BRIEF COMMUNICATIONS

Calcium Uranium Titanate—A New Pyrochlore

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Calcium uranium dititanate pyrochlore ($A_2B_2O_7$), a component of a high-level nuclear waste ceramic, was characterized by powder X-ray diffraction, analytical electron microscopy and selected area electron diffraction. The cubic unit cell ($a = 10.1579(5)$ Å) has symmetry $Fd\bar{3}m$ with A in 16(c), B in 16(d), O_1 in 48(f), and O_2 in 8(a). A preliminary examination of the peak intensity in X-ray powder patterns and chemical analyses by energy dispersive X-ray spectroscopy suggest that although this pyrochlore can be approximately described by the crystallochemical formula [Ca,U][Ti$_2$]O$_7$ the Ca/U ratio may deviate from unity with some trivalent titanium partitioning onto the A-site. © 1989 Academic Press, Inc.

Introduction

One of the principal phases of a titanate ceramic, designed for immobilization of high-level radioactive waste derived from

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amine reprocessing of heavy water reactor fuel, has a pyrochlore-type structure (1, 2). To a first approximation, its stoichiometry conforms to $A_2B_2O_7$, where $A = $ Ca, and U and $B = $ Ti. The coordination spheres of the cations are AO_8 and BO_6. Using the first setting for $Fd\bar{3}m$ with the origin at 16(c), $\bar{4}3m$, the O_2 48(f) x-coordinate is the only positional variable. It was found that a calculated X-ray pattern based upon the ideal formulation [CaU][Ti$_2$]O$_7$ gave a poor match to the intensities of some reflections.
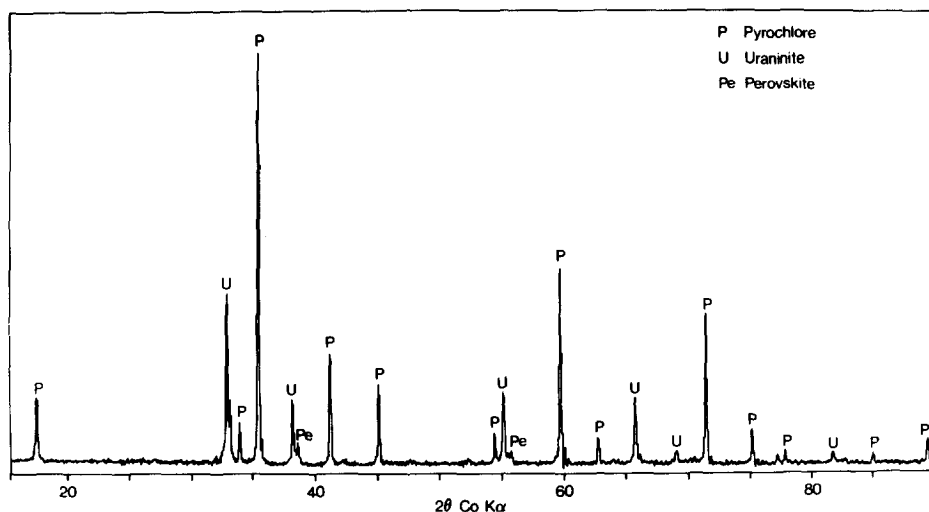
FIG. 1. X-ray diffraction pattern of a nuclear waste ceramic containing perovskite, uraninite, and calcium uranium dititanate pyrochlore.

Therefore, a brief study was undertaken to examine the dependence of diffraction intensities upon nonintegral partitioning over the cation sites. This pyrochlore is also of interest since it adds to the limited number of substituted 3:4 titanate pyrochlores.

Experimental Methods

Pyrochlore as a component of the waste form was studied by powder X-ray diffraction (XRD) and analytical electron microscopy (AEM); the predominant coexisting phases were perovskite and uraninite (Fig. 1). Earlier studies had shown that there was no overlap of pyrochlore reflections with those of other phases (3). The ceramic was crushed finely with an internal Si standard prior to XRD examination. Diffraction patterns were recorded by scanning from 15–95° 2θ with a stepwidth of 0.02° 2θ using Co radiation ($\lambda = 1.79026$ Å). Under these conditions the number of counts at the centroid of the strongest (222) pyrochlore reflection was approximately 8000. Data collection was repeated several times to establish the

reproducibility of the results. Additional data, collected from the polished surface of the ceramic, gave identical results to those obtained from crushed samples, suggesting that preferred orientation was not affecting the relative intensities. The data were subjected to three-interval smoothing followed by stripping of $K\alpha_2$ reflections (4). Pyrochlore unit cells were refined using an iterative least-squares program (5) to yield a cell edge of 10.1579(5) Å. Reflections with 2θ less than that of the Si(111) peak were excluded from the refinement. Selected area electron diffraction (SAD) patterns were consistent with the cubic unit cell derived from XRD and failed to reveal any superlattice reflections indicative of long-range ordering of the calcium and uranium atoms or oxygen vacancies.

Standardless energy dispersive X-ray spectra (EDS) were collected from thin (<100 Å) sections in which corrections for absorption and fluorescence effects were unnecessary. Assuming an integral oxygen stoichiometry of 7, manipulation of cation ratios yielded structural formulae close to $[Ca_{0.92}U^{4+}_{1.08}][Ti^{4+}_{1.93}Ti^{3+}_{0.16}]_{\Sigma1.99}O_7$. The limita-
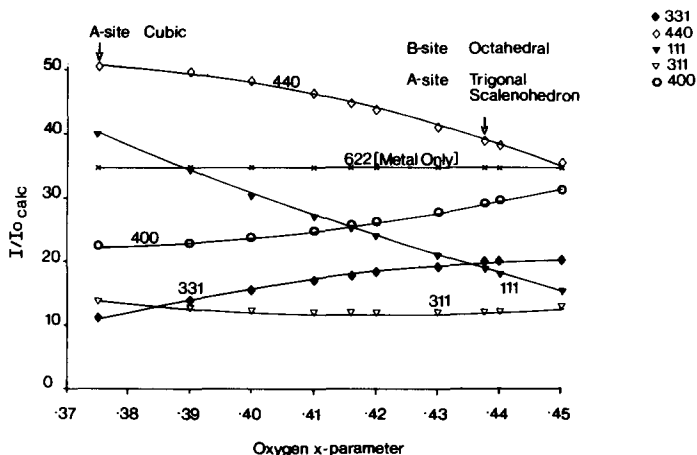
FIG. 2. Intensity variation of major reflections in pyrochlore XRD pattern simulations as a function of oxygen 48(f) x-parameter.

tions of the EDS quantitation technique are given elsewhere (6).

Discussion

An estimate of a suitable oxygen 48(f) x-parameter was derived from the polynomial expression of Chakoumakos (7) which relates the oxygen parameter to the A–O and B–O bond lengths as

$$x = -0.751846 + 3.63005R - 5.03230R^2$$
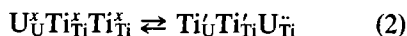$$+ 3.57083R^2 - 1.09316R^4 + 0.051435R^6,$$

where $R = (A - O)/(B - O)$.

Using the ionic radii of Shannon (8), the average (Ca,U)–O bond length was 2.44 Å and the Ti–O bond length was 1.985 Å, leading to an oxygen parameter (x) of 0.420. An X-ray diffraction pattern simulated using this x-value and the stoichiometry [CaU][Ti$_2$]O$_7$ produced satisfactory intensity matches for all reflections except the (111) and (311).

Figure 2 illustrates fluctuations in intensity for the dominant reflections of [CaU][Ti$_2$]O$_7$ as a function of x. The intensity of reflections arising from metal-only planes, e.g., (622), is invariant with x. Oxygen-only

reflections, viz., (220), (620), and (642), had calculated intensities less than 0.1% of the strongest line, and were below detectability. With respect to the anomalous intensities, only the (111) reflection was sensitive to the x-parameter while (311) was not. Therefore, an alternate explanation for the behavior of these reflections was sought.

As EDS had shown the stoichiometric ratio of Ca to U may deviate from unity, the effect of altering the partitioning of various ions over the A and B sites was investigated. Because the sample was prepared under reducing conditions, several altervalent substitutions are possible. Using Kröger notation (9) these replacements are represented as follows:[1]

$$Ca_{Ca}^x Ti_{Ti}^x Ti_{Ti}^x \rightleftarrows U_{Ca}^{\cdot\cdot} Ti_{Ti}^{\prime} Ti_{Ti}^{\prime} \qquad (1)$$

$$U_U^x Ti_{Ti}^x Ti_{Ti}^x \rightleftarrows Ti_U^{\prime} Ti_{Ti}^{\prime} U_{Ti}^{\cdot\cdot} \qquad (2)$$

$$Ca_{Ca}^x U_U^x Ti_{Ti}^x \rightleftarrows U_{Ca}^{\cdot\cdot} Ti_U^{\prime} Ti_{Ti}^{\prime} . \qquad (3)$$

The effect of these substitutions was examined by simulating X-ray diffraction pat-

[1] In Kröger symbolism, ^{x}, $^{\cdot}$, and $^{\prime}$ represent effective site changes of zero, $+q$ and $-q$, respectively, while elemental subscripts indicate the prototypical occupant of the site.

TABLE I

Unit Cell Data for Calcium Uranium Dititanate $Fd\bar{3}m$, $a = 10.1579(5)$ Å

d calc(Å)	2θ calc(°)	2θ obs(°)	$h\ k\ l$	I/I_0 obs	Partitioning mechanism (I/I_0 calc)			
					Ideal[a]	(1)[b]	(2)[c]	(3)[d]
5.87	17.56	17.29	1 1 1	15	24	27	11	21
3.5921	28.86		2 2 0		<1	<1	<1	<1
3.0627	33.99	33.96	3 1 1	9	12	14	5	10
2.9323	35.55	35.53	2 2 2	100	100	100	100	100
2.5395	41.28	41.27	4 0 0	26	26	27	25	25
2.3304	45.18	45.17	3 3 1	19	18	19	13	18
2.0739	51.14		4 2 2		<1	<1	<1	<1
1.9549	54.50	54.48	5 1 1	9	8	8	5	7
1.9533	54.50		3 3 3		<1	<1	<1	<1
1.7957	59.80	59.79	4 4 0	47	44	43	44	44
1.7170	62.84	62.83	5 3 1	8	7	7	3	6
1.6933	63.82		4 4 2		<1	<1	<1	<1
1.6064	67.73		6 2 0		<1	<1	<1	<1
1.5494	70.58		5 3 3		1	1	1	1
1.5314	71.48	71.50	6 2 2	36	34	35	34	34
1.4662	75.19	75.22	4 4 4	8	8	8	7	7
1.4224	77.98		5 5 1		<1	<1	<1	<1
1.4224	77.98	77.95	7 1 1	4	2	3	1	2
1.3577	82.49		6 4 2		<1	<1	<1	<1
1.3224	85.12	85.15	5 3 3	2	2	2	1	2
1.3224	85.18		7 3 1		1	1	1	1
1.2697	89.57	89.58	8 0 0	5	6	6	6	6
					$R = 8.0$	9.4	12.2	8.0

[a] $[Ca_{1.0}U_{1.0}][Ti_{2.0}]O_7$.

[b] $[Ca_{0.9}U_{1.1}][Ti_{2.0}]O_7$.

[c] $[Ca_{1.0}U_{0.8}Ti_{0.2}][Ti_{1.9}U_{0.1}]O_7$.

[d] $[Ca_{0.9}U_{0.9}Ti_{0.2}][Ti_{2.0}]O_7$.

terns for a number of compositions that deviated from the ideal formulation [CaU][Ti$_2$]O$_7$ to a degree consistent with the EDS data (Table I). An estimate of the R-factor for each model was derived from the formula

$$R = \frac{\sum_{hkl} \left| I\text{obs}\ (hkl) - I\text{calc}\ (hkl) \right|}{\sum_{hkl} I\text{obs}\ (hkl)} \times 100$$

This analysis shows that when substitution (1), with Ca/U < 1 or substitution (2), with Ca/U > 1 are used, the resultant R-factors are less satisfactory than those obtained from the prototypical formulation. Alternatively, the implementation of mechanism (3) in which Ca/U = 1 but some Ti^{3+} partitions to the A-site, yields an R-factor identical to that derived from [CaU][Ti$_2$]O$_7$. Thus, within the limitations of this data, both the ideal composition [CaU][Ti$_2$]O$_7$ and [Ca$_{0.9}$U$_{0.9}$Ti][Ti$_2$]O$_7$ provide an equally good account of the X-ray data.

A more accurate analysis of the partitioning data could be carried out by refinement of single-crystal data or Rietveld refinement of polyphasic powder data, taking into ac-

TABLE II

COMPARISON OF IONIC RADII AND UNIT CELL DATA FOR $[A^{2+}A^{4+}][Ti_2]O_7$ PYROCHLORES AND ZIRCONOLITES

$A^{2+}A^{4+}$	$\bar{r}A(\text{Å})$	$rA^{2+}-rA^{4+}$	Phase	Unit cell data	Ref.
CaHf	0.98	0.29	Zirconolite	Not determined	10
CaZr	0.98	0.28	Zirconolite	$a = 12.4458(7)$, $b = 7.2734(4)$, $c = 11.3942(9)$ Å, $\beta = 100.533(7)$ (Pseudocubic cell edge = 10.29 Å)	11
CaCe	1.05	0.15	Pyrochlore	$a = 10.211 \pm 2$ Å	10
CaU	1.06	0.12	Pyrochlore	$a = 10.1579(5)$ Å	This work
CdCe	0.94	0.07	Pyrochlore	$a = 10.1365 \pm 1$ Å	10
CdZr	0.87	0.06	Pyrochlore	$a = 10.02 \pm 2$ Å	10

count all positional parameters, isotropic temperature factors, and site occupancies, but this was beyond our immediate objective. Furthermore, reconnaissance syntheses in which starting compositions of [CaU][Ti_2]O_7 were sintered to near liquidus temperatures (1400°C) under various atmospheres (air, N_2, N_2/3% H_2) or hot pressed in graphite dies (1200°C, 20 MPa) failed to produce single-phase materials or significant grain growth. Pyrochlore invariably coexisted with substantial portions of perovskite ($CaTiO_3$) and uraninite (UO_2).

Table II compares the unit cell parameter of calcium uranium dititanate with other mixed valence 3:4 titanate pyrochlores. Although there is no simple correlation between the average size of the A cation and the cell constants, increasing differences in ionic radii of the A cations progressively dilate the unit cell. Substantial dissimilarities ($0.15 < rA^{2+} - rA^{4+} < 0.28$) between the radii of A cations leads to the stabilization of monoclinic zirconolite (11) or its polytypes (12, 13). However, the data set is too restrictive to predict which phase will crystallize preferentially (10).

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