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Letter to the Editors

Preparation and characterisation of Pu-pyrochlore: $[La_{1-x}Pu_x]_2\ Zr_2O_7$ ($x = 0$–1)

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Abstract

Thermal and X-ray powder diffraction studies were carried out on mixtures of PuO_2, ZrO_2 and graphite and La_2O_3, PuO_2, ZrO_2 and graphite. $Pu_2Zr_2O_7$, a new cubic phase with pyrochlore structure ($a = 1.0592$ nm), was identified and characterised. The studies also established the existence of a continuous range of solid solution, $[La_{1-x}Pu_x]_2Zr_2O_7$ with $x = 0$ to 1. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Titania- and zirconia-based ceramics are under active consideration as precursors for the immobilization of high level radioactive waste (HLW) [1]. Establishing the existence of compounds that can incorporate radioactive elements of interest is the first step in proposing their use as host matrices in solid solution forms. The stability and durability of a compound in solid solution with respect to leaching is an equally important consideration. $La_2Zr_2O_7$ has a pyrochlore structure and lanthanide and actinide elements can occupy its La sites because their ionic radii are close to that of La^{3+} [2]. The systems $La_2Zr_2O_7$–$Nd_2Zr_2O_7$ and $La_2Zr_2O_7$–$2CeO_2$–ZrO_2 have been studied in this context [3]. Thermal and X-ray powder diffraction studies on La–Ce–Zr–O systems have shown the formation of a solid solution, $[La_{1-x}Ce_x]_2Zr_2O_7$, with pyrochlore structure [4]. Cerium is only one of the lanthanides, which, in addition to the 3+ state, exists in the 4+ state. This, together with its trivalent and tetravalent radii, makes cerium analogous to plutonium in its chemical and crystallochemical behaviour.

A principal concern with the pyrochlore type structure is the effect of α-recoil damage associated with the presence of actinides, since naturally occurring minerals of the same structure occur in radiation-damaged metamict state due to the constituent uranium and thorium [5]. Pyrochlores which are doped with actinides can be used to simulate the long term radiation effects that are observed in naturally occurring pyrochlores which contain uranium and thorium. Thus, ^{244}Cm-doped $Gd_2Zr_2O_7$ pyrochlore has been found to readily amorphize as a result of self-radiation from α-decay events [6]. Also, recent studies have shown that α-decay-induced amorphization in $Gd_2Zr_2O_7$ can be readily simulated by irradiation with heavy ions such as Kr^+, and it has been observed that pyrochlores in the $Gd_2(Zr_xTi_{1-x})_2O_7$ system become increasingly radiation-resistant with increase in zirconium content [7]. Synthesis of Zr-based pyrochlores thus becomes important.

There are crystal chemical constraints for the synthesis of actinide pyrochlores which have been well brought out by Chakoumakos and Ewing [8]. Thus, despite the synthesis of many pyrochlore compositions, few have included actinide elements. $Pu_2Ti_2O_7$ has been prepared [9] by the solid state reaction

$$2PuO_2 + 0.5TiN + 1.5TiO_2 \rightarrow 0.25N_2 + Pu_2Ti_2O_7. \quad (1)$$

The XRD data of $Pu_2Ti_2O_7$ are comparable to monoclinic $Ce_2Ti_2O_7$. Here, TiN was successfully used to reduce Pu(IV) to Pu(III). $Pu_2Zr_2O_7$ has not been reported in literature. The aim of the present work was to prepare $Pu_2Zr_2O_7$ and study the solid-solution behaviour of $Pu_2Zr_2O_7$ in $La_2Zr_2O_7$.

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2. Experimental

Mixtures of PuO_2, ZrO_2 and graphite and La_2O_3, PuO_2, ZrO_2 and graphite were taken in appropriate ratios and heated in helium atmosphere upto 1400°C in a Mettler thermoanalyser at a rate of heating of 15°C/min. The PuO_2 contained 4% moisture, which was taken into account in calculating the amount of PuO_2 required. Graphite was added to reduce Pu(IV) to Pu(III). XRD data of the products were obtained using Cu-K_α radiation ($\lambda = 0.15418$ nm) with a Diano X-ray diffractometer. Both the diffractometer and the thermoanalyser were enclosed in a glove box to handle radioactive material.

3. Results and discussion

A typical TG and DTA curve of $2PuO_2 + 2ZrO_2 + C$ mixture is given in Fig. 1. The figure shows, after initial moisture loss, a loss in the temperature range 1000–1400°C. The loss above 1000°C can be attributed to the reduction of Pu(IV) to Pu(III) accompanied by evolution of CO. The reaction was slow, extending over a temperature range of 1000–1400°C associated with a broad endothermic peak. The XRD of the product showed the absence of PuO_2 and ZrO_2 lines (with a limit of detection of <5%), and the pattern was similar to that of $La_2Zr_2O_7$ [10] except for some shift in line position to a higher angle. The composition of the compound worked out to be $Pu_2Zr_2O_7$.The high temperature chemical reaction can be given as

$$2PuO_2 + 2ZrO_2 + C \rightarrow Pu_2Zr_2O_7 + CO. \quad (2)$$

Chemical analysis for Pu in $Pu_2Zr_2O_7$ was carried out after dissolution of the sample in an $HNO_3 + H_2SO_4$ mixture by the procedure given by Drummond and Grant [11]. The experimental result was found to be 61.5%, which is in agreement with the calculated value, 61.88%, for Pu.

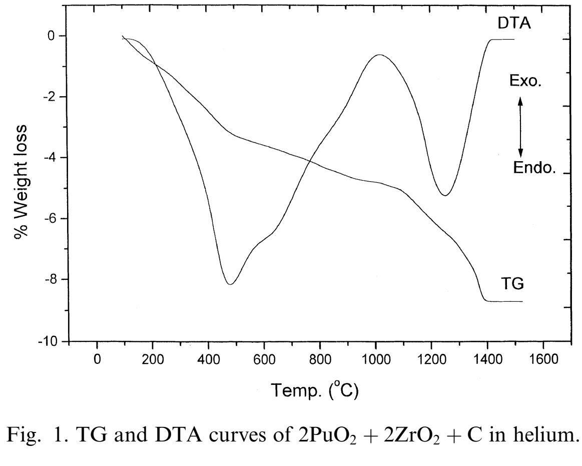

Fig. 1. TG and DTA curves of $2PuO_2 + 2ZrO_2 + C$ in helium.

The XRD of $Pu_2Zr_2O_7$ was indexed, based on the structure of $La_2Zr_2O_7$ [10], on a cubic system with lattice parameter $a = 1.0592(2)$ nm. The refinement of the cell parameter was carried out by least squares method using a computer programme [12]. Table 1 gives the X-ray data of $Pu_2Zr_2O_7$ with the calculated and observed d values, $h\,k\,l$ indices and observed intensities.

Mixtures of La_2O_3, PuO_2, ZrO_2 and graphite in different molar ratios were heated upto 1400°C in a helium atmosphere. Fig. 2 gives the X-ray patterns obtained for the different compositions. The compositions obtained can be represented as $(Pu_xLa_{1-x})_2Zr_2O_7$ with $x = 0$, 0.25, 0.5 and 1. $La_2Zr_2O_7$ was obtained by heating mixtures of La_2O_3 and ZrO_2 in 1:2 molar ratio at 1300°C for 18 h in air, and the X-ray powder pattern obtained is also given in Fig. 2 for comparison. The patterns were similar, with a systematic shift in the line positions with increase in La concentrations, indicating solid solution of $Pu_2Zr_2O_7$ in $La_2Zr_2O_7$. The chemical reaction involved is

$$2xPuO_2 + 2ZrO_2 + xC + 2(1-x)LaO_{1.5} \rightarrow (Pu_xLa_{1-x})_2Zr_2O_7 + xCO. \quad (3)$$

All the patterns could be indexed on a cubic lattice with pyrochlore structure. A plot of lattice parameter with x ($x = 0$, 0.25, 0.5, 1) is shown in Fig. 3, which shows linear variation of lattice parameter.

$Pu_2Zr_2O_7$, on heating in air, was readily oxidized below 600°C. On the basis of weight gain, the composition corresponded to $Pu_2Zr_2O_8$. The XRD patterns were similar to those of $Pu_2Zr_2O_7$ except for the

Table 1
X-ray powder data on $Pu_2Zr_2O_7$ ($a = 1.0592$ nm)

$h\,k\,l$	d obs. (nm)	d cal. (nm)	I/I_0
1 1 1	0.6121	0.6116	15
3 1 1	0.3198	0.3194	10
2 2 2	0.3061	0.3058	100
4 0 0	0.2651	0.2648	34
1 3 3	0.2430	0.2430	9
5 1 1	0.2037	0.2039	5
4 4 0	0.1873	0.1872	43
5 3 1	0.1790	0.1790	4
6 2 2	0.1597	0.1597	35
4 4 4	0.1529	0.1529	8
7 1 1	0.1483	0.1483	3
6 4 2	0.1415	0.1415	1
7 3 1	0.1379	0.1379	3
8 0 0	0.1324	0.1324	5
6 6 2	0.1214	0.1215	10
8 4 0	0.1185	0.1184	7
7 5 3	0.1163	0.1163	3
8 4 4	0.1080	0.1081	9
7 7 1	0.1064	0.1064	2
10 2 2	0.1019	0.1019	9

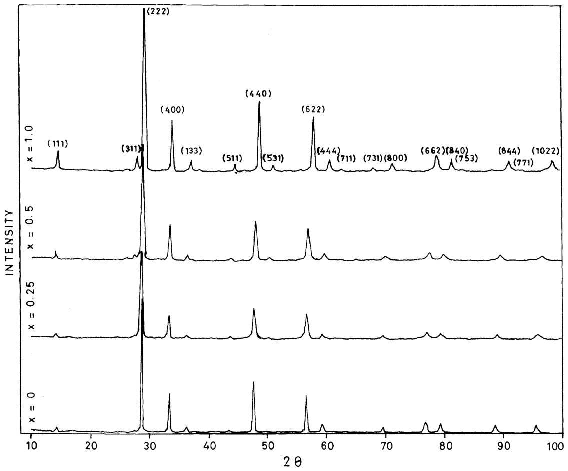

Fig. 2. X-ray powder diffraction patterns of $[La_{1-x}Pu_x]_2Zr_2O_7$ ($x = 0, 0.25, 0.5, 1$).

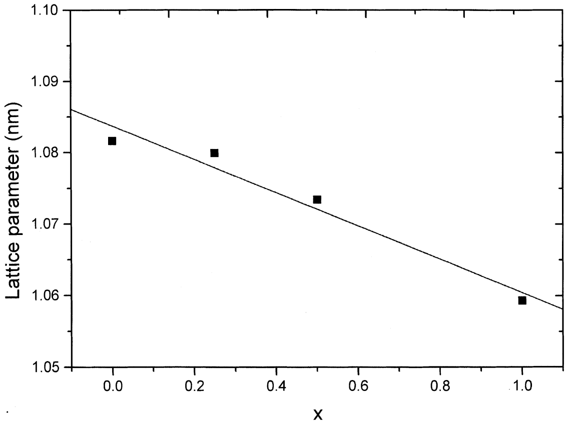

Fig. 3. Plot of lattice parameter vs. x in $[La_{1-x}Pu_x]_2Zr_2O_7$ ($x = 0, 0.25, 0.5, 1$).

contraction of the lattice due to the oxidation of Pu(III) to Pu(IV) ($Pu_2Zr_2O_8$, $a = 1.054$ nm). However, on heating at 1400°C for 1 h, the X-ray pattern changed and a fluorite lattice, $(Pu_{0.5}Zr_{0.5})O_2$, with a lattice parameter $a = 0.5273(2)$ nm was obtained. This is in agreement with the phase diagram of Pu–Zr–O systems reported in literature [13].

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