Intermediate Cubic Phase Crystallized from Synroc Alkoxide Precursor at 800°C

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When the alkoxide precursor to Synroc is heated to 800°C in air, a cubic oxide is formed. This phase is shown by X-ray and neutron powder diffraction to have the fluorite ($a = 4.99$ Å) rather than the pyrochlore structure. This has important implications for waste encapsulation.

Key Words: alkoxides; pyrochlore; fluorite; powder diffraction.

INTRODUCTION

Synroc is a dense titanate-based ceramic (1) designed for the incorporation of high-level waste (HLW) from the reprocessing of spent nuclear fuel. Synroc is made from an alkoxide-based precursor (2), which on drying is amorphous. On calcining in the temperature range 700–900°C the precursor forms a crystalline cubic phase, and on heating above 900°C the final Synroc phases begin to crystallize. This process is complete in the final stage of Synroc processing, namely, hot-pressing at 1100–1200°C.

A cubic phase, together with the perovskite ($CaTiO_3$), was observed (3) to form on heating a $Ca(OH)_2$–$Ti(OH)_4$ mixture in the temperature range ~600–1100°C. This cubic phase is similar to the cubic phase forming on calcination of the Synroc precursor (4). It was deduced (3) from powder X-ray diffraction (XRD) that the phase had a $Ca_2Ti_5O_{12}$ stoichiometry. However, Ball and White (5) pointed out deficiencies in this attribution, and a $Ca_2Ti_2(O,OH)_7$ pyrochlore structure was assigned.

Radiocesium in HLW tends to be volatile at the elevated temperatures involved in the processing of solids used for its immobilization. The structure of the cubic phase has implications for the Cs volatility in the calcination stage of Synroc processing since if the cubic phase has the pyrochlore structure, Cs could be incorporated into the channels of the structure and would presumably be protected to a significant extent from loss by volatility; this would not be the case for the fluorite structure.

Pyrochlore is an ordered variant of the fluorite structure, with a doubled unit cell. Distinction between the two structures is drawn from the appearance of extra reflections in XRD diffraction; the intensities of these reflections in the present case are proportional to the square of the difference of the scattering powers of Ca^{2+} and Ti^{4+}. This difference is very small and these extra peaks were not observed in XRD (3, 5). However, the thermal neutron scattering lengths of these two ions are of opposite sign, so neutron diffraction should easily distinguish between the structures.

EXPERIMENTAL

Synroc precursors were made by hydrolyzing ethanolic solutions of Ti, Zr, and Al alkoxides by the addition of aqueous slurries of Ca and Ba hydroxides (2). The overall composition was (wt%) Al_2O_3 (5.4), BaO (5.6), CaO (11.0), TiO_2 (71.4), ZrO_2 (6.6). Ti–Ca hydroxide mixtures were prepared by combining 0.01 mol/liter $Ca(OH)_2$ solutions with $Ti(OH)_4$ sols made by hydrolyzing ethanolic Ti isopropanate solutions. After being dried at ~110°C, the materials were lightly ground in a pestle and mortar and then heated in air for 1 h at temperatures between 600 and 1100°C.

X-Ray diffraction data were collected using a Siemens D500 instrument with $CoK\alpha$ radiation ($\lambda = 1.7889$ Å). Powder neutron diffraction data were obtained using a wavelength of 1.8823(2) Å on the high-resolution powder diffractometer instrument (6) attached to the Lucas Heights HIFAR reactor. Analytical transmission electron microscopy was carried out with a JEM 2000FX apparatus fitted with a Tracor Northern energy-dispersive spectrometer.

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RESULTS AND DISCUSSION

XRD and neutron powder diffraction data are shown in Figs. 1 and 2, respectively, for a Synroc precursor heated at 800°C.

The XRD pattern showed mainly the cubic phase, but weak peaks due to rutile and $CaTi_2O_5$ (7) (see also below) were also present (see Fig. 1). The major contributions to the neutron pattern were from rutile. When the rutile peaks were subtracted, the most significant remaining peaks had d spacings of 2.49 and 1.764 Å, where approximately 30% of the intensity of the $d = 2.49$ Å line derived from the (101) reflection of rutile. The peaks at $d = 2.49$ and 1.764 Å correspond to the $(200)_f$ and $(220)_f$ peaks, respectively, from a fluorite cell ($a = 4.99$ Å) or to the $(400)_p$ and $(440)_p$ peaks from the pyrochlore structure ($a = 9.98$ Å). However, the absence of the $(200)_p$ and $(220)_p$ peaks rules out the pyrochlore structure, since these peaks would be expected to be strong if pyrochlore-type ordering was present.

Given that the cubic material has the fluorite structure, with the Ca and Ti ions being disordered, the structure factors of the $h + k + l = 4n \pm 1$, $4n$, and $4n + 2$ peaks (n = integer) would be proportional to b_m^2, $(b_m + 2b_o)^2$, and $(b_m - 2b_o)^2$, respectively, where b_m and b_o are the thermal neutron scattering lengths of the average metal (m) and the oxygen ions (O), respectively. Thus the absence of the $(111)_f$, $(311)_f$, and $(331)_f$ reflections can be understood if $b_m \sim 0$, corresponding to a Ti/Ca ratio of 5:4, assuming no Zr is present in the fluorite structure under consideration. A different ratio of Ti/Ca would be applicable if Zr is present. The structure factors of the allowed $4n$ and $4n + 2$ fluorite reflections would then be proportional to b_o^2, assuming all the O positions in the fluorite structure are filled (but see below).

There was poor agreement between the intensities of the lower-index fluorite peaks calculated on the above basis and the intensities calculated using a typical value of ~ 0.8 Å^2 for the Debye–Waller temperature factor. However, the presence of a Ca ion in the fluorite structure leads to an oxygen vacancy, so for a nominal fluorite composition of $(Ti_{5/9}Ca_{4/9})O_{2-x}$, x would correspond to 4/9. Though the presence of oxygen vacancies would not in itself lead to changes in relative intensities of the observed fluorite reflections, the vacancies would lead to local displacements of the oxygen ions.

As a first approximation, the oxygen disorder present in the fluorite structure could be described by an artificial temperature factor of ~ 15 Å^2.
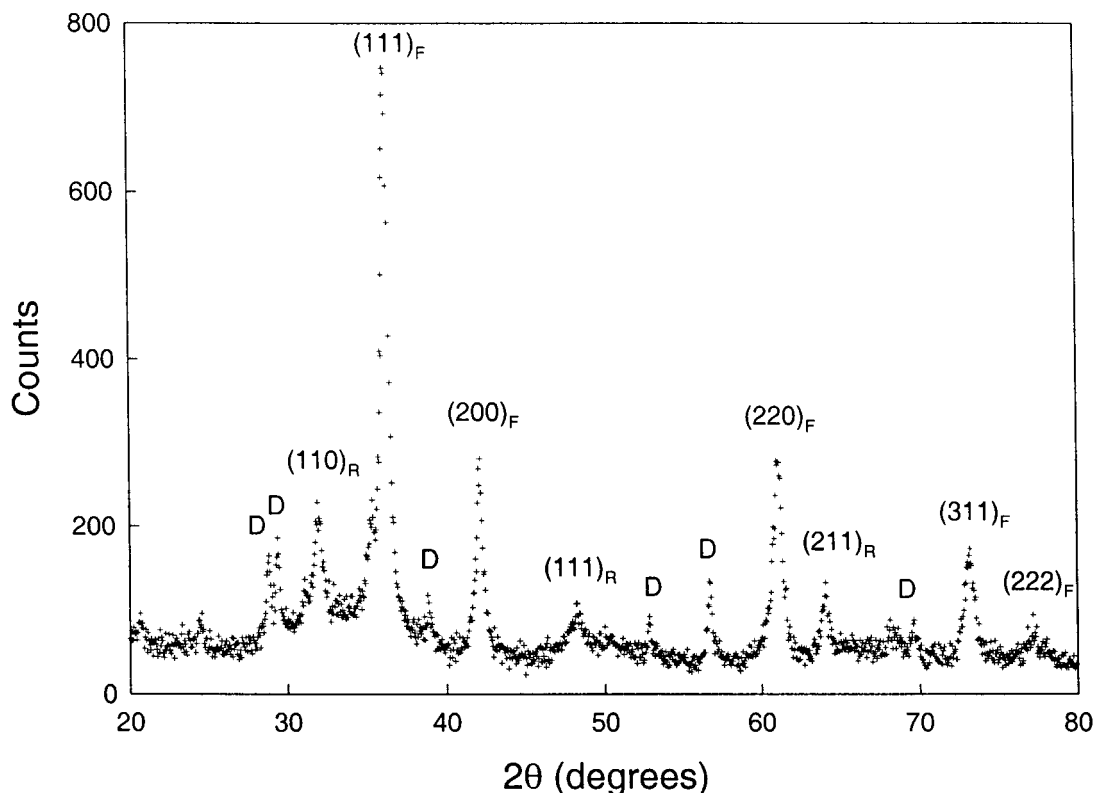

FIG. 1. X-Ray diffraction pattern of Synroc alkoxide precursor after heating 1 h in air at 800°C using $CoK\alpha$ radiation. F = cubic phase, R = rutile phase, D = $CaTi_2O_5$ phase.
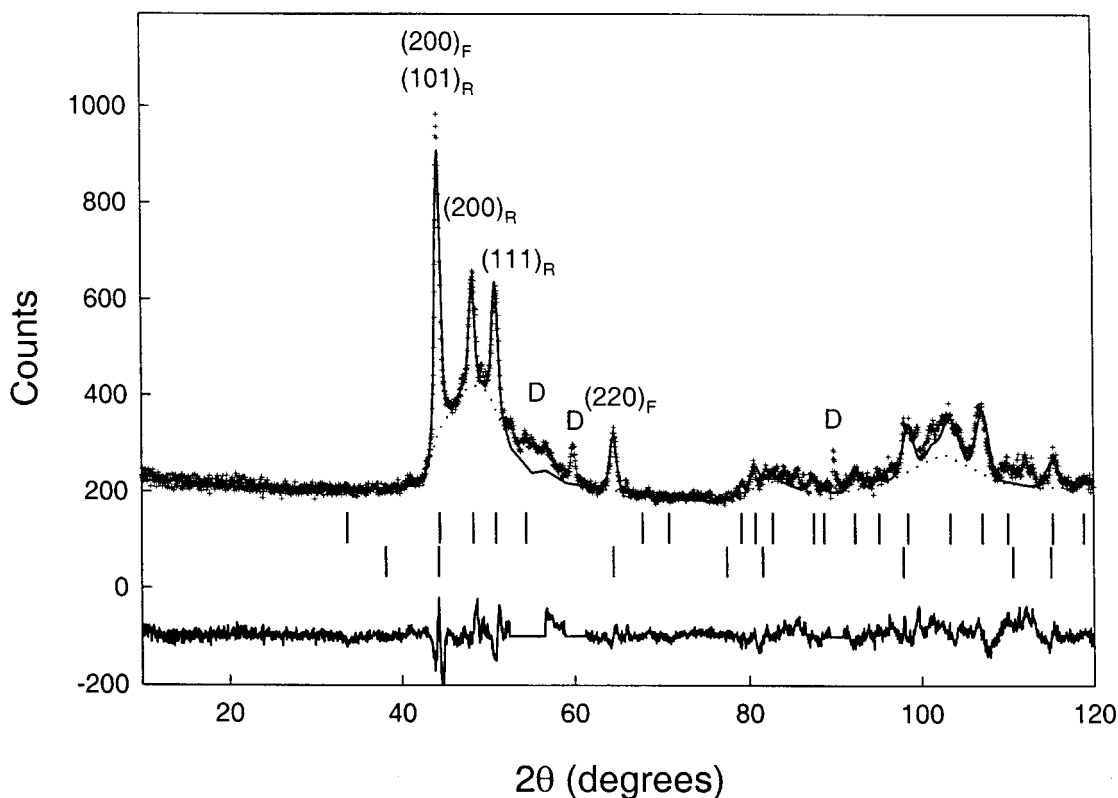
FIG. 2. Powder neutron diffraction pattern of Synroc alkoxide precursor after heating for 1 h at 800°C in air. The Rietveld fit is also shown; it includes peaks for rutile (R) and fluorite (F) structures. Major peaks from the $CaTi_2O_5$ phase are marked with the symbol D, and have been excluded from the fit.

A two-phase Rietveld analysis was carried out on the neutron powder data. The scale factors of the two phases, the fluorite-structured Ca–Ti–O phase and rutile phase, were allowed to vary and a quantitative phase analysis using the method of Hill and Howard (8) was carried out. A nonisotropic background, due to an amorphous rutile phase, was included in the refinement. The shapes of the Bragg peaks, from the essentially crystalline Ca–Ti–O and rutile phases, were initially set at the instrumental parameters of the diffractometer (6), but were eventually allowed to vary using a strain broadening model to accommodate the significant increase in widths of the Bragg peaks over the instrumental resolution function. A fixed Lorentzian term, equivalent to a particle size of 500 Å, was added to account for the large particle size-related widths.

The structural parameters were initially fixed to their ideal values for a disordered fluorite lattice. The lattice parameters were allowed to vary from those given previously (5) but the fit did not lead to significant changes.

A significant improvement in the fit was obtained by allowing the oxygen thermal parameter to vary. The value of this parameter obtained in the fit was extremely large, $B = 20(1)$ Å^2, and indicates that the oxygen in the fluorite structure is not adequately modeled. The high thermal para-

meter may be due to static displacements associated with vacancies in the oxygen sublattice or to some other structural feature not accounted for in the model. The metal site thermal parameters were also allowed to vary and refined to a small negative value. They were then fixed at a positive value of 0.5 Å^2 for the final refinement.

Using a fully occupied constraint model for the cations, the Ca/Ti sites were refined down to Ti = 0.54(1) and Ca = 0.46(1), in good agreement with the estimated values given above. The final refined values for both phases are given in Table 1, along with the measures of fit.

Quantitative phase analysis yielded a gravimetric ratio of the crystalline rutile phase to the Ca–Ti–O fluorite phase of 1 : 5.7. The quantity of amorphous phase could not be estimated due to its unknown composition. No estimates of the amount of $CaTi_2O_5$ could be made in the absence of structural information in Ref. (7). Significant lines in the neutron pattern at d spacings of 2.111, 1.885, and 1.332 Å may derive from this source. These regions were excluded from the Rietveld refinement.

The composition of the fluorite phase discussed above is not the same as that of the precursor, so noncrystalline material, as discussed above, is present. Synroc precursors heated at various temperatures between 700 and 850°C and

Rutile phase	
a (Å)	4.5977(7)
c (Å)	2.9547(8)
Ti	
$\quad x = y = z$	0
$\quad B$ (Å^2)	0.1(3)
O	
$\quad x = y$	0.3034(9)
$\quad z$	0
$\quad B$ (Å^2)	0.4(2)
CaTiO phase	
a (Å)	4.9911(7)
Ti/Ca	
$\quad x = y = z$	0
$\quad B$ (Å^2)	0.5
$\quad n$	0.54(1)/0.46(1)
O	
$\quad x = y = z$	0.25
$\quad B$ (Å^2)	20(1)
wR_p	6.29
χ^2	7.26

[a] The figures in parentheses are statistical errors in the last digit. Values without parentheses were fixed in the final refinement.

all showing mainly the cubic phase in XRD were studied by ATEM, but all were too fine-grained to obtain sufficient isolation of individual crystals. Selected area diffraction gave mainly randomly diffracted beams.

XRD and neutron diffraction results qualitatively similar to those described for the Synroc precursor were obtained with equimolar Ca(OH)$_2$–Ti(OH)$_4$ mixtures made by the alkoxide route (2) and heated to 800°C, as well as Synroc precursors containing 20 wt% simulated HLW heated to similar temperatures.

As mentioned earlier the XRD patterns of the Synroc precursor heated to 800°C yielded weak lines attributed to CaTi$_2$O$_5$ (7). Such lines were evident also in equimolar Ca(OH)$_2$–Ti(OH)$_4$ mixtures heated to 600–1100°C. Contrary, however, to the results of (7), we did not observe any XRD lines with d spacings > 9 Å. This disagreement, however, does not necessarily invalidate their conclusions about the unit cell geometry. On varying the Ca/Ti ratio between 0.5 and 10 in these mixtures, and heating in the 700–1100°C range, it could only be concluded that the yield of the CaTi$_2$O$_5$ phase was a maximum for a molar Ti/Ca ratio between 2 and 4.

CONCLUSION

The intermediate cubic phase forming when Synroc precursors are calcined at 800°C is shown to have the fluorite and not the pyrochlore structure. This has important implications in the encapsulation of waste materials.

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