CONF-951155--115

UCRL-JC-122949
PREPRINT

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This paper was prepared for submittal to
The Materials Research Society 1995 Fall Meeting
in Boston, MA on November 27-December 1, 1995

December 1995

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# THE $CaO$-$TiO_2$-$ZrO_2$ SYSTEM AT 1200 °C AND THE SOLUBILITIES OF Hf AND Gd IN ZIRCONOLITE

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## ABSTRACT

Phase equilibria are established in the $CaO$-$TiO_2$-$ZrO_2$ system at 1200 °C, using X-ray diffraction and electron probe microanalysis. The existence of two previously reported ternary phases, zirconolite ($CaZrTi_2O_7$) and calzirtite ($Ca_2Zr_5Ti_2O_{16}$), is confirmed. Each of these phases exhibits a significant range of homogeneity between $TiO_2$ and $ZrO_2$ while maintaining a nearly constant concentration of CaO. The ternary solubilities of the constituent binary phases are found to be negligible, with the exceptions of the perovskites, which display mutual solubility of at least 22 mol.% and may in fact form a series of continuous solid solutions. The solubilities of Hf and Gd in zirconolite are also investigated. While Hf-bearing samples did not reach thermodynamic equilibrium under the experimental conditions employed, the existence of a Hf analog to zirconolite, $CaHfTi_2O_7$, is conclusively demonstrated. The phase is stable at the stoichiometric composition, and its lattice parameters are very close to those reported in the literature for stoichiometric zirconolite. A Gd-bearing sample of the composition $Ca_{0.88}Zr_{0.88}Gd_{0.24}Ti_2O_7$ is found to be essentially single phase zirconolite, in agreement with previous investigations at higher temperatures.

## INTRODUCTION

In recent years, significant technological advancements have been made in the Synroc scheme for the immobilization high-level nuclear waste[1]. However, many basic scientific issues related to Synroc fabrication have yet to be addressed. For example, the $CaO$-$TiO_2$-$ZrO_2$ system is an integral part of the Synroc formulation. Indeed, of the four phases comprising Synroc ($Ba_{1.2}(Al,Ti)_8O_{16}$, $CaTiO_3$, $CaZrTi_2O_7$ and $TiO_2$), the latter three are members of this ternary system. In spite of its great technological importance, however, the $CaO$-$TiO_2$-$ZrO_2$ system has never been investigated in detail. To date, some cursory studies[2-5] of the system have been performed using X-ray diffraction, and many questions remain pertaining to phase relationships at temperatures typically employed during Synroc production.

Additionally, there currently exists interest in refining the basic Synroc formulation for the immobilization of excess weapons Pu. The issues which must be addressed in arriving at a Pu Synroc formulation have been outlined by Jostsons *et al*[6]. Prominent among these concerns are chemical durability, maximum Pu loading levels, and criticality safety. It is well-known that zirconolite ($CaZrTi_2O_7$) is the most durable phase in Synroc[1,7]. Moreover, it is the phase most capable of incorporating actinides[1], and hence reformulated Pu Synroc will undoubtedly be composed primarily of zirconolite[8]. Accordingly, much experimental effort has been expended recently to determine the solubility limits of Pu and Pu analogs in zirconolite[9-12]. However, relatively little attention has been paid to the incorporation of neutron absorbing elements, such as Hf and Gd, into zirconolite, even though such incorporation is essential to the prevention of criticality in heavily Pu-loaded wasteforms.

In consideration of the preceding discussion, phase equilibria have been determined in the $CaO$-$TiO_2$-$ZrO_2$ system at 1200 °C at concentrations below 50 mol.% CaO, using X-ray diffraction and electron probe microanalysis. Furthermore, the solubility limits of Hf and Gd in zirconolite have also been explored, utilizing the same experimental techniques.

## EXPERIMENT

$TiO_2$ (anatase, 99.5%, nanocrystalline) $ZrO_2$ (>95.0%, Hf as the major impurity, nanocrystalline), dried calcium oxalate ($CaC_2O_4$, 99.9%, annealed at 200 °C for one week), $Gd_2O_3$ (99.9%) and $HfO_2$ (98.0%, Zr as the major impurity, particle size < 1 μm) powders were combined to form samples with nominal weights of 3 g. These samples were hand-milled, placed in Pt crucibles and calcined for 2 hr in air at 1200 °C. They were subsequently air-cooled, and again hand-milled. The milled powders were then pressed into 0.75 in diameter pellets using an hydraulic press with an applied pressure of approximately 25 ksi. The sample pellets were placed on Pt sheets and annealed in air for 10-14 days at 1200 °C, after which time they were air-cooled. One half of each pellet was ground into a powder and analyzed by X-ray diffraction, using $CuK_\alpha$ radiation. The other half of each sample was mounted in epoxy, metallographically cross-sectioned and analyzed for composition using electron probe microanalysis (EPMA), employing a 10 kV, 20 nA electron beam and utilizing wollastonite ($CaSiO_3$), rutile ($TiO_2$), zircon ($ZrSiO_4$) and $HfO_2$ as standards. The Gd-bearing sample was not analyzed for composition.

## RESULTS

### The $CaO-TiO_2-ZrO_2$ System at 1200 °C

Prior to the presentation of experimental results, previous experimental investigations of the ternary $CaO-TiO_2-ZrO_2$ system will be discussed. For information on the constituent binary oxide systems $CaO-TiO_2$, $CaO-ZrO_2$ and $TiO_2-ZrO_2$, the reader is referred to [13].

As was mentioned in the Introduction, some previous work has been performed pertaining to phase equilibria in the $CaO-TiO_2-ZrO_2$ system. Coughanour *et al.*[2] have utilized X-ray diffraction analysis to investigate phase equilibria in the $CaO-TiO_2-ZrO_2$ system in the temperature range of 1450-1550 °C. The results of their investigation are depicted in Fig. 1. They found a single ternary phase, zirconolite ($CaZrTi_2O_7$), to exist at this temperature. Additionally, they found that the perovskite phases $CaTiO_3$ and $CaZrO_3$ formed a series of continuous solid solutions, and further observed the existence of extensive ternary regions of $ZrO_2$(c) and $ZrO_2$(t). (The letters *c*, *t* and *m* denote cubic, tetragonal and monoclinic modifications of $ZrO_2$, respectively.)

Rossell and coworkers[5,14,15] were the first to determine the crystal structure of zirconolite. They described the phase as a monoclinically distorted, anion-deficient, fluorite related superstructure. Rossell also determined the phase boundaries of zirconolite as a function of temperature, using X-ray diffraction analysis[5]. He found it to contain a relatively constant concentration of 24.0-25.0 mol.% CaO. However, he observed that zirconolite existed over a significant range of compositions of $TiO_2$ and $ZrO_2$, and therefore is more correctly termed $CaZr_xTi_{3-x}O_7$. The values of $x$ were found to extend from 0.833-1.250 at 1300 °C and 0.968-1.364 at 1480 °C. Rossell also detected evidence of partial melting in Ti-rich zirconolite at 1480 °C.

A second ternary phase, calzirtite ($Ca_2Zr_5Ti_2O_{16}$), was discovered by Pyatenko and Pudovkina[16]. Its crystal structure was also determined by Rossell[17], who considered the phase to be a tetragonal, fluorite-based superlattice structure comprising 18 anion-deficient fluorite subcells . According to Rossell, calzirtite decomposes into zirconolite, perovskite and $ZrO_2$ at about 1400 °C, which explains its absence in the phase diagram of Coughanour *et al.*

Figueiredo and coworkers[3,4] used X-ray diffraction analysis to investigate phase equilibria in the $CaO-TiO_2-ZrO_2$ system at 1300 °C. Their results are in general agreement with those of Coughanour *et al.* and Rossell and coworkers. They confirmed the existence of zirconolite and calzirtite, and established some additional phase equilibrium relationships in the ternary system. However, some of their experimental results, primarily those for samples containing more than 40-50 mol.% CaO, were not self-consistent, nor were they consistent with the results obtained from samples containing lower concentrations of CaO. The experimental results of Figueiredo and coworkers for samples containing less than 40 mol.% CaO have been reproduced in Fig. 2.

The results of the present investigation are depicted in Fig. 3. Gross sample compositions, the phases detected in each sample by X-ray diffraction analysis, and the compositions of the phases

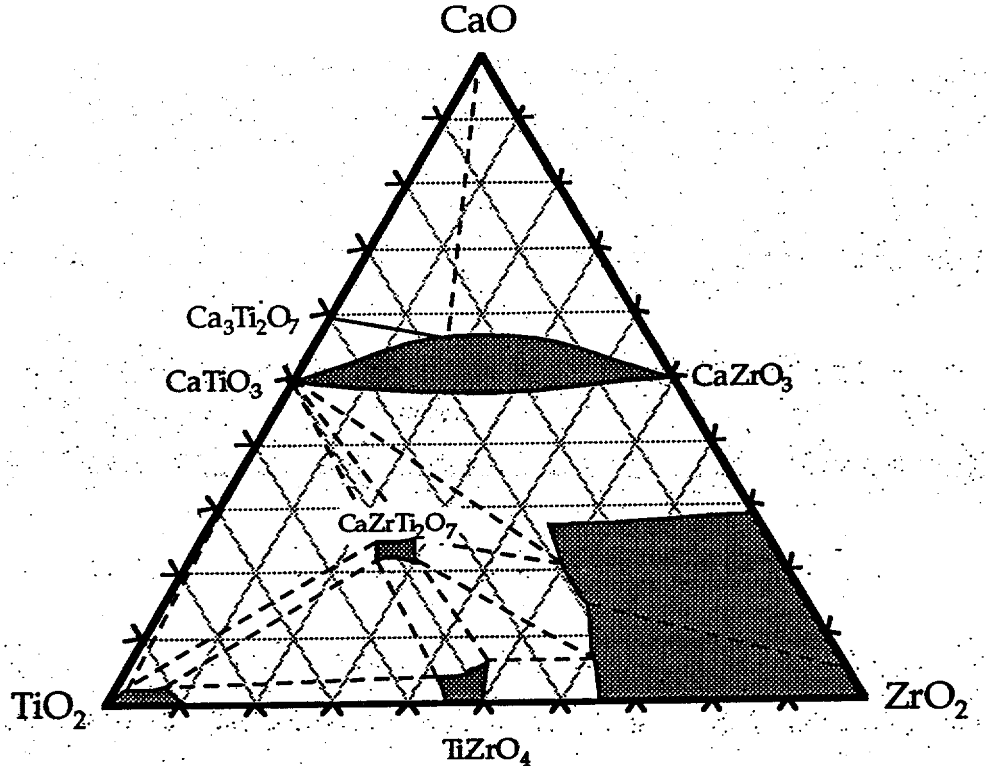

**Fig. 1.** **Phase Equilibria in the CaO-$TiO_2$-$ZrO_2$ System at 1450-1550 °C according to Coughanour et al.[2]. The dashed line in the phase $ZrO_2$ denotes the approximate boundary between the region of stability of $ZrO_2(t)$ (lower) and the region of stability of $ZrO_2(c)$ (upper).**

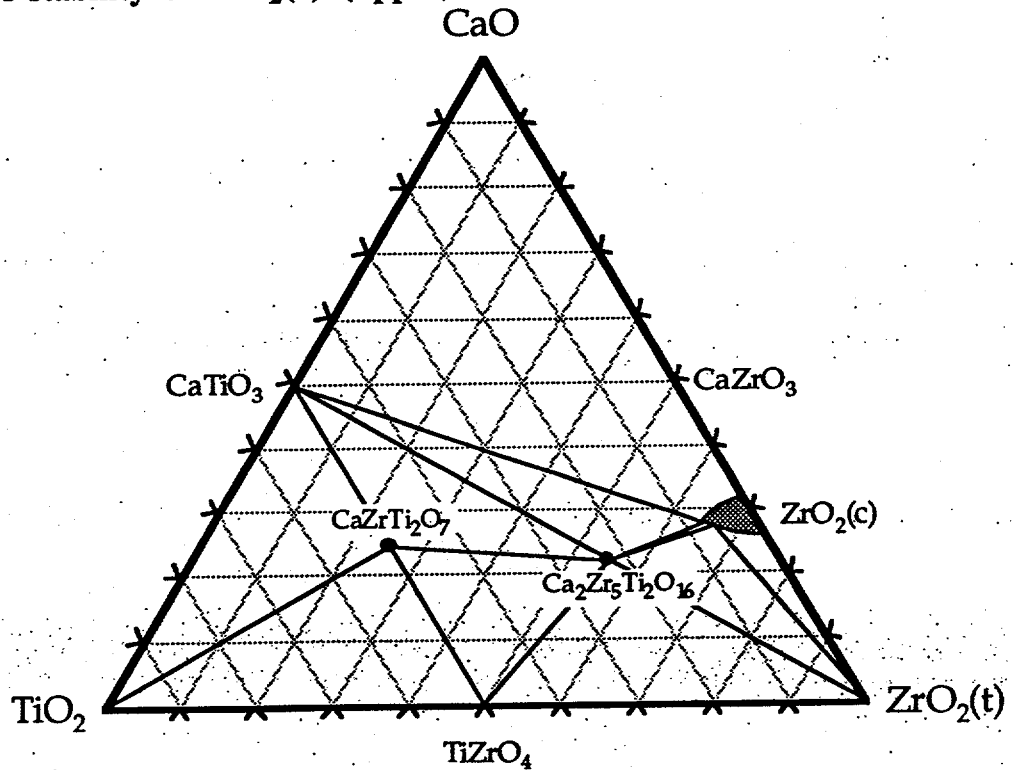

**Fig. 2.** **Phase equilibria in the CaO-TiO2-ZrO2 system at 1300 °C, based on the work of Figueiredo and coworkers[3,4]. Only those samples containing less than 40 mol.% CaO have been considered in drawing the figure.**

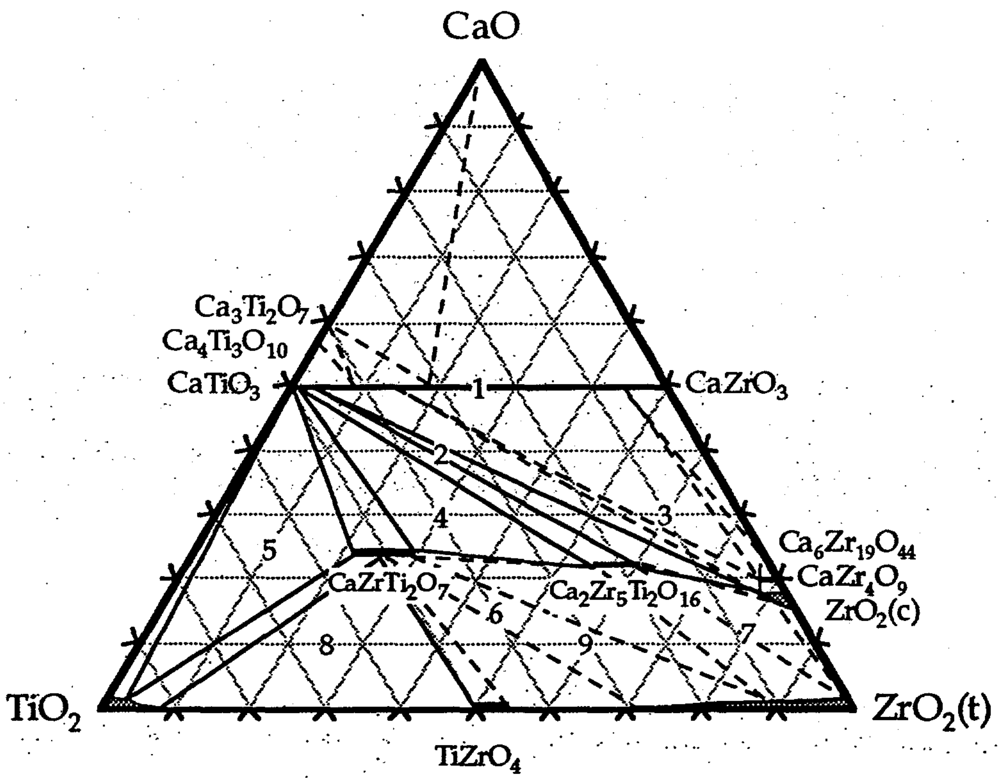

**Fig. 3. Phase equilibria in the CaO-$TiO_2$-$ZrO_2$ system at 1200 °C. The numerals within the diagram represent the gross sample compositions and sample numbers used in the present investigation. The phases identified in each sample by X-ray diffraction and the compositions of these phases as determined by EPMA are given in Table 1. Dashed lines represent tie-lines inferred from the phase rule.**

as determined by EPMA are given in Table 1. The presently determined 1200 °C isotherm is consistent with the 1450-1550 °C diagram of Coughanour *et al.* (Fig. 1), considering the fact that calzirtite, $CaZr_4O_9$ and $Ca_6Zr_{19}O_{44}$ are all unstable above 1400 °C. The results of the present investigation are also in relative agreement with those of Figueiredo and coworkers at 1300 °C in the compositional region below 40 mol.% CaO (Fig. 2). The only major difference between the two isotherms is that Figueiredo and coworkers found a two-phase equilibrium to exist between $TiZrO_4$ and calzirtite, whereas a tie-line between zirconolite and $ZrO_2$(t) was found to be more stable in the present investigation. There is also a slight discrepancy in the range of homogeneity of $ZrO_2$(c).

Zirconolite was found to exhibit a rather wide range of homgeneity at a constant CaO composition, in accordance with the work of Rossell[5]. In terms of the chemical formula $CaZr_xTi_{3-x}O_7$, $0.836 \leq x \leq 1.157$ at 1200 °C, based upon EPMA of samples 4 and 5. This range of values is slightly smaller than that observed by Rossell at 1300 °C. The lattice parameters of zirconolite at these limiting compositions are in very good agreement with those found by Rossell at the same compositions.

Calzirtite was found to exhibit a range of homogeneity as well, a phenomenon which has not previously been reported in the literature. As was the case for zirconolite, calzirtite is stable at a constant composition of CaO, while variation may occur in the relative amounts of $TiO_2$ and $ZrO_2$. Therefore, the chemical formula for calzirtite is more correctly written as $Ca_2Zr_{7-x}Ti_xO_{16}$, where $1.564 \leq x \leq 2.112$ at 1200 °C, according to EPMA data for samples 2 and 4. As ideally $x = 2$, it may be seen that the most $TiO_2$-rich composition of calzirtite essentially corresponds to the ideal stoichiometric formula unit. The lattice parameters of calzirtite do not change significantly with composition. Those of sample 4 (corresponding to the $TiO_2$-rich limit) were found to be $a = 1.5105$ nm and $c = 1.0258$ nm, whereas those of sample 2 (corresponding to the $ZrO_2$-rich limit) were determined to be $a = 1.5217$ nm and $c = 1.0130$ nm.

Table I. Gross Sample Compositions, Phases Identified by X-Ray Diffraction, and Composition of Phases in the $CaO$-$TiO_2$-$ZrO_2$ System Determined by EPMA

| Sample Number | Gross Composition (mol.%) | | | Phases Identified by X-Ray Diffraction | Composition of Phases (mol.%) | | |
|---|---|---|---|---|---|---|---|
| | $CaO$ | $TiO_2$ | $ZrO_2$ | | $CaO$ | $TiO_2$ | $ZrO_2$ |
| 1 | 50.0 | 25.0 | 25.0 | $CaZrO_3$ | 49.7(4)[a] | 10.8(28) | 39.5(27) |
| | | | | $CaTiO_3$ | 49.9(1) | 39.2(1) | 11.0(1) |
| 2 | 40.0 | 35.0 | 25.0 | $CaTiO_3$ | 49.3(6) | 47.8(13) | 2.9(13) |
| | | | | $ZrO_2$(c) | 18.3(3) | 3.7(1) | 78.0(3) |
| | | | | $Ca_2Zr_5Ti_2O_{16}$[b] | 22.1 | 17.4 | 60.5 |
| 3 | 30.0 | 10.0 | 60.0 | $CaZrO_3$ | 49.4(4) | 17.0(12) | 33.6(11) |
| | | | | $CaZr_4O_9$ | 19.8(4) | 2.6(4) | 77.6(7) |
| 4 | 30.0 | 40.0 | 30.0 | $Ca_2Zr_5Ti_2O_{16}$ | 22.1(3) | 23.5(3) | 54.4(4) |
| | | | | $CaZrTi_2O_7$ | 24.9(4) | 46.2(6) | 29.0(3) |
| | | | | $CaTiO_3$ | 48.7(5) | 50.5(3) | 0.8(5) |
| | | | | $ZrO_2$(m)[b] | 0.2 | 3.4 | 96.4 |
| 5 | 25.0 | 65.0 | 10.0 | $CaZrTi_2O_7$ | 24.6(2) | 54.4(4) | 21.0(3) |
| | | | | $CaTiO_3$ | 49.1(4) | 50.8(4) | 0.3(0) |
| | | | | $TiO_2$ | 1.1(6) | 96.0(2) | 2.6(3) |
| 6 | 15.0 | 40.0 | 45.0 | $CaZrTi_2O_7$ | 24.3(3) | 49.9(5) | 25.8(5) |
| | | | | $ZrO_2$(m) | 0.4(2) | 13.8(1) | 86.0(4) |
| | | | | $TiO_2$ | 0.4(1) | 91.6(0) | 8.1(0) |
| 7 | 12.0 | 8.0 | 80.0 | $ZrO_2$(m) | 1.9(7) | 1.4(4) | 96.7(11) |
| | | | | $Ca_2Zr_5Ti_2O_{16}$ | 21.8(1) | 18.0(4) | 60.3(3) |
| 8 | 10.0 | 65.0 | 25.0 | $CaZrTi_2O_7$ | 23.5(1) | 51.1(9) | 25.5(8) |
| | | | | $TiZrO_4$ | 0.2(1) | 50.1(12) | 49.8(13) |
| | | | | $TiO_2$ | 0.3(1) | 91.9(3) | 7.8(3) |
| | | | | $ZrO_2$(m)[b] | 0.1 | 29.2 | 70.7 |
| 9 | 10.0 | 30.0 | 60.0 | $CaZrTi_2O_7$ | 24.1(3) | 49.6(6) | 26.3(9) |
| | | | | $ZrO_2$(m) | 0.1(1) | 13.8(1) | 86.1(1) |

[a] Numerals in parentheses represent the estimated standard deviations in the last significant digit of the composition, based on an average value of several experimental data points.

[b] Composition based on one experimental data point.

As was mentioned previously, Coughanour *et al.* found a series of continuous solid solutions to exist between $CaTiO_3$ and $CaZrO_3$. However, in the present investigation only limited, although significant, mutual solubility was observed. According to EPMA of sample 1, a symmetrical miscibility gap exists between the phases, with each perovskite phase dissolving a maximum of 22 mol.% of the other. A variation of a 1-3 mol.% $TiO_2$ and $ZrO_2$ was found in each perovskite phase during probing, suggesting that the samples were inhomogeneous. The X-ray diffraction pattern of sample 1 exhibited very broad peaks, ranging roughly from those expected for a $CaTiO_3$ to those anticipated for $CaZrO_3$. The diffraction pattern therefore indicated either that the individual perovskite grains were very small or that ternary perovskites of several different compositions were present simultaneously, and hence the sample was not at thermodynamic equilibrium. In support of the latter possibility, sample 3 contained a perovskite phase with a composition inside the miscibility gap present in sample 1. However, it should be noted that a variation of a 1 mol.% $TiO_2$ and $ZrO_2$ was also found in the composition of the perovskite phase in sample 3. Based on these observations and the work of Coughanour *et al.*, it seems likely that sample 1 is not in a state of thermodynamic equilibrium, and a series of continuous solid solutions exists between $CaTiO_3$ and $CaZrO_3$ at 1200 °C. A series of continous solid solutions between the two perovskite phases has therefore tentatively been depicted in Fig. 3. However, more work, involving longer annealing times and repeated sample grindings, must be performed to resolve this issue.

Finally, it should be noted that samples 4 and 6 contained $ZrO_2$ in addition to three other phases, indicating that they did not fully reach thermodynamic equilibrium. Moreover, sample 8 contained rutile in addition to zirconolite and $ZrO_2$, which is inconsistent with thermodynamic equilibrium in the system. However, the amount of nonequilibrium phase in each sample was very small, and therefore the majority phases present in all three samples are likely to represent the true equilibrium state of the system.

## The Solubility of Hf in Zirconolite

As Zr and Hf are in the same group of the periodic table and have virtually identical ionic radii[18], one would expect that Hf would substitute readily for Zr in zirconolite. Only one such attempt to fabricate a Hf analog of zirconolite ($CaHfTi_2O_7$) has been reported in the literature. McCauley and Hummel[19] fabricated a sample of the composition $CaHfTi_2O_7$ during an investigation of the existence of ordered pyrochlores of the type $A^{2+}B^{4+}Ti_2O_7$. The sample, which was fabricated directly from the oxides, was annealed at 1450 °C for 48 hr and analyzed by X-ray diffraction analysis. While no diffraction pattern or crystal structure was reported, the resulting diffraction pattern was described as being similar, although not identical to that of zirconolite.

In the present investigation, three $HfO_2$-bearing samples were fabricated, with gross sample compositions of $CaHfZrTiO_7$, $CaHfTi_2O_7$, and $25CaO:10HfO_2:65TiO_2$. The latter composition was anticipated to correspond to that of a Ba-hollandite-free, Hf analog Synroc, *i.e.*, $CaHfTi_2O_7 + CaTiO_3 + TiO_2$. For purposes of comparison, a stoichiometric zirconolite sample was also fabricated under the same experimental conditions. All samples were annealed at 1200 °C for 14 days. While the zirconolite sample was found to be single phase, none of the $HfO_2$-bearing samples exhibited single phase X-ray diffraction patterns subsequent to heat treatment. Moreover, each of the samples was found to contain a zirconolite-structured phase, $CaTiO_3$, $TiO_2$ and $HfO_2$, indicating that equilibrium was not achieved.

As all of the $HfO_2$-bearing samples contained the same four phases, only the sample with the gross composition corresponding to $CaHfTi_2O_7$ was analyzed in detail. Using EPMA, Hf analog zirconolite was found to be stoichiometric within experimental uncertainty, corresponding to the formula $Ca_{1.000(8)}Hf_{0.968(44)}Ti_{2.032(36)}O_7$. Nevertheless, these data indicate that $CaHfTi_2O_7$ exhibits a slight range of homogeneity between $TiO_2$ and $HfO_2$ at a constant concentration of CaO, in analogy with the ternary solubility found in zirconolite. However, the range of homogeneity of $CaHfTi_2O_7$ seems to be somewhat less $TiO_2$-rich than that of zirconolite at this temperature.

The lattice parameters of $CaHfTi_2O_7$ are only slightly larger than those of zirconolite itself ($a = 1.2455$ nm, $b = 0.7273$ nm, $c = 1.1351$ nm, and $\beta = 100.59$ °, as compared with $a = 1.24404(9)$ nm, $b = 0.72663(6)$ nm, $c = 1.13815(12)$ nm, $\beta = 100.554(8)$ ° for zirconolite[5]).

## The Solubility of Gd in Zirconolite

The dissolution of Gd into zirconolite is not as straightforward as was the case for Hf. $Gd^{3+}$ cations cannot be substitute individually for $Ca^{2+}$, $Ti^{4+}$ or $Zr^{4+}$ without violating the requirement of electroneutrality. However, electroneutrality may be maintained if two $Gd^{3+}$ cations are substituted for one $Ca^{2+}$ cation plus one $Ti^{4+}$ or one $Zr^{4+}$ cation. Owing to size considerations[18], substitution of $Ti^{4+}$ cations by $Gd^{3+}$ cations is unfeasible, and a coupled substitution of the type

$$2Gd^{3+} \longrightarrow Ca^{2+} + Zr^{4+} \qquad (1)$$

must be employed if Gd is to be incorporated into zirconolite. This coupled substitution corresponds to the general formula $Ca_{1-x}Gd_{2x}Zr_{1-x}Ti_2O_7$. Such a substitution was attempted by Rossell[9], who fabricated samples of the preceding formula with $0.12 \leq x \leq 0.20$, using the constituent oxides as starting materials and adopting a 1400 °C, 4-7 day heat treatment. Utilizing X-ray diffraction analysis, Rossell found that samples with $x = 0.20$ comprised zirconolite, a hexagonal phase and $CaTiO_3$. By reducing $x$ to 0.12, Rossell was able to eliminate the hexagonal phase, and the diffraction pattern corresponded to that of zirconolite, along with a trace of perovskite as a secondary phase.

Rossell's experiments were repeated by the present investigators at 1200 °C. A sample of the composition $Ca_{0.88}Zr_{0.88}Gd_{0.24}Ti_2O_7$ ($x = 0.12$) was fabricated and analyzed by X-ray diffraction. It was found to consist of zirconolite and a trace amount (< 2 mol.%) of $CaTiO_3$, in accordance with the work of Rossell. The lattice parameters of the zirconolite phase were determined to be $a = 1.2520$ nm, $b = 0.7288$ nm, $c = 1.1413$ nm and $\beta = 100.57°$, which agree well with the values reported by Rossell[9] ($a = 1.24997(8)$ nm, $b = 0.72863(6)$ nm, $c = 1.14029(11)$ nm, and $\beta = 100.563(8)$ °). Therefore, the phase equilibria in this system appear to change very little between 1200 and 1400 °C.

## CONCLUSIONS

Phase equilibria have been established in the $CaO$-$TiO_2$-$ZrO_2$ system at 1200 °C, using X-ray diffraction analysis and electron probe microanalysis (EPMA). The results of the present investigation are in general agreement with those of previous researchers. The existence of two ternary phases, zirconolite ($CaZrTi_2O_7$) and calzirtite ($Ca_2Zr_5Ti_2O_{16}$), has been confirmed. Zirconolite was found to exhibit a significant range of homogeneity between $TiO_2$ and $ZrO_2$ while maintaining a constant concentration of CaO. Its range of homogeneity may be expressed using the chemical formula $CaZr_xTi_{3-x}O_7$, where $0.836 \leq x \leq 1.157$ at 1200 °C. Calzirtite exhibits a range of homogeneity as well, again at a constant concentration of CaO. It may be described by the chemical formula $Ca_2Zr_{7-x}Ti_xO_{16}$, where $1.564 \leq x \leq 2.112$ at 1200 °C. A sample fabricated along the $CaTiO_3$-$CaZrO_3$ join portrays some mutual solubility between the two perovskite phases. However, owing to the appearance of its X-ray diffraction pattern and some compositional variations observed during EPMA, it appears that the sample did not reach thermodynamic equilibrium. It is possible that a series of continuous solid solutions exists between the phases under equilibrium conditions at 1200 °C, as has been found by previous researchers at higher temperatures.

X-ray diffraction analysis and EPMA have also been employed to study the solubility limits of Hf in zirconolite. Subsequent to heat treatment, all $HfO_2$-bearing samples were found to contain a zirconolite-structured phase, $CaTiO_3$ and $TiO_2$ some unreacted $HfO_2$, indicating that thermodynamic equilibrium was not achieved. Nevertheless, it was possible to demonstrate conclusively that a stoichiometric Hf analog of zirconolite, $CaHfTi_2O_7$, is thermodynamically stable at 1200 °C. Its lattice parameters have been found to be very close to those of stoichiometric zirconolite. The apparent coexistence of $CaHfTi_2O_7$, $CaTiO_3$ and $TiO_2$ strongly suggests the feasilbility of fabricating a Hf analog to Synroc. Owing to the neutron absorbing capabilities of Hf, such a formulation would be extremely attractive for use in situations where criticality is an issue, such as the immobilization of weapons-grade Pu.

Using X-ray diffraction analysis, it has also been demonstrated that Gd may be incorporated into zirconolite by the coupled substitution of 2 $Gd^{3+}$ cations for one $Ca^{2+}$ cation plus one $Zr^{4+}$ cation, which corresponds to the chemical formula $Ca_{1-x}Gd_{2x}Zr_{1-x}Ti_2O_7$. It has been found that such a substitution will lead to the formation of virtually single phase zirconolite up to at least $x = 0.12$, in agreement with the findings of other researchers working at higher temperatures. As Gd is also a good neutron absorber, the present findings indicate the potential of a Gd-bearing Synroc for use in immobilizing radioactive actinides.

## ACKNOWLEDGMENT

This work was performed under the auspices of the United States Department of Energy by Lawrence Livermore National Laboratory under Contract Number W-7405-Eng-48.

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