

## Solid Solution of Metal Oxides in the Zirconolite Phase $\text{CaZrTi}_2\text{O}_7$ . II: The Ternary Phase $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$

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The extent of solid solution of  $\text{CaO}$ ,  $\text{ZrO}_2$ , and  $\text{TiO}_2$  in the  $\text{CaZrTi}_2\text{O}_7$  phase has been determined using powder X-ray diffraction methods. The  $\text{CaO}$  content always lies between 24.0 and 25.0 mole%, while the atomic ratio  $[\text{Ti}]/[\text{Zr}]$  may vary from 1.4 to 2.6 at  $1300^\circ\text{C}$  and from 1.2 to 2.1 at  $1480^\circ\text{C}$ . The relevant portion of the ternary phase diagram  $\text{CaO}-\text{ZrO}_2-\text{TiO}_2$  has been drawn. Structure refinement based on powder X-ray diffraction intensities has been carried out on zirconolite phases  $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$  with  $x = 0.9, 1.0$ , and  $1.2$ : the resultant cation distributions agree with those from a previous study. © 1992

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### Introduction

In the study of the  $\text{CaO}-\text{ZrO}_2-\text{TiO}_2$  system, the zirconolite phase, formally  $\text{CaZrTi}_2\text{O}_7$ , was inferred to have a range of composition (1), and it has been observed that the atomic ratio  $[\text{Ti}]/[\text{Zr}]$  for zirconolites synthesized at  $1300^\circ\text{C}$  and at  $1500^\circ\text{C}$  was 2.75 and 1.31, respectively (2). The structural study of zirconolites with  $[\text{Ti}]/[\text{Zr}]$  of 2.55 and 1.31 showed how the exchange of  $\text{Ti}^{\text{IV}}$  and  $\text{Zr}^{\text{IV}}$  was accommodated (3). However, there has been no detailed study either of the nature or extent of the compositional variation exhibited by the zirconolite phase in the ternary system, or of its temperature dependence. The present work includes such a study, with additional structural information from the phase at three representative compositions.

### Experimental

The starting materials and preparative procedures were described in Part I (8). The

principal materials prepared were  $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$ ,  $0.75 \leq x \leq 1.43$  ( $2.9 \leq [\text{Ti}]/[\text{Zr}] \leq 1.1$ ), quenched from  $1300^\circ$ ,  $1480^\circ$ , and  $1530^\circ\text{C}$  ( $\text{CaZr}_9\text{Ti}_{2.1}\text{O}_7$ ,  $\text{CaZrTi}_2\text{O}_7$ , and  $\text{CaZr}_{1.2}\text{Ti}_{1.8}\text{O}_7$  from  $1480^\circ\text{C}$  were used for structure refinement), and  $\text{Ca}_{.95}\text{Zr}_x\text{Ti}_{3.025-x}\text{O}_7$ ,  $0.75 \leq x \leq 1.50$  ( $3.0 \leq [\text{Ti}]/[\text{Zr}] \leq 1.0$ ), quenched from  $1300^\circ$ ,  $1450^\circ$ , and  $1480^\circ\text{C}$ .

Lattice parameters were determined by a least-squares procedure from measurements of 40-50 diffraction lines on a powder X-ray diffraction pattern recorded with a Guinier camera, using  $\text{CuK}\alpha_1$  radiation and with  $\text{ThO}_2$  ( $a = 5.5972 \text{ \AA}$ ) as an internal standard. The esd's of the lattice parameters were calculated from the measurements of individual films: the weighting scheme used was based on the assumption that all lines could be measured with equal precision. The overall procedure produced internally consistent results in that lattice parameters determined for duplicate specimens agreed to within twice the esd's.

Structure refinement based on powder

X-ray diffraction intensities was carried out using data obtained with a diffractometer. As described in Part I, a model structure of composition  $\text{CaZrTi}_2\text{O}_7$ , with the metal atoms on their ideal sites and the published atomic coordinates for this phase (3), was assumed, and then scale factor, overall isotropic temperature factor, all variable atomic coordinates, and occupancies of the metal atom sites were refined. From these last quantities, a value for the number of electrons ( $n(e)$ ) at each site could be determined, and the distribution of metal atoms over the available sites estimated. Refinements were completed using appropriately combined scattering factors for the metal atoms.

For determination of the distribution of the metal atoms, it was noted that there are three metal atom types in known proportions to be distributed over five sites such that the sites are filled, and the number of electrons at each site matches the experimental values. There are therefore 15 unknowns (the fractions of each metal type at each site), but only 11 linear constraint equations. As described in Part I, basic feasible solutions were sought by systematically setting four of the unknowns to zero and solving for the remainder. There was only one basic feasible solution for  $\text{CaZr}_9\text{Ti}_{2.1}\text{O}_7$  and  $\text{CaZrTi}_2\text{O}_7$ , but there were two for  $\text{CaZr}_{1.2}\text{Ti}_{1.8}\text{O}_7$  (so that any linear combination of these two solutions,  $a_1S_1 + a_2S_2$ , where  $a_1, a_2 \geq 0$  and  $a_1 + a_2 = 1$ , is also a solution).

## Results and Discussion

### *The Zirconolite Phase in the Ternary System CaO–ZrO<sub>2</sub>–TiO<sub>2</sub>*

It was established from preliminary experiments that the CaO content of the zirconolite phase was restricted: materials of approximately 50 mole% Ti and  $\leq 24.0$  mole% CaO, fired at 1400°C, contained zirconolite and  $\text{ZrO}_2$ , while similar materials

of  $\geq 25.0$  mole% CaO contained zirconolite and the perovskite phase  $\text{Ca}(\text{Zr}, \text{Ti})\text{O}_3$ . Also, the structure studies of zirconolite single crystals prepared from different reaction mixtures (3) showed that the CaO content lay between 24.3 and 24.8 mole%. Therefore, materials of overall composition  $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$  and  $\text{Ca}_{.95}\text{Zr}_x\text{Ti}_{3.025-x}\text{O}_7$  quenched from various temperatures were studied: lattice parameters of the resultant zirconolite phase are given in Table I, and are summarized, in effect, in the unit cell volume vs composition curves shown in Fig. 1. It may be noted that the  $a$  parameter is largely unaffected by changes in composition, all variation occurring in  $b$ ,  $c$ , and  $\beta$ .

Table I also shows any extra phases that were detected in the X-ray powder patterns of the specimens. Since the compositions of these two series of materials lay very close to the zirconolite phase field, the relative amounts of any coexisting phases were small, and only the strongest lines of their diffraction patterns appeared as very faint lines on the Guinier photographs. The diffraction patterns of  $\text{ZrTiO}_4$  and  $\text{TiO}_2$  were such that detection of small amounts of these phases was difficult or impossible. Therefore, the compositions at which these extra phases first appeared were uncertain. The horizontal sections at the ends of the curves in Fig. 1 correspond to regions where the zirconolite phase was judged to be in equilibrium with two other phases (and thus compositionally invariant under the experimental conditions), while the sloping portions correspond to zirconolite of varying composition, either in two-phase equilibrium, or as a single phase. These slope changes are mirrored in curves of  $b$ ,  $c$ , and  $\beta$  vs composition.

In the series  $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$ , partial melting occurred at 1530°C for  $x < 1.03$  ( $[\text{Ti}]/[\text{Zr}] > 1.9$ ), and there was evidence that a liquid phase was present at 1480°C in  $\text{Ca}_{.95}\text{Zr}_x\text{Ti}_{3.025-x}\text{O}_7$  at the highest  $[\text{Ti}]/[\text{Zr}]$  values. The phase equilibria are complicated further

TABLE I

## LATTICE PARAMETERS OF THE ZIRCONOLITE PHASE IN VARIOUS PREPARATIONS

CaZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>, 1300 °C

x	[Ti]/[Zr]	a	b	c	β	*
.769	2.900	12.4421(16)	7.2511(8)	11.3201(16)	100.616(11)	p
.789	2.800	12.4427(10)	7.2506(6)	11.3217(12)	100.615(9)	p
.811	2.700	12.4427(8)	7.2520(5)	11.3240(9)	100.626(6)	p
.833	2.600	12.4436(9)	7.2534(5)	11.3277(10)	100.626(7)	p?
.857	2.500	12.4417(11)	7.2541(6)	11.3361(13)	100.611(8)	
.882	2.400	12.4401(9)	7.2575(5)	11.3413(11)	100.626(7)	
.909	2.300	12.4406(10)	7.2591(6)	11.3481(13)	100.599(8)	
.938	2.200	12.4412(8)	7.2611(5)	11.3570(11)	100.588(7)	
.968	2.100	12.4407(9)	7.2645(5)	11.3694(10)	100.563(7)	
1.000	2.000	12.4404(9)	7.2663(6)	11.3815(12)	100.554(8)	
1.034	1.900	12.4393(10)	7.2676(6)	11.3858(12)	100.532(8)	
1.034	1.900	12.4392(8)	7.2668(5)	11.3862(10)	100.533(7)	
1.071	1.800	12.4397(8)	7.2688(5)	11.3992(9)	100.528(6)	
1.071	1.800	12.4403(9)	7.2693(5)	11.4003(10)	100.512(8)	
1.111	1.700	12.4425(9)	7.2713(5)	11.4174(10)	100.490(7)	z
1.154	1.600	12.4394(9)	7.2731(4)	11.4294(9)	100.477(8)	z
1.200	1.500	12.4376(11)	7.2724(6)	11.4428(14)	100.461(10)	z
1.250	1.400	12.4421(11)	7.2747(5)	11.4506(12)	100.447(9)	c, z
1.304	1.300	12.4400(11)	7.2739(5)	11.4547(11)	100.445(9)	c, z

CaZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>, 1480 °C

x	[Ti]/[Zr]	a	b	c	β	*
.900	2.333	12.4446(13)	7.2705(8)	11.3750(14)	100.550(11)	p
.960	2.125	12.4454(8)	7.2723(4)	11.3864(9)	100.535(7)	p
1.000	2.000	12.4458(7)	7.2734(4)	11.3942(9)	100.533(7)	
1.040	1.885	12.4451(5)	7.2750(11)	11.4026(11)	100.519(8)	
1.120	1.679	12.4462(7)	7.2794(3)	11.4206(11)	100.453(6)	
1.200	1.500	12.4444(10)	7.2829(5)	11.4626(11)	100.432(9)	
1.240	1.419	12.4463(7)	7.2844(4)	11.4750(8)	100.410(6)	
1.400	1.143	12.4468(12)	7.2867(5)	11.4981(13)	100.373(10)	z, p

CaZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>, 1530 °C<sup>†</sup>

x	[Ti]/[Zr]	a	b	c	β	*
1.111	1.700	12.4383(9)	7.2742(5)	11.4398(10)	100.461(7)	p
1.154	1.600	12.4369(9)	7.2761(5)	11.4446(11)	100.449(7)	p
1.200	1.500	12.4362(9)	7.2740(4)	11.4418(11)	100.449(7)	p
1.250	1.400	12.4381(7)	7.2785(3)	11.4674(7)	100.420(6)	p
1.304	1.300	12.4398(8)	7.2791(4)	11.4918(8)	100.392(6)	p
1.364	1.200	12.4446(7)	7.2836(3)	11.5123(6)	100.356(5)	p
1.429	1.100	12.4401(8)	7.2817(4)	11.5133(10)	100.365(7)	z, p

Ca<sub>99</sub>Zr<sub>x</sub>Ti<sub>100-x</sub>O<sub>3</sub>, 1300 °C

x	[Ti]/[Zr]	a	b	c	β	*
.756	3.000	12.4441(10)	7.2502(6)	11.3220(12)	100.638(8)	p, r
.796	2.800	12.4446(13)	7.2538(8)	11.3313(16)	100.630(11)	p, r
.818	2.700	12.4442(13)	7.2545(8)	11.3286(16)	100.621(10)	
.840	2.600	12.4436(13)	7.2552(7)	11.3323(15)	100.623(10)	
.864	2.500	12.4420(6)	7.2549(4)	11.3335(8)	100.624(5)	
.890	2.400	12.4409(12)	7.2577(6)	11.3398(13)	100.624(9)	
.917	2.300	12.4392(11)	7.2582(6)	11.3474(13)	100.597(8)	
.945	2.200	12.4392(9)	7.2609(5)	11.3531(10)	100.593(7)	
.976	2.100	12.4400(12)	7.2625(6)	11.3606(14)	100.582(9)	
1.008	2.000	12.4377(11)	7.2645(6)	11.3690(13)	100.562(9)	z
1.043	1.900	12.4407(10)	7.2688(6)	11.3807(11)	100.554(8)	z
1.080	1.800	12.4393(9)	7.2668(5)	11.3865(10)	100.549(7)	z
1.120	1.700	12.4380(8)	7.2690(5)	11.3980(10)	100.519(7)	z
1.163	1.600	12.4399(10)	7.2693(6)	11.4106(12)	100.510(8)	z
1.210	1.500	12.4413(13)	7.2709(5)	11.4298(12)	100.473(10)	z
1.260	1.400	12.4400(10)	7.2733(5)	11.4388(11)	100.465(8)	z
1.375	1.200	12.4415(12)	7.2736(5)	11.4445(12)	100.464(9)	z, c

Ca<sub>99</sub>Zr<sub>x</sub>Ti<sub>100-x</sub>O<sub>3</sub>, 1480 °C<sup>†</sup>

x	[Ti]/[Zr]	a	b	c	β	*
.756	2.800	12.4343(10)	7.2594(6)	11.3541(11)	100.592(8)	p
.864	2.500	12.4356(13)	7.2595(7)	11.3616(13)	100.571(10)	p?
.890	2.400	12.4366(11)	7.2599(7)	11.3612(16)	100.571(11)	p?
.917	2.300	12.4367(9)	7.2608(5)	11.3592(11)	100.573(8)	p?
.945	2.200	12.4375(8)	7.2670(7)	11.3607(13)	100.581(10)	p?
.976	2.100	12.4366(11)	7.2605(9)	11.3615(19)	100.581(14)	p?
1.008	2.000	12.4369(10)	7.2629(6)	11.3594(10)	100.586(8)	p?
1.043	1.900	12.4358(15)	7.2619(8)	11.3652(16)	100.576(12)	
1.080	1.800	12.4388(7)	7.2682(4)	11.3877(9)	100.524(6)	z
1.120	1.700	12.4367(12)	7.2697(6)	11.4011(12)	100.512(9)	z
1.163	1.600	12.4347(12)	7.2717(6)	11.4142(10)	100.490(9)	z
1.210	1.500	12.4377(12)	7.2735(5)	11.4348(10)	100.470(8)	z
1.260	1.400	12.4383(9)	7.2761(4)	11.4496(8)	100.447(6)	z
1.375	1.200	12.4407(9)	7.2795(4)	11.4882(10)	100.405(7)	z
1.513	1.000	12.4443(11)	7.2816(5)	11.5001(12)	100.388(8)	z, p

Ca<sub>99</sub>Zr<sub>x</sub>Ti<sub>100-x</sub>O<sub>3</sub>, 1450 °C

x	[Ti]/[Zr]	a	b	c	β	*
.756	3.000	12.4396(9)	7.2581(6)	11.3419(12)	100.588(8)	p
.796	2.800	12.4407(11)	7.2600(6)	11.3468(14)	100.586(10)	p
.818	2.700	12.4391(8)	7.2598(5)	11.3464(11)	100.589(7)	p
.840	2.600	12.4403(12)	7.2597(8)	11.3440(16)	100.594(11)	p
.864	2.500	12.4370(10)	7.2615(6)	11.3494(12)	100.578(8)	
.890	2.400	12.4387(12)	7.2613(6)	11.3458(15)	100.572(11)	
.917	2.300	12.4362(12)	7.2605(7)	11.3521(13)	100.578(9)	
.945	2.200	12.4364(13)	7.2605(8)	11.3559(15)	100.575(12)	
.976	2.100	12.4373(13)	7.2631(7)	11.3586(16)	100.570(10)	
1.008	2.000	12.4350(11)	7.2640(7)	11.3617(11)	100.555(10)	
1.043	1.900	12.4362(11)	7.2658(7)	11.3720(14)	100.557(9)	
1.080	1.800	12.4369(9)	7.2675(5)	11.3802(10)	100.549(7)	
1.120	1.700	12.4361(9)	7.2691(5)	11.4009(11)	100.517(7)	z
1.163	1.600	12.4375(9)	7.2705(5)	11.4181(10)	100.494(7)	z
1.210	1.500	12.4367(16)	7.2740(8)	11.4334(16)	100.474(13)	z
1.260	1.400	12.4357(13)	7.2758(8)	11.4470(14)	100.453(11)	z
1.375	1.200	12.4408(12)	7.2799(6)	11.4833(10)	100.419(9)	z
1.513	1.000	12.4420(7)	7.2807(3)	11.4946(10)	100.393(6)	z, c?

Note. Axial lengths  $a$ ,  $b$ , and  $c$  are in Å,  $\beta$  in degrees. Numbers in parentheses are esd's, and apply to the last quoted place. \*Extra phases detected: c—calzirtite, Ca<sub>2</sub>Zr<sub>5</sub>Ti<sub>3</sub>O<sub>16</sub>;

z—monoclinic ZrO<sub>2</sub>;

p—perovskite, Ca(Zr,Ti)O<sub>3</sub>;

r—rutile, TiO<sub>2</sub>.

† Partial melting occurred in materials with  $0.756 \leq x \leq 1.080$ .

‡ Partial melting occurred in materials with  $x = .756$ , and possibly in materials with  $x = .796$ .

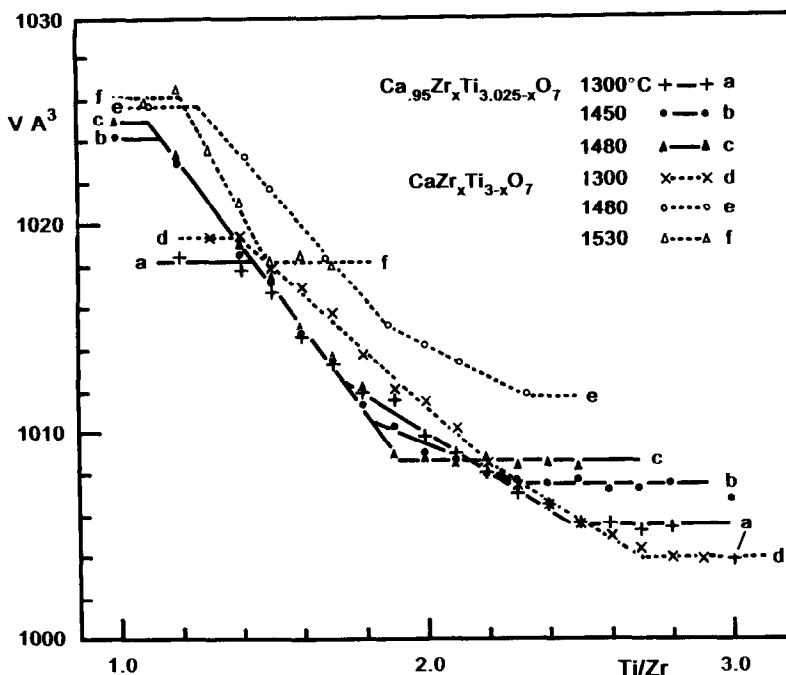


FIG. 1. Variation in unit cell volume with overall [Ti]/[Zr] for the zirconolite phase in two formulations at different temperatures.

by the appearance of the calzirtite phase ( $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$ ) (4, 5) within the three-phase field zirconia-perovskite-zirconolite at temperatures below about 1370°C. This phase does not appear in the published  $\text{CaO-ZrO}_2\text{-TiO}_2$  phase diagram (1), which refers to equilibria above 1450°C. The lattice parameters of  $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$  (tetragonal,  $I4_1/acd$ ,  $a = 15.2203$ ,  $c = 10.1224$  Å) do not vary greatly with overall composition, so the phase appears to have little homogeneity range.

A zirconolite phase field consistent with the above data for 1300° and 1480°C is shown in Fig. 2. It is evident that the [Ti]/[Zr] ratio exhibited by a given zirconolite is not a function of formation temperature alone, as has been suggested (2), but is also a function of the overall composition. The [Ti]/[Zr] range of the phase contracts in extent and moves to lower values as the temperature is raised,

so that use of the [Ti]/[Zr] ratio of a natural zirconolite as an indicator of geological formation temperature would be feasible, but only if the zirconolite was formed in one of the three-phase regions at the extremities of its existence range.

The results of structure refinement of  $\text{CaZr}_9\text{Ti}_{2.1}\text{O}_7$ ,  $\text{CaZrTi}_2\text{O}_7$ , and  $\text{CaZr}_{1.2}\text{Ti}_{1.8}\text{O}_7$  prepared at 1400°C are given in Table II. The atomic coordinates agree with those determined from single crystal data (3), although esd's from powder data are about an order of magnitude larger. The atomic populations at the metal-atom sites for  $\text{CaZr}_9\text{Ti}_{2.1}\text{O}_7$  and  $\text{CaZr}_{1.2}\text{Ti}_{1.8}\text{O}_7$  are similar to those found for single crystals of zirconolites with like deviations from stoichiometry (3). However, the metal-atom populations for  $\text{CaZrTi}_2\text{O}_7$  differ from those published previously (6), and are to be preferred, since in that earlier structure determination the

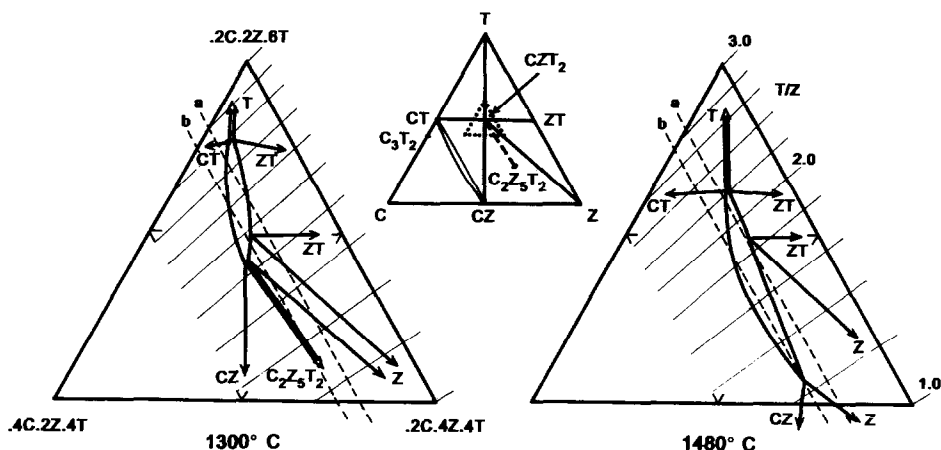


FIG. 2. Suggested behavior of the zirconolite phase at two temperatures. The basic CaO–ZrO<sub>2</sub>–TiO<sub>2</sub> diagram is inset. The truncated regions shown are identical in extent. Lines *a* and *b* are the loci of the two sets of compositions studied, i.e., Ca contents 0.95 and 1.00, respectively. Lines of constant [Ti]/[Zr] are the same for each figure and are labelled on the right-hand one. Phases are indicated as follows: T = TiO<sub>2</sub> rutile; C = CaO; Z = ZrO<sub>2</sub> tetragonal; CT, ZT = CaTiO<sub>3</sub> and CaZrO<sub>3</sub> perovskite; ZT = ZrTiO<sub>4</sub>; C<sub>2</sub>Z<sub>5</sub>T<sub>2</sub> = Ca<sub>2</sub>Zr<sub>5</sub>Ti<sub>2</sub>O<sub>16</sub> calzirtite; and CZT<sub>2</sub> = CaZrTi<sub>2</sub>O<sub>7</sub> zirconolite.

existence of the fivefold-coordinated Ti was not detected, which would influence the resultant occupancies, and the procedure of population assignment was less soundly based than is the case here.

It can be seen that variation in [Ti]/[Zr] is accommodated in the structure by simultaneous adjustments to the amount of Ti substituting at the Zr site (M2) and to the Zr substituting at the six-coordinate Ti site M3 and at the five-coordinate Ti site M4. The Ca site M1 always contains a few at.% of Zr, a result in agreement with the single crystal findings (3). Since the scattering factors for Ca and Ti are close (20 and 22 electrons), Ca and Ti in small amounts at the Zr site (M2) cannot be distinguished using X-ray data. Thus, either there is a slight Ca/Zr exchange at M1 and M2, or the materials have a genuine deficiency in Ca, or both. Although the former case is less likely considering the results from the phase equilibrium study above, it was assumed here for ease of calculation: the adjustments to atomic populations at M2, M3, and M4 re-

quired for conformation with the more likely case of a genuine Ca deficiency are all less than the quoted esd's.

If the CaO content of the ternary zirconolite phase is ~24.5 mole%, then the M<sub>4</sub>O<sub>7</sub> stoichiometry required for the structure cannot be achieved unless

(a) there is present an unidentified impurity cation of valence <4, or

(b) the structure contains defects, probably of the stacking type noted in Part I, which can accommodate a slight anion excess (the material would have the formula Ca<sub>0.98</sub>Zr<sub>x</sub>Ti<sub>3.02-x</sub>O<sub>7.02</sub>, because of the structural requirement of an intact cation array), or

(c) the cation Ti<sup>iii</sup> is stabilized in a small amount at the M2 site, as in Ca<sub>0.98</sub>Zr<sub>x</sub>Ti<sub>0.04</sub><sup>iii</sup>Ti<sub>2.98-x</sub><sup>iv</sup>O<sub>7</sub>.

It would seem that (a) is unlikely. Starting materials of >99.95% purity (checked by atomic absorption analyses, see Part I) were used, and care was taken to avoid contamination of the specimens during preparation. As neither (b) nor (c) was

TABLE II  
ATOMIC COORDINATES OF TERNARY ZIRCONOLITES

CaZrTi <sub>2</sub> O <sub>7</sub>					CaZr <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						
R = .038 N <sub>obs</sub> = 155					R = .047 N <sub>obs</sub> = 133						
site	n(g)	x	y	z	occupancy	site	n(g)	x	y	z	occupancy
M1	20.8(3)	.373(1)	.123(2)	.4949(8)	.96Ca + .04(1)Zr	M1	20.7(3)	.371(1)	.124(2)	.494(1)	.98Ca + .02(2)Zr
M2	37.8(3)	.1222(5)	.1222(9)	.9744(5)	.04Ca + .88(2)Zr + .08(2)Ti	M2	38.1(7)	.1224(8)	.121(1)	.9746(7)	.02Ca + .88(4)Zr + .10(4)Ti
M3	22.5(3)	.2497(9)	.122(2)	.7467(8)	.03(2)Zr + .97Ti	M3	22.2(5)	.247(2)	.127(3)	.746(1)	Ti
M4	11.8(2)	.474(2)	.056(2)	.250(3)	.10(5)Zr + .90Ti	M4	10.5(4)	.470(4)	.049(3)	.255(5)	Ti
M5	11.2(2)	0	.127(2)	1/4	Ti	M5	10.8(3)	0	.127(3)	1/4	Ti
O1		.311(3)	.137(5)	.275(3)		O1		.304(3)	.106(7)	.283(4)	
O2		.470(3)	.144(4)	.102(3)		O2		.470(4)	.130(6)	.121(4)	
O3		.196(3)	.082(4)	.574(3)		O3		.197(5)	.075(5)	.578(4)	
O4		.404(3)	.175(4)	.720(3)		O4		.403(4)	.171(7)	.710(4)	
O5		.703(3)	.168(4)	.591(3)		O5		.708(5)	.178(6)	.596(4)	
O6		.001(3)	.111(4)	.414(3)		O6		.000(3)	.131(7)	.406(4)	
O7		.119(3)	.054(4)	.787(2)		O7		.114(4)	.066(6)	.800(3)	

CaZr <sub>2</sub> Ti <sub>4</sub> O <sub>7</sub>					R = .047 N <sub>obs</sub> = 144				
site	n(g)	x	y	z	occupancy S <sub>1</sub> <sup>a</sup>	occupancy S <sub>2</sub> <sup>a</sup>			
M1	20.8(4)	.373(1)	.128(2)	.495(1)	.98Ca + .02(2)Zr	.96Ca + .01(2)Zr + .03(3)Ti			
M2	38.9(8)	.1224(7)	.122(1)	.9749(6)	.02Ca + .95(3)Zr + .03(3)Ti	.04Ca + .96(4)Zr			
M3	24.8(5)	.249(1)	.120(2)	.742(1)	.15(3)Zr + .85Ti	.15(3)Zr + .85Ti			
M4	12.5(3)	.434(3)	.059(2)	.255(4)	.16(2)Zr + .84Ti	.16(2)Zr + .84Ti			
M5	11.0(3)	0	.131(3)	1/4	Ti	Ti			
O1		.298(3)	.137(6)	.276(3)					
O2		.470(4)	.157(5)	.096(4)					
O3		.206(4)	.078(5)	.568(3)					
O4		.411(4)	.169(6)	.725(4)					
O5		.702(4)	.160(6)	.581(3)					
O6		.005(4)	.121(5)	.410(4)					
O7		.112(4)	.055(5)	.787(3)					

Note. Space group  $C2/c$ . All sites are of the general eightfold type  $f$ , except M5, which is the fourfold type  $e$ . M4 is the "split-atom" site, with occupancy 0.5 atoms.

<sup>a</sup>  $S_1$  and  $S_2$  are the basic feasible solutions for the occupancy of the M sites; any linear combination,  $a_1S_1 + a_2S_2$ ,  $a_1 + a_2 = 1$ , is also a solution.

investigated here, further work would be necessary to establish the origin of the apparent Ca deficiency.

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