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Studies on stabilised zirconia as host phase for the fixation of actinides, rare-earths and sodium

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Abstract

Titania, zirconia and alumina based ceramic materials are potential solid waste forms being assessed to determine their suitability for long term immobilisation of radionuclides. The preparation, characterisation, solid solubilities and leachability studies on stabilised zirconia containing actinides, rare earths and sodium are reported. The range of solid solubilities of cerium, uranium, neodymium, plutonium and sodium was established in stabilised zirconia. Leaching studies in water and 0.1 M HCl at room temperature and 70°C showed very low leachabilities of uranium, plutonium and rare earths. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

High-level radioactive waste (HLW) from spent fuel contains highly radioactive isotopes of alkali elements (Rb, Cs), alkaline earth elements (Sr, Ba), rare earth elements (Ce, Nd) and actinide elements (U, Pu, Np, Am). One way to dispose of high level radioactive wastes would be to immobilize them into inert and stable materials such as glass or an assemblage of crystalline phases [1]. Among the radioactive elements in HLW, actinide elements have a great biological hazard because of their long half lives and alpha activities. Therefore, it is desirable that they are fixed into chemically and physically stable host phases resistant to self irradiation and environmental degradation. In titanium based ceramics known as SYNROC, the incorporation of lanthanides and actinides into zirconolite, $CaZrTi_2O_7$ and perovskite, $CaTiO_3$ phases, their leachability and resistance to radiation damage have been studied extensively [2]. Of these two phases, zirconolite is the more durable in leaching tests and in alpha damage studies. A monazite-type phase is one of the hosts for actinide elements in supercalcine-ceramics [3] and is promising for the immobilization of actinide wastes.

The most important criteria for choosing crystalline phases are (1) good irradiation stability, (2) ability to confine actinides and fission products in solid solution and (3) good chemical durability. Zirconium oxide is suitable as a major constituent of high level waste forms because of the following three reasons [4]:

(1) Zirconium oxide is stable under hydrothermal conditions.
(2) Zirconium oxide forms a hydroxide with low solubility in a pH range of 1.7–10.5.
(3) Zirconium oxide compounds with other metal cations tend to confine considerable amounts of actinide and lanthanide elements.

It is well known that the oxides with the fluorite (CaF_2) structure are resistant to irradiation [5]. Important natural analogues include uraninite, pitchblende (UO_{2+x}), thorianite (ThO_2) and cerianite (CeO_2). In high level waste, it has been observed that this type of phase is formed not only in the calcine obtained after calcination of HLW but also in many of the waste forms such as supercalcine ceramics [6], alumina based forms [7] and titania forms [8]. Calcia-stabilized zirconia, with the CaF_2 structure, has been investigated in the present work as a possible host phase for the immobilization of lanthanides and actinides. Sodium, a reprocessing additive, has been reported to be soluble in UO_2 with fluor-

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ite structure forming a solid solution, $Na_{0.2}U_{0.8}O_{2+x}$ [9]. The present work deals with the preparation, characterisation, solid solubilities and preliminary leachability studies of stabilised zirconia containing actinides, rare earths and sodium.

2. Experimental

In the present study, the preparations of ceramic oxides were carried out by two different methods: (i) solid state synthesis and (ii) using the glycerol method.

2.1. Solid state method

This technique is conventionally used for the preparation of multi-component oxide; oxides, carbonates and hydroxides are blended together and then wet or dry milled, after which the mixture is repeatedly calcined and mechanically ground to assist completion of reaction. Compaction of the powder mixture before sintering increases the rate of the reaction.

Calcia stabilized zirconia is chosen as a host ceramic for the fixation of cerium (Ce), uranium (U), neodymium (Nd), plutonium (Pu) and sodium (Na) in a fluorite matrix. Solid solutions were prepared using "AnalaR" chemicals including $CaCO_3$, ZrO_2, CeO_2, Nd_2O_3 and Na_2CO_3. Stoichiometric $UO_{2.00}$ was prepared by equilibration of U_3O_8 in Ar/H_2 at 800°C [10]. They were mixed in appropriate ratios keeping the $Ca/(Ca+Zr)$ ratio, in the range 0.15–0.23. The mixtures were pelletized and heated at 1200–1400°C in air or, in case of $UO_{2.00}$, in vacuum.

2.2. Glycerol method

The glycerol method is newly developed in our laboratory; the respective nitrate solutions were mixed in appropriate molar ratios, followed by addition of the calculated quantity of glycerol. For 0.1 M of nitrate, this is 9 ml of glycerol (99%) [11]. The contents are heated slowly on a hot plate and when the temperature reaches around 70°C reaction starts: as long as water has not completely evaporated, the reaction temperature remains below 100°C. Once the water has completely evaporated, the reaction temperature increases, reaction becomes vigorous and NO_2 and CO_2 gases are evolved until a dark brown pasty mass remains. This pasty mass was air dried at around 300°C. Glycerol decomposes at this temperature and finally a dark brown porous mass is obtained which is very soft and can be crushed into a fine powder. This powdered mass is heated at 500–800°C in air for about 4 h to remove all organic matter and free carbon, followed by pelleting and heating at 1200°C. This method was not, however, used for preparations involving UO_2 as it is not stable in air and oxidises to U_3O_8. In the present work the nitrates of calcium, zirconium, cerium, neodymium, sodium and plutonium were prepared by dissolving oxides, hydroxides, carbonates or nitrates in HNO_3 or in distilled water. The concentrations of elements in solution were determined by standard gravimetric, titrimetric or potentiometric methods.

The characterisation of the heated products at different stages were carried out by X-ray powder diffraction (XRD) technique using CuK_α radiation in a diffractometer enclosed in a glove box for handling radioactive materials. The oxidation studies were carried out on $CaO–ZrO_2–UO_2$ in fluorite single phase region using thermogravimetric (TG) technique.

For the samples containing volatile elements like sodium, the calcined powder was hot pressed at 20 MPa between graphite dies at 1200°C using a uniaxial hot press. Some of the samples were also examined using a scanning electron microscope (Model JSM-T330 A, Jeol, Japan), followed by energy dispersive X-ray analysis (SEM/EDX); the pressed pellets were fixed in a mould of 30 mm diameter, using mould resin and then polished with diamond-impregnated cloth using diamond paste. The polished pellets were coated with carbon by vacuum evaporation.

Leaching studies were carried out by two methods. In one method, solubility tests were carried out on powdered samples. The particle size of the powdered samples was found to be less than 100 μm by using standard mesh. The powder samples were leached in quartz distilled water (QDD) or in 0.1 M HCl in the ratio of 1:10 in Teflon tubes. These tubes were fixed on a rotor and the samples were stirred continuously for 7 days at room temperature. The leachate is then filtered through Whatman 542 filter paper. In this method, as per MCC-3 [12] there was a very slight reduction in the volume of the solvent.

In another method, as per standard procedure MCC-1 [12], leaching experiments were carried out on hot pressed pellets in an acid digestion bomb with a Teflon container at 70°C. The pellets were kept in the container with a measured volume of solvent. The solvents used in our experiments were QDD water or 0.1 M HCl.

Analysis of the leachate was carried out using inductively coupled plasma–atomic emission spectroscopic (ICP–AES) and atomic absorption spectrometric (AAS) techniques. Elements other than Cs were determined by ICP–AES using a Jobin-Yvon Panorama ICP emission spectrometer with a combination of polychromator and sequential facilities. The determination of Cs was done by flame-AAS using a GBC-906 atomic absorption spectrometer. After the leachate was collected and analysed, the pellets were subsequently subjected to further cycles of leaching and the analysis of the leachate.

3. Results and discussion

3.1. CaO–ZrO$_2$–CeO$_2$ system

Solid solutions of compositions $[(ZrO_2)_{1-x}$-$((CeO_2)_x]_{0.9}(CaO)_{0.1}$ with $0<x<1$ have been studied by Carriat et al. [13] to determine the influence of the lattice parameter on electric conductivity of fluorite-type ternary oxide systems. The lattice parameter was found to increase linearly with cerium concentration.

In the system CaO–ZrO$_2$–CeO$_2$, the solid solubility of CeO$_2$ in phases of the CaO–ZrO$_2$ system was determined emphasizing the fluorite region. The samples were prepared by solid state as well as the glycerol method with varying concentrations of cerium maintaining the Ca/(Ca+Zr) ratio=0.23, at 1200°C in air. The powder XRD patterns of the heated mixtures obtained were fluorite structured solid solutions.

Fig. 1 gives X-ray powder diffraction patterns obtained for different concentrations of cerium oxide for the composition of solid solution $[Ca_{0.23}Zr_{0.77}]_{1-y}Ce_yO_{1-x}$ where $y=0$–1. It is seen that in the region y (cerium concentration)=0.05–0.35 and 0.75–0.95, the products were found to be single phase fluorite type. A shift in the position of reflections with change in y is observed. The equilibrium condition was reached in less than 8 h. In the region $y=0.45$–0.65, the XRD patterns of the products were found to be mixtures of two phases, both fluorite type, C_1 (zirconium rich) and C_2 (cerium rich). Repeated heating in the region $y=0.45$–0.65 did not show any change in XRD patterns, indicating the attainment of the equilibrium.

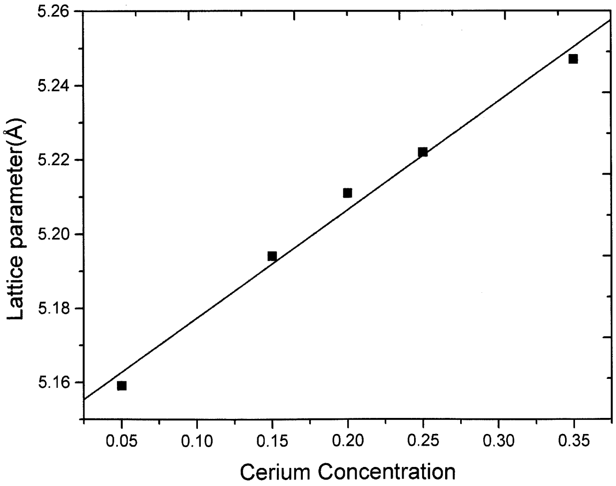

Fig. 2. Plot of lattice parameter versus Ce concentration in $[Ca_{0.23}Zr_{0.77}]_{1-y}Ce_yO_{2-x}$ ($y=0$–0.35).

Fig. 2 shows the correlation between lattice parameter, a, in (Å) and cerium concentration ($y=0$–0.35). The lattice parameter varied linearly with increase in cerium concentration and its equation of fit is:

$$a(\text{Å}) = 5.148 + 0.29y \tag{1}$$

3.2. CaO–ZrO$_2$–UO$_2$ system

Potential nuclear fuels in the system UO$_2$–ZrO$_2$–CaO have been investigated at high temperatures by Handwerk et al. [14] and a continuous solid solution was found between urania and stabilised zirconia after sintering in hydrogen at 1750°C.

In the present work, the solid solubility of uranium oxide in stabilized zirconia region was determined at Ca/(Ca+Zr) ratio 0.23, varying the concentrations of uranium in the range of 0.1–0.9, and heating at 1400°C in vacuum. Fig. 3 shows the X-ray powder diffraction patterns of the heated products with different concentrations of uranium. From the XRD results, the formation of complete solid solution of fluorite type of

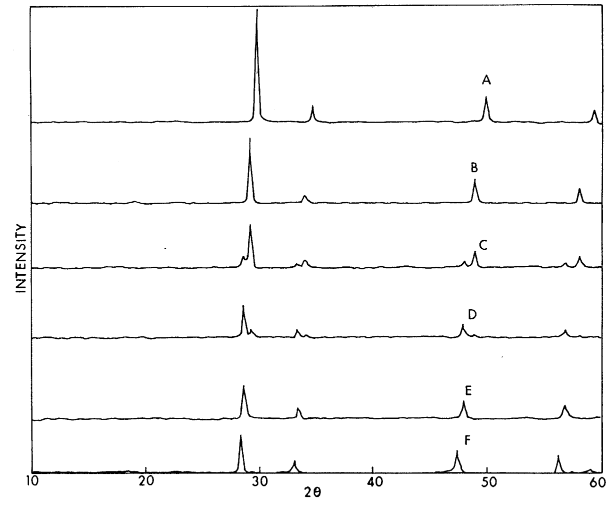

Fig. 1. XRD patterns of $[Ca_{0.23}Zr_{0.77}]_{1-y}Ce_yO_{2-x}$. A: $y=0.05$, B: $y=0.35$, C: $y=0.45$, D: $y=0.65$, E: $y=0.75$, F: $y=0.95$.

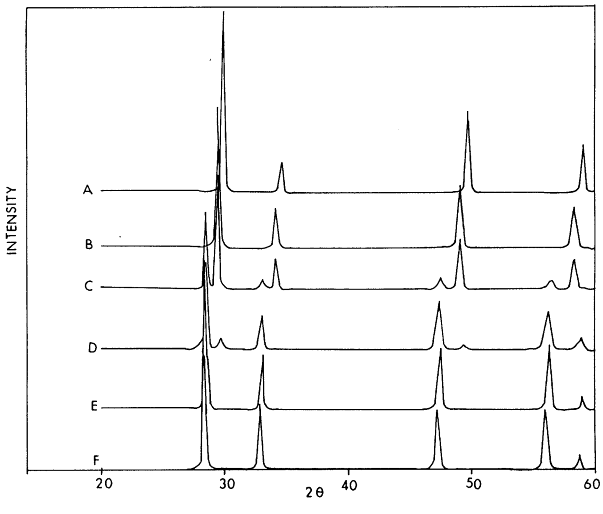

Fig. 3. XRD patterns of $[Ca_{0.23}Zr_{0.77}]_{1-y}U_yO_{2-x}$. A: $y=0.1$, B: $y=0.3$, C: $y=0.35$, D: $y=0.7$, E: $y=0.8$, F: $y=0.9$.

composition $(Ca_{0.23}Zr_{0.77})_{1-y}U_yO_{2-x}$ has been observed in the range of $y=0.1$–0.3 (C_1: zirconium rich). On further increase in the concentration of uranium (y), in the range $y=0.35$–0.7, the products were found to be mixtures of two fluorite phases, C_1 and C_2. In the range $y=0.8$–0.9 the products were found to be single phase fluorite type (C_2: uranium rich). The results observed in this system were found to be similar as compared with the CaO–ZrO_2–CeO_2 system. The only difference is that the region of C_2 solid solution is found to be very small compared to its extent in the Ca–Zr–Ce–O system. The results on heating in air at 1200°C showed that up to 10 mol% of uranium can go in solid solution in calcia-stabilized zirconia.

Fig. 4 shows the graph of lattice parameter versus concentration of uranium. The lattice parameter 'a' in (Å) varied linearly with increase in uranium concentration in the range $y=0$–0.3. The lattice parameter data could be fitted to the equation:

$$a(\text{Å}) = 5.153 + 0.33y \quad (2)$$

3.3. Oxidation studies

Thermogravimetric (TG) studies were carried out on the solid solution samples of uranium in calcia-stabilized zirconia of composition $(Ca_{0.23}Zr_{0.77})_{1-y}U_yO_{2-x}$, where $y=0$–0.3 in air up to 1200°C. Weight change data and XRD were utilized to determine the structural stability and stoichiometry of the oxidised compositions. The O/M (M = Ca + Zr + U) and the O/U ratios were calculated from weight gain assuming the O/U of the starting uranium oxide as 2.00. Fig. 5 shows the variation of O/U ratio with respect to temperature up to 900°C for 10, 20 and 30 mol% UO_2 in solid solution in stabilized zirconia as well as that of sintered UO_2 for comparison. From the figure, the solid solution has an oxidation step from 200 to 400°C but there is no further change up to 900°C: the O/U of the product at 900°C was around 2.3. In contrast, UO_2 (sintered) had oxidised to an O/U of 2.66 at 900°C. Table 1 gives oxidation data obtained from thermogravimetric experiments.

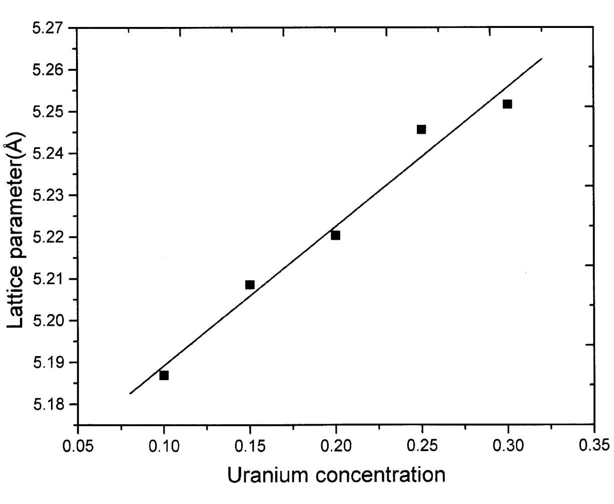

Fig. 4. Plot of lattice parameter versus U concentration in $[Ca_{0.23}Zr_{0.77}]_{1-y}U_yO_{2-x}$ ($y=0$–0.3).

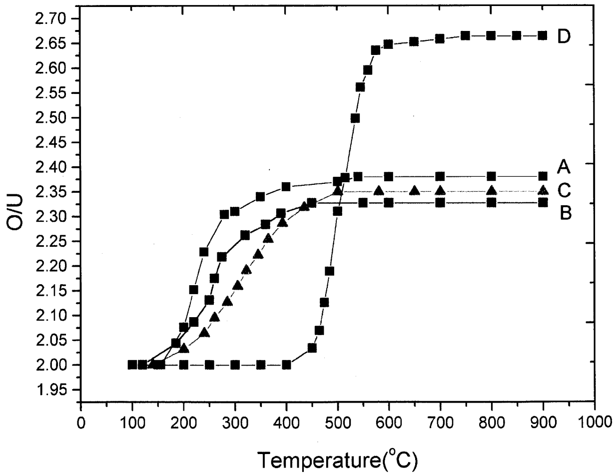

Fig. 5. Plots of O/U versus temperature of $[Ca_{0.23}Zr_{0.77}]_{1-y}U_yO_{2-x}$ in air. A: $y=0.1$, B: $y=0.2$, C: $y=0.3$, D: $y=1.0$.

X-ray powder diffraction results of the oxidised samples at 900°C showed that there was no change in XRD patterns, except for a very small shift in reflection positions towards higher angle, indicating contraction of the lattice. Above 900°C, further weight gain was observed in the solid solutions and the XRD patterns of the oxidised samples at 1200°C with 20–30 mol% uranium consisted of a mixture of calcium uranates and zirconium oxide, indicating breakdown of the fluorite lattice. The solid solution of 10 mol% of uranium in calcia stabilized zirconia, even after oxidation at 1200°C, did not show any change in XRD pattern and thus it retained the fluorite structure; formation of solid solutions of 10 mole% of uranium in calcia stabilized zirconia has been observed in air. The oxidation products of the solid solution of uranium in stabilized zirconia in the range 10–30 mol% of uranium at temperatures of 900 and 1200°C were identified by XRD and the lattice parameter was calculated for the single-phase fluorite. The results are summarised in Table 2. The better ther-

Table 1
Thermogravimetric (TG) results of the solid solution of uranium in stabilized zirconia of composition $(Ca_{0.23}Zr_{0.77})_{1-y}U_yO_{2-x}$, where $y=0$–0.3 in air at 900°C

Concentration of uranium (y)	Initial O/U	O/U after oxidation	Initial O/M	O/M after oxidation
0.1	2.00	2.38	1.793	1.827
0.2	2.00	2.33	1.816	1.877
0.3	2.00	2.35	1.839	1.955
1.0	2.00	2.66	–	–

Table 2
Oxidation products identified by XRD for solid solution of composition $(Ca_{0.23}Zr_{0.77})_{1-y}U_yO_{2-x}$, where $y = 0.1$–0.3

Concentration of uranium (y)	Oxidation temperature (°C)	Phases identified by XRD	Lattice parameter (Å)
0.1	900	Fluorite (C_1)	5.184
	1200	Fluorite (C_1)	
0.2	900	Fluorite (C_1)	5.212
	1200	$CaUO_4 + ZrO_2$	
0.3	900	Fluorite (C_1)	5.238
	1200	$Ca_2U_2O_7 + ZrO_2$	

mal stability of UO_2 in air in stabilised zirconia matrix is clearly established by TG and XRD results.

3.4. CaO–ZrO$_2$–Nd$_2$O$_3$ system

Phase relationships in this system are not known in detail. The fluorite phase in the binary system of ZrO_2–Nd_2O_3 is reported to be completely stabilized in the composition range of 25–36 wt.% Nd_2O_3 [15].

In the present study, the solid solubility of Nd_2O_3 in calcia stabilized cubic zirconia was determined. Single-phase fluorite type solid solutions of composition $(Ca_{0.2}Zr_{0.8})_{1-y}Nd_yO_{2-x}$, were formed with different concentrations of neodymium (y) in the range 0–0.2. It has been observed from the XRD data that only up to 20 mol% of neodymium can go in to the solid solution in calcia stabilised zirconia. The lattice parameters were calculated from the XRD patterns; Fig. 6 shows the linear variation. The lattice parameter data could be fitted in to the equation:

$$a(\mathring{A}) = 5.145 + 0.44y \tag{3}$$

On further increase in concentration of neodymium from $y = 0.3$ to 0.4, another cubic phase of pyrochlore type was found to be obtained along with fluorite phase. This phase is $Nd_2Zr_2O_7$. In the range of $y = 0.5$ and above the phases identified were the mixtures of fluorite, pyrochlore and excess monoclinic Nd_2O_3. Table 3 shows the different phases identified from the XRD in Ca-stabilized zirconia–Nd_2O_3 system in air at 1200°C.

3.5. CaO–ZrO$_2$–PuO$_2$ system

The phase diagram of the Pu–Zr–O system has been reported in literature [16]. However, the Ca–Pu–Zr–O system has not been studied. Samples were prepared by the glycerol method, with appropriate concentrations of plutonium to Ca/(Ca + Zr) ratio equal to 0.15.

Fig. 7 shows a typical thermogram (TG) and DTA. It was observed that weight losses associated with exothermic peaks due to burning of carbonaceous matter were complete below 800°C. The samples were further sintered at 1400°C for 1–3 h. The heated products were characterised by X-ray powder diffraction patterns.

Fig. 8 shows the X-ray powder diffraction patterns; the products were formed as single-phase fluorite type and no reflections due to CaO, ZrO_2 and PuO_2 were observed. The phases were identified as solid solutions of plutonium in calcia stabilized zirconia of compositions $(Ca_{0.15}Zr_{0.85})_{1-y}Pu_yO_{2-x}$ where $y = 0$–0.3. Fig. 9 shows the lattice parameter variation with plutonium concentration (y); it varied linearly with increase in

Table 3
Phases obtained in the Ca–Zr–Nd–O system in air at 1200°C

Neodymium concentration	Ca/(Ca + Zr)	Phases identified
0–0.2	0.2	Fluorite
0.25–0.4	0.2	Fluorite + $Nd_2Zr_2O_7$
0.5 and above	0.2	Fluorite + $Nd_2Zr_2O_7$ + Nd_2O_3

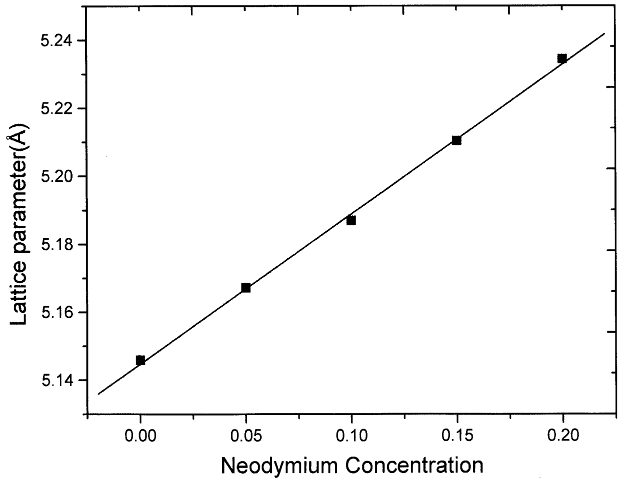

Fig. 6. Plot of lattice parameter with Nd concentration in $[Ca_{0.20}Zr_{0.80}]_{1-y}Nd_yO_{2-x}$ ($y = 0$–0.2).

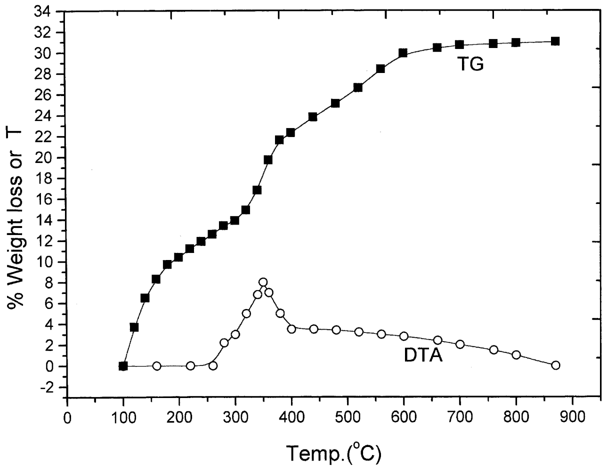

Fig. 7. TG/DTA of glycerol product (final product = $[Ca_{0.15}Zr_{0.85}]_{0.7}Pu_{0.3}O_{2-x}$.

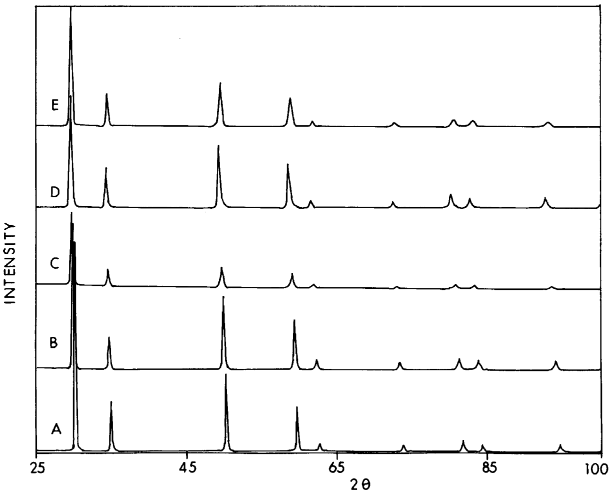

Fig. 8. XRD patterns of $[Ca_{0.15}Zr_{0.85}]_{1-y}Pu_yO_{2-x}$. A: $y=0$, B: $y=0.1$, C: $y=0.2$, D: $y=0.3$, E: $y=0.2$ (reduced sample).

plutonium concentration in the range $y=0$–0.3. The lattice parameter data fit gave the equation:

$$a(\text{Å}) = 5.135 + 0.295y \quad (4)$$

Plutonium in solids exists in both +4 and +3 oxidation states. It has been confirmed that up to 30 mol% PuO_2 (Pu^{4+}) can go in to the solid solution in cubic calcia stabilized zirconia in air at 1400°C. It was thought interesting to determine the solid solubility of Pu^{3+} in the fluorite matrix. A sample with 20 mol% of plutonium in stabilised zirconia was mixed with graphite and heated in a helium atmosphere at 1400°C. From the thermogravimetric (TG) experiments, weight loss was observed above 1000°C due to the reduction of Pu(IV) to Pu(III). The experimental weight loss was in agreement with the calculated loss. The X-ray powder pattern of the reduced product, shown in Fig. 8(E) was found to be a single fluorite phase with a small increase in lattice parameter compared to Pu(IV) solid solution, indicating that Pu(III) can also go in to the solid solution in a fluorite matrix.

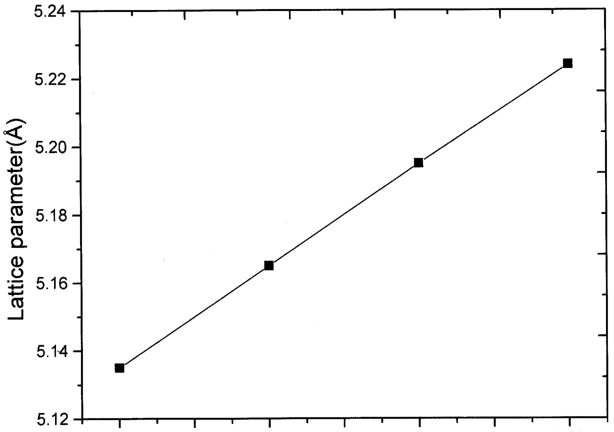

Fig. 9. Plot of lattice parameter with Pu concentration in $[Ca_{0.15}Zr_{0.85}]_{1-y}Pu_yO_{2-x}$ ($y=0$–0.3).

3.6. CaO–ZrO_2–Na_2O system

The Na–U–O system shows a limited range of solid solubility of sodium in a UO_2 fluorite lattice [9]. Cubic calcia stabilized zirconia is considered to be a good host phase for the fixation of actinides and lanthanides. But sodium is a common reprocessing additive, either as NaOH or as Na_2CO_3, and sodium-bearing phases may render a waste form more prone to leaching. The CaO–ZrO_2–Na_2O system has been studied to determine if sodium is soluble in stabilized zirconia. The samples were prepared by taking $CaCO_3$, ZrO_2 and Na_2CO_3 in appropriate ratios, keeping the Ca/(Ca + Zr) ratio constant at 0.15, with varying concentrations of sodium in the range of 0–0.6. The samples were heated in air at 1000°C for about 3–4 h, followed by heating at 1200°C for about 48 h.

The X-ray powder diffraction patterns of the heated products at 1000°C were found to be mixtures of Na_2ZrO_3 and stabilized zirconia. This showed that initially the reaction of Na_2CO_3 and ZrO_2 led to the formation of Na_2ZrO_3 which further reacted with $CaCO_3$ and excess ZrO_2 at higher temperatures. Thus the problems of melting of Na_2O or Na_2CO_3 were avoided. At 1200°C, they showed the formation of a single FCC phase up to 40 at.% of sodium without any shift in X-ray line positions: Fig. 10 shows the sample containing 20 at.% sodium. On further increase in sodium concentration, above 40 at.%, Na_2ZrO_3 crys-

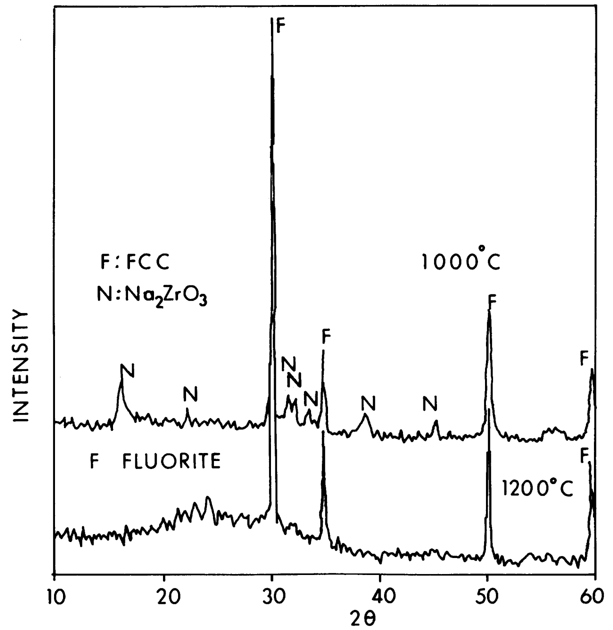

Fig. 10. XRD patterns of $[Ca_{0.15}Zr_{0.85}]_{0.8}Na_{0.2}O_{2-x}$ at 1000 and 1200°C.

Table 4
Phase identified in air at different temperature in the Ca–Zr–Na–O system

Starting mixture	Ca/(Ca + Zr)	Na/(Na + Ca + Zr)	Temperature (°C)	Phases identified
$CaCO_3 + ZrO_2 + Na_2CO_3$	0.15	0.1–0.4	1000	Na_2ZrO_3 + fluorite
		0.1–0.4	1200	Fluorite
		> 0.4	1200	Na_2ZrO_3 + fluorite[a]
$Ca_{0.15}Zr_{0.85}O_{1.85} + Na_2ZrO_3$	0.135	0.1–0.2	1200	Fluorite

[a] Small amount.

tallised together with a fluorite phase. In the Na–Zr–O system, the only compound reported in the literature is Na_2ZrO_3 [17]. Hence Na_2ZrO_3 was prepared by heating Na_2CO_3 and ZrO_2 in 1:1 ratio at 900°C in air, and the purity of the compound confirmed by XRD. The mixture of calcia-stabilized zirconia ($Ca_{0.15}Zr_{0.85}O_{1.85}$) and Na_2ZrO_3 containing up to 20 at.% of sodium was heated in air at 1200°C. The XRD of the heated product showed a single phase fluorite type. However, there was no significant change in lattice parameter. Density measurements showed a decrease in density values with increasing sodium concentration. The heated products were treated with water and the leachate checked for pH and found to be neutral. These observations indicate the possibility of substitution of sodium atoms at calcium sites forming substitution-type solid solutions. Table 4 shows the different phases formed in the Ca–Zr–Na–O system in air at different temperatures.

The samples in the Ca–Zr–Na–O system were analysed for sodium by AAS after dissolution in acid digestion bomb. The results are shown in Table 5. The analytical values for sodium are found to be less than the calculated values. This could be due to the very slow evaporation of sodium at high temperature (1200°C) during the long heating time.

Since evaporation of sodium from the matrix at high temperature was suspected, the sample was prepared containing 20 at.% of sodium in calcia stabilized zirconia at 1200°C in the hot press using a graphite die under a pressure of 20 MPa for about one hour to avoid volatilization of sodium. The X-ray powder diffraction of the hot pressed sample showed a single fluorite type phase without change in X-ray line positions.

SEM/EDX studies were carried out on hot pressed pellet. The results obtained were average relative values of the elements on different locations on the surface of the pellet. The considerably high standard deviation obtained in the analysis of sodium indicates some segregation of sodium on the surface of the pellet.

Table 5
Analytical results of sodium in $(Ca_{0.15}Zr_{0.85})_{1-y}Na_yO_{2-x}$

Concentration of sodium (y)	Obs. wt.% of sodium in the sample	Cal. wt.% of sodium in the sample
0.1	1.07	2.2
0.2	1.79	4.7
0.3	2.38	7.8
0.4	1.34	11.5

3.7. Leaching results of the fluorite matrices

Sintered pellets of solid solution samples containing 20 at.% of cerium, uranium and neodymium in calcia-stabilized zirconia were powdered. The particle sizes of the powdered samples were determined by using standard mesh and were found out to be less than 100 μm. The powdered samples were leached in 0.1 M HCl with continuous stirring for 7 days, as per standard method MCC-3. The ratio of volume of leachant to sample surface area was constant within the series of tests for each sample and was generally maintained at a value between 1 and 2 cm. The leachates were analysed by ICP–AES; results are shown in Table 6. The percentage leached of cerium, neodymium and uranium were found to be very low and comparable to those reported [4,18].

The leaching test was carried out for the sample containing 20 at.% of sodium in calcia stabilized zirconia matrix, which was prepared under the hot press condition. The method used here is as per MCC-1 procedure using QDD water for 2 days. Table 7 shows the results of analysis of various elements, amount leached out, amount originally present in the pellet and percentage leached out. The percentage of sodium leached from the matrix is more compared to cerium, uranium and neodymium. Usually alkali elements are found to be easily leached from the matrix. There was a decrease in leaching values with time of elements other than zirconium,

Table 6
Analysis results of elements leached at room temperature from powdered samples (MCC-3). Leachant: 0.1 M HCl; sample mass: 1 g; volume of leachant:10 ml; leaching period: 7 days

Composition	Ion	ppm	% Leached
$[Ca_{0.15}Zr_{0.85}]_{0.8}Ce_{0.2}O_{2-x}$	Ce	0.85	0.016
	Zr	0.03	10^{-4}
$[Ca_{0.15}Zr_{0.85}]_{0.8}U_{0.2}O_{2-x}$	U	4.8	0.2
	Zr	0.12	10^{-4}
$[Ca_{0.15}Zr_{0.85}]_{0.8}Nd_{0.2}O_{2-x}$	Nd	7.2	0.15
	Zr	15.4	0.15

Table 7
Analysis results of elements leached from hot pressed pellet $(Ca_{0.15}Zr_{0.85})_{0.8}Na_{0.2}O_{2-x}$

Element	ppm	Amount leached out (mg)	Amount originally present (mg)	wt.% Released
Na	31.1	0.789	15.0	5.26
Ca	9.0	0.245	15.7	1.5
Zr	BDL[a]	–	–	–

[a] BDL: below detection limit.

which could be due to lack of complete equilibration during heat treatment and preferential leaching of elements leading to enrichment of surface layers in zirconium oxide.

The solid solution sample, 20% of plutonium in calcia-stabilized zirconia, was leached in quartz distilled water (Q.D.D) for 7 days at room temperature. The pellet was intact. The leachate was assayed by α-liquid scintillation counting: 5 ml of dioxane-based liquid scintillator was taken in scintillation vial, to which 50–100 μl of the leachate (to be assayed for plutonium) was added with proper washings. The percentage of plutonium leached was found out to be 1×10^{-4}. The results were comparable with the leachabilities reported for plutonium in plutonium titanates [18]. XRD of the solid residues after leaching in all cases showed no change in the X-ray patterns in comparison with those of the samples before leaching.

4. Conclusions

Solid solubility and preliminary leach studies have shown stabilised zirconia with fluorite structure as a suitable host phase for fixation of lanthanides and actinides. In stabilised zirconia matrix, thermal stability of UO_2 in air was found to be enhanced and also plutonium was found to be soluble both in +3 and +4 oxidation states, whereas sodium was found to be soluble to a limited extent. Leach studies have shown satisfactory leach rates for uranium, plutonium, neodymium and cerium.

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References

[1] W. Lutze, R.C. Ewing, Summary and evaluation of nuclear waste forms, in: W. Lutze, R.C. Ewing (Eds.), Radioactive Waste Forms for the Future, Elsevier Science, Amsterdam, 1988, p. 699.

[2] A.E. Ringwood, V.M. Oversby, S.E. Kesson, W. Sinclair, N. Ware, W. Hibberson, A. Major, Immobilisation of high level nuclear reactor wastes in SYNROC: a current appraisal, Nuclear and Chemical Waste Management 2 (1981) 287.

[3] G.J. McCarthy, High level waste ceramics: material considerations, process simulation and product characterisation, Nucl. Technol. 32 (1977) 92.

[4] I. Hayakawa, H. Kamizono, Durability of an $La_2Zr_2O_7$ waste form containing various amounts of simulated HLW elements, J. Nucl. Mater. 202 (1993) 163.

[5] W.J. Weber, J.W. Wald, W.J. Gray, Radiation effects in crystalline high level nuclear waste solids, in: J.G. Moore (Ed.), Scientific Basis for Nuclear Waste Management, Vol. 3, Plenum Press, NY, 1981, p. 441.

[6] A.B. Harker, Tailored ceramics, in: W. Lutze, R.C. Ewing (Eds.), Radioactive Waste Forms for the Future, Elsevier Science, Amsterdam, 1988, p. 335.

[7] P.E.D. Morgan, D.R. Clarke, C.M. Jantzen, A.B. Harker, High alumina-tailored nuclear waste ceramics, J. Am. Ceram. Soc. 64 (1981) 249.

[8] J.A. Cooper, D.R. Cousens, R.A. Lewis, S. Myhra, R.L. Segall, R.S.T.C. Smart, P.S. Turner, T.J. White, Microstructural characterization of Synroc C and E by electron microscopy, J. Am. Ceram. Soc. 68 (1985) 64.

[9] S.K. Sali, S. Sampath, V. Venugopal, Existence of fluorite-type solid solutions in alkali metal-uranium-oxygen systems, J. Nucl. Mater. 232 (1996) 23.

[10] C.E. Mcneilly, T.D. Chikalla, Determination of oxygen/metal ratios for uranium, plutonium and (U,Pu) mixed oxides, J. Nucl. Mater. 39 (1971) 77.

[11] K.T. Pillai, R.V. Kamath, V.N. Vaidya, D.D. Sood, Synthesis of yttrium-aluminium garnet by glycerol route, Mater. Chem. Phys. 44 (1996) 225.

[12] D.M. Strachan, B.O. Barnes, R.P. Turcotte, Standard leach tests for nuclear waste materials, in: J.G. Moore (Ed.), Scientific Basis for Nuclear Waste Management, Vol. 3, Plenum Press, New York, 1981, p. 347.

[13] J. Carriat, E. Debray, M. Gouet, M. Guillou, Influence of the lattice parameter on electric conductivity of cubic fluoritic ternary oxide systems, High Temperatures High Pressures 13 (1981) 681.

[14] J.H. Handiwerk, G.D. White, D.C. Hill, Ceramic nuclear fuels in the system UO_2–ZrO_2–CaO, J. Am. Ceram. Soc. 46 (1963) 29.

[15] R. Rouanet, High temperature study of the system zirconium oxide-neodymium sesquioxide, C.R. Acad. Sci. Ser C 270 (1970) 802.

[16] R.E. Skavdahl, T.D. Chikalla, Plutonium refractory compounds, in: O.J. Wick (Ed.), Plutonium Handbook — A Guide to the Technology, The American Chemical Society, Illinois, 1980, p. 249.

[17] S.G. Ampian, X-ray and optical crystallographic data for Na_2ZrO_3, J. Am. Ceram. Soc. 51 (1968) 607.

[18] S.S. Shoup, C.E. Bamberger, T.J. Haverlock, J.R. Peterson, Aqueous leachability of lanthanide and plutonium titanates, J. Nucl. Mater. 240 (1997) 112.