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Synthesis, characterization and structural refinement of polycrystalline uranium substituted zirconolite

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Ceramic precursors of Zirconolite ($CaZrTi_2O_7$) family have a remarkable property of substitution on Zr^{4+} cationic sites. This makes them potential material for nuclear waste management in 'synroc' technology. In order to simulate the mechanism of partial substitution of zirconium by tetravalent actinides, a solid phase of composition $CaZr_{0.95}U_{0.05}Ti_2O_7$ has been synthesized through ceramic route by taking calculated quantities of oxides of Ca, Ti and nitrates of uranium and zirconium respectively. Solid state synthesis has been carried out by repeated pelletizing and sintering the finely powdered oxide mixture in a muffle furnace at 1050°C. The polycrystalline solid phase has been characterized by its typical powder diffraction pattern. Step analysis data has been used for *ab initio* calculation of structural parameters. The SEM and EDAX analysis also confirm that zirconolite acts as a host material for uranium. The powder diffraction data of 3500 points between $2\theta = 10$–80° has been analysed by GSAS (general structure analysis system) software to obtain the best fit of the observed data points. The uranium substituted zirconolite crystallizes in monoclinic symmetry with space group C2/c (#15). The following unit cell parameters have been calculated: $a = 12.4883(15)$, $b = 7.2448(5)$, $c = 11.3973(10)$ and $\beta = 100.615(9)^\circ$. The calculated and observed values of the intensities, lattice parameters and density measurement shows good agreement. The Rietveld analysis and GSAS based calculations for bond distance Ti–O, Ca–O, Zr–O, and O–M–O bond angles have been made. The structure was refined to satisfactory completion.The and Rp and Rwp are found to be 7.48 and 9.74 % respectively.

1. Introduction

The applications of synthetic titanates and zirconates for fixation of nuclear waste in "synroc" technology are well established [1–4]. Leach rate experiments demonstrate that at temperatures above 100°C, titanate waste-forms leach out hazardous cations at much slower rate than glass encapsulated forms. The constituent synthetic titanate minerals namely hollandite ($BaAl_2Ti_6O_{16}$), perovskite ($CaTiO_3$) and zirconolite ($Ca\ Zr_2Ti_2O_7$) are found to be kinetically stable in extreme geohydrothermal conditions (upto 900°C and 5000 bar) for over hundreds of years. They are more stable than borosilicate glasses [5–8]. It has also been reported that the zirconolite phase has a characteristic capability of converting several rare earths and actinides into titanate solid solutions at temperatures between 700–1000°C [9]. In this context it becomes interesting to simulate and understand the structure property relationship of the uranium waste form of title composition. As a part of ongoing work on synthetic titanate minerals the authors have reported the synthesis and characterization of Sr and La substituted perovskites elsewhere[10–12].

2. Experimental

To understand the crystallochemical interaction of actinides with calcium zirconium titanates in nuclear waste forms, a simulation synthesis of uranium substituted zirconolite has been carried out as follows: calculated quantities (molar ratio 1.0:0.95:0.05:2.0) of calcium, zirconium, uranium and titanium have been thoroughly grinded and mixed in glycerol medium using mortar and pestle. AR quality $CaCO_3$, $ZrO(NO_3)_2{\cdot}xH_2O$, $UO_2(NO_3)_2{\cdot}6H_2O$ and titanium oxide powder were used in appropriate quantities as source of Ca, Zr, U and Ti, respectively. The oxide route solid state synthesis of ceramic phase was carried

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TABLE I Crystallographic data for $CaZr_{0.95}U_{0.05}Ti_2O_7$ at room temperature

Structure	Monoclinic
Space group	C2/c (#15)
Lattice parameters	$a = 12.4883(15)$
	$b = 7.2448(5)$
	$c = 11.3973(10)$
	$\alpha = \gamma = 90.0$
	$\beta = 100.615(9)$
Z	8
Rwp	9.74%
Rp	7.48%
wR expected	7.84%
RF^2	12.951%
Volume of unit cell	1013.53(21)
$Density_{cal}$	4.897 gm / cm^3
$Density_{exp}$	4. 85 gm / cm^3
Chi^2	1.559
Slope	1.289

TABLE II Refined atomic coordinate of $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic powder at room temperature

Atom	x	y	z	Occupancy	Uiso (Å^2)
Ca1	0.37562	0.12633	0.49916	1.04105	0.01514
Zr2	0.1195	0.1202	−0.0258	0.95	0.09046
U3	0.1195	0.1202	−0.0258	0.05	0.8
Ti4	0.24854	0.13266	0.74421	1.06504	0.03584
Ti5	0.4415	0.0572	0.251	0.9077	0.4333
Ti6	0.0001	0.112	0.25	0.9061	0.18571
O7	0.318	0.12031	0.28196	1.07826	0.03575
O8	0.48094	0.14222	0.13916	1.23819	0.36183
O9	0.22596	0.08815	0.5784	1.22708	0.00465
O10	0.405	0.154	0.719	1.0	0.38291
O11	0.715	0.105	0.568	1.32811	0.1104
O12	−0.007	0.14	0.419	1.10728	0.01068
O13	0.115	0.055	0.778	0.88144	0.16007

TABLE III EDAX analysis of the $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic powder

Element	Weight (%)
U	4.76
Ca	21.68
Ti	49.53
Zr	24.03

TABLE IV Observed and calculated structure factors of $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic powder. The seven column within each group contain the values h, k, l, d spacing, Fosq, Fcsq, and intensity respectively. The reflections detected from the final cycles in the least—squares refinement

h	k	l	d-space	Fosq	Fcsq	I%
1	1	0	6.21955	1.95E + 04	1.96E + 04	4.4692
1	1	0	6.21955	1.94E + 04	1.97E + 04	2.2115
0	0	2	5.58397	1.75E + 04	1.40E + 04	1.6123
0	0	2	5.58397	2.37E + 04	1.41E + 04	1.0865
1	1	−1	5.66626	1.25E + 04	1.30E + 04	2.3617
1	1	−1	5.66626	1.36E + 04	1.30E + 04	1.2798
1	1	1	5.22768	2.78E + 04	2.78E + 04	4.471
1	1	1	5.22768	2.84E + 04	2.79E + 04	2.2704
1	1	2	3.97252	6.70E + 04	6.98E + 04	6.0675
1	1	2	3.97252	5.97E + 04	6.99E + 04	2.6905
0	2	0	3.6106	6.26E + 04	7.54E + 04	2.3164
0	2	0	3.6106	6.21E + 04	7.56E + 04	1.1431
3	1	0	3.55233	2.23E + 04	2.02E + 04	1.5929
3	1	0	3.55233	2.92E + 04	2.03E + 04	1.039
0	2	1	3.43552	2.01E + 04	4.24E + 04	1.3399
0	2	1	3.43552	4.83E + 04	4.25E + 04	1.5973
1	1	−3	3.33624	9.78E + 04	1.10E + 05	6.1077
1	1	−3	3.33624	1.06E + 05	1.10E + 05	3.2914
3	1	−2	3.24476	1.36E + 05	1.27E + 05	8.0082
3	1	1	3.23709	1.70E + 05	1.60E + 05	9.9211
3	1	−2	3.24476	1.43E + 05	1.27E + 05	4.1765
3	1	1	3.23709	1.61E + 05	1.60E + 05	4.6839
2	2	−1	3.0718	3.09E + 04	4.94E + 04	1.6122
2	2	1	2.92517	2.13E + 06	2.16E + 06	100
4	0	−2	2.92255	1.96E + 06	1.94E + 06	45.8361
2	2	1	2.92517	2.20E + 06	2.16E + 06	51.2378
4	0	−2	2.92255	1.99E + 06	1.95E + 06	23.116
0	0	4	2.79199	2.11E + 06	1.84E + 06	44.5532
0	0	4	2.79199	2.19E + 06	1.84E + 06	23.0591
2	2	−3	2.50604	5.88E + 05	6.57E + 05	19.5236
2	2	−3	2.50604	6.59E + 05	6.59E + 05	10.8789
4	0	2	2.49501	8.08E + 05	7.61E + 05	13.2852
4	0	2	2.49501	9.97E + 05	7.63E + 05	8.1566
1	1	4	2.46163	3.73E + 04	6.63E + 04	1.1902
4	0	−4	2.2851	2.34E + 05	2.12E + 05	3.1396
2	2	3	2.28277	3.13E + 05	2.97E + 05	8.4017
4	0	−4	2.2851	2.13E + 05	2.13E + 05	1.4263
2	2	3	2.28277	2.70E + 05	2.98E + 05	3.6028
5	1	1	2.19441	4.55E + 04	3.67E + 04	1.1136
5	1	1	2.19441	8.50E + 04	3.68E + 04	1.035
3	3	0	2.07318	1.27E + 05	1.03E + 05	1.3519
3	1	−5	2.04615	1.07E + 05	8.50E + 04	2.2134
6	0	−2	2.04264	1.22E + 05	1.54E + 05	1.2569
3	1	4	2.04038	1.30E + 05	1.55E + 05	2.6799
3	1	4	2.04038	1.41E + 05	1.55E + 05	1.4465
1	3	−3	2.02752	8.04E + 04	8.83E + 04	1.6342
1	3	−3	2.02752	1.02E + 05	8.85E + 04	1.0332
5	1	2	2.01894	7.37E + 04	4.96E + 04	1.4825
3	3	1	2.00463	2.56E + 05	1.83E + 05	5.0583
3	3	1	2.00463	2.50E + 05	1.83E + 05	2.4614
0	0	6	1.86132	1.22E + 05	1.22E + 05	1.0121
0	2	5	1.89951	3.17E + 05	1.85E + 05	5.5151
0	0	6	1.86132	5.96E + 04	1.23E + 05	0.2453
0	2	5	1.89951	1.83E + 05	1.85E + 05	1.579
1	1	−6	1.83138	9.41E + 04	1.88E + 05	1.4978
6	0	−4	1.81604	1.75E + 05	1.04E + 05	1.3617
6	0	2	1.81067	1.77E + 05	9.98E + 04	1.3728
0	4	0	1.8053	2.40E + 06	1.99E + 06	18.4701
0	4	0	1.8053	2.13E + 06	2.00E + 06	8.1335
6	2	−1	1.79994	2.05E + 06	1.94E + 06	31.276
6	2	−1	1.79994	2.10E + 06	1.95E + 06	15.9494
5	1	−5	1.77217	8.92E + 04	7.04E + 04	1.3101
3	1	−6	1.77088	1.13E + 05	1.13E + 05	1.6524
4	2	−5	1.74213	9.84E + 04	6.96E + 04	1.3855
4	0	−6	1.74056	2.04E + 06	1.78E + 06	14.3335

(*Continued on next page*)

out by repeated grinding, pelletizing and sintering the glycerol paste at 1050°C. After 72 h of sintering, densification of the material took place and a polycrystalline solid solution was formed. Powder X-ray diffractogram was recorded on a Rigaku multiflex diffractometer at room temperature by step scanning from 10°–80° 2θ, in increments of 0.02° (0.2°/min) and a counting rate of 6 s/step. Scanning electron microscopic imaging and EDAX analysis have been performed to study the morphological characteristics and elemental profile respectively.

3. Result and discussion

The preliminary powder diffractogram of the single phase polycrystalline uranium substituted zirconolite ($CaU_{0.05}Zr_{0.95}TiO_7$) gives prominent reflections

TABLE IV (*Continued*)

h	k	l	d-space	Fosq	Fcsq	I%
2	2	5	1.73795	1.47E+06	1.43E+06	20.5941
4	0	−6	1.74056	1.72E+06	1.78E+06	6.0046
2	2	5	1.73795	1.19E+06	1.44E+06	8.3066
6	2	−3	1.71465	8.99E+04	9.47E+04	1.2175
2	0	6	1.69514	1.14E+06	1.37E+05	3.7414
2	4	−2	1.67905	9.05E+04	5.36E+03	1.1642
0	4	3	1.62437	8.56E+04	8.13E+04	1.0154
7	1	−4	1.58458	1.10E+05	7.25E+04	1.2269
4	4	−2	1.5359	1.02E+06	8.03E+05	10.5614
8	0	0	1.53006	6.57E+05	7.85E+05	3.3587
8	0	0	1.53006	7.80E+05	7.88E+05	1.9816
0	4	4	1.51599	9.00E+05	7.20E+05	8.9997
6	2	−5	1.5149	8.35E+05	7.00E+05	8.3303
0	4	4	1.51599	7.74E+05	7.23E+05	3.8483
6	2	−5	1.5149	7.07E+05	7.02E+05	3.5079
6	2	3	1.51074	6.28E+05	6.53E+05	6.223
6	2	3	1.51074	4.17E+05	6.55E+05	2.0527
2	2	−7	1.47738	7.35E+05	6.06E+05	6.8963
2	2	−7	1.47738	6.54E+05	6.08E+05	3.0492
4	0	6	1.47318	7.12E+05	6.77E+05	3.3189
4	0	6	1.47318	9.56E+05	6.79E+05	2.214
4	4	2	1.46259	6.88E+05	4.55E+05	6.3012
8	0	−4	1.46128	3.63E+05	3.15E+05	1.6593
4	4	2	1.46259	4.37E+05	4.57E+05	1.9901
0	0	8	1.39599	2.81E+05	2.10E+05	1.1481
1	3	−7	1.34464	2.59E+05	6.56E+04	1.9392
2	0	8	1.30924	3.13E+05	8.75E+04	1.1036
4	4	−6	1.25302	7.35E+05	6.10E+05	4.7081
4	4	−6	1.25302	5.44E+05	6.12E+05	1.7334

between $2\theta = 10^\circ$–80° with maxima at 30.56° which corresponds to $d = 2.92517$ Å. The reflections match in intensity and position with the standard pattern of synthetic zirconolite [13]. The powder diffraction data consisting 3500 reflections, has been subjected to processing and analysis on computer software GSAS package (general structure analysis system) which is capable of handling such data simultaneously for completion of structure refinement [14]. Scattering factors for Ca, Zr, Ti and O atoms were obtained from international tables for crystallography, [15]. Rietveld plot of the synthetic phase shows satisfactory fit between the experimental and the theoretical values of intensities at most of the data points (Fig. 1). Zirconolite framework, ideally $CaZrTi_2O_7$, has five cation acceptor sites, Ca in 8 coordination (M8), Zr in 7 coordination (M7) and three Ti sites: (M6) in 6 coordination and a pair of 5 coordinated (M5) sites [16]. The large variation in polyhedral volumes provides a structure capable of accommodating many elements. This is confirmed by the presence of several substituting cations, *viz* REE^{3+}, Th^{4+}, $Fe^{3+}$and Nb^{3+} etc in natural samples of zirconolites as well [17]. In synthetic samples these sites are occupied by cations whose ionic radii vary from 0.051 to 0.112 nm including several rare earth and transition element cations. UO_2 can be incorporated as a solid solution in the crystal structure of zirconolite. The U^{4+} cation (ionic radius 0.98) is largely accommodated on

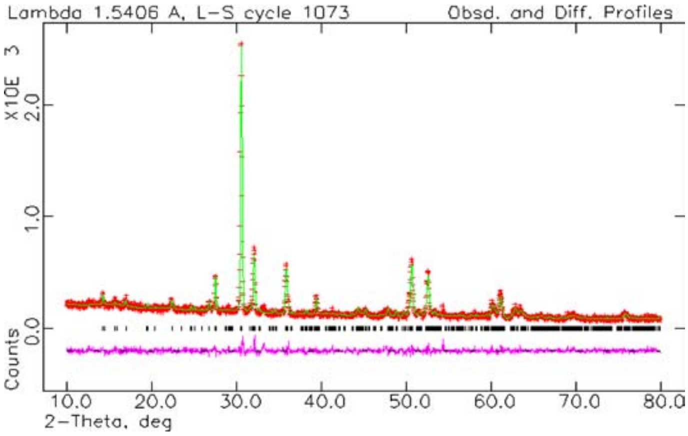

Figure 1 Rietveld refinement pattern of $CaZr_{0.95}U_{0.05}Ti_2O_7$. The '+' are the raw X-ray diffraction data, and the overlapping continuous line is the calculated pattern. Black vertical lines in the profile indicate the position of the allowed reflections for $CuK_{\alpha1}$ and Cu $K_{\alpha2}$. The curve at the bottom is the difference in the observed and calculated intensities in the same scale.

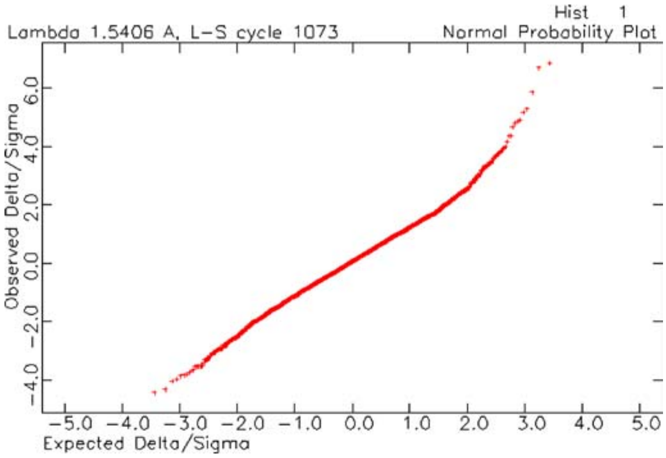

Figure 2 Probability plot between $I_0 - I_C$ for polycrystalline $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic sample.

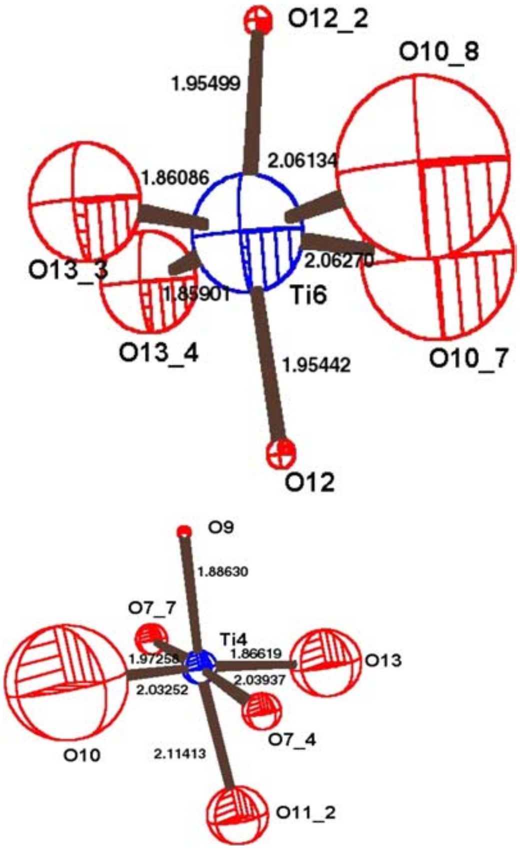

Figure 3 ORTEP view of Ti(6) and Ti(4) coordination in TiO_6 with their respective bond lengths.

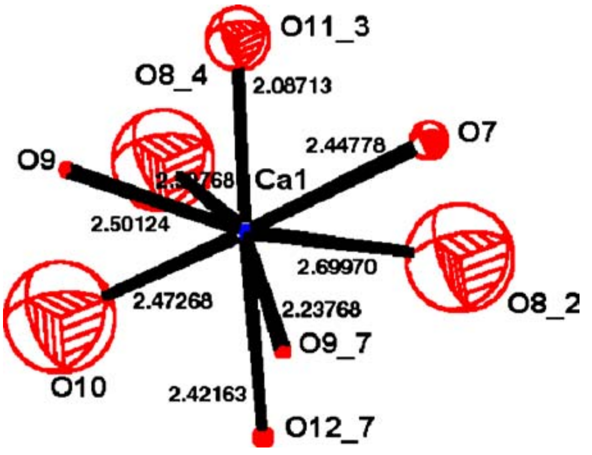

Figure 4 ORTEP view of eight oxygen coordination on Ca(1) site with their respective Ca–O bond lengths.

Zr site [18]. It is this important property of this material, which has led to its potential application in radioactive waste management using "synroc" technology. In the $CaO–ZrO_2–TiO_2$ system, the existence of stable phase with molar ratio 1:1:2 was first established by Coughanour [19] followed by crystallographic work on the single crystal of $CaZrTi_2O_7$ which is reported in monoclinic symmetry having space group C2/c (# 15), $Z = 8$. The reflection statistics generated by GSAS showed that reflection hkl and $h0l$ were absent for $h + k = 2n + 1$ and $l = 2n + 1$ respectively which suggested the possible space group C2/c in the title compound. Other reflection conditions for this space group have been verified by Istats (intensity statistics) data of the GSAS program. Similar observations have been made by Rossel for single crystal of zirconolite [20]. The GSAS based calculations on synthetic phase $CaU_{0.05}Zr_{0.95}TiO_7$ generally support the earlier single crystal diffraction results. The M–O bond lengths and various O–M–O bond angles at each site have been calculated precisely. The structure was determined by method of General Least Squares. The Rietveld refinement converged satisfactorily to $Rp = 0.0748$ and $Rwp = 0.0974$ with reasonable values for refined cell parameters and their calculated standard deviation as evident in the normal probability plot between I_0 and I_C which reflects a satisfactory linear fit (Fig. 2). The bond distances Ti–O, Ca–O, Zr–O, and bond angels O–Ti–O, O–Ca–O, O–Zr–O, have been calculated (Appendix I & II). The M–O distances an O–M–O angles match with the earlier investigations on single crystal of zirconolite [21]. Tables I and II detail the final structural data on this new polycrystalline uranium substituted calcium zirconium titanate. The Ca atoms are coordinated by 8 oxygen atoms at the corners of octahedra while Zr atoms are coordinated by oxygen at seven of the eight vertices of distorted cube and each Ti atom by six oxygen atoms either at the vertices of the octahedra of Ti(4) and Ti(6) or a trigonal prism Ti(5). All these results are in accordance with crystallochemical expectations for zirconolite framework. The interplanar spacing and their observed and calculated structure factors are listed in Table IV. The ORTEP view of TiO_6 octahedra shows that the O(10) and O(13) occupy positions that are coplanar while O(12)–Ti(6)–O(12) angle is 168.00863(13)° in the distorted octahedra. The two O(12) atoms are mirror image, above and below the plane (Fig. 3). Ti(4) atom occupy the central position of the octahedra where it is coordinated by six oxygen atoms: two O(7) and O(9), O(10), O(11), O(13). These six oxygen atoms are located at the corners of an irregular octahedra. Ca is in eight coordination with varying Ca-O bond lengths from minimum 2.08713(13) to maximum 2.69970(18) Å. Ca(1) is coordinated to O(7), O(10), O(11), O(12) and a pair of O(8) and O(9) respectively (Fig. 4). Compositional analysis of the material by EDAX maps the elemental distribution of various elements. The weight % data of the elements have confirmed uranium substitution at zirconium sites (Table III and Fig. 5). The morphological examination of the specimen by scanning electron microscopy shows that the ceramic phase consists of tiny crystals of $\approx 3.5 \times 9.0\ \mu m$ size (Fig. 6). Further crystallographic refinement of uranium and thorium substituted zirconolites of various degree of substitutions at zirconium site is under investigations.

Acknowledgement

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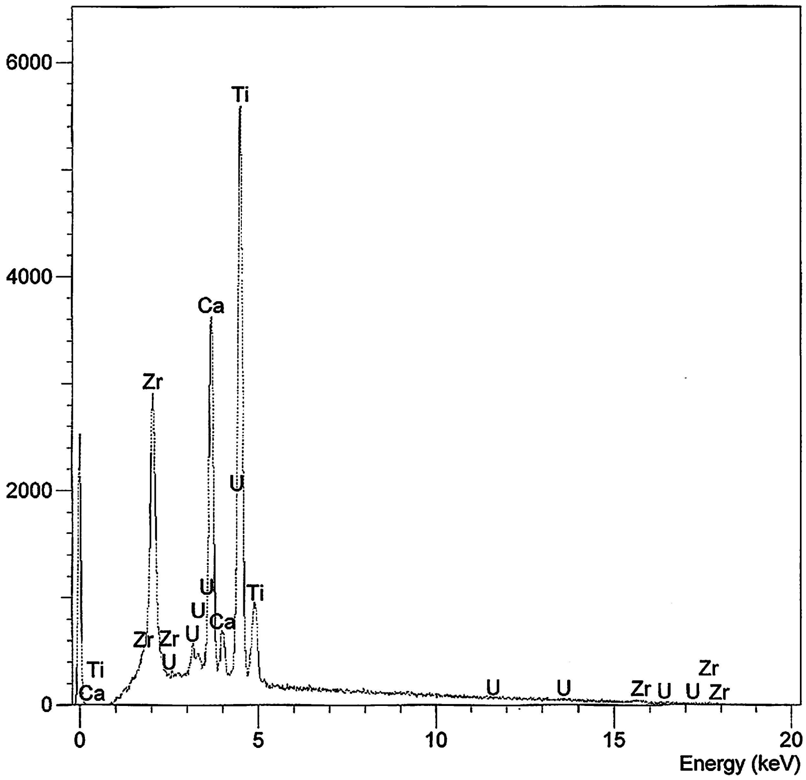

Figure 5 EDAX spectrum of polycrystalline $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic powder.

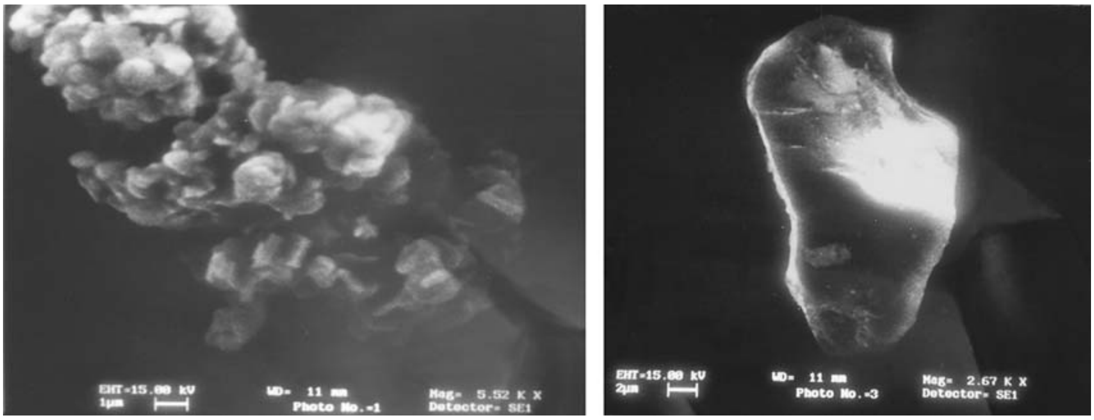

Figure 6 Scanning electron microphotographs of $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic sample.

Appendix- I

Metal-oxygen distances (Å) for $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic powder

Ca1	O7	2.44778(24)	Ti4	O7	2.03937(13)
Ca1	O8	2.59768(26)	Ti6	O10	2.06134(13)
Ca1	O8	2.69970(18)	Ti6	O10	2.06270(13)
Ca1	O9	2.23768(24)	Ti6	O12	1.95499(17)
Ca1	O9	2.50124(16)	Ti6	O12	1.95442(17)
Ca1	O10	2.47268(23)	Ti6	O13	1.86086(14)
Ca1	O11	2.08713(13)	Ti6	O13	1.85901(14)
Ca1	O12	2.42163(18)	Ti4	O7	2.03937(13)
Zr2	O8	2.36816(16)	Ti4	O7	1.97258(12)
Zr2	O9	2.20791(16)	Ti4	O9	1.88630(17)
Zr2	O11	2.20939(25)	Ti4	O10	2.03252(23)
Zr2	O11	2.46153(16)	Ti4	O11	2.11413(20)
Zr2	O12	2.02635(20)			
Zr2	O12	2.46555(16)			
Zr2	O13	2.27604(19)			

Appendix - II

O—M—O Bond angles in $CaZr_{0.95}U_{0.05}Ti_2O_7$ ceramic powder

O7	Ca1	O8	59.611(8)
O7	Ca1	O8	127.255(4)
O7	Ca1	O9	107.111(9)
O7	Ca1	O9	67.780(5)
O7	Ca1	O10	170.8777(12)
O7	Ca1	O11	64.931(5)
O7	Ca1	O12	117.006(6)
O8	Ca1	O8	94.317(6)
O8	Ca1	O9	166.1796(21)
O8	Ca1	O9	96.336(5)
O8	Ca1	O10	128.401(7)
O8	Ca1	O11	101.593(5)
O8	Ca1	O12	73.065(6)
O8	Ca1	O9	91.410(6)
O8	Ca1	O9	164.8061(13)
O8	Ca1	O10	59.623(5)
O8	Ca1	O11	79.065(8)
O8	Ca1	O12	93.117(8)
O9	Ca1	O9	80.674(5)
O9	Ca1	O10	65.172(8)
O9	Ca1	O11	67.172(5)
O9	Ca1	O12	119.206(5)
O9	Ca1	O10	105.190(5)
O9	Ca1	O11	109.210(8)
O9	Ca1	O12	79.718(8)
O10	Ca1	O11	113.951(5)
O10	Ca1	O12	65.761(6)
O11	Ca1	O12	170.3100(4)
O10	Ti6	O12	87.434(5)
O10	Ti6	O13	164.9424(4)
O10	Ti6	O13	96.004(8)
O10	Ti6	O12	87.381(5)
O10	Ti6	O12	82.785(5)
O10	Ti6	O13	95.900(8)
O10	Ti6	O13	165.0511(4)
O12	Ti6	O12	168.0863(13)
O12	Ti6	O13	93.591(7)
O12	Ti6	O13	94.132(7)
O12	Ti6	O13	94.092(7)
O12	Ti6	O13	93.668(7)
O13	Ti6	O13	98.842(8)
O8	Zr2	O9	175.0779(4)
O8	Zr2	O11	109.888(6)
O8	Zr2	O11	79.320(8)
O8	Zr2	O12	85.418(6)
O8	Zr2	O12	99.578(8)
O8	Zr2	O13	72.547(6)
O9	Zr2	O11	65.687(6)
O9	Zr2	O11	97.110(8)
O9	Zr2	O12	98.088(6)
O9	Zr2	O12	84.754(8)
O9	Zr2	O13	106.860(6)
O11	Zr2	O11	74.753(5)
O11	Zr2	O12	156.092(4)
O11	Zr2	O12	119.174(5)
O11	Zr2	O13	68.320(9)
O11	Zr2	O12	90.912(5)
O11	Zr2	O12	164.9319(17)
O11	Zr2	O13	121.122(4)
O12	Zr2	O12	74.029(5)
O12	Zr2	O13	135.275(6)
O12	Zr2	O13	72.057(6)
O7	Ti4	O10	73.473(4)
O7	Ti4	O13	86.397(5)
O7	Ti4	O11	72.380(4)
O7	Ti4	O13	92.698(5)
O7	Ti4	O9	91.294(4)
O7	Ti4	O10	107.385(4)
O7	Ti4	O11	104.195(4)
O9	Ti4	O10	80.887(9)
O9	Ti4	O11	164.2796(18)
O9	Ti4	O13	100.419(8)
O10	Ti4	O11	96.714(9)
O10	Ti4	O13	166.1663(17)
O11	Ti4	O13	78.257(9)
O7	Ti5	O8	119.475(7)
O7	Ti5	O8	100.329(8)
O7	Ti5	O10	94.135(4)
O8	Ti5	O8	104.739(7)
O8	Ti5	O10	107.730(4)
O8	Ti5	O10	131.3629(8)

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