Mechanical and Thermophysical Properties of Hot-Pressed SYNROC B

C. L. Hoenig
H. W. Newkirk
R. A. Otto
R. L. Brady
A. E. Brown
A. R. Ulrich
R. C. Lum

Manuscript date: May 6, 1981

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. It contains certain information that may be regarded as proprietary or confidential. It is to be distributed only to persons authorized by the Department of Energy. It is not to be distributed outside the Department of Energy. It is not to be used for any purpose other than that for which it was prepared. It is not to be reproduced or transmitted in any form or by any means electronic or mechanical, including photocopying and recording, or by any information storage or retrieval system, except as may be permitted in writing by the Department of Energy. The views and conclusions contained herein are those of the authors and are not necessarily endorsed by the United States Government.

LAWRENCE LIVERMORE LABORATORY
University of California • Livermore, California • 94550

Available from: National Technical Information Service • U.S. Department of Commerce
5285 Port Royal Road • Springfield, VA 22161 • \$5.00 per copy • (Microfiche \$3.50)

CONTENTS

List of Illustrations	iii
List of Tables	iii
Abstract	1
Introduction	1
Experimental	1
Sample Preparation	1
Flexural Strength (Modulus of Rupture)	6
Compressive Strength	7
Ultrasonic Properties	8
Thermal Expansion	8
Thermal Conductivity	9
Microhardness	10
Results and Discussion	10
Conclusions	14
References	15

LIST OF ILLUSTRATIONS

1. Vibro Energy Mill for use in grinding SYNROC powder	2
2. A 75-ton Centorr hot press	3
3. Graphite die for hot pressing a 15.2-cm-diam SYNROC sample	3
4. SYNROC sample after hot pressing	4
5. SYNROC sample after surface grinding	4
6. SYNROC sample after being cut and ground into special shapes	5
7. Scanning electron microscopy of SYNROC B	6
8. Probe assembly of thermal comparator	9
9. Thermal expansion of SYNROC B	12

LIST OF TABLES

1. Nominal oxide composition of SYNROC	1
2. Reference standards used for thermal conductivity test	10
3. Ultrasonic test report on SYNROC B M05HP4A	10
4. Mechanical properties of SYNROC	11
5. Thermal expansion of SYNROC B	13
6. Thermal-expansion coefficients of various titanates and SYNROC B	13
7. Thermal conductivity of TiO_2 , titanates, and SYNROC B and C	14

Mechanical and Thermophysical Properties of Hot-Pressed SYNROC B

ABSTRACT

The optimal SYNROC compositions for use with commercial waste are reviewed. Large amounts of powder (about 2.5 kg) were prepared by conventional ceramic operations to test the SYNROC concept on a processing scale. Samples, 15.2 cm in diameter, were hot pressed in graphite, and representative samples were cut for microstructural evaluations. Measured mechanical and thermophysical properties did not vary significantly as a function of sample location and were typical of titanate ceramic materials.

INTRODUCTION

The SYNROC concept for incorporating radiation-waste (rad-waste) elements in a synthetic, titanate mineral assemblage was introduced by Ringwood in 1978.^{1,2} These concepts are being applied to U. S. defense wastes by the Mineral Waste Form Program at LLNL. SYNROC B, a basic waste form without rad-waste elements, consists primarily of three titanate-mineral phases—zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3), and a hollandite analogue ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). The results of

other studies on the application of SYNROC C to commercial wastes³⁻⁶ and of SYNROC D to U. S. defense waste⁷⁻¹¹ are reported elsewhere.

The purpose of this study is to evaluate some of the mechanical and thermophysical properties of basic SYNROC B that are important to risk-analysis studies concerned with the preparation, transportation, and storage of nuclear waste. These results will also be compared with later formulations of SYNROC C and D.

EXPERIMENTAL

SAMPLE PREPARATION

The oxide composition (M05) used in this study is shown in Table I. Also shown in Table I is a recent and improved formulation recommended by Ringwood² in which the nominal molecular ratio for hollandite ($\text{BaO}:\text{Al}_2\text{O}_3:\text{TiO}_2$) was changed from 1:1:6 to 1:1:7.

In a typical formulation for commercial waste, Ringwood proposes 88 wt% SYNROC, 2 wt% Ti metal, and 10 wt% waste.

The starting materials were pigment-grade TiO_2 rutile (N.L. Chemical Co., South Amboy, N. J. 08879); zirconium dioxide (ZrO_2) reactor grade, Teledyne Wah Chang, Albany, Oregon 97321); and reagent grade hydroxides of barium, calcium, and aluminum. We now prefer to use an

TABLE I. Nominal oxide composition of SYNROC.

Oxide	M05 ^a (wt%)	Ringwood's ^b preferred (wt%)
TiO_2	57.2	62.2
CaO	16.2	10.0
ZrO_2	12.8	6.9
BaO	8.3	15.0
Al_2O_3	5.5	5.9
	100.0	100.0

^aComposition calculated on the basis of 40 wt% hollandite (1:1:6), 38 wt% zirconolite, and 25 wt% perovskite.

^bComposition calculated on the basis of 37.0 wt% hollandite (1:1:7), 32.4 wt% zirconolite, 23.1 wt% perovskite, 7 wt% TiO_2 , and 1 wt% Al_2O_3 .

anatase grade of TiO_2 , which we find to be more reactive in the synthesis of SYNROC mineral phases.

A batch with an oxide equivalent of about 2.5 kg was cone blended with a high intensity bar for 16 hours. The powders were then calcined in air at 1000°C for 16 hours to a constant weight and

ground as an aqueous slurry with Al_2O_3 balls in a Sweco Vibro Energy Mill, model M18-5 (see Fig. 1). The powder mixture was air dried at 200°C and cone blended a second time for 18 hours. An x-ray pattern of this powder showed only perovskite formation plus unreacted TiO_2 , ZrO_2 , and some unidentified peaks.

FIG. 1. Vibro Energy Mill for use in grinding SYNROC powder.

We conducted preliminary small-scale 1.6-cm-diam hot pressings to establish the temperature, pressure, and time parameters necessary to achieve 99% of theoretical density which was taken as 4.23 g/cm³ and was based on the pycnometric density of SYNROC B crushed and ground to -325 mesh powder.

For the large hot pressing (15.2-cm-diam), we prepressed 800 g of powder at 2000 psi in an ATJ graphite die to a density of 1.91 g/cm³ (45% of theoretical). The graphite die was positioned by hand onto the lower platen of a double-acting hot press (Fig. 2 and 3), which could be operated in either a vacuum or an inert-atmosphere. A 3-phase, tungsten-mesh heating element surrounded the graphite die and punches. Temperature was measured by thermocouple and optical pyrometer.

The sample (M05HP4A) was slowly heated under vacuum (10^{-4} Torr) to 1200°C in 4 hours under a uniaxial pressure on the sample of 800 psi. At 1200°C, the maximum pressure of 2000 psi was applied and maintained for a 1-hour period under a

FIG. 2. A 75-ton Centorr hot press.

FIG. 3. Graphite die for hot pressing a 15.2-cm-diam SYNROC sample.

vacuum of 7.0×10^{-5} Torr. At the end of the hold period, the pressure was released and furnace power was terminated. The sample cooled slowly to room temperature over a period of 16 hours. The sample was easily removed from the graphite die, and no visual reactions between the sample and graphite die were observed. The hot-pressed sample is shown in Fig. 4, and the sample after surface grinding in Fig. 5.

The sample was then cut and ground into special shapes for studies of mechanical and thermophysical properties. The finished specimens are shown in Fig. 6. Four samples for ultrasonic testing (a) were taken from the center and edge locations, two each, of the large disc to assess property variations across the diameter. Two larger samples (b) for tests of flexural strength (modulus of rupture) were taken from an intermediate edge-to-center location. Two samples for thermal expansion (c) were taken from edge and center locations. Samples for compression testing (d) and bearing blocks to minimize end effects were also taken from edge and center locations.

FIG. 4. SYNROC sample after hot pressing.

FIG. 5. SYNROC sample after surface grinding.

FIG. 6. SYNROC sample after being cut and ground into special shapes for use in studies of mechanical and thermophysical properties. Specimens were cut from center and edge locations of sample disc to assess property variations across the diameter. (a) Samples for ultrasonic testing. (b) Samples for flexural strength (modulus of rupture). (c) Samples for thermal expansion. (d) Samples for compression testing and for bearing blocks to minimize end effects.

The microstructure and phase development of SYNROC B were studied by scanning electron microscopy (SEM) and x-ray diffraction. In Fig. 7, the SEM micrograph shows grain sizes on the order of 1 μm . The mottled phase is a mixture of perovskite and zirconalite, and the dark phase is hollandite. An x-ray diffraction pattern showed all three SYNROC phases to be well developed, with only trace amounts of unknown phases.

The broken samples from flexural strength testing were sent to Dr. S. M. Wiederhorn, Fracture and Deformation Division, National Bureau of Standards, for fracture property studies including critical stress intensity to determine fracture and stress corrosion resistance.

FLEXURAL STRENGTH (MODULUS OF RUPTURE)

Tests for tensile strength of brittle ceramics are difficult to conduct. The low ductility of these materials makes them sensitive to the high localized stresses present at the grip contacts near the ends of samples. Therefore, a very high probability exists that premature fracture will be initiated in the grip region of the specimen.

Close approximations of the monotonic tensile strength can be obtained by two alternate tests, the

flexural (modulus of rupture) test and the diametral compression test.¹²⁻¹⁴ The latter test uses a compressive loading applied along the diameter of a cylinder and results in tensile stresses across the specimen.

For this investigation, we have chosen the flexural test in which an increasing force is applied, either by one centered or by two evenly spaced contacts. For valid testing of brittle material, such contacts with the beam must be with transfer members having a rounded impresser and pivotal action. The radius of the support assures a nonlocalized distribution of bearing stress. The pivotal action of these contacts is desired so that any possible bowing existing in the specimens may be matched. The two usual parameters recorded in this test are, first, bending force and, second, deflection of the center lower surface of the beam. These measurements are taken on an X-Y recorder as a force-vs-deflection plot. A pre-test alignment procedure is performed to position the specimen and the deflection transducer accurately. In this procedure, loading cycles at low levels (safely below yielding) are first imposed on the specimen. Positional accuracy is then noted on the plotter output and corrections are made by refinement of the specimen position.

The dimensions of flexural specimens in this study were selected within a given relationship of thickness, width, and length and were 0.190, 0.50,

FIG. 7. Scanning electron microscopy of SYNROC B.

and 4 in., respectively. We decided to perform a four-point rather than a three-point test. The former produces a "field" of maximum stress on the lower surface of the specimen. The selected specimens were supported during the test on 3-in. centers to oppose a bending force applied by a pair of contacts having 0.125-in. radii and a 1-in. separation. These dimensions agree with relationships suggested by ASTM specifications.¹⁵ Two material properties are determined from these flexural tests, specifically, modulus of rupture (M/R) and bending modulus (E_B).

Modulus of rupture (flexural strength) is essentially a measure of the maximum stress (during bending) at the lower beam surface at the instant of fracture. The formula for determining maximum stress for the four-point flexure test is as follows:

$$S_{\max}(M/R) = \frac{PL}{bd^2}$$

where $S_{\max}(M/R)$ is maximum stress (psi), P is maximum force (lb), L is support span (in.), b is beam width (in.), and d is beam thickness (in.).

Bending modulus (modulus of elasticity in bending) is a measure of the elastic stiffness of the material in a simple beam configuration. A plot of bending force vs bending deflection for a specimen of consistent density and regularly distributed surface flaws is expected to exhibit a linear elastic response. The slope of this line is the bending modulus of elasticity. The formula for a four-point flexure test is as follows:

$$E_B = \frac{0.21 L^3 m}{bd^3}$$

where E_B is modulus of elasticity in bending (psi), 0.21 is constant for rectangular beam, L is support span length (in.), m is slope of tangent of initial straight line of the plot (lb/in.), b is specimen width (in.), and d is specimen thickness (in.).

COMPRESSIVE STRENGTH

The determination of valid compressive mechanical properties of a material requires the careful selection of appropriate specimens and

procedures.¹⁶ One of the first considerations is the specific dimensions of the specimen. To determine properties (i.e., elastic modulus and monotonic compressive strength) with precision, a right-circular-cylindrical specimen is a virtual necessity. A minimum cylinder-length-to-diameter ratio of 6 to 1 must be maintained to assure a condition of pure uniaxial (monotonic) stress. Under this criterion, specimen length will be sufficient to provide uniform strain in the center region of the specimen during the entire test. This central region is the site for the fixing of electrical strain gages, clip gages, or other types of deflection transducers. This region should be restricted to only one-third of the specimen length, to again assure that this included volume of material is unaffected by the frictional constraint of the specimen ends.

Only a single specimen, 0.5 in. in diameter by 3 in. in length, was available at this stage of our test program. Bearing blocks, 1.25 by 1.25 by 0.5 in., were cut of the same material and were used as loading members at the ends to reduce the likelihood of premature spallation. The use of bearing blocks serves to modify and distribute stress concentrations caused by the mismatch between SYNROC with its high degree of stiffness and steel platens that have a low degree of stiffness.

Pretest alignment of the specimen to eliminate or minimize bending loads is a necessity for accurate compression determinations on a brittle material. For this test, an LLNL-designed alignment fixture is employed. This fixture is a manually operated assembly that is topped by a circular platen upon which the specimen is centered. The unit is capable of producing both a tipping action (off the horizontal) and a lateral displacement of the platen. Adjustment for correctional specimen alignment is guided by the mounting of three clip gages (Instron extensometers) at 120° positions around the center third of the specimen. The deflection output signal of each of these transducers, as well as that for corresponding force, is directed to a plotter. By observing the relation of these traces, we can modify specimen bending (an indication of misalignment).

Two material properties of the specimen are evaluated. In addition to the ultimate compression fracture strength, a stiffness measurement that is expressed by elastic modulus (Young's modulus) is determined.

The compressive fracture strength is expressed as follows:

$$S_c = \frac{P_B}{A_0}$$

where S_c is compressive fracture strength (psi), P_B is breaking load (lb), and A_0 is specimen cross-sectional area (in.²).

Through interpretation of the load-vs-deflection plot, we obtain the value for Young's modulus by determining the slope of the line to the limit of its linear region. The modulus is calculated, from the load increments and the corresponding extension increments at two points on the line, by applying the following equation:

$$E_c = L_0 \Delta_p / A_0 \Delta_e$$

where E_c is Young's modulus-compression (psi), L_0 is original gage length (in.), Δ_p is load increment (lb), A_0 is original cross-sectional area (in.²), and Δ_e is extension increment (in.).

ULTRASONIC PROPERTIES

The method used to determine the ultrasonic properties of materials is well documented in the literature.¹⁷⁻²¹ The technique employed (in part) in these SYNROC studies is the "Pulse-Overlap Method" developed by Papadakis.²²⁻²⁴ One pulse overlap system was purchased from Matec Corporation and another from Panametrics, Inc. No absolute corrections were attempted for phase shifts caused by the junction of the near-field and far-field echoes of ultrasound. Neither were corrections made for the seal interfaces. The ultrasound velocity corrections as a percentage of the measured velocities are very small unless the specimen is thin and also has very high moduli. The use of highly damped, high-frequency, ultrasonic transducers coupled with a digital exciting pulse permits an accuracy of one part per thousand with most specimens. The additional computational and experimental time required to correct the velocities to an accuracy of one part per hundred thousand is usually not justified. First, it may not be cost effective; and second, the thickness and parallelism of

the specimens may not be uniform enough or accurate enough to meet the stringent requirements for making such velocity corrections.

THERMAL EXPANSION

Thermal expansion measurements on SYNROC were performed according to ASTM E-228-71 (Standard Test Method for Linear Expansion of Rigid Solids with a Vitreous Silica Dilatometer). Minor modifications were made to the dilatometer and test procedure.

The thermal linear-expansion apparatus consists of a Brinkman furnace with a two-inch constant heating zone, a West cam-driven temperature-ramping controller, an LLNL designed, horizontal-positioned, quartz dilatometer with a linear voltage-displacement transducer (LVDT). Type S (Pt-10% Rh) thermocouples are used for temperature measurement and control.

A thermocouple is attached to the test specimen by tightly wrapping a platinum wire around both the bead of the thermocouple and the test specimen. The latter is then inserted into the quartz-tube dilatometer, ensuring the correct alignment of the test specimen, transmission rod, and LVDT. This entire assembly is inserted into a quartz protection tube such that the test specimen is located in the furnace zone of constant temperature. Inert argon gas flows around the test specimen for the duration of the test. The heating rate to 950°C is approximately 3°C/minute. The length change versus temperature is traced with an X-Y recorder during the test.

The SYNROC test specimens were rods, 2.54 by 0.48 by 0.48 cm. Two test runs were made for each of the two specimens submitted. Ten points were selected from the trace of the change in length vs temperature. For the reported data, we made corrections for changes in length of the quartz dilatometer by using the following formula:

$$\Delta L/L_0 = (\Delta L)_a/L_0 + (\Delta L)_s/L_0$$

where L_0 is length of test specimen at ambient temperature, $(\Delta L)_a$ indicates apparent changes in specimen length in going from test temperature T_1 to temperature T_2 , and $(\Delta L)_s/L_0$ is change in length per unit length of quartz in going from T_1 to T_2 .

THERMAL CONDUCTIVITY

The thermal conductivity at room temperature was measured approximately and compared to reference standards by using a thermal comparator (TPRC Thermal Comparator, Model 100, McCloye Park Corporation, 2595 Yeager Road, West Lafayette, Indiana 47906).

The thermal comparator registers the rate of cooling experienced by the tip of a heated probe in contact with the surface of a material. The probe assembly, shown schematically in Fig. 8, consists of a sensing tip, a heater, and a thermal reservoir, held at temperature T_1 above the room temperature T_2 . Upon contact of the surface of the material (thermal conductivity λ_2) with the probe tip, of thermal conductivity λ_1 , the temperature of the tip of the probe quickly drops to an intermediate temperature T_c , according to the relation

$$T_c = \frac{T_1 \lambda_1 + T_2 \lambda_2}{\lambda_1 + \lambda_2}$$

The thermal comparator employs a thermocouple whose thermoelectric junction is very

near the end of the sensing tip and is differentially connected with another junction located within the thermal reservoir. This differential reading $T_1 - T_c$ is given by

$$T_1 - T_c = \lambda_2(T_1 - T_2)/(\lambda_1 + \lambda_2)$$

The exact location of the sensing thermocouple tip is vital to the proper operation of the comparator. Maximum sensitivity and freedom from influence of load (pressure) is obtained when the thermocouple junction is at the contact interface. This condition obtains when the probe material and the test sample constitute the two elements of the thermocouple. Because this condition does not generally obtain in practice, experience requires that the thermocouple be located as close to the tip as possible and that the load on the probe be carefully controlled to a constant value. The reference standards used in this test are given in Table 2. Our measured values were accurate to within $\pm 10\%$.

FIG. 8. Probe assembly of thermal comparator.

MICROHARDNESS

Hardness measurements were made with a Knoop indenter using a Leitz Durimet Small-Hardness Tester (Ernst Leitz (Canada) Ltd., Midland, Ontario). Measurements were taken with 50-, 100-, and 500-gram loads. Average values were determined from three to six measurements, and errors were reported as the standard deviation (σ).

TABLE 2. Reference standards used for thermal conductivity test.

Material	Thermal conductivity (W/m/K)
Ebonite	0.18
Code 7740 glass	1.15
Fused quartz	1.4
No. 110 AT (Ti, 5Al, 2.5Sn) alloy	7.8
No. 316 stainless steel	14
Armco iron	75

RESULTS AND DISCUSSION

The ultrasonic test results of four samples from edge and center locations are shown in Table 3. Averaged values are shown in Table 4 with the combined results of the other tests.

The ultrasonic velocity measurements on SYNROC were performed with highly damped transducers having nominal frequencies of 5 and 10 MHz for determining the distortional and compressional wave speeds, respectively. The transducers were fitted with a low-acoustic-impedance delay line to avoid phase reversals between echoes from the SYNROC samples. The first and second echoes returning from the SYNROC overlapped on the os-

cilloscope screen, and the frequency required to produce this overlap was recorded. The frequency is easily measured to six or seven places. The visual ability to produce the overlap depends on the surface finish, thickness, parallelism, and homogeneity of the specimen. The surface finish of the SYNROC samples was such that it was amenable to visual overlap precisions of one in twenty thousand frequency. Rotation of the distortional-wave-particle direction did not change the frequency that produced the overlap. Therefore, it is concluded that the samples were each isotropic and essentially strain free in rotation through the faces.

TABLE 3. Ultrasonic test report^a on SYNROC B M05HP4A.

Property	Edge location		Center location	
	1	2	1	2
Geometry	1.27 by 1.27 by 0.38 cm			
Frequency (V_L)	10 MHz			
Frequency (V_S)	5 MHz			
Thickness (mm)	3.795	3.798	3.797	3.796
Density (kg/m^3)	4232	4232	4234	4236
Long. velocity (m/s)	7945	7952	7948	7950
Shear velocity (m/s)	4327	4327	4325	4330
Thin-rod velocity (m/s)	6947	6949	6946	6953
Poisson's ratio	0.28919	0.28966	0.28968	0.28907
Bulk modulus (MPa)	161,484	161,951	161,671	161,798
Shear modulus (MPa)	79,219	79,240	79,194	79,423
Young's modulus (N/mm^2)	204,255	204,386	204,271	204,765

^aMFE 80-177, ET No. 7007 Nov. 7, 1980: Ultrasonic velocities are estimated to be correct to about 1%. All specimens appeared isotropic to shear wave propagation.

TABLE 4. Mechanical properties of SYNROC.

Property ^a	SYNROC B ^b		SYNROC C ^c
	Edge location	Center location	
Tensile strength (MPa)	—	—	75.6
Flexural strength (MPa)	295 ± 31	—	—
Compressive strength (MPa)	—	574 (single sample)	810
Elastic constants:			
Young's modulus (GPa):			
Ultrasonic	204.3	204.5	203.3
Modulus of rupture	182 ± 6	—	—
Compression	—	288	—
Bulk modulus (GPa):			
Ultrasonic	161.8	161.8	161.2
Shear modulus (GPa):			
Ultrasonic	79.2	79.3	78.8
Microhardness (kg/mm ²):			
HK _{N50}	1079 ± 35	1109 ± 13	—
HK _{N100}	1028 ± 9	1017 ± 10	—
HK _{N500}	884 ± 37	875 ± 21	—

^aErrors are calculated as standard deviations (σ).^bHot pressed in graphite at 1200°C, 2000 psi, for 1 hour to a density of 4.23 g/cm³, which is taken as theoretical for SYNROC B. Sample diameter is 15.2 cm.^cFrom Ringwood.¹⁰ Density is 4.35 g/cm³ for SYNROC C with 10% simulated high-level waste. Tensile test done by diametral compression. Compressive specimens were 0.5 cm long by 0.5 cm in diameter, giving an L/D ratio of 1.0.

The results of flexural and compressive tests and microhardness measurements are shown in Table 4. Also shown are the data of Ringwood¹⁰ for SYNROC C containing 10% simulated high-level waste.

The densities of SYNROC C combinations with high-level waste and with small percentages of metal are approximately 4.35 g/cm³. This is slightly higher than the 4.23 g/cm³ taken as theoretical for SYNROC B alone, without these additions. The 4.23 density value is based on mercury porosimetry measurement of hot-pressed samples.

The results in Table 4 indicate little variation in properties from center to edge in the large 15.2-cm-diameter hot-pressed sample. The strength values are unfortunately based on only a few measurements and more data is needed. The flexural strength of 295 ± 31 MPa compares very well with a commercial grade 85% Al₂O₃ ceramic. The elastic properties of our sample also compare well with commercial alumina. The difference between the elastic properties of SYNROC B and C is minor, in-

dicating that the addition of 10% high-level waste does not appreciably alter the mechanical properties of SYNROC. We believe the compressive strength of 810 MPa reported by Ringwood¹⁰ may be high due to the low L/D ratios of the samples tested. We have also found compressive strengths as high as 847 MPa on SYNROC samples with L/D ratios of 3.5.

The microhardness values in Table 4 show a characteristic decrease with increasing indenter load. There is no significant variation from edge to center in the hardness. The values taken under 100-g loads are of the order of 1000 kg/mm². This compares very well with the work of Hirthe²⁵ who measured the microhardness of near stoichiometric single-crystal rutile (TiO₂) along the (111) plane. In these experiments, using a 200-g load, Hirthe found values that ranged from a low of 960 kg/mm² at a 90°-indenter orientation to a high of 1040 kg/mm² at 180°-indenter orientation. Hirthe also found that slightly reduced titania, TiO_{1.998}, showed a higher hardness with values ranging from 1000 kg/mm² at

90° to 1140 kg/mm² at 180°C. We believe SYNROC hot pressed in graphite is in a slightly reduced state.

A plot of expansion versus temperature for a sample cut from a center location is shown in Fig. 9. Data for the first and second runs show a slight change in expansion behavior on the second run. The sample cut from an edge location showed similar behavior. The results of both runs are expressed in Table 5 as expansion coefficients (α) for several temperature ranges. The low-temperature coefficients for edge and center locations in the range of 22 to 80°C are inconsistent. The edge location showed a 20% increase in α during reheat, and the center sample showed no change. For coefficients calculated at higher ranges (22 to 264°C and above) both samples show 3 to 8% increases in α during reheat. We believe this indicates some residual stress existed in the hot-pressed samples, which was relieved during the first run.

The overall expansion behavior for multiphase SYNROC is comparable to other titanate ceramics. For comparison, we list the reported coefficients of other titanates together with SYNROC in Table 6. The expansion of SYNROC B is about the same as that reported by Eichelberger²⁷ for synthetic

polycrystalline CaTiO₃ (perovskite), cold pressed and sintered at 1600°C.

The thermal conductivity of LLNL SYNROC B measured at room temperature was 2 W/m/°C. Higher values have been measured on SYNROC C prepared by Reeve et al.²⁸ at the Australian Atomic Energy Commission. They measured thermal diffusivity and specific heat as a function of temperature up to 973 K and calculated thermal conductivity according to the relation:

$$a = \frac{k}{\rho \cdot C_p}$$

where a is thermal diffusivity, k is thermal conductivity, C_p is specific heat, and ρ is density. These values are listed in Table 7 along with values for TiO₂ and other titanates similar to SYNROC. The value for SYNROC C at room temperature as measured by Reeve et al.²⁸ is 4.0 W/m/°C or twice the value we measured for SYNROC B. We believe the value of 4.0 W/m/°C is more reliable because a more accurate method of measurement was employed. For comparison, the value for polycrystalline TiO₂ is 8.4 W/m/°C, and the values for single-crystal BaTiO₃ and SrTiO₃ are 5.7 and 11.2

FIG. 9. Thermal expansion of SYNROC B. (Specimen of M05HP4A taken from center region of sample disc.)

TABLE 5. Thermal expansion of SYNROC B.^a

Thermal-expansion temp. range (°C)	Expansion coefficient ($\alpha \times 10^6$)			
	Edge location		Center location	
	1st run	2nd run	1st run	2nd run
22-80	6.93	8.84	8.32	8.32
22-264	8.71	9.41	8.68	9.30
22-425	9.38	9.63	9.46	9.85
22-625	9.79	10.09	10.03	10.40
22-814	10.12	10.44	10.39	10.83
22-949	10.47	10.81	10.83	11.04

^aSpecimens cut from M05HP4A sample (15.2-cm diam) that had been hot pressed at 1250°C, 2000 psi for 1 hour, to a density of 4.23 g/mm³ (approximately 100% theoretical density).

TABLE 6. Thermal-expansion coefficients of various titanates and SYNROC B.^a

Material	Expansion coefficient ($\alpha \times 10^6$)		
	22-250°C	22-600°C	22-950°C
TiO ₂ , rutile, polycrystalline ²⁶	7.3	8.8	9.6
BaTiO ₃ (barium titanate, polycrystalline) ²⁶	5.6	10.9	14.4
CaTiO ₃ (calcium titanate, polycrystalline) ²⁷	8.8	10.5	11.4
SYNROC B	9.4	10.2	10.4

^aOn the second run, SYNROC B values were averaged for both edge and center samples.

W/m/°C, respectively. Polycrystalline values for these titanates are significantly below the single-crystal values. The wide spread in the values at room temperature cannot be due entirely to grain boundary and porosity effects of the polycrystalline materials at high density. Both hot-pressed SYNROC materials were approximately 99% of theoretical density.

Charvat and Kingery²⁹ studied the effect of microstructure and porosity on the thermal conductivity of ceramics. They found good agreement between the thermal conductivity values of single crystals and the corresponding, pure, dense polycrystalline material at temperatures below the onset of radiant-heat transfer. For titania, radiant-heat transfer becomes significant at temperatures above 400 to 500°C. In the case of TiO₂, they also noted a strong influence of crystal-orientation ef-

fects on thermal conductivity. At 400°C, values were approximately 7.5, 5.4, and 5.0 W/m/°C, respectively, for single crystals parallel to the c-axis, those perpendicular to c-axis, and for polycrystalline TiO₂ corrected to zero porosity.

Charvat and Kingery²⁹ found that pore corrections could be made for isometric pores according to the relation

$$K_s = K_p / (1 - p)$$

where K_s is the conductivity of the solid, K_p is the experimental conductivity, and p is the pore fraction. Because of the anisotropic nature of TiO₂, irregular, nonisometric-shaped pores in some TiO₂ microstructures did not follow this relation.

TABLE 7. Thermal conductivity of TiO_2 , titanates, and SYNROC B and C.

Material ²⁷	Thermal conductivity (W/m/K)						
	300 K	400 K	500 K	600 K	800 K	1000 K	1200 K
TiO_2 :							
Polycrystalline ^a	8.4	7.0	5.9	5.0	3.9	3.5	3.3
BaTiO_3 :							
Single crystal	5.7	4.6	-	-	-	-	-
Polycrystalline	1-4	-	-	-	-	-	-
CaTiO_3 :							
Polycrystalline	3-5	3-5	-	-	-	-	-
SrTiO_3 :							
Single crystal	11.2	-	-	-	-	-	-
Polycrystalline ^b	5.5	-	-	-	-	-	-
SYNROC B	2.0	-	-	-	-	-	-
SYNROC C ²⁹	4.0	-	-	5.0	-	6.6	-

^a99.5% pure, 98.0% theoretical density.^b94% theoretical density.

However, the microstructure of SYNROC B (see Fig. 7) indicates that the small amount of remaining porosity is isometric. If we use the preceding expression for pore correction, the measured porosity values for the two SYNROC

samples and TiO_2 are within 2% of those for a fully dense solid. The large difference in values between single crystals of BaTiO_3 and of SrTiO_3 indicates that chemical composition has a strong influence on titanate thermal conductivity.

CONCLUSIONS

The SYNROC B mineral waste form can be hot pressed in graphite at 1200°C into a dense ceramic monolith. The mechanical and thermophysical properties are typical of titanate ceramics. The properties of SYNROC C containing 10% simulated commercial waste are similar to SYNROC B, indicating no adverse degradation in

properties as a result of waste additions. The properties of SYNROC with waste loadings higher than 10% are unexplored, however, and additional studies are needed to establish the relation between these properties and the waste loading of SYNROC.

REFERENCES

1. A. E. Ringwood, *Safe Disposal of High-Level Nuclear Reactor Wastes: A New Strategy*, Australian National University Press, Canberra, Australia (1978).
2. A. E. Ringwood, V. M. Overshy, S. E. Kesson, W. Sinclair, N. Ware, W. Hibberson, and A. Major, "Immobilization of High Level Nuclear Reactor Wastes in SYNROC: A Current Appraisal," *J. Nucl. Chem. Waste Management* (1981), in press.
3. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, "The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization," *Geochem. J.* **13**, 141-165 (1979).
4. A. E. Ringwood, *Safe Disposal of High-Level Radioactive Wastes*, Australian National University, Canberra, Australia, Publ. No. 1438 (1980).
5. D. G. Coles and F. Bazan, *Continuous Flow Leaching Studies of Crushed and Cored SYNROC*, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-84679 (1980).
6. A. E. Ringwood and S. E. Kesson, "Immobilization of High-Level Wastes in SYNROC Titanate Ceramic," in *Proceedings of Conference on Ceramics in Nuclear Waste Management*, Cincinnati, Ohio, April 30-May 2, 1979 (CONF-790420).
7. H. W. Newkirk, C. L. Hoenig, F. J. Ryerson, J. D. Tewhey, G. S. Smith, C. C. Rossington, A. J. Brackmann, and A. E. Ringwood, *Status of SYNROC D Technology for Immobilizing U. S. Defense Wastes*, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-84395 (1981).
8. J. Tewhey, H. Newkirk, F. Ryerson, D. Coles, C. Hoenig, R. Rozsa, C. Rossington, and F. Bazan, *Phase Equilibria, Leaching Characteristics, and Ceramic Processing of SYNROC D Formulations for U. S. Defense Wastes*, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-83658 (1981).
9. J. D. Tewhey, C. L. Hoenig, H. W. Newkirk, R. B. Rozsa, D. G. Coles, and F. J. Ryerson, *The Application of SYNROC to High-Level Defense Wastes*, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-85032 (1980).
10. A. E. Ringwood, W. Sinclair, and G. M. McLaughlin, *Nuclear Waste Immobilization*, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-15457 (1979).
11. J. Campbell, C. Hoenig, F. Ryerson, F. Bazan, T. Wolery, M. Guinan, R. Rozsa, and R. Van Konynenburg, "Immobilization of High-Level Defense Wastes in SYNROC: An Appraisal of Product Performance," presented at conference on *High-Level Waste Technical Review*, Atlanta, Ga., May 18-19, 1981; also Lawrence Livermore National Laboratory, Report UCRL-85913 (April 28, 1981).
12. R. H. Marion and J. K. Johnstone, *A Parametric Study of the Diametral Compression Test for Ceramics*, Sandia Laboratories, Albuquerque, N. Mex., SAND-75-0347 (1975).
13. R. M. Spriggs, L. A. Brissette, and T. Vasilos, "Tensile Strengths of Dense Polycrystalline Ceramics by the Diametral-Compression Test," *Mater. Res. Stand.* **4**, 218 (1964).
14. A. Rudnick, A. R. Hunter, and F. C. Holden, "An Analysis of the Diametral Compression Test," *Mater. Res. Stand.* **3**, 283-289 (1963).
15. American Society for Testing Materials, "Standard Test Methods for Flexural Properties of Plastics and Electrical Insulating Materials," in *1979 Annual Book of ASTM Standards: Part 35, Plastics General Test Methods* (ASTM, Philadelphia, Pa., 1979), Specification D-790-71, p. 329.
16. American Society for Testing Materials, "Standard Test Methods for Compressive Strength of Fired Whiteware Materials," in *1979 Annual Book of ASTM Standards: Part 13, Electronics* (ASTM, Philadelphia, Pa., 1979), Specification C-773-74, pp. 15-18.
17. H. Seki, A. Granato, and R. Truell, "Diffraction Effects in the Ultrasonic Field of a Piston Source and Their Importance in the Accurate Measurement of Attenuation," *J. Acous. Soc. Am.* **28**, 230-238 (1956).
18. H. J. McSkimin, in *Physical Acoustics*, Vol. 1, Part A, W. P. Mason, Ed. (Academic Press, Inc., New York, 1964), Chapter 4.
19. H. J. McSkimin, "Pulse Superposition Method for Measuring Ultrasonic Wave Velocities in Solids," *J. Acoust. Soc. Am.* **33**, 12-16 (1961).
20. H. J. McSkimin and P. Andreatch, Jr., "Elastic Moduli of Germanium Versus Hydrostatic Pressure at 25.0°C and -195.8°C," *J. Appl. Phys.* **34**, 651-655 (1963).

21. E. Schreiber and O. L. Anderson, "Pressure Derivatives of the Sound Velocities of Polycrystalline Alumina," *J. Am. Ceram. Soc.* **49**, 184-190 (1966).
22. E. P. Papadakis and K. A. Fowler, "Broadband Transducers: Radiation Field and Selected Applications," *J. Acous. Soc. Am.* **50**, 729-745 (1971).
23. E. P. Papadakis, "Absolute Accuracy of the Pulse-Echo Overlap Method and the Pulse-Superposition Method for Ultrasonic Velocity," *J. Acous. Soc. Am.* **52**, 843-846 (1972).
24. E. P. Papadakis, "Ultrasonic Diffraction Loss and Phase Change in Anisotropic Materials," *J. Acous. Soc. Am.* **40**, 863-876 (1966).
25. W. M. Hirthe, D. R. McCann, and E. H. Greener, "Influence of a Departure from Stoichiometry on the Microhardness of Rutile at Room Temperature," *Trans. Am. Soc. Mech. Eng.* **227**, 1467-1468 (1967).
26. Y. S. Touloukian, Ed., *Thermophysical Properties of Matter* (Plenum Publishing Corp., New York, 1977), Vol. 13: Thermal Expansion of Nonmetallic Solids, and Vol. 2: Thermal Conductivity, Non-metallic Solids.
27. R. L. Eichelberger, "Lime Bonded and Stabilized with Titanium Oxide as a Refractory for Special Applications," *U. S. Atomic Energy Commission, Rept. No. 8*, 25 (1954).
28. K. D. Reeve, D. M. Levins, E. J. Ramm, J. L. Woolfrey, W. J. Buyck, R. K. Ryan, and J. F. Chapman, "The Development and Testing of SYNROC for High-Level Radioactive Waste Fixation," *Waste Management 1981*, American Nuclear Society, February 23-26, 1981.
29. F. R. Charvat and W. D. Kingery, "Thermal Conductivity: XIII. Effect of Microstructure on Conductivity of Single-Phase Ceramics," *J. Am. Ceram. Soc.* **40**, 306-315 (1957).