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Alpha-decay induced amorphization of Cm-doped Gd_2TiZrO_7

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ABSTRACT

The sample of pyrochlore-based ceramic doped with a ^{244}Cm isotope with a target composition $Gd_{1.935}Cm_{0.065}TiZrO_7$ was prepared by cold pressing and sintering. The pyrochlore structure phase was predominant in the sample but minor perovskite and gadolinium zirconate (ideally $Gd_2Zr_2O_{7-x}$) were also present. The Ti/Zr pyrochlore phase was rendered amorphous at a dose of 4.6×10^{18} α-decays/g (0.60 dpa). Volume expansion of the pyrochlore lattice was found to be 2.7 vol.% at a dose of 3.85×10^{18} α-decays/g.

1. Introduction

Pyrochlore is considered as a perspective host phase for excess weapons plutonium and other actinides as well as rare earths occurred in high level waste [1]. A number of U-, Th- [2,3], Cm- and Pu-bearing [4–8] titanate pyrochlore compositions have been synthesized and examined in details. Numerous works were performed on α-decay induced amorphization of the pyrochlores doped with ^{238}Pu and ^{244}Cm [4–8] and studies of the structure of natural analogues containing U, Th and their decay products [3,9–11]. Excellent radiation stability [12] and high chemical durability [13] of zirconate pyrochlore with nominal formula $Gd_2Zr_2O_7$ makes it one of the most promising actinide waste forms. Titanium substitution for zirconium decreases both radiation resistance and chemical durability but they remain quite high for the intermediate composition Gd_2TiZrO_7 [1,12,13]. Most of radiation damage tests were conducted using heavy ion irradiation. In the present work, we studied amorphization of the ^{244}Cm-doped Zr/Ti-pyrochlore with a target composition $Gd_{1.935}Cm_{0.065}TiZrO_7$.

2. Experimental

Oxides of Gd, Ti and Zr taken in stoichiometric ratio were intermixed and mechanically activated in an AGO-2U planetary mill. Curium nitrate solution with curium isotopes concentration of 1.556 mg/mL and isotopic composition (wt%): ^{244}Cm – 75.5 ± 10.13, ^{245}Cm – 15.18 ± 0.12, ^{246}Cm – 8.65 ± 0.09, ^{247}Cm – 0.48 ± 0.03, ^{248}Cm – 0.18 ± 0.02 was added in drops to the oxide mixture. The mixture was air-dried at 100 °C, the powder obtained was denitrated at 500 °C for 1 h and calcined at 800 °C for 2 h. The calcine was ground in a mortar with ethanol, dried, compacted in pellets each of 6 mm in diameter and ~1.5 mm in thickness under 200 MPa followed by sintering at a temperature of 1470 °C for 46 h, re-milling in ethanol, repeated compaction and sintering at 1400 °C for 24 h.

X-ray diffraction (XRD) study was performed using a DRON-3M diffractometer (Cu K_α radiation, scan range is 20–120° 2Θ) and by photo-method using a Debye–Sherrer chamber. In the first case, the ceramic pellet was placed on an aluminum holder and sealed with a thin (~10 μm) Teflon film. In the second case, powdered pellet specimen was placed within thin-walled quartz capillary.

3. Results

XRD pattern of the as-prepared sample contains a set of strong reflections due to Ti–Zr-pyrochlore (Fig. 1). Moreover, weak reflections due to minor phases such as orthorhombic structure perovskite and cubic pyrochlore structure gadolinium zirconate (nominally $Gd_2Zr_2O_{7-x}$), orthorhombic zirconium titanate ($ZrTiO_4$) and unreacted baddeleyite (monoclinic ZrO_2) are present. The results of calculation and indexing of XRD pattern of the as-prepared specimen are given in Table 1.

The reflections due to predominant pyrochlore phase are observed within whole range of 2Θ angles, although distant

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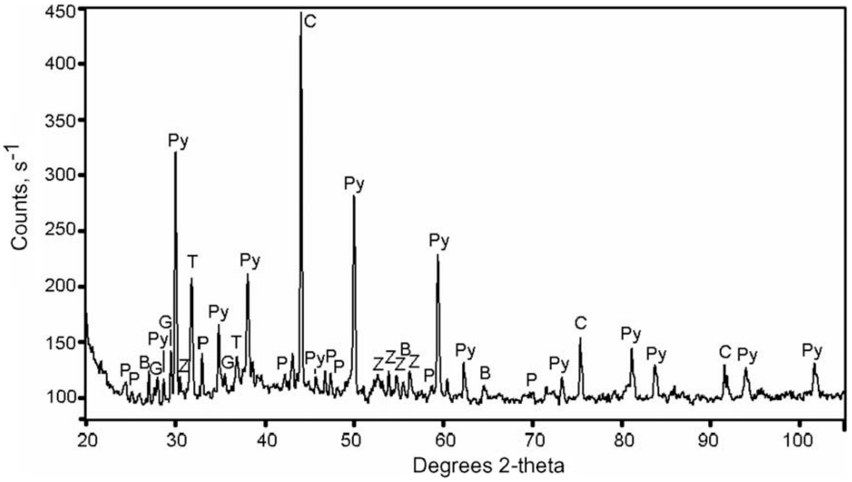

Fig. 1. XRD pattern of the as-prepared pyrochlore-based ceramic. Py – Ti/Zr pyrochlore, G – Gd/Zr pyrochlore ($Gd_2Zr_2O_{7-x}$), P – perovskite structure phase, Z – zirconium titanate ($\sim ZrTiO_4$), B – baddeleyite ($\sim ZrO_2$), C – diamond (used as an internal standard), T – Teflon.

Table 1
Assigning indices to reflections on XRD pattern of the as-prepared pyrochlore ceramic (photo-method).

No	d_{exp}, Å	d_{calc}, Å	*I*, %	hkl
1	5.9803	5.955	4	111
2	3.1144	3.110	4	113
3	2.9757	2.978	100	222
4	2.5765	2.579	15	004
5	2.3677	2.366	8	313
6	1.9778	1.985	4	115
7	1.8231	1.824	80	404
8	1.5554	1.555	70	226
9	1.4877	1.489	9	444
10	1.2884	1.289	8	008
11	1.1807	1.183	13	626
12	1.1527	1.153	9	408
13	1.0521	1.053	18	448
14	0.9919	0.993	15	2.2.10
15	0.8723	0.872	15	6.2.10
16	0.8603	0.860	13	848

reflections are not sharp and α-doublets are poorly-resolved. The pyrochlore crystal lattice parameter in the as-prepared ceramic specimen is $a = 10.328(1)$ Å. This value is nearly average between those for $Gd_2Zr_2O_7$ ($a = 10.50–10.52$ Å) and $Gd_2Ti_2O_7$ ($a = 10.18$ Å) indicating that the Ti/Zr ratio in the phase in our ceramic is close to 1.

Alpha-irradiation due to Cm isotopes decay resulted in gradual reduction in intensity of the pyrochlore reflections and their shift to lower angles on XRD patterns (Fig. 2) due to disordering of the lattice and its expansion (Fig. 3). Gradual changes of the intensity of the [222] reflection due to the target pyrochlore phase with time are given in Table 2. Volume expansion of the pyrochlore lattice increases with a cumulative dose and was found to be 2.7 vol.% at a dose of 3.85×10^{18} α-decays/g. The unit-cell lattice expansion exhibits behaviour typical of pyrochlore [9] and other potential actinide host phases [14].

After 500 days since preparation at a cumulative dose of 2.46×10^{18} α-decays/g the XRD pattern within the range of 20–120° 2Θ contains only 8 of 13 initial reflections due to the pyrochlore phase and the *a* parameter increases from 10.328(1) Å to 10.399(10) Å. At a dose of $3.30 \cdot 10^{18}$ α-decays/g most of reflections due to minor phases disappeared and the XRD pattern contained reflections due to two phases only: target Ti/Zr pyrochlore and traces of Zr-pyrochlore whose reflections were observed even after complete amorphization of the target phase. For the Ti/Zr pyrochlore relative lattice expansion was 0.8% and volume expansion –~2.5%. The Ti/Zr pyrochlore structure phase was rendered to be fully X-ray amorphous after ~970 days since preparation of the ceramic specimen at a cumulative dose of $\sim 4.6 \cdot 10^{18}$ α-decays/g (0.60 dpa). At this dose the intensity of the [222] reflection due to minor Zr-pyrochlore reduced by a factor of ~2. The XRD reflections due to the perovskite structure phase and baddeleyite disappeared at a dose of 2.00×10^{18} α-decays/g (0.26 dpa). This means that both the phases also contained curium.

4. Discussion

In spite of the fact that the Ti/Zr pyrochlore structure phase is predominant in the ceramic, minor phases in amount of ~10 vol.% are present. Since these minor phases are also susceptible to amorphization, they contain curium and, therefore, actual chemical composition of the Ti/Zr pyrochlore phase is some different from the target one. Nevertheless, estimation of the amorphization dose for the Ti/Zr pyrochlore is quite correct. If to compare the amorphization doses for $Gd_2Ti_2O_7$ and Gd_2ZrTiO_7 pyrochlores from point of view of the effect of chemical composition on radiation resistance, then the values at room temperature are $(2.5–3) \times 10^{18}$ α-decays/g (~0.2 dpa) [15,16] and 4.6×10^{18} α-decays/g (~0.6 dpa) for the Ti-pyrochlore and Ti/Zr pyrochlore, respectively. Thus, Zr substitution for Ti increases radiation resistance of the pyrochlore structure phase at both ion bombardment and actinide doping [14]. Moreover advantage of the Zr-bearing pyrochlores over Ti-pyrochlore is the effect of reduction of the critical temperature, T_c, for instance, T_c of the Ti/Zr pyrochlore was found to be 330 K, whereas this value is 600 K for the Ti-pyrochlore [16]. If for the pyrochlore studied in the present work the amorphization dose is ~0.60 dpa, then for the pyrochlore with formula Gd_2TiZrO_7 irradiated with 1 MeV Kr^+ ions the critical dose value at room temperature was found to be some lower (~0.33–0.35 dpa) [17].

Thus, the Zr-bearing pyrochlores are capable to recover their structure, damaged due to self-irradiation, faster than the Ti-bearing varieties. However, actual isolating properties of host phase will be determined by its capability to retention of radionuclides in both crystalline and amorphous states. At loading of

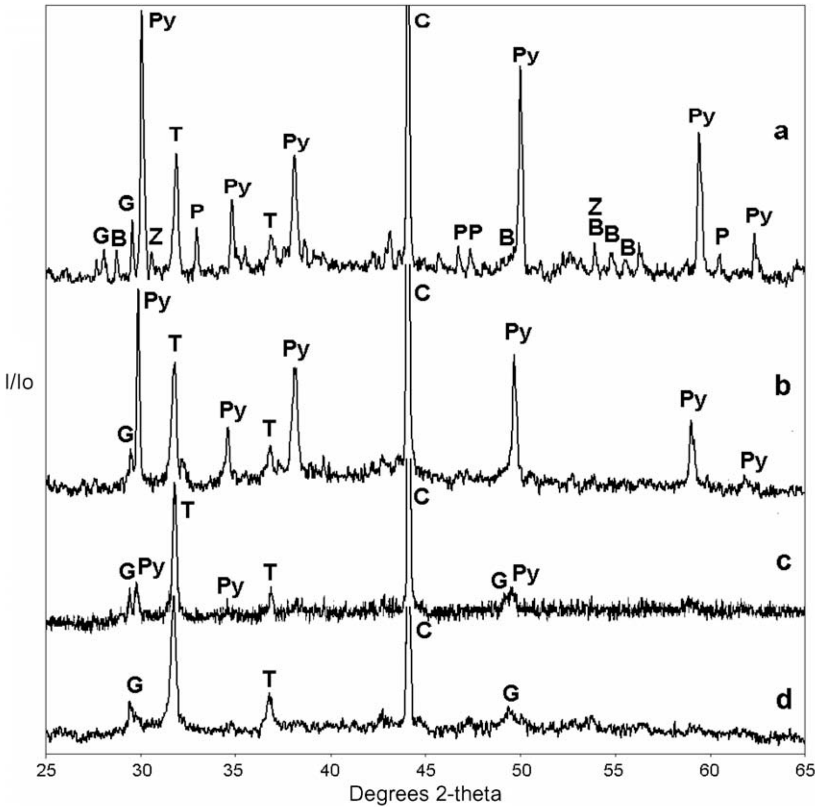

Fig. 2. XRD patterns of the pyrochlore-based ceramic vs cumulative dose, D × 10^{18} α-decays/g (dpa): a – 0.15 (0.02), b – 2.00 (0.26), c – 3.62 (0.47) and d – 4.58 (0.60). Py – Ti/Zr pyrochlore, G – Zr-pyrochlore, P – perovskite structure phase, C – diamond, T – Teflon.

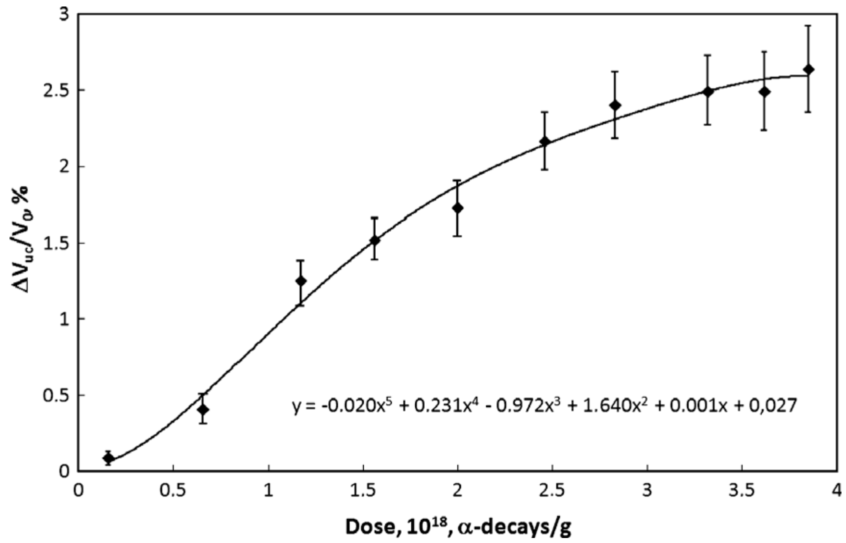

Fig. 3. The effect of cumulative dose on unit-cell volume expansion in the Cm-Doped Ti/Zr pyrochlore.

the matrix with waste with alpha-emitters content equivalent to 10 wt% ^{239}Pu both titanate and titanate-zirconate matrices will be amorphized in 400–1000 years. This time is much shorter than the half-life periods for such isotopes as ^{239}Pu, ^{237}Np, ^{243}Am, ^{93}Zr. Therefore, strong retention of long-lived radionuclides by amorphized matrix is of great importance. The key factor in favour of Ti/Zr pyrochlores may be low critical amorphization temperature (300–350 K) actually achievable in underground repository. Thermal effect may hinder strongly the amorphization process right up till conservation of crystalline state for a long time comparable with life-time of dangerous radionuclides.

Table 2
Change in Intensity of the [222] reflection from the pyrochlore lattice with time.

Time since preparation, days	Dose, α-decays/g, (dpa)	I_{max}, rel.%	$2\theta_{max}$, degrees	a, Å(Δa)	Storage time of the matrix with 10 wt% ^{239}Pu, years
32	1.55×10^{17} (0.02)	100	30.04	10.328(1)	20
129	6.65×10^{17} (0.09)	95	30.00	10.339(3)	100
410	2.0×10^{18} (0.26)	64	29.88	10.384(4)	290
502	2.46×10^{18} (0.32)	55	29.90	10.399(4)	350
580	2.83×10^{18} (0.37)	39	29.86	10.407(5)	400
685	3.32×10^{18} (0.44)	20	29.88	10.410(7)	480
755	3.62×10^{18} (0.48)	17	29.80	10.410(10)	520
804	3.85×10^{18} (0.51)	12	29.76	10.415(12)	550
852	4.05×10^{18} (0.53)	7	Cannot be exactly determined		600
889	4.22×10^{18} (0.55)	4			620
970	4.60×10^{18} (0.60)	~0	Amorphization		690

5. Conclusion

The pyrochlore ceramic specimen with chemical composition recalculated to target formula $Gd_{1.935}Cm_{0.065}TiZrO_7$ was synthesized from mechanically activated precursor and curium nitrate solution by cold pressing and sintering at a temperature of 1470 °C for 46 h, re-milling in ethanol, repeated compaction and sintering at 1400 °C for 24 h. The ceramic was composed of major zirconate/titanate pyrochlore (~90 vol.%) and minor extra phases (~10 vol.%). Volume expansion of the pyrochlore lattice was found to be 2.7 vol.% at a dose of 3.85×10^{18} α-decays/g. Critical amorphization dose of the zirconate/titanate pyrochlore structure phase at room temperature (~300 K) was found to be 4.6×10^{18} α-decays/g (0.60 dpa).

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