. Nevertheless, some perovskite tends to form at the expense of zirconolite [3] and, while it is a leach-resistant phase, perovskite is less durable in aqueous conditions than is zirconolite [4]. Therefore, to obtain an optimum waste form, it is necessary to use only relatively mildly reducing conditions (see below).

Several rare earths and actinides were of interest in the present work. Nd and Ce are abundant components of unpartitioned HLW. Nd^{3+} has an ionic size very close to that of the trivalent actinides from Np to Cm in the periodic table, so it was used as a simulant for trivalent actinides. Ce should be a very good simulant of Pu, because, on heating in air at 1000–1400 °C, both form tetravalent metal fluorite-structured dioxides and trivalent metal monazite-structured phosphates [5]. The ability to form trivalent or tetravalent compounds under the same oxygen partial pressure illustrates the importance of chemical coordination in the final valence state adopted by the Ce and Pu. While NpO_2 is formed in air on heating Np oxide to about 1000 °C, the phosphate formed under these conditions is NpP_2O_7 and not $NpPO_4$ [6], so it is clearly more difficult to form Np^{3+} than it is Pu^{3+} [7] on heating oxide systems in air. Obviously, trivalent ions will be more likely to form than will tetravalent ions under more reducing conditions. U will always be included in actinide wastes, depending on the efficiency of the chemical separations in reprocessing, and the formation of U^{4+} in oxides normally requires reducing conditions, especially for U oxide itself.

We now briefly note the relevant literature on ions incorporated into zirconolite. Nd^{3+} has been found [7] to enter the Ca site rather than the Zr site, because of ionic size considerations. Smith and Lumpkin [8] stated that the polytype adopted by Nd-bearing zirconolite fabricated at temperatures above 1300 °C depends on the Nd content. U^{4+} can enter both the Ca [9] and Zr [9, 10] sites. The pyrochlore-structured Ce analogue of zirconolite has been observed [11] but no progressive substitution of Ce for Zr has been reported. Clinard and coworkers [12, 13] anticipated that Pu^{4+}

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would be accommodated in the Zr site in high temperature sintering of Ca(Pu_x, Zr_{1-x})Ti_2O_7 ($x=0.2$, 1), but their preparations were by no means of single-phase form, so the assumption of Pu^{4+} cannot be wholly substantiated (see below). Matzke and coworkers [14, 15] and Smith *et al.* [16] were able to observe that Np and Pu partitioned preferentially into the perovskite and zirconolite phases in synroc, but the questions of site locations and valence states were not addressed.

In the present work, we have deduced the valence of selected substitutions of variable-valence ions in zirconolite using a well-known strategy. If a model single phase can actually be made to form on heating to equilibration, then the unknown valence is self-consistently defined, using an ionic model, *i.e.* the electroneutrality condition, and assuming vacancy concentrations are negligible.

2. Experimental details

Nearly all the samples were made using our standard preparative method [2] in which Ti and Zr alkoxides are first mixed with aqueous nitrate solutions of Ca, rare earths or actinides and any charge-compensating ions, such as Al, deemed necessary. After stir drying, the mixtures were calcined in air (for rare earths) or 3.5% H_2+N_2 (for actinides) at about 700 °C to remove water, NO_x and organics. The reducing conditions were used for actinide-bearing preparations, to avoid the formation of metastable +5 and +6 species.

Final consolidation and equilibration of the rare earth samples were achieved by pelletizing and sintering for 1–3 days at 1350–1400 °C, sometimes with intermediate grinding and resintering steps. While these temperatures are higher than those envisaged in synroc production, the emphasis here was to achieve equilibration by prolonged heating within about 100 °C of the melting points (1525 °C for pure $CaZrTi_2O_7$ [17]). Consolidation of the actinide-bearing samples was achieved by hot pressing in graphite dies of bore 1 cm at 1250 °C and 18 MPa for 2 h, to yield two samples 2 mm thick per pressing. A disadvantage was that the reducing conditions promote the formation of a minor fraction of perovskite (see above). The hot-pressed samples were reheated to try to equilibrate them in air and neutral conditions.

X-ray diffraction (XRD) was carried out using conventional diffractometers. For this, the rare-earth-containing samples were in the form of powders, the U-bearing samples were in the form of hot-pressed or sintered pellets 1 cm in diameter, and the Np- and Pu-bearing samples consisted of hot-pressed pellets cut in half along their diameters, set in a resin and finally polished to a finish of 1 μm. JEOL scanning and transmission electron microscopes were used on the polished pellets and ion-thinned materials as appropriate.

3. Results and discussion

3.1. Nd

Samples having compositions of $Ca_{(1-x-y/2)}Nd_{(x+y)}$-$Zr_{(1-y/2)}Al_{(x)}Ti_{(2-x)}O_7$ were studied. The formation of a single zirconolite phase would imply that $(x+y/2)$ formula units of Nd would inhabit the Ca site and $y/2$ units the Zr site. For $x=y=0.1$–0.3, the samples all showed perovskite in addition to zirconolite. Samples with $y=0$ and x up to 0.65 were found to be single-phase, monoclinic zirconolites. For $x=0.7$–0.85 an orthorhombic phase was observed and, at $x>0.85$, additional phases, such as zirconia and alumina, were observed. Transmission electron microscopy (TEM) studies of $x=0.5$ ($y=0$) material showed that the zirconolite crystallites were of the 2M polytype, with very few lattice defects.

3.2. Ce

To look at the Ce valence state and site locations, three samples were prepared. In sample Ce-1, of composition $Ca_{0.8}Ce_{0.2}ZrTi_{1.8}Al_{0.2}O_7$, the formation of a single phase would imply that Ce was in the +3 state and substituted on the Ca site, with Al as a charge compensator on a Ti^{4+} site. Samples Ce-2 and Ce-3, of respective compositions $Ca_{0.8}Ce_{0.2}ZrTi_{1.6}Al_{0.4}O_7$ and $CaZr_{0.8}Ce_{0.2}Ti_2O_7$, would have Ce in the +4 state and substituting in the Ca and Zr sites, respectively, if single phases formed.

Ce-1 was found to be essentially phase pure zirconolite, according to XRD and scanning electron microscopy (SEM) investigation. Thus, it was concluded that Ce^{3+}, substituting in the Ca site, was a viable complete model of Ce entry into zirconolite. However, additional X-ray absorption spectroscopy, and detailed TEM structural and SEM compositional studies are in progress to examine this conclusion further. Sample Ce-2 showed alumina in addition to zirconolite, while Ce-3 contained two zirconolites, one of which was relatively dilute in Ce and the other (possibly a pyrochlore) was relatively rich in Ce.

It is concluded that perhaps some (but certainly not all) of the Ce substituted as per the models in Ce-2 and Ce-3. The result for Ce-3 was similar to the result of Clinard for an analogous Pu-doped composition [13]. A set of samples of composition $Ca_{(x)}Ce_{(1-x)}ZrTi_{(2-x)}$-$Al_{(x)}O_7$ gave XRD results which were broadly similar to the analogous Nd-doped series described above.

TABLE 1. Model valences and site locations for Np and Pu in zirconolites

Sample	Composition	Valence	Site
Np-1	$Ca_{0.8}Np_{0.2}ZrTi_{1.8}Al_{0.2}O_7$	+3	Ca
Np-2	$CaZr_{0.8}Np_{0.2}Ti_2O_7$	+4	Zr
Pu-1	$Ca_{0.8}Pu_{0.2}ZrTi_{1.8}Al_{0.2}O_7$	+3	Ca
Pu-2	$CaZr_{0.8}Pu_{0.2}Ti_2O_7$	+4	Zr

3.3. U

Here, the samples investigated corresponded to (a) U^{4+} substituting on the Zr site, *i.e.* of formula $CaZr_{(1-x)}U_{(x)}Ti_2O_7$, and (b) U^{4+} substituting in the Ca site, with two Al ions substituted on the Ti^{4+} sites for charge compensation, giving a formula of $Ca_{(1-x)}U_{(x)}$-$ZrAl_{(2x)}Ti_{(2-2x)}O_7$. The samples of composition (a) showed that the transformation from the zirconolite structure to pyrochlore occurred at an x value of around 0.5, which is in reasonable agreement with published data [9, 10], with equilibration being assisted by short (about 2 h) heat treatments at 1300 °C after hot pressing, to remove metastable perovskite, etc. However, it was found that prolonged heating (about 20 h) caused severe disproportionation. This was not investigated in detail, however, because the effect appeared to be present only at temperatures and times well outside reasonable limits for synroc hot consolidation.

The other group of samples did not display such effects on heating in the range 1300–1400 °C, and it was concluded that the limits of U^{4+} solubility in the Ca site of zirconolite corresponded to $x = 0.3$–0.4. Extra phases observed at $x > 0.4$ were mainly UO_2–ZrO_2 solid solutions and alumina.

3.4. Np and Pu

The samples are described in Table 1 and the XRD results are shown in Table 2. Guided by the results obtained for the U-bearing samples, we restricted the high temperature treatments after hot pressing to short times at 1300 °C, to avoid possible disproportionation effects. The immediate conclusion from the XRD results was that, given the more than 90% abundance of zirconolite in all the heated samples, essentially both trivalent and tetravalent Np and Pu are viable valence states in zirconolite in which charge compensators are present, after heating in air or nitrogen (estimated oxygen partial pressure of about 10^{-5} atm), assuming initial hot pressing under reducing conditions to prevent the formation of metastable +5 and +6 valence states.

In the Np-2 and Pu-2 Al-free formulations, SEM analyses of the zirconolites showed that the Np and Pu contents are less than those of the model compositions. These zirconolites coexist with a significant fraction of a more actinide-rich pyrochlore-like phase. These results indicate that the solubility limits for Np and Pu have been exceeded, just as for the analogous Ce-3 sample mentioned above. Thus, the Np and Pu species can only be incorporated to a maximum limit of about 0.15–0.17 cations per formula unit. In contrast, zirconolites in the Al-bearing Np-1 and Pu-1 formulations generally contain the same or slightly more Np and Pu than do the model compositions, and any extra phases present do not contain actinides. For the Np formulations, the phase assemblages and compositions are the same whether they were heated in air or nitrogen, while nitrogen favours the entry of Pu into the Ca site in the presence of charge-balancing Al.

TEM studies of Np-2 gave results in excellent agreement with the corresponding SEM studies, and the

TABLE 2. Phase assemblages from XRD and SEM for hot-pressed Np- and Pu-doped zirconolites before and after heat treatment

Sample	Heat treatment[a]	Zirconolite (wt.%)	"Pyrochlore" (wt.%)	Perovskite (wt.%)	Rutile (wt.%)	Zirconium titanate (wt.%)
Np-1	–	100				
	H1	89			8	3
	H2	89			8	3
Np-2	–	80		20		
	H1	93[b]	7	<1	<1	
	H2	93	7	<1	<1	
Pu-1	–	85		15		
	H1	100				
	H2	95		5		
Pu-2	–	70		30		
	H1	90	10		<1	
	H2	88	7		5	

[a] H1 and H2 correspond to 2 h at 1300 °C in air and nitrogen respectively.

[b] Small peak observed at *d* spacing of 0.284 nm — very similar to the result obtained for Ce-3 above.

high-resolution lattice images showed the zirconolite crystallites (2M polytype) to be almost free of defects.

4. Further discussion and conclusions

As stated previously, the main aim of this work is to understand the ranges of viable valence states and site locations of rare earth fission products and actinides in high-level nuclear fuel reprocessing wastes, to enable crystal–chemical design of titanate ceramics containing a large fraction of zirconolite. This has largely been achieved. For simplicity, the use of slightly reducing conditions would allow all rare earths and actinides in partitioned or unpartitioned HLWs of the Purex type to be incorporated into zirconolite as trivalent species, with the exception of U, which would be tetravalent. Moreover, since this conclusion appears to be true for an air atmosphere (with the exception of U), there appears to be no significant sensitivity of valence state to the processing atmosphere oxygen partial pressure, in the range between about 10^{-3} and 10^{-8} atm, below which separate problems derive from the instability of zirconolite with respect to perovskite formation. Of course, such sensitivity could be controlled by operating at an appropriate buffer, such as the Ni–NiO system, which would yield an oxygen partial pressure of about 10^{-4} atm at 1200 °C.

The above conclusions on the valence state and site location are being further examined via calculations of XRD peak intensities, electron microscopy (to confirm the detailed chemical compositions, and to check on the polytypic nature and general defect structure of the zirconolite phases) and X-ray absorption spectroscopy to check more directly the deduced Ce valences.

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