Research Article

Synthesis, Characterization, and Crystal Structure Refinement of Lanthanum and Yttrium Substituted Polycrystalline 2M Type Zirconolite Phases: $\text{Ca}_{1-x}\text{M}_x\text{ZrTi}_2\text{O}_7$ ($\text{M} = \text{Y, La}$ and $x = 0.2$)

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Solid phases of zirconolite-2M with composition $\text{Ca}_{0.8}\text{M}_{0.2}\text{ZrTi}_2\text{O}_7$ ($\text{M} = \text{La, Y}$) have been synthesized through ceramic route and their structures refined to a satisfactory convergence using Rietveld analysis. Zirconolites crystallize in space group C2/c with $Z = 8$. The powder diffraction data of $\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ (CZTY) and $\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$ (CZTLA) have been subjected to General Structural Analysis System software to arrive at a satisfactory structure fit with $R_p = 0.1128$ and $R_{wp} = 0.1805$ for CZTY and $R_p = 0.1178$ and $R_{wp} = 0.1874$ for CZTLA, respectively. The unit cell parameters are $a = 10.1708$ (6) Å, $b = 6.2711$ (4), and $c = 11.2779$ (6) Å for CZTY and $a = 11.2548$ (6) Å, $b = 6.2601$ (4), and $c = 11.2606$ (7) Å for CZTLA. Calculated interatomic distances and bond angles are in good agreement with their standard values. Particle size along prominent reflecting planes calculated by Scherrer's formula ranges between 67 and 107 nm. The polyhedral (CaO_8 , ZrO_7 , and $\text{TiO}_6/\text{TiO}_5$) distortions and valence calculation based on bond strength analysis have been reported. The compositions of the zirconolites were determined using energy dispersive X-ray (EDAX) analysis. Cation site occupancies were determined by applied compositional constraints which were found consistent with the expected zirconolite-2M cation site occupancies.

1. Introduction

Borosilicate glass has long been the first choice of material for the immobilization of high-level radioactive wastes (HLW) due to its good glass-forming ability, chemical durability, radiation stability, and so forth. However, there is a potential risk that the conventional borosilicate glass waste forms partially crystallize either during annealing or during long-term storage in deep geological environment [1, 2]. Another proposed method for the long-term storage of high-level radioactive waste is the encapsulation of the waste in a ceramic matrix, followed by storage in an underground repository. One such ceramic, which has many of the properties thought to be favorable for waste storage, is zirconolite ($\text{CaZrTi}_2\text{O}_7$). Zirconolite is a rare accessory mineral found in a wide range of rock types and geological environments. The chemical composition of natural zirconolite can vary

extensively, with the main substitutions involving lanthanides (Ln), actinides (Act), Nb, and Fe. Zirconolite is one of the three major phases in the synthetic ceramic "Synroc" which is evaluated as a host for high-level radioactive waste [3]. Ceramics made from pyrochlore, titania, and zirconia have been suggested as potential waste forms because they seem to be more stable than nuclear waste forms made from glass [4, 5]. Zirconolite was proposed as a potential nuclear waste form for the incorporation of lanthanides, plutonium, and minor actinides such as Np, Am, and Cm. Solid solutions containing zirconolite appear to be very stable with respect to hydrothermal alteration [6–9]. Zirconolite was identified as anion deficient superstructure derived from eight fluorite subcells with a monoclinic distortion. Zirconolites of the type $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$ are monoclinic with two-layer repeat sequence [10–13]. These are referred to as 2M type zirconolites. In 2M zirconolites two-layer repeat sequence consists of TiO_6

TABLE 1: Crystallographic data for type $\text{Ca}_{1-x}\text{M}_x\text{ZrTi}_2\text{O}_7$ ($M = \text{Y}, \text{La}$ and $x = 0.2$) ceramic phases at room temperature.

Phase	CZTY	CZTLa
Lattice parameters		
a	10.1708 (6)	11.2548 (6)
b	6.2711 (4)	6.2601 (4)
c	11.2779 (6)	11.2606 (7)
$\alpha = \gamma =$	90°	90°
$\beta =$	100.589 (5)°	100.586 (6)°
R-pattern (Rp)	0.1128	0.1178
R-weighted pattern (Rwp)	0.1805	0.1874
Rwp expected (R_e)	0.804	0.0802
R-structure factor (RF^2)	0.32158	0.25482
Volume of unit cell ($\text{\AA}^3$)	1018.25 (7)	1108.66 (7)
Density _{X-ray} (gm/cm^3)	3.90	3.705
Unit cell formula weight	2636.215	2674.158
S (goodness-of-fit)	1.98	2.05
Slope	1.4879	1.4798
Number of parameters refined	39	39

Structure: rhombohedral; space group; C2/c; $Z = 8$.TABLE 2: Refined atomic coordinate of $\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ and $\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$ ceramic powders at room temperature.

Atom	x	y	z	Occupancy	U_{iso} ($\text{\AA}^2$)
$\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$					
Ca	0.38053	0.13313	0.49857	0.80257	0.01789
Y	0.38053	0.13313	0.49857	0.21057	0.01789
Zr	0.12371	0.11665	-0.02253	0.892	0.02874
Ti1	0.2506	0.125	0.7445	0.78474	0.00621
Ti2	0.4655	0.018	0.27	0.50797	0.00648
Ti3	0.0001	0.124	0.25	0.5759	0.00674
O1	0.318	0.12031	0.28196	1.0	0.05487
O2	0.48094	0.17522	0.13916	1.0	0.05487
O3	0.22596	0.08815	0.5784	1.0	0.05315
O4	0.405	0.154	0.719	1.0	0.05485
O5	0.715	0.105	0.568	1.0	0.05379
O6	-0.007	0.14	0.419	1.0	0.05789
O7	0.115	0.055	0.778	1.0	0.05748
$\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$					
Ca	0.37732	0.13897	0.49715	0.8	0.02756
La	0.37732	0.13897	0.49715	0.097	0.02556
Zr	0.12567	0.11477	-0.02248	0.935	0.02537
Ti1	0.2506	0.125	0.7445	0.94854	0.01285
Ti2	0.4655	0.018	0.27	0.42369	0.01487
Ti3	0.0001	0.124	0.25	0.54178	0.01235
O1	0.318	0.12031	0.28196	1.0	0.06679
O2	0.48094	0.17522	0.13916	1.0	0.05678
O3	0.22596	0.08815	0.5784	1.0	0.06658
O4	0.405	0.154	0.719	1.0	0.05617
O5	0.715	0.105	0.568	1.0	0.05618
O6	-0.007	0.14	0.419	1.0	0.05614
O7	0.115	0.055	0.778	1.0	0.05674

FIGURE 1: X-ray diffraction patterns of $\text{Ca}_{1-x}\text{M}_x\text{ZrTi}_2\text{O}_7$ ($\text{M} = \text{Y, La}$ and $x = 0.2$) samples sintered at 1100°C and 1300°C .

FIGURE 2: Plots of the observed X-ray powder pattern from the zirconolite $\text{Ca}_{1-x}\text{M}_x\text{ZrTi}_2\text{O}_7$ ($\text{M} = \text{Y, La}$ and $x = 0.2$) together with the superimposed calculated pattern. A weighted difference plot is included to highlight the differences between observed and calculated patterns.

and TiO_5 polyhedra that form a hexagonal bronze motif (HTB) as $0\ 0\ 1$ plane. The Ca and Zr ions form in sheets between the HTB layers ordered in rows along $(1\ \bar{1}\ 0)$ plane [14–16]. The Ca and Zr sites are of particular importance in radwaste effluent cation substitution because these sites are used to accommodate trivalent rare earth lanthanides. Several polytypes of zirconolite have been observed in natural

and synthetic systems, including 2M, 3T, 3O, 4M, and 6T polytypes [17]. Zirconolite solid solutions with the general formula $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$ (where $x < 1.3$) crystallize in the 2M polytype [18–20]. The other polytypes like 3T, 3O, and 4M do not occur for ideal zirconolite but crystallize with increasing levels of substitution of Ca and Zr by lanthanides and actinides. The site occupancies of zirconolites- $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$

FIGURE 3: Probability plots between I_0 and I_C for polycrystalline (a) $\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ and (b) $\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$ ceramic samples.

FIGURE 4: PLATON projection of the molecular structure depicting the interlinking of CaO_8 , ZrO_7 and $\text{TiO}_6/\text{TiO}_5$ polyhedra in the framework of zirconolite structure.

FIGURE 5: DIAMOND view of stick and ball presentation of CZTY sample.

over different values of x are determined by crystal structure refinement [21]. This present communication is basically aimed at synthesis, solid state reactivity, and crystallographic characterization of substituted zirconolite based ceramic materials, which have been identified as potential matrix for process development in technology of radioactive waste management. Though their applications in this area are well documented, their structure-property relationship is not yet investigated to the desired level; therefore, it is necessary to understand thoroughly the structural complexities of the interactions of the effluent cations vis-à-vis ceramic precursors. Powder diffraction data and GSAS software based calculations of cell parameters, crystal symmetry, isotropic and thermal parameters, interatomic distances, and other structural factors provide a good database for process development. It is in this context that the author has selected substituted zirconolite for crystallochemical investigations. Herein we reported synthesis and Rietveld refinement of lanthanum and yttrium substituted 2M type zirconolites and their structure models evolved from powder diffraction data.

2. Experimental

2.1. Ceramic Route Synthesis of $\text{Ca}_{1-x}\text{M}_x\text{ZrTi}_2\text{O}_7$ ($\text{M} = \text{Y}$, La and $x = 0.2$) Phases. Calculated quantities of AR grade CaCO_3 , ZrO_2 , TiO_2 , Y_2O_3 , and La_2O_3 for the stoichiometry $\text{Ca}_{0.8}\text{M}_{0.2}\text{ZrTi}_2\text{O}_7$ ($\text{M} = \text{Y}$, La) were thoroughly mixed with about 10 mL of 1,2,3-propanetriol to form a semisolid paste. The glycerol paste was gradually heated initially at 600°C for 4 hours in a crucible. The mixture was reground to micron

size, pressed into pellets, and sintered in a platinum crucible at 1300°C for 12 hours. The process was repeated to get a polycrystalline dense material.

2.2. Characterization. The powder X-ray diffraction pattern has been recorded at $2\theta = 10^\circ$ – 90° on a Pan Analytical diffractometer (XPRT-PRO) using $\text{CuK}\alpha$ radiation at step size of $2\theta = 0.017^\circ$ and a fixed counting time of 5 sec/step. Scanning electron microscopy (SEM) has been carried out on an electron microscope system (HITACHI S-3400) equipped with ThermoNoran ultra dry detector facility for energy dispersive X-ray (EDAX) analysis.

3. Results and Discussion

3.1. Rietveld Refinement and Crystallographic Model of the Phases. Yttrium and lanthanum substituted zirconolite ($\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ or CZTY and $\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$ or CZTLA) synthesized at 1100°C give monoclinic zirconolite phase with some traces of unreacted compounds (Figures 1(a) and 1(b)), whereas samples sintered at 1300°C result in the formation of single phase denser solid solutions that give prominent reflections at $2\theta = 10$ – 80° with maxima at 30.46 and 30.44 for CZTY and CZTLA, respectively (Figures 1(c) and 1(d)). The reflections match in intensity and position with the standard pattern of synthetic zirconolite [22]. The powder diffraction data of each phase consisting of 4867 reflections has been subjected to processing and analysis on computer software GSAS package which is capable of handling such data simultaneously for completion of structure refinement.

FIGURE 6: (a) Scanning electron microphotograph of $\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ sample at magnifications of 7.5 k. (c) SEM of $\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ and (b) EDAX spectra of $\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ and (d) EDAX spectra of $\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$ phases.

Atomic coordinates for Ca, Zr, Ti, and O atoms were obtained from international tables for crystallography [23]. Zirconolite framework, ideally $\text{CaZrTi}_2\text{O}_7$, has five cation acceptor sites, Ca in 8 coordination (M8), Zr in 7 coordination (M7), and three Ti sites (M5) in 5 coordination and a pair of 6 coordinated (M6) sites [24]. Y_2O_3 and La_2O_3 can be incorporated as a solid solution in the crystal structure of zirconolite. The Y^{3+} and La^{3+} cations (ionic radius) are largely accommodated on Ca site. It is this important property of this material which has led to its potential application in radioactive waste management using “Synroc” technology. In the $\text{CaO-ZrO}_2\text{-TiO}_2$ system, the existence of stable phase with molar ratio 1 : 1 : 2 was first established by Coughanour et al. [25], followed by crystallographic work on the single crystal of $\text{CaZrTi}_2\text{O}_7$ which is reported in monoclinic symmetry having space group C2/c (#15), $Z = 8$. The reflection statistics generated by GSAS showed that reflections hkl and hOl were absent for $h + k = 2n + 1$ and $l = 2n + 1$, respectively, which suggested the possible space group C2/c in the compounds. The structure was determined by method of general least squares. Rietveld plot of the synthetic phases shows satisfactory fit between the experimental and the theoretical values of intensities at most of the data points (Figure 2). The refinement converged

satisfactorily to $R_p = 0.1128$ and $R_{wp} = 0.1805$ for CZTY and $R_p = 0.1178$ and $R_{wp} = 0.1874$ for CZTLa sample, with reasonable values for refined cell parameters (Table 1) as evident in the normal probability plot between I_0 and I_C which reflects a satisfactory linear fit (Figure 3). Determination of atomic positions in the unit cell of the compounds was carried out by Rietveld analysis. Computation was started with a structure model based on the parent zirconolite structure. Y and La ions were assumed in the structure model to occupy the Ca atomic site with occupancies adopted from analytical data. The relevant atomic parameters, site occupation factors, and isotropic thermal parameters obtained from their refinement are presented in Table 2.

The bond distances Ca–O, Zr–O, and Ti–O (Table 3) and bond angles O–Ca–O, O–Zr–O, and O–Ti–O (Table 4) have been calculated precisely. The M–O distances and O–M–O angles match with the earlier investigations on single crystal of zirconolite [26]. Figure 4 shows the PLATON projection of molecular structure depicting the interlinking of CaO_8 , ZrO_7 , and $\text{TiO}_6/\text{TiO}_5$ polyhedra in the framework of zirconolite structure. 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

TABLE 3: Interatomic distances (Å) for $\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$ and $\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$ ceramic powders.

$\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$					
Ca/Y-O1	2.44859 (15)	Ti1-O1	1.98617 (8)	Ti2-Ti2	1.04422 (5)
Ca/Y-O2	2.55158 (13)	Ti1-O1	2.03767 (9)	Ti1-Ti2	2.83723 (12)
Ca/Y-O2	2.9158 (12)	Ti1-O3	1.87934 (10)	Ca/Y-Ca/Y	3.54641 (13)
Ca/Y-O3	2.29789 (11)	Ti1-O4	2.00482 (9)	Ca/Y-Ca/Y	3.67475 (14)
Ca/Y-O3	2.49148 (10)	Ti1-O5	2.10339 (12)	Ca/Y-Zr	3.64459 (14)
Ca/Y-O4	2.47791 (14)	Ti1-O6	1.86777 (8)	Ca/Y-Zr	3.76732 (19)
Ca/Y-O5	2.15874 (8)	Ti2-O1	2.01446 (8)	Ca/Y-Zr	3.52244 (18)
Ca/Y-O6	2.35648 (9)	Ti2-O2	1.91349 (7)	Ca/Y-Zr	3.58109 (14)
Zr-O2	2.26148 (10)	Ti2-O2	1.60418 (7)	Ca/Y-Ti1	3.48736 (19)
Zr-O3	2.14917 (9)	Ti2-O4	2.02817 (7)	Ca/Y-Ti1	3.57798 (17)
Zr-O5	2.16485 (10)	Ti2-O4	1.51432 (6)	Ca/Y-Ti1	3.42492 (17)
Zr-O5	2.45348 (10)	Ti3-O4	1.99876 (8)	Ca/Y-Ti2	3.09889 (15)
Zr-O6	2.03887 (11)	Ti3-O4	1.99816 (8)	Ca/Y-Ti2	3.15781 (18)
Zr-O6	2.48648 (9)	Ti3-O6	1.94956 (10)	Ca/Y-Ti2	3.26467 (18)
Zr-O7	2.29685 (12)	Ti3-O6	1.94899 (10)	Ca/Y-Ti3	3.45802 (17)
Zr-Ti1	3.32627 (18)	Ti3-O7	1.91452 (7)	Ti2-Ti3	2.91319 (14)*2
Zr-Ti3	3.26664 (16)	Ti3-O7	1.91774 (7)		
Zr-Ti3	3.26674 (16)	Ti3-Ti3	0.00279		
$\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$					
Ca/La-O1	2.42719 (15)	Ti1-O1	1.97120 (9)	Ti2-Ti3	2.90539 (15)
Ca/La-O2	2.56430 (14)	Ti1-O1	2.03661 (9)	Ti2-Ti3	2.90580 (15)
Ca/La-O2	2.95126 (13)	Ti1-O3	1.87550 (11)	Ca/La-Ca/La	3.65709 (14)
Ca/La-O3	2.27255 (12)	Ti1-O4	2.00481 (10)	Ca/La-Ca/La	3.56708 (15)
Ca/La-O3	2.43456 (10)	Ti1-O5	2.09821 (13)	Ca/La-Zr	3.60524 (15)
Ca/La-O4	2.48768 (15)	Ti1-O7	1.86797 (9)	Ca/La-Zr	3.81833 (20)
Ca/La-O5	2.16519 (9)	Ti2-O1	2.00846 (9)	Ca/La-Zr	3.46808 (18)
Ca/La-O6	2.34869 (10)	Ti2-O2	1.91558 (8)	Ca/La-Zr	3.61316 (15)
Zr-O2	2.27834 (10)	Ti2-O2	1.59878 (7)	Ca/La-Ti1	3.46905 (20)
Zr-O3	2.12595 (10)	Ti2-O4	2.02515 (8)	Ca/La-Ti1	3.5655 (18)
Zr-O5	2.13885 (11)	Ti2-O4	1.51705 (6)	Ca/La-Ti1	3.37752 (18)
Zr-O5	2.45278 (11)	Ti3-O4	1.99078 (8)	Ca/La-Ti2	3.11141 (16)
Zr-O6	2.05856 (11)	Ti3-O4	1.99217 (8)	Ca/La-Ti2	3.19491 (20)
Zr-O6	2.48798 (10)	Ti3-O6	1.94159 (11)	Ca/La-Ti2	3.29465 (19)
Zr-O7	2.28861 (13)	Ti3-O6	1.94103 (11)	Ca/La-Ti3	3.45485 (18)
Zr-Ti1	3.30877 (19)	Ti3-O7	1.91666 (7)	Ca/La-Ti3	3.45657 (18)
Zr-Ti3	3.26337 (17)	Ti3-O7	1.91488 (7)	Ti2-Ti1	2.83413 (13)
Zr-Ti3	3.26234 (17)	Ti3-Ti3	0.00249	Ti2-Ti2	1.04354 (6)

and pair of Ti atoms by six oxygen atoms at the vertices of the octahedra of Ti(4) and Ti(6) and a trigonal prism Ti(5) (Figure 5). All these results are in accordance with crystallochemical expectations for zirconolite framework [27]. Table 5 lists the calculated valence of Ca, Zr, and Ti in the respective phase. Valence sum for Ca, Zr, and Ti shows that the Ca–O and Ti–O bonds are in relative compression while the Zr–O bonds are under tension in the large-cation layers. Particle size calculation using full wavelength at half maxima (FWHM) of major prominent reflections shows that the particle size of specimens ranges from 67 to 107 nm (Table 6). Compositional analysis of the materials by EDAX maps the elemental distribution of various elements (Figures 6(b)

and 6(d)). The weight% and atomic% data of the elements have confirmed Y and La substitution at calcium site. The morphological examination of the specimens by scanning electron microscopy shows that the ceramic phases consist of crystals of $\approx 1\text{--}5\text{ }\mu\text{m}$ size (Figures 6(a) and 6(c)).

4. Conclusions

Refinement of powder X-ray diffraction data shows that the solid solutions of Y and La zirconolite crystallize in the monoclinic (C12/c1 space group) system. Crystal data and structural parameters of the material have been refined to a

TABLE 4: O–M–O bond angles in CZTY and CZTLa ceramic powders.

$\text{Ca}_{0.8}\text{Y}_{0.2}\text{ZrTi}_2\text{O}_7$			
O1-Ca-O2	60.816 (4)	O3-Zr-O7	108.825 (4)
O1-Ca-O3	106.177 (5)	O5-Zr-O5	76.1297 (26)
O1-Ca-O3	69.2880 (31)	O5-Zr-O6	159.2397 (19)
O1-Ca-O4	170.3787 (8)	O5-Zr-O6	120.6788 (25)
O1-Ca-O5	64.2639 (28)	O5-Zr-O7	69.031 (5)
O1-Ca-O6	120.4205 (35)	O5-Zr-O6	90.2427 (25)
O2-Ca-O3	166.8666 (12)	O5-Zr-O6	163.0753 (11)
O2-Ca-O3	94.6279 (26)	O5-Zr-O7	120.8052 (24)
O2-Ca-O4	128.749 (4)	O6-Zr-O6	73.0430 (28)
O2-Ca-O5	104.9508 (25)	O6-Zr-O7	131.759 (4)
O2-Ca-O6	71.1752 (31)	O6-Zr-O7	71.277 (4)
O3-Ca-O3	81.4828 (27)	O1-Ti1-O1	176.14021 (30)
O3-Ca-O4	64.255 (5)	O1-Ti1-O3	94.1837 (28)
O3-Ca-O5	65.1166 (23)	O1-Ti1-O4	75.3278 (22)
O3-Ca-O6	120.2787 (27)	O1-Ti1-O5	73.7796 (23)
O3-Ca-O4	106.7528 (32)	O1-Ti1-O7	94.2665 (27)
O3-Ca-O5	109.464 (5)	O1-Ti1-O3	89.6886 (27)
O3-Ca-O6	82.289 (5)	O1-Ti1-O4	105.6577 (21)
O4-Ca-O5	110.4121 (30)	O1-Ti1-O5	102.3748 (23)
O4-Ca-O6	66.510 (4)	O1-Ti1-O7	84.6988 (26)
O5-Ca-O6	168.09560 (20)	O3-Ti1-O4	81.563 (5)
O2-Zr-O3	177.13270 (10)	O3-Ti1-O5	167.6345 (10)
O2-Zr-O5	110.3632 (33)	O3-Ti1-O7	100.244 (5)
O2-Zr-O5	81.812 (5)	O4-Ti1-O5	97.466 (6)
O2-Zr-O6	82.7689 (34)	O4-Ti1-O7	169.7887 (7)
O2-Zr-O6	93.786 (5)	O5-Ti1-O7	78.252 (5)
O2-Zr-O7	68.158 (4)	O1-Ti2-O2	93.158 (4)
O3-Zr-O5	68.248 (32)	O1-Ti2-O2	88.247 (4)
O3-Zr-O5	99.671 (5)	O1-Ti2-O4	162.0644 (7)
O3-Zr-O6	99.7264 (32)	O1-Ti2-O4	86.6597 (35)
O3-Zr-O6	85.824 (5)	O2-Ti2-O2	89.304 (4)
O4-Ti3-O4	71.840 (4)	O2-Ti2-O4	102.833 (4)
O4-Ti3-O6	84.7296 (33)	O2-Ti2-O4	107.853 (4)
O4-Ti3-O6	89.5539 (34)	O2-Ti2-O4	99.560 (4)
O4-Ti3-O7	168.167 (20)	O2-Ti2-O4	162.159 (11)
O4-Ti3-O7	96.770 (4)	O4-Ti2-O4	81.231 (4)
O4-Ti3-O6	89.6968 (34)	O6-Ti3-O7	92.012 (4)
O4-Ti3-O6	84.7067 (33)	O6-Ti3-O7	92.953 (4)
O4-Ti3-O7	96.865 (4)	O6-Ti3-O7	92.615 (4)
O4-Ti3-O7	168.27790 (20)	O6-Ti3-O7	92.255 (4)
O6-Ti3-O6	173.2187 (5)	O7-Ti3-O7	94.450 (4)
$\text{Ca}_{0.8}\text{La}_{0.2}\text{ZrTi}_2\text{O}_7$			
O1-Ca-O2	60.786 (4)	O3-Zr-O7	108.785 (4)
O1-Ca-O3	106.177 (5)	O5-Zr-O5	76.1597 (26)
O1-Ca-O3	69.1780 (31)	O5-Zr-O6	159.8997 (19)
O1-Ca-O4	170.2887 (8)	O5-Zr-O6	120.7988 (25)
O1-Ca-O5	64.7539 (28)	O5-Zr-O7	69.091 (5)
O1-Ca-O6	120.7805 (35)	O5-Zr-O6	90.4917 (25)
O2-Ca-O3	166.7266 (12)	O5-Zr-O6	163.0753 (11)

TABLE 4: Continued.

O2-Ca-O3	94.5999 (26)	O5-Zr-O7	120.7972 (24)
O2-Ca-O4	128.739 (4)	O6-Zr-O6	73.0430 (28)
O2-Ca-O5	104.7908 (25)	O6-Zr-O7	131.389 (4)
O2-Ca-O6	71.1852 (31)	O6-Zr-O7	71.197 (4)
O3-Ca-O3	81.2828 (27)	O1-Ti1-O1	176.29021 (30)
O3-Ca-O4	64.185 (5)	O1-Ti1-O3	94.11737 (28)
O3-Ca-O5	65.1866 (23)	O1-Ti1-O4	75.1778 (22)
O3-Ca-O6	120.1887 (27)	O1-Ti1-O5	73.7396 (23)
O3-Ca-O4	106.7528 (32)	O1-Ti1-O7	94.2965 (27)
O3-Ca-O5	109.784 (5)	O1-Ti1-O3	89.8686 (27)
O3-Ca-O6	82.189 (5)	O1-Ti1-O4	105.7977 (21)
O4-Ca-O5	110.3411 (30)	O1-Ti1-O5	102.4548 (23)
O4-Ca-O6	66.480 (4)	O1-Ti1-O7	84.5988 (26)
O5-Ca-O6	168.08960 (20)	O3-Ti1-O4	81.593 (5)
O2-Zr-O3	177.28270 (10)	O3-Ti1-O5	167.5945 (10)
O2-Zr-O5	110.3932 (33)	O3-Ti1-O7	100.294 (5)
O2-Zr-O5	81.782 (5)	O4-Ti1-O5	97.796 (6)
O2-Zr-O6	82.7989 (34)	O4-Ti1-O7	169.4887 (7)
O2-Zr-O6	93.179 (5)	O5-Ti1-O7	78.282 (5)
O2-Zr-O7	68.189 (4)	O1-Ti2-O2	93.186 (4)
O3-Zr-O5	68.1975 (32)	O1-Ti2-O2	88.191 (4)
O3-Zr-O5	99.891 (5)	O1-Ti2-O4	162.0784 (7)
O3-Zr-O6	99.4584 (32)	O1-Ti2-O4	86.1897 (35)
O3-Zr-O6	85.489 (5)	O2-Ti2-O2	89.189 (4)
O4-Ti3-O4	71.179 (4)	O2-Ti2-O4	102.846 (4)
O4-Ti3-O6	84.7996 (33)	O2-Ti2-O4	107.783 (4)
O4-Ti3-O6	89.7939 (34)	O2-Ti2-O4	99.780 (4)
O4-Ti3-O7	168.15820 (20)	O2-Ti2-O4	162.1786 (11)
O4-Ti3-O7	96.780 (4)	O4-Ti2-O4	81.541 (4)
O4-Ti3-O6	89.7568 (34)	O6-Ti3-O7	92.172 (4)
O4-Ti3-O6	84.7847 (33)	O6-Ti3-O7	92.483 (4)
O4-Ti3-O7	96.685 (4)	O6-Ti3-O7	92.615 (4)
O4-Ti3-O7	168.17290 (20)	O6-Ti3-O7	92.1255 (4)
O6-Ti3-O6	173.2485 (5)	O7-Ti3-O7	94.7854 (4)

TABLE 5: Bond valence calculation for substituted calcium zirconium titanate ceramic phases.

Phase	Element				
	Ca	Zr	Ti(1)	Ti(2)	Ti(3)
$\text{Ca}_{0.80}\text{Y}_{0.20}\text{ZrTi}_2\text{O}_7$	2.79	3.47	4.18	5.97	4.39
$\text{Ca}_{0.80}\text{La}_{0.20}\text{ZrTi}_2\text{O}_7$	2.70	3.55	4.21	5.94	4.35

satisfactory convergence with reasonable values of Rietveld parameters (Rp and Rwp). Calculations of Ca–O, Zr–O, and Ti–O bond distances and O–M–O bond angles quantify the extent of distortion in the CaO_8 , ZrO_7 , and $\text{TiO}_6/\text{TiO}_5$ polyhedron. Zirconolites have been identified as a potential material for immobilization and solidification of Y^{3+} and La^{3+} cations. Analytical evidence has been found to conclude that the yttrium and lanthanum are crystallochemically fixed in the ceramic matrix.

TABLE 6: Particle size along prominent reflections of CZTY and CZTLA phases.

h, k, l planes	$\text{Ca}_{0.80}\text{Y}_{0.20}\text{ZrTi}_2\text{O}_7$	$\text{Ca}_{0.80}\text{La}_{0.20}\text{ZrTi}_2\text{O}_7$
	Particle size (nm)	
112	95.85	95.85
311	81.21	81.21
221	100.95	100.95
40–2	100.98	100.98
004	67.49	67.49
22–3	102.28	102.28
62–1	107.70	107.70
42–5	86.79	86.79

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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