

Self-irradiation induced structural changes in the transplutonium pyrochlores $An_2Zr_2O_7$ ($An = Am, Cf$)

Richard E. Sykora^{a,*}, P.E. Raison^b, Richard G. Haire^a

^aChemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6375, USA

^bEuropean Commission, Institute for Energy, Joint Research Center of Petten, Postbus 2, 1755 ZG Petten, The Netherlands

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Abstract

We have pursued the fundamental chemistry of actinide pyrochlore oxides, $An_2Zr_2O_7$ ($An = Am, Cm, Bk, \text{ and } Cf$), using X-ray diffraction as well as optical spectroscopy. One recent facet of our studies has been to observe the structural changes of these materials under self-irradiation as a function of time. It has been reported that both titanate and silicate materials transform from a crystalline to an amorphous state under irradiation. With the Zr-based actinide pyrochlores studied here, we have observed a phase change from a pyrochlore structure to a fluorite-type structure with the retention of crystallinity. We focus here on the impact of α -radiation (^{243}Am and ^{249}Cf), rather than that from neutrons (^{248}Cm) or β -radiation (^{249}Bk), on the $An_2Zr_2O_7$ pyrochlore structures. As a result of this phase change, the local coordination environments of both the actinide and zirconium atoms are altered. We consider a defect/ion deficiency driven mechanism and also address the occurrence of oxidation of the trivalent actinides during the self-irradiation process as being potential mechanisms responsible for the observed phase change.

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Keywords: Zirconium pyrochlore; Actinide; Californium; Americium; X-ray diffraction; Radiation stability; Phase transformation

1. Introduction

In the past several years, there has been a search for materials for different nuclear applications; which include hosts for the long-term storage of nuclear wastes, for fuels, and for the transmutation of long-lived radionuclides. Researchers have examined the materials science properties of a number of silicate [1–3], titanate [4–7], and zirconate systems [8–11]. These inorganic ceramics are candidates for a new generation of “designer” matrices for such applications, but before their potential can be realized fully, a firm understanding of their fundamental chemistry and materials science is essential. Several properties are important when considering these ceramics; included are neutron

capture cross sections, thermal conductivity, radiation resistance, structural and chemical stability, etc.

One requirement of a particular ceramic material for nuclear applications is the ability to retain structural integrity under irradiation. Many ceramics transform from crystalline to amorphous states from irradiation, and one result of structural breakdown is that dopant ions (e.g., actinides, fission products) can leach out from the host into the surrounding environment [5], making these host materials unsuitable for long term storage.

One ceramic, zircon ($ZrSiO_4$), has been widely studied as a host material for the long term storage of weapons grade plutonium. Natural zircon is known to contain quantities of ^{232}Th , ^{235}U , and ^{238}U at levels as high as 7% [12]. For this reason, both natural and synthetic zircon has been used for studying the long-term effects of radiation. The critical amorphization dose for zircon, D_c , has been estimated using X-ray diffraction (XRD) [13], polarized light microscopy [14], HRTEM [15], and

*Corresponding author. Fax: +865-574-4987.

E-mail address: sykorare@ornl.gov (R.E. Sykora).

IR [16], NMR [17], and Raman [3] spectroscopies. Reported D_c values for it range from 6.7×10^{15} to 23×10^{15} α -decay events/mg. A recent study has dealt with the durability in aqueous environments of several self-irradiated zircon samples having varying amorphous contents [2]. That study, which involved hydrothermal treatments of zircon in CaCl_2 solutions, revealed two dramatic decreases in the durability in aqueous environments of zircon samples that corresponded to amorphous domain contents of 0.3 and 0.7.

Pyrochlore-type systems offer alternate ceramics for nuclear applications [18]. The f -element materials of general formula $A_2B_2O_6O'$ acquired their generic name from the mineral pyrochlore, $[\text{Na,Ca}]_2\text{Nb}_2\text{O}_6(\text{O,OH,F})$. Their cubic pyrochlore structures are described as a fluorite-type structure having a doubled unit cell with ordered oxygen vacancies. It can also be described as a three-dimensional framework of corner-shared BO_6 octahedra intertwined with A_2O' chains, where the A cations are eight coordinate. As revealed in earlier studies, these pyrochlores contain either a trivalent lanthanide or actinide in the A site and a tetravalent transition-metal (e.g., Ti, Zr, Hf) in the B site.

The radiation-induced conversion of crystalline $\text{Gd}_2\text{Ti}_2\text{O}_7$ to an amorphous state has been studied by partial doping of the A site with ^{244}Cm [5]. The radiation resistance of titanate pyrochlore, $A_2\text{Ti}_2\text{O}_7$ ($A = \text{Sm}$ to Lu , Y), single crystals has also been studied using 1-MeV Kr^+ ion bombardment [7]. The susceptibility of the latter series of pyrochlores to amorphization by ion beam irradiation is discussed in terms of cation radius ratio, defect formation, and the tendency of the pyrochlore structure to transform to a defect-fluorite structure.

Zirconium pyrochlores, such as the Am and Cf compounds studied here, appear to be more resistant to the effects of radiation than titanates. A Xe^+ ion bombardment study on the system $\text{Gd}_2\text{Ti}_{2-x}\text{Zr}_x\text{O}_7$ revealed that with increasing Zr content, the materials became more resistant to structural transformation, and $\text{Gd}_2\text{Zr}_2\text{O}_7$ remained crystalline even after a dose of ~ 15 dpa [8]. A comprehensive review of pyrochlores for nuclear waste disposal also addresses the radiation effects on them [18]. In a report by workers at the European Institute for Transuranium Elements (Joint Research Centre, Karlsruhe, Germany), the effects from 120 MeV iodine ion bombardment of $\text{Nd}_2\text{Zr}_2\text{O}_7$ were given; it was found that after a dose of 3×10^{14} ions/cm² this ceramic was still crystalline, although a new unidentified phase was detected by XRD [9]. Our work focuses on self-irradiation effects in the transplutonium-zirconate pyrochlores $\text{An}_2\text{Zr}_2\text{O}_7$ ($\text{An} = \text{Am}$, Cm , Bk , Cf), and we report here some results with the ^{243}Am and ^{249}Cf compounds, where both actinides are alpha emitting nuclides. We shall discuss the observed behavior of these actinide pyrochlore oxides in terms

of both radiation damage and the potential that the actinide ions in the materials underwent oxidation due to self-irradiation.

2. Experimental

2.1. Materials and methods

High-purity (99.99%) commercial grade zirconyl nitrate was used in the studies, together with comparable quality CfCl_3 and AmO_2 . The actinide materials were obtained as part of the Basic Energy Sciences production program involving the High-Flux Isotope Reactor at Oak Ridge National Laboratory. The syntheses of the pyrochlores involved mixing chloride or nitrate solutions of the stoichiometric milligram quantities of the components, evaporating the solutions to dryness, and then calcining the resulting solids in alumina boats at elevated temperatures in appropriate atmospheres. Temperatures up to 1500 °C were employed, with heating cycles totaling 10–20 h in most cases. For the californium pyrochlore, an air atmosphere was satisfactory. For americium, a hydrogen (4% in Ar) atmosphere was used to maintain a trivalent Am state. Greater details of the syntheses have been reported previously [19]. For the self-radiation studies, the pyrochlore samples reported here were stored in flame-sealed, quartz capillaries with an air atmosphere.

2.2. X-ray diffraction

Sub-milligram quantities of the pyrochlore products were sealed under air in quartz capillaries for the diffraction studies. XRD patterns were obtained at room temperature from these powder samples using 114.6 mm Debye–Scherrer cameras and $\text{Mo K}\alpha$ radiation. This analysis approach was required given the small sizes of the samples. Lattice parameters were refined by a least squares program [20], and the program PowderCell [21] was employed for calculating theoretical patterns for indexing and comparison purposes. XRD patterns were taken periodically to follow the changes in the pyrochlore samples. The measured and calculated 2-Theta values, as well as the visually estimated intensities, for a $\text{Cf}_2\text{Zr}_2\text{O}_7$ sample after 1 month and 2 years of exposure to self-irradiation are listed in Tables 1 and 2, respectively.

3. Results and discussion

3.1. Aspects of pyrochlore oxides

We report here results of an XRD study of the americium and californium pyrochlore oxides with time

Table 1
Line list and indexing for a one month old $\text{Cf}_2\text{Zr}_2\text{O}_7$ sample

<i>hkl</i>	2θ (Mo $K\alpha$)		Intensity	
	Calc. ^a	Obs.	Calc. ^a	Obs. ^b
111	6.69	6.68	2.1	3
311	12.82	12.83	1.2	1
222	13.39	13.47	10.0	10
400	15.48	15.46	3.7	4
331	16.88	16.89	1.3	2
511, 333	20.15	20.14	<1	1
440	21.96	21.93	5.3	5
531	22.98	23.03	<1	1
622	25.81	25.76	5.3	5
444	26.98	27.03	1.3	2
711, 551	27.82	27.82	<1	1
731, 553	29.97	30.01	<1	1
800	31.25	31.26	<1	1
662	34.13	34.20	2.3	3
840	35.05	35.07	1.8	2
844	38.52	38.52	1.7	2
1022, 666	40.96	41.01	1.3	2
880	44.78	44.72	<1	1
1062	46.95	46.91	1.6	1
1200, 884	47.65	47.63	<1	1
1240	50.41	50.38	<1	1
10102, 1422	57.48	57.41	<1	1
1284	60.51	60.54	<1	1
1462, 10106	62.28	62.29	<1	1

^aBased on the cubic lattice parameter $a=10.556(2)$ Å, $\lambda(\text{Mo } K\alpha)=0.71073$ Å.

^bObserved intensities were estimated by visual inspection of X-ray films.

to ascertain the changes in the structural aspects of the materials due to self-irradiation. Pyrochlore oxides of the general formula, $\text{An}_2\text{Zr}_2\text{O}_7$ (where *An* is a trivalent actinide), have been synthesized and characterized for Pu, Am, Cm, Bk, and Cf [11,19,22,23]. Characterization of these materials was mainly by XRD and solid state spectroscopy (Raman, fluorescence, and absorption).

Care must be taken in the small scale syntheses of these americium and californium pyrochlores to maintain the ~1:1 An to Zr ratio and obtain the pure pyrochlores. If the actinide content is low, one obtains the actinide in a zirconia matrix, where the actinide stabilizes the cubic structure of the zirconia. If the actinide content is high, then either a solid solution of dioxides or a diphasic system can be encountered. These aspects of the structures of the *f*-element-zirconium pyrochlores have been published [19,23].

These pyrochlore oxides exhibit cubic symmetry, having a comparable structure to that of the mineral, *pyrochlore*. Table 1 lists the powder diffraction results for the pyrochlore, $\text{Cf}_2\text{Zr}_2\text{O}_7$, that was indexed in the *Fd3m* space group, and is representative of the americium compound and other transneptunium pyrochlores that contain a trivalent actinide.

Table 2
Line list and indexing for a two year old $\text{Cf}_2\text{Zr}_2\text{O}_7$ sample after transformation to $\text{Cf}_{0.5}\text{Zr}_{0.5}\text{O}_{2-x}$ due to self-irradiation

<i>hkl</i>	2θ (Mo $K\alpha$)		Intensity	
	Calc. ^a	Obs.	Calc. ^a	Obs. ^b
111	13.43	13.41	10.0	10
200	15.52	15.50	3.3	4
220	22.02	21.99	5.8	5
311	25.88	25.86	5.3	4
222	27.05	27.00	1.1	1
400	31.33	31.38	<1	1
331	34.23	34.24	2.3	2
420	35.14	35.22	1.6	2
422	38.63	38.63	2.0	1
511, 333	41.07	41.10	1.3	1
440	44.90	44.94	<1	1
531	47.08	47.03	1.6	1
600, 442	47.79	47.79	<1	1
620	50.55	50.51	<1	1
533	52.55	52.52	<1	1
622	53.20	53.12	<1	1
711, 551	57.65	57.74	<1	1
642	60.69	60.64	<1	1
731, 553	62.47	62.46	<1	1

^aBased on the cubic lattice parameter $a=5.264(1)$ Å, $\lambda(\text{Mo } K\alpha)=0.71073$ Å.

^bObserved intensities were estimated by visual inspection of X-ray films.

The An^{3+} cations in the pyrochlore, which are larger than the zirconium cations, are eightfold coordinated, with six oxygen atoms at the $48f$ and two at the $8b$ crystallographic positions. The Zr^{4+} cations are coordinated with six oxygen atoms located at $48f$ positions, as shown in Fig. 1. There are other criteria that need to be met in order for these pyrochlore structures to form, for example the An^{3+} ion's radius must be between 0.130 and 0.105 nm. Using published radii [24,25], this suggests that these pyrochlores form with trivalent actinide ions of actinium through einsteinium (and possibly even fermium, element 100). The californium-zirconium pyrochlore contains the highest *Z* of any pyrochlore that has been reported. Some of the actinides included in this range of radii and that form pyrochlores, may not remain trivalent ions in the solid after heating in air, but can be oxidized and result in the formation of dioxide solid solutions.

The cubic lattice parameters as a function of the A^{3+} radius are plotted in Fig. 2 for several lanthanide and actinide pyrochlores. A linear fit is obtained with these pyrochlores, with perhaps the exception of the berkelium pyrochlore. The latter parameter probably reflects that complete reduction of the Bk to its trivalent state had not been achieved. The relationship between the two variables in Fig. 2 has been fit to a linear function (excluding the Bk point), which allows one to calculate

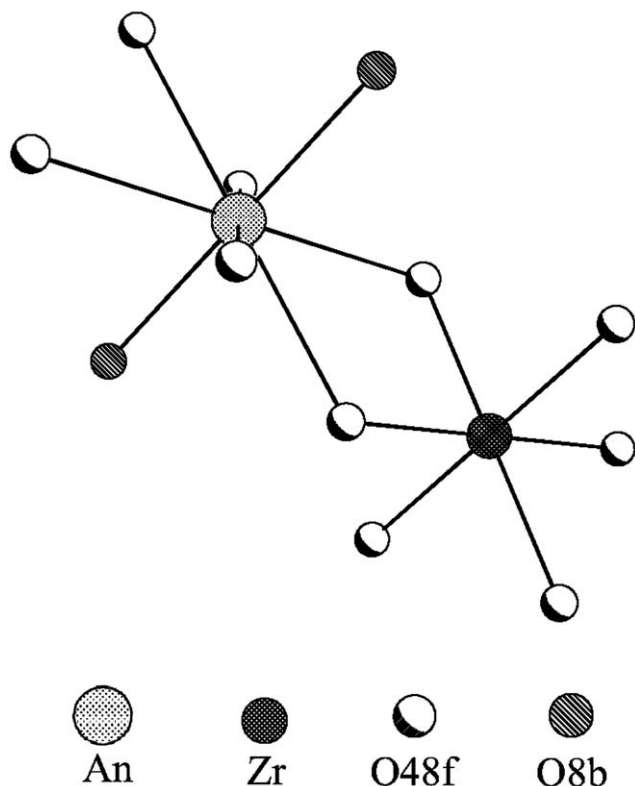


Fig. 1. The An^{3+} cations in the pyrochlore, which are larger than the zirconium cations, are eightfold coordinated, with six oxygen atoms at the 48f and two at the 8b crystallographic positions. The Zr^{4+} cations are coordinated with six oxygen atoms located at 48f positions.

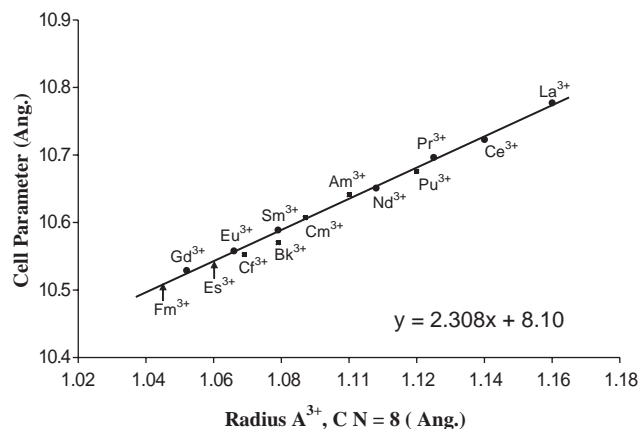


Fig. 2. The cubic lattice parameters as a function of the A^{3+} radius for several lanthanide- and actinide-zirconium pyrochlores. The relationship between the two variables in Fig. 2 can be fit to a linear function.

lattice parameters from a radius (or radii in mixed f -element pyrochlores), estimate the composition that may be allowed to obtain pyrochlore formation, or determine if the f -element in the pyrochlore product may or may not be fully reduced.

3.2. Radiation effects on the pyrochlore structure

Given the general interest in the stability of inorganic matrices for potential nuclear applications, we pursued to ascertain the effects of self-irradiation on the americium and californium pyrochlores over time via XRD. This study examined the effects of alpha radiation taking advantage of the shorter half-life of ^{249}Cf ($t_{1/2} = 351$ y, 5.8–6.2 MeV alpha emissions), while studies on the americium pyrochlore are still in progress. With both actinide products, a slight “swelling” of the lattice parameter was noted during the early part of the studies. The latter was attributed to the accumulation of point defects caused by α -decay events, and perhaps the inclusion of He in the matrices. With the californium compound, the diffraction lines unique to the pyrochlore faded slowly with time, and the material displayed XRD data consistent with a face-centered cubic structure, interpreted to represent a solid solution of dioxides. After 6 months, and a combined dose of 1.17×10^{15} α -decay events/mg, the pyrochlore diffraction lines were no longer visible for the californium product. Heating of this dioxide solid solution regenerated the initial pyrochlore structure.

With actinides that can display both a III and IV oxidation state, a competing process that occurs is the oxidation of the actinides [11]. This oxidation depends upon the pseudo-oxidation potential (III to IV) for the actinide. With some actinides, the pyrochlore must be prepared by reducing the actinide to the trivalent state (i.e., heating in hydrogen). This is the case for the americium-zirconium oxide system, but with the californium-zirconium pyrochlore the trivalent californium pyrochlore can be prepared in air.

The appearance of a fluorite structure after storage of an actinide pyrochlore in air creates a paradox. The question arises whether the change reflects a loss of pyrochlore diffraction lines (dislocation of ions) or whether the trivalent actinide has been oxidized and formed a solid solution of face-centered cubic dioxides. And the lattice parameter will not resolve this question, as the “swelling” of the matrix from radiation brings changes in the lattice parameter. In essence, the lattice parameter observed can reflect damage, oxidation, or a combination of the two effects.

It has been shown for the f -elements that exhibit both a trivalent and a tetravalent oxidation state, that oxidation of the trivalent f -element in a pyrochlore to a tetravalent state can generate a 50 atom% solid solution of dioxides [11]. It has also been determined that for these f -element pyrochlores, an oxidation–reduction cycle can be established [11]. This cycle involves: (1) the pyrochlore oxide; (2) an oxygen rich pyrochlore oxide; (3) an oxygen deficient solid solution (1:1 fluorite structure); and (4) a 1:1 solid solution of the two dioxides. The cycle has been studied with americium and

berkelium pyrochlores but has not been observed to date for the curium and californium pyrochlores of zirconium. Although these latter actinide elements can form pure dioxides, attaining oxidation is difficult and they are not considered candidates for this thermal oxidation–reduction cycle as their dioxides are not thermally stable and their trivalent state is generated from their dioxides at the temperatures used for synthesizing the pyrochlores [25]. As a first approximation then, both curium and californium in their pyrochlores resist oxidation when heated in air. Thus, ascertaining the specific behavior of the pyrochlore matrices over time with lattice parameters alone is difficult. However, there is one important aspect regarding these actinide-zirconia products; the material remains crystalline rather than becoming amorphous, as observed with titanium-based ceramics [4,5,18].

With the californium pyrochlores, we have observed conversion of the pyrochlore structure to a fluorite-type structure over periods of 1 to 2 years. There is a small reduction rather than expansion in the expected lattice parameter (expected parameter of the fluorite phase without oxidation or “swelling” should be $\sim \frac{1}{2}$ of the initial pyrochlore lattice parameter). We have interpreted this structural change to indicate an oxidation phenomena (i.e., Cf^{3+} going to Cf^{4+}), as a result of alpha radiation (i.e., generation of localized atomic oxygen or ozone in the matrix that could oxidize the californium). It is assumed that the initial swelling of the pyrochlore lattice observed was due to radiation effects that reached saturation before formation of the mixed-dioxide solid solution. In the pure CfO_2 system, it has been reported that the lattice swelling due to radiation damage alone was rapid and saturated at about 1.2% after 27 days [26].

Preliminary findings with the americium-zirconium pyrochlore also suggest it undergoes a phase change and eventually forms a solid solution of dioxides due to self-irradiation. Due to the longer half-life and lower decay energy of ^{243}Am ($t_{1/2} = 7370$ y, 4.7–5.4 MeV alpha emissions), the study of the radiation damage in the americium pyrochlore system has not been completed.

Different changes may be observed in these systems depending on the specific processes occurring in them. The lattice parameters of partially oxidized actinide pyrochlore structures are smaller than that of the pure pyrochlore, while the fluorite lattice parameter of the incompletely oxidized dioxide is larger than that of the fully-oxidized solid solution of the dioxides. There are also order–disorder transitions in going from the pyrochlore structures to the fluorite solid solutions (or the reverse), which involves insertion or removal of oxygen atoms from the lattices, and an alteration of interatomic distances in the materials. In addition, the Zr atoms are converted from six coordinate to eight coordinate during the transition from the pyrochlore

structure to a fluorite-type structure. The actinide atoms remain eight coordinate in both structures, although their coordination environments shift from an irregular coordination environment in the pyrochlore structure to a regular square prismatic coordination in the fluorite structure type.

To complement our experimental observations from XRD and aid in interpretation of the results, we have performed an empirical calculation to address the changes. These are discussed in the following section.

3.3. Oxidation states of f-elements in the solid solutions

The amounts of An^{3+} and An^{4+} in the transplutonium-zirconium fluorite-type solid solutions can be estimated using the method devised by Kim [27]. This empirical method was developed to calculate the lattice parameter of solid solutions of fluorite composition between host and dopant cations, and has been successful for other systems [28].

The lattice parameter for solid solutions containing Zr as the host cation can be expressed by Eq. (1):

$$d_{\text{Zr}} = 0.5098 + \sum_k (0.0203\Delta r_k + 0.00022\Delta z_k)m_k, \quad (1)$$

where d_{Zr} is the lattice constant of the fluorite solid solution in nanometers, Δr_k is the difference in the ionic radius ($r_k - r_h$) of the k th dopant (r_k) and the host cation (r_h) in eightfold coordination [24,28], Δz_k is the valency difference ($z_k - z_h$), and m_k is the mole percent of the k th dopant and can be represented by Eq. (2):

$$m_k = \frac{n_k M_k}{100 + \sum_k (n_k - 1)M_k} \times 100, \quad (2)$$

where n_k is the number of cations in the k th solute oxide and M_k is the mole percent of the k th dopant oxide [28]. Similar expressions have been developed for hafnium, cerium, thorium, and uranium as host cations [28].

For the californium-zirconium solid solution that appears after 2 years of self-irradiation of the initial $\text{Cf}_2\text{Zr}_2\text{O}_7$ pyrochlore (Table 2), a Cf(IV):Cf(III) ratio of approximately 6:1 is calculated from the above equations, corresponding to a formula of $(\text{Cf}_{0.43}^{4+}) (\text{Cf}_{0.07}^{3+})\text{Zr}_{0.5}\text{O}_{1.965}$. Lattice expansion due to radiation damage not involving a change in oxidation state (i.e., $\sim 1.2\%$ change) [26] is not factored into this calculation. An additional consideration in these calculations is the choice of radii for the actinide ions since multiple values have been published [24,25,29]. A similar calculation to determine the relative amounts of Am^{3+} and Am^{4+} in the americium pyrochlore samples will be made after additional data are acquired.

4. Conclusion

A previous study revealed that the americium and berkelium pyrochlores undergo a reduction–oxidation cycle, where the f -element cations in the pyrochlore were oxidized to An^{4+} cations by heating in an oxygen-containing atmosphere, or reduced by heating in an appropriate atmosphere [11]. The curium and californium pyrochlores do not undergo such a thermal cycle, presumably because these actinides are not significantly oxidized during heating.

In the present study, the effects of self-irradiation of the americium- and californium-zirconium pyrochlores were followed with time and “swelling” and subsequent formation of fluorite lattices are both observed. Oxidation of the trivalent actinides to a tetravalent state generates a reduction in the lattice parameter of a material, while radiation damage and dislocation of ions often lead to a lattice expansion. The damage associated with the alpha-particle ionization and collisions with the recoiling fragments are believed to be the main influence to the phase change observed in the pyrochlores discussed here. Additional work will evaluate these processes in the americium pyrochlore, the self-irradiation from neutrons and fission fragments ($^{248}\text{Cm}_2\text{Zr}_2\text{O}_7$), and β -radiation effects ($^{249}\text{Bk}_2\text{Zr}_2\text{O}_7$).

The present studies employing XRD have followed the structural transformation of the pyrochlores with time. A substantial change in bonding and coordination was found for both the actinide and zirconium atomic positions. The coordination of the zirconium positions changes from six coordinate in the pyrochlores to eight coordinate for the dioxide solid solutions. For the actinide position, the irregular eight-coordinate environment in the pyrochlore compounds is replaced by a regular square-prismatic environment in the fluorite-type solid solution. The coordination changes result from cation-site disordering in going from the pyrochlore to the fluorite structure. The computational method to estimate the average oxidation state of the actinide cations found in the solid dioxide solutions provided support that the californium had been oxidized as one effect of the self-irradiation.

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