Thermodynamic and Diffusivity Measurements in Potential Ultra High Temperature Composite Materials


The Ohio State University
Research Foundation
Department of Materials Science and Engineering
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Columbus OH 43212

August 1990

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Project Engineer

FOR THE COMMANDER

WALTER H. REIMANN, Chief
Materials Development Branch
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1. BACKGROUND

Calcium zirconate, barium zirconate and strontium zirconate have been identified as potential ultra-high temperature composite materials. These materials are proposed as candidate materials for use in advanced aeropropulsion systems where the engines operate in severe operating conditions of 1650°C to 2200°C. The advantage of such high operating temperatures includes the reduction of specific fuel consumption and thus operating costs.

In order to achieve such an objective, quite a few new materials have been proposed. But many of these new materials have been proposed only on the basis of their high melting points and their good mechanical strength. Very often the chemical stability of these materials at the ultra-high operating temperatures of 1650°C to 2200°C are neglected.

There is a paucity of thermodynamic and kinetic data in the temperature range 1650-2200°C for many of the potential materials. This is especially true in the case of mixed oxides, although the vapor pressures of pure oxides [1] as well as the relative rate of evaporation for solid solutions in systems like CaO-ZrO₂ [2] have been measured.

Hence the purpose of this research is to provide fundamental thermodynamic and kinetic data in the temperature range 1650-2200°C for calcium, barium and strontium zirconates. The evaluation of the kinetics of vaporization of these materials addresses such issues as the weight loss per unit area per hour (mg/cm²/hr) anticipated for zirconates if they are used as the wall of the combustion compartment of jet engines operating at about 2000°C. In this manner the potential of the material to serve as a matrix or coating for high temperature composites can be evaluated.

One also has to consider the corrosive oxygen-containing environments in which these materials are expected to operate. If these materials are to act as oxygen barriers to prevent oxidation of metallic or non-oxide ceramic components, knowledge of oxygen
diffusivity is important. Therefore another objective of this project is to study oxygen
diffusion in the alkaline-earth zirconates.

The literature was searched for diffusion data on these zirconates but no data was
found. Available data in the literature include oxygen diffusivity in alkaline-earth
stabilized zirconia and in some related mixed oxides with the perovskite structure.
Kingery et al. [3] measured oxygen diffusivity in calcia-doped zirconia having a
defective fluorite structure, over the temperature range of 700°C to 1100°C. Because of
the high concentration of oxygen vacancies in this defective fluorite structure, diffusion in
stabilized zirconia is expected to be significantly higher than in zirconates which have the
perovskite structure.

The available data on oxygen diffusion in perovskites were measured over the
temperature range of 800°C to 1100°C for BaTiO₃ [4,5] and from 1000°C to 1300°C for
SrTiO₃ [6]. If diffusion coefficient measurements are extrapolated over the temperature
range of 1650°C to 2200°C, calculated results show that oxygen diffusivity in BaTiO₃
SrTiO₃ are two and three orders of magnitude lower than in stabilized zirconia
respectively. Diffusion coefficients may be determined through the introduction into the
system of a tracer which is frequently an isotope with a low natural abundance. For
oxygen, the isotope ¹⁸O is commonly used. In a gas exchange experiment, an
atmosphere of O₂ enriched with ¹⁸O is brought into contact with the sample at a given
temperature and annealing time. After this anneal the tracer profile in the solid is
determined and compared to an expected profile based on a solution to the diffusion
equation.

Nuclear Reaction Analysis (NRA) is a proven technique for determining the ¹⁸O tracer
centration versus depth. This technique is composed of two methods, 1) the proton
induced non-resonant nuclear reaction using the ¹⁸O(p,α)¹⁵N reaction [7], and 2) the
nuclear resonance technique employing the 1169 keV resonance of the ¹⁸O(p,γ)¹⁹F
nuclear reaction. Both nuclear reactions are described by the compound nuclear model.
where an incoming projectile strikes the target nucleus, creates an excited nucleus which then decays via an alpha (gamma-ray) for the non-resonant (resonant) nuclear reaction. Both techniques have their advantages and disadvantages which will be discussed fully in their respective experimental sections.

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

CaZrO$_3$ powder was obtained from Alfa Products, BaZrO$_3$ from TAM and SrZrO$_3$ from Universal Energy Systems. The chemical analyses of the zirconates are shown in Table 1. X-ray diffraction analyses of the starting powders showed that CaZrO$_3$ was a single phase material containing the low temperature orthorhombic phase. BaZrO$_3$ and SrZrO$_3$ were also single-phase materials of the cubic and orthorhombic forms, respectively.

The as-received powders were hot pressed using a Vacuum Industries vacuum hot press sintering furnace. CaZrO$_3$ samples were hot pressed at three different temperatures and pressures to determine the effect of temperature and pressure on its sintering behavior. The temperature and pressure chosen for hot pressing CaZrO$_3$ was 1400°C and 20.7 MPa. These conditions were also used in hot pressing BaZrO$_3$ and SrZrO$_3$.

Hot-pressed samples of the three zirconates were characterized by density measurements and by scanning electron microscopy. In addition, further observation of the CaZrO$_3$ and BaZrO$_3$ microstructures was performed using transmission electron microscopy (TEM). Quantitative analysis of the grains and grain boundaries were done using energy dispersive spectroscopy (EDS).

Because of the significant amounts of impurities in the commercial powders
Table 1. Chemical Analyses of the Alkaline-Earth Zirconates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Major Impurities (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaZrO₃</td>
<td>Alfa Products</td>
<td>Fe(200), Al(3000), Si(700), Ti(1000), Mg(50), Ba(10000), Hf(10000), Mn(5), K(2)</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>TAM</td>
<td>Fe(1000), Al(1000), Si(30000), Ti(2000), Mg(100), Ca(1000), Na(100), Sr(300), K(10)</td>
</tr>
<tr>
<td>SrZrO₃</td>
<td>Universal Energy</td>
<td>Fe(200), Al(200), Si(500), Ti(50), Mg(3000), Ba(100), Mn(3000), Ga(1000), Na(300)</td>
</tr>
</tbody>
</table>

* Coors Analytical Laboratory, Golden Col., CO
(Table 1), zirconates were also prepared by solid state reaction using alkaline-earth carbonates and zirconia as starting powders. Samples prepared by this method were used in vaporization studies; however fully dense samples could not be achieved within the time frame of this project and so no diffusion anneals were performed on these materials. The powder preparation procedure for the diffusion samples is described in Appendix A.

For the vaporization experiments, calcium zirconate samples were synthesized starting from powders of CaCO$_3$ and ZrO$_2$ following a procedure developed by Okubo et al. for calcium, barium and strontium zirconates [8]. CaCO$_3$ grain size was large to start with (about 20 μ) and hence it was ball milled separately in acetone for 8 hours. Then equimolar proportions of CaCO$_3$ and ZrO$_2$ were mixed and ball milled in acetone for 17 hours. Tablets of calcium zirconate were then prepared by dry pressing the mixture at a pressure of 1 MPa and then calcining at 1400°C for 1 hour. X-ray diffraction revealed a single phase CaZrO$_3$ structure.

Dry-pressed tablets of calcium zirconate, about 9 mm in diameter and 1 mm in height were used. A couple of experiments using the hot-pressed samples of CaZrO$_3$ were also performed. The hot-pressed samples were parallelopiped in shape with one of the dimension being small compared to the other two.

A similar procedure was followed for synthesizing barium zirconate and preparing dry-pressed samples. However, these samples were very difficult to handle and additional sintering at 1450°C for three hours did not significantly improve the mechanical strength. So hot-pressed samples were used for all tests with BaZrO$_3$. The samples were heated in air at 1000°C for 24 hours in order to reoxidize samples which were hot pressed in the carbon saturated reducing environment.

Diffusion specimens were prepared from the hot-pressed samples of the three commercial powders. The hot-pressed disks which were 1.7 inch in diameter were cut into half-inch square specimens using a diamond wafering blade. The hot-pressed samples were greyish in color due to the reducing atmosphere of the hot press. Cut
specimens were oxidized in air at 1000ºC for 12 hours. After oxidizing in air, the specimens were polished to a mirror finish using 6, 3, 1 and 1/4 micron diamond pastes.

2.2 Vaporization Studies

2.2.1 Experimental Set-Up

The experimental investigation of calcium and barium zirconates were carried out in a vacuum microbalance apparatus. This apparatus is illustrated schematically in Figure 1. The salient features include a vacuum system, a Cahn 2000 electrobalance and an induction coil.

The vacuum system consists of an oil diffusion pump backed by a mechanical pump and a liquid nitrogen trap and is capable of achieving a level of vacuum of about 10⁻⁶ torr at low temperatures. The microbalance is capable of measuring weight changes as small as 0.1 micrograms. The heating of the sample is achieved by using a Lepel high frequency induction unit.

Figure 2 shows the reaction chamber in slightly greater detail. The sample is suspended by a molybdenum wire in the center of a graphite susceptor. The sample is heated indirectly by radiation from the graphite susceptor which couples to the RF coil directly. The graphite susceptor is machined in such a way so as to enable the temperature measurements to be carried out from the bottom through a black body hole. The lower portion of the susceptor consists of a hole, 4 mm in diameter and extending 20 mm deep to a point very close to the bottom of the susceptor. The temperature measurement is carried out using a disappearing filament type optical pyrometer.

The suspension system consists of two segments of quartz wires and a final segment of molybdenum wire which is attached to the sample by making small grooves on the sample. The insulating system consists of a layer of zirconia felt, 0.1 inch thick, surrounded by an outer alumina tube, 0.125 inch thick. The whole assembly is housed
Figure 1. The microbalance experimental set-up used for the vaporization studies.
Figure 2. A schematic showing the details of the reaction chamber in the experimental set-up.
in a water jacketed quartz chamber, cooled by circulating water. The top of the hot zone is insulated by two layers of zirconia felt, each 0.1 inch thick, with a central opening for inserting the sample into the hot zone. The zirconia felt lining has proved to be an excellent heat insulator and an added advantage in that it does not couple to the RF induction coil in the kilocycle range used in these experiments.

2.2.2 Temperature Calibration

Temperature calibration has been carried out in order to obtain meaningful temperature readings. For the purposes of temperature calibration, the experimental set-up was slightly modified. The microbalance was removed and a glass stopper with an optical window was inserted to allow direct observation of samples. The melting point of elemental standards was correlated with the optical pyrometer temperature readings taken through the blackbody hole at the bottom.

Two pure elements (purity > 99.0%), Fe and Ni, were used. The samples were suspended from the glass stopper into the center of the graphite susceptor. The melting point was noted by observing the metal from the top through a prism and noting the temperature reading of the pyrometer as soon as the metal melted and dropped off into the shallow graphite crucible at the bottom. The experiment proved to be repeatable and the results are shown in Figure 3. The graphite susceptor completely surrounds the metal sample and hence there is no direct RF coupling between the induction coil and the metal sample.

Calibration of the optical pyrometer was made in accordance with Wien's law concerning the spectral distribution of energy in the emission spectrum which yields a relationship between the true temperature and the apparent temperature [9] as follows:

\[
\frac{1}{T_{\text{true}}} - \frac{1}{T_{\text{app}}} = \frac{\lambda}{C_2} \ln(\alpha \varepsilon_{\lambda})
\]

where \( \lambda \) = wavelength of radiation, 0.653 \times 10^{-4} \text{cm} for the optical pyrometer

\( C_2 = \text{constant} = 1.438 \text{ cm-deg} \)
Figure 3. A plot of the true melting point vs. the apparent melting point, obtained from an optical pyrometer, for Fe and Ni.
\( \varepsilon_\lambda \) = emissivity of body at wavelength

\( \alpha \) = absorption coefficient to take into account the absorption effect due to the optical path

\( T_{\text{true}} \) = true temperature in °K and

\( T_{\text{app}} \) = apparent temperature in °K.

The right hand side of the above equation is nearly constant with a value of about \(-4.6 \times 10^{-5}/°\text{K}\) from independent measurements with Fe and Ni. Both Fe and Ni have melting points lying in the medium range of the optical pyrometer reading. But independent experiments have shown that the low range of the pyrometer (775-1225°C) always reads 25°C lower than the medium range (1075-1750°C) in the region of overlap between the two ranges while the high range of the pyrometer (1500-2850°C) always reads 50°C higher than the medium range in the region of overlap between the two ranges. The complete temperature calibration for all the three ranges of the optical pyrometer is shown in Figure 4.

2.2.3 Procedure

The samples were suspended from the microbalance and heated in vacuum. The heating rates used were rapid, as is typical of induction heating. Usually a temperature of 1800°C was achieved in about half an hours time. The weight loss experienced by the materials at a given temperature was recorded continuously by a chart recorder connected to the Cahn electrobalance. The measurements were usually carried out for about 2 hours. The measurements were carried out in the most appropriate recorder range depending on the rate at which the material was losing weight at that given temperature. The vacuum was usually maintained below \(10^{-3}\) torr.

Calcium zirconate and barium zirconate were each tested at three different temperatures. Two experiments were carried out at each temperature to check the reproducibility of the measurements. After the vaporization experiments, the samples
Figure 4. A temperature calibration plot for the three ranges of the optical pyrometer.
were characterized by XRD, SEM and EDS to obtain information regarding the microstructural and chemical transformations accompanying the vaporization process.

2.3 Diffusion Studies

2.3.1 Gas-Exchange Diffusion Apparatus

A schematic diagram of the gas-exchange diffusion apparatus is shown in Figure 5. The apparatus is a closed system consisting of an alumina tube which has one closed end and the other connected to pyrex glass tubing using a vacuum quick disconnect. At the end of the glass tubing is a mechanical pump which was used as a backup equipment for evacuating the system of air.

The alumina tube was placed inside a Lindberg single-zone, global-type tube furnace with a maximum temperature of 1500°C. A Lindberg controller was used to maintain the temperature within ±5°C. A platinum/platinum-10% rhodium thermocouple placed inside the alumina tube was used to measure the temperature of the samples.

Between the furnace and the mechanical pump are two Varian Vacsorb pumps one of which was used to store the 16O:18O gas mixture and the other to evacuate the system of air. The Varian Vacsorb pump is a sorption pump capable of pumping ultrahigh vacuum systems from atmospheric pressure to 1 x 10^-2 Torr using synthetic zeolite [10]. This sorption pump provides clean vacuum without the oil contamination usually present when mechanical pumps are used. The gas pressure in the system was monitored using a standard barometric pressure/vacuum gauge and a thermocouple vacuum gauge.

2.3.2 Procedure

Before a diffusion anneal experiment samples were preannealed in air, using a vented tube, for 24 hours at the diffusion temperature for equilibration. The vents were then closed and the air evacuated by submerging one of the sorption pumps in liquid
Figure 5. The gas-exchange apparatus used in diffusion experiments.
nitrogen. After pressure was reduced to 60-80 microns, this sorption pump was closed and the 70:30 $^{16}$O:$^{18}$O mixture was introduced into the system by opening the other. After the desired diffusion anneal time elapsed, the oxygen gas mixture was then collected back by submerging the sorption pump in liquid nitrogen. Samples were taken out of the alumina tube and coated with gold prior to analysis of the oxygen tracer penetration using the nuclear reaction technique.

2.4 Nuclear Reaction Analysis (NRA)

In the nuclear reaction analysis experiments it proved useful to employ vitreous silica "standards". These samples of $\nu$-SiO$_2$, General Electric type 124 vitreous silica, were given diffusion anneals in a furnace [11] similar to the one described in Section 2.3.1. The $\nu$-SiO$_2$ samples were 0.4032 cm$^2$, 0.3175 cm thick, and both faces were polished to a mirror finish.

2.4.1 Non-resonant Nuclear Reaction: $^{18}$O(p,α)$^{15}$N

The non-resonant $^{18}$O(p,α)$^{15}$N (Q=3.97 MeV) nuclear reaction employs a beam of protons in the energy range of 750-800 keV directed on the sample surface. Protons striking an $^{18}$O nucleus create an excited $^{15}$N nucleus which have a certain probability of decaying via an alpha particle of $E_{\alpha}=3.4$ MeV. Our experiments were performed on the 45°S beam line, Figure 6, at the Ohio State University Van de Graaff Laboratory. Details of the experimental beam line are described in J. Cumming's thesis [11]. The experiment is performed in an ORTEC scattering chamber. Figure 7 shows the geometry of the experimental set up. Emitted alpha particles are detected at the lab angle $\theta=150^\circ$ in a ORTEC Surface Barrier (500 μm thick) detector with detector characteristics of 16.7 keV Full Width at Half Maximum (FWHM) at $E_{\alpha}=5.486$ MeV and a noise width of 10 keV FWHM. A collimator defines a 1.1012 m sr solid angle and the $^{58}$Ni (2.54 μm thick):
Figure 6. The 45°S beam line used for the non-resonant nuclear reaction analysis.
Figure 7. Geometrical set-up of the non-resonant experiment.
0.0022 g/cm² foils in front of the detector reduces the scattered proton flux from the low energy (p,p) reaction and also reduces the computer data acquisition dead-time.

The OSU accelerator is a 6.0 MV CN type Van de Graaff (VdG). At the low proton energy of 750 keV this accelerator performs poorly producing unsteady beam characteristics (energy and current). To overcome these difficulties a Hydrogen (H₂) beam is used at an energy of 1.50 MeV (2Eₚ) producing a steady 0.75 MeV energy proton beam with an average 300 nA beam current. The proton beam energy width (FWHM) is measured using the known 0.992 MeV resonance of the $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ nuclear reaction and was determined to be close to 1 keV.

A schematic of the electronics used for data processing of the signals from the detector is shown in Figure 8. The alpha energy electronic pulse is amplified and split into unipolar and bipolar signals. Unipolar linear energy signals are then processed by the LRS 3511 Analog to Digital Converter (ADC) which is a peak (voltage) sensing ADC of 8 k gain with a 5 μs conversion time. ADC signal linearity is better than ±0.0375% over 99% of its range. Bipolar signals are sent to the EG&G 455 Single Channel Analyzer (SCA, discriminator) and then to the gate and delay generator which creates the gate for the ADC. A Faraday cup at the end of the beam line is not used because the target is thick and completely stops the proton beam. Charge integration of the beam is therefore measured on the target and its signal is sent to the scaler via a TTL/NIM logic level converter. Typical total proton beam flux at the target in these experiments was approximately $3 \times 10^{15}$ protons. A 10 Hz clock pulse is used to determine total beam time of typically 2 hour duration due to the high cross-section of this non-resonant (p,α) reaction.

Data acquisition is performed on a CAMAC based system that utilizes the LeCroy 3500 system and the Digital Equipment Corporation microVax II minicomputer which runs under Virtual Memory System (VMS). Acquisition Code for Research on Nuclei (ACORN) [13] is a CAMAC based data acquisition program written at the VdG lab.
Figure 8. A schematic diagram of the electronics used for data processing of signals produced via the non-resonant nuclear reaction.
ACORN acquires events in real time from user-defined CAMAC module configurations, and sorts the events into histograms, based on conditions defined by the user. Another option is to generate event files of the data onto the System Industries 689 Mbyte disks for eventual play back and resorting.

A $^{18}\text{O}(p,\alpha)^{15}\text{N}$ nuclear reaction cross-section [14] versus energy at the detected alpha angle of 150° is shown in Figure 9a and a typical alpha energy spectrum from a $\nu\text{-SiO}_2$ "standard" target annealed in $^{18}\text{O}$ for 24 hrs. at 1100°C is displayed in Figure 9b. These "standard" targets were used to develop the NRA technique and data analysis routines. Both histograms are plotted with the x-axis in the $500 \leq E_\alpha \leq 1000$ keV energy region. Characteristic features of the alpha energy spectrum, Figure 9b, are the location of the sample surface at 750 keV and the position of the 629 keV resonance from the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction.

Incoming proton's and outgoing alpha's lose energy primarily through two processes, 1) electronic energy losses (where energy is lost through ionization and excitation of the target atoms, and 2) elastic energy losses to the screened nuclei (nuclear stopping). A typical energy loss diagram ($dE/dx$ (keV/μm)) for an oxide ceramic is shown in Figure 10 calculated from proton and alpha stopping power tabulations [15,16,17]. The program $dE/dX$ [18], a chi-squared minimization fitting routine presented in Appendix B, is used to fit the stopping powers for alpha's ($2000 \leq E_\alpha \leq 3500$ keV) and proton's ($200 \leq E_p \leq 750$ keV) in the energy regions of interest. A linear fit for the alpha and proton stopping powers in the energy region of interest,

$$S = \frac{dE}{dx} = - M_\alpha(p) E_\alpha(p) + B_\alpha(p),$$

is demonstrated in Figure 11. In fitting NRA spectra constant stopping powers, the average over the energy range of interest, were assumed.
Figure 9a. Experimental cross-section obtained from G. Amsel et al., Anal. Chem. 39, 1689 (1967).

Figure 9b. Experimental spectrum and its relation to cross-section data.
Figure 10. Energy loss diagram for an oxide ceramic
Figure 11. Energy loss calibration for alpha's (top) and proton's (bottom).
Including the nuclear kinematics of the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction, i.e., the linear relationship of the proton and alpha energies at the angle of interest,

$$E_{\alpha} = M_{nr}E_p + B_{nr},$$

and combining this with the solutions to the differential equations produces a unique function of the detected alpha particle energy, initial incoming proton energy, and the depth of the reaction,

$$E_{\alpha}(d) = E_p(x)[M_{nr} - S_{\alpha}/(S_p\cos\theta)] + E_p(x=0)S_{\alpha}/(S_p\cos\theta) + B_{nr},$$

where

- $x$ = depth of reaction ($\mu$m),
- $E_p(x)$ = proton particle energy at $x$ (keV)
- $E_{\alpha}(d)$ = detected alpha particle energy (keV),
- $S_{\alpha}, S_p$ = stopping powers
- $B_{nr}, M_{nr}$ = constants of the fitted proton and alpha energies,
- $E_p(x=0) = 750$ keV; initial proton energy,
- $\theta = 150^\circ$; detected angle of the alpha particle.

Determination of the $^{18}\text{O}$ tracer concentration also requires knowledge of the energy calibration and linearity of the ADC (2.8 keV/Channel) as depicted in Figure 12b, along with the spreading of the electronic noise shown in Figures 12a and 12c. Figure 12c, the electronic noise width, depicts a constant FWHM/Channel ratio of 0.00742 over the region of interest.

Spreading of the proton and alpha particle energy within the sample was also included in data analysis. Varying the energy of the proton beam, the position of the 629 keV resonance of the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ nuclear reaction, Figure 13, interacts at various depths, since energy loss is dependent upon the initial beam energy and the material. This energy straggling is linearly proportional to the depth in the energy region of interest [19]. The program ERRFIT [19], a gaussian fitting routine, determines the FWHM, $\Gamma_s$, of the resonance for the various depths of interaction. The solid line in Figure 13 is drawn to
Figure 12. Pulser spectrum (top), linearity calibration (b), and FWHM calibration (c) for the ADC.
Figure 13. Effect of varying the proton beam energy on the 629 Kev resonance position and spreading.
guide the eye and does not represent a fit using an assumed concentration profile.

Lastly, carbon build-up on the target must also be included in the analysis. Carbon build-up is produced from carbon molecules in the diffusion pump oil located along the beam line, Figure 6, which are attracted to the target due to charging of the target by the proton beam. Reduction of the carbon level in the target chamber is performed by the use of LN2 cold traps located at various positions along the beam line. Since carbon on the sample surface degrades the beam resolution (FWHM), it is monitored by performing a Rutherford Backscattering (RBS) experiment before and after the nuclear (p,α) experimental run. Figure 14 shows a typical RBS spectrum for v-SiO2 with a thin $^{197}$Au coating. This thin $^{197}$Au coating prevents a build-up of charge on the target which would yield a reduced measurement of the proton flux. Comparing the FWHM of the $^{197}$Au(p,p) peak before and after the nuclear (p,α) experiment provides an assessment of the increase of the proton energy width (FWHM) due to carbon build-up on the sample surface. Build-up of carbon was determined not to be a problem due to the relatively short, 2 hour, experimental runs.

Calculation of the diffusion coefficient involves a trial and error convolution process where an ideal spectrum is obtained from knowledge of the energy loss (dE/dx) together with the known solution to the diffusion equation. The ideal number of counts in each energy sector, $N_i$, is related to the concentration by

$$N_i = C(x_i) \Delta x_i \sigma(x_i) \rho_{ox} L \Delta\Omega$$

where

- $C(x_i) = \text{average fractional concentration of the tracer in the interval } x_i$
- $\sigma(x_i) = \text{nuclear reaction cross section for energies over } x_i$
- $\rho_{ox} = \text{number density of oxygen in the material}$
- $L = \text{number of incident protons}$
- $\Delta\Omega = \text{detector solid angle of observation}$.
RBS Spectrum

Target: \( \text{SiO}_2 \) with \( ^{197}\text{Au} \) coating

\( E_p = 0.75 \text{ MeV}; \ \theta = 150^\circ \)

Figure 14. RBS spectrum of silicon oxide coated with a thin layer of gold.
The ideal spectrum obtained using the above equation is then convoluted with the various experimentally determined spreading functions as shown in Figure 15 and then compared with the experimental spectrum. The assumed diffusion coefficient which gives the best fit to the experimental depth profile is taken as the experimental value of the apparent oxygen tracer diffusion coefficient.

2.4.2 Resonant Nuclear Reaction: $^{18}\text{O}(p,\gamma)^{19}\text{F}$

The main advantage of the resonant versus non-resonant techniques is that gamma-rays ($\gamma$-rays) do not lose energy but are only affected by absorption in the material via three processes, 1) photoelectric effect, 2) Compton effect, and 3) pair production. This allows a tracer concentration to be probed deeper within the sample, i.e., 10's of microns versus a few microns for the non-resonant ($p,\alpha$) technique. Depth profiling is accomplished by detecting the $\gamma$-ray yield ($E = 6.321$ MeV @ $\theta = 60^\circ$) from the $E_p = 1169$ keV resonance of the $^{18}\text{O}(p,\gamma)^{19}\text{F}$ nuclear reaction at various depths within the target sample [21].

The resonance energy resolution, $\Gamma_r = 0.6$ keV FWHM, with a proton beam energy resolution, $\Gamma_p = 1$ keV, provides a 0.03 $\mu$m depth resolution for SiO$_2$. The cross-section at energies of off resonance is negligible in comparison to that of on resonance. The energy of the proton beam enters the target at an energy above resonance, the proton loses energy as the particle traverses the material until at a depth ($x$) the resonance energy is attained. At this thin particular depth the reaction of interest creates the $\gamma$-ray of interest which is detected. At a greater depth the proton energy is less than the resonance where again the cross-section is negligible.

The $^{18}\text{O}(p,\gamma)^{19}\text{F}$ cross-section at a lab angle $\theta=60^\circ$ is $4.45 \mu$b/sr for the decay of the $9101\rightarrow2780$ keV state of $^{19}\text{F}$ [22]. Acquiring acceptable statistics requires approximately 8 hours of beam time. Due to the long beam time experimental runs, carbon build-up was observed to be a problem. Although initially promising, the low
Figure 15. Theoretical (without energy spreading; dash) and experimental spectrum (with energy spreading; solid).
counting rate coupled with the contamination limited the usefulness of this technique.

3. RESULTS AND DISCUSSION

3.1 Microstructural Characterization

3.1.1 Calcium Zirconate

A scanning electron micrograph of a sample cut from the interior of the CaZrO$_3$ disk hot-pressed at 1400°C and 20.7 MPa using the powder from Alfa Products is shown in Figure 16. The density, measured using a Micromeritics multivolume pycnometer, was found to be 97.6% of the theoretical density, 4.97 g/cm$^3$. Using a Zeiss Videoplan, the average grain size was measured as 12.13 microns based on 100 grains.

Some of the hot-pressed CaZrO$_3$ samples which were thermally etched had microstructures which clearly showed small particulates in the grain boundaries and in the grains. Figure 17 shows scanning electron micrographs of these particulates within the grain boundaries. Using a 200 kV JEOL 200cx Transmission Electron Microscope, these particulates were observed using two samples cut from the hot-pressed disk at 1400°C and 20.7 MPa. The surface was studied using a sample which was ion-milled from one side only. To study the inner surface, a second sample was ion-milled from both sides.

Based on the TEM micrographs, diffraction patterns and EDS spectra, precipitates found on the grain boundaries very near the free surface of the sample during annealing (Figure 18) were identified as cubic zirconia (ZrO$_2$). Formation of zirconia is presumably due to calcium depletion of the exposed surface [23]. The grain boundary region contained a glassy phase with isolated crystalline particulates. Figure 19 shows a selected area diffraction pattern confirming the glassy nature of the grain boundary phase. The glassy phase was initially presumed to have been formed as a result of the impurities
Figure 16. A SEM image, using secondary electrons, of CaZrO$_3$ hot pressed at 1400°C and 20.7 MPa taken at 30 KV and 1100x magnification.
Figure 17. A TEM micrograph of particulates observed in the CaZrO$_3$ grain boundary taken at 200 KV and 31.6 KX magnification.

Figure 18. A TEM micrograph of a cubic zirconia grain in the CaZrO$_3$ grain boundary taken at 200 KV and 5 KX magnification.
Figure 19. A TEM micrograph of a selected area diffraction pattern of the glassy phase in the CaZrO$_3$ grain boundary.
present in the sample which segregated at the grain boundaries. However, energy dispersive X-ray analysis of the grain boundaries and the precipitates showed a significant amount of molybdenum and silicon which suggests contamination of the sample surface by the molydisilicide heating elements. Because of this observation, subsequent samples were loosely wrapped in platinum foil to prevent contamination.

Grain boundaries in the sample interior (greater than 100 microns away from the sample surface during annealing) showed no glassy grain boundary phase but did reveal a crystalline phase. EDS analysis of this crystalline phase did not show any molybdenum but showed calcium, aluminum and silicon. This phase was determined to be gehlenite \((2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2)\) based on electron diffraction results.

3.1.2 Barium Zirconate

A TEM micrograph of \(\text{BaZrO}_3\) hot pressed at 1400°C and 20.7 MPa using the powder from TAM is shown in Figure 20. The density of \(\text{BaZrO}_3\) was measured to be 95.8% of the theoretical density. The average grain size is about 0.6 micron. X-ray diffraction analysis of the hot-pressed sample showed a single phase \(\text{BaZrO}_3\). This is corroborated by TEM observations which revealed neither second phases nor glassy phases in the grains or in the grain boundaries as shown in Figure 21. EDS analyses within the grains as shown in Figures 22a and b indicate that impurities such as silicon and aluminum are in solid solution with \(\text{BaZrO}_3\). Similar results are obtained across a grain boundary as shown in Figure 22c. Small precipitate-like grains shown in Figure 23 were also analyzed by EDS (Figures 24a and b) indicating the same result of impurities forming a solid solution with \(\text{BaZrO}_3\).

3.1.3 Strontium Zirconate

When the as-received \(\text{SrZrO}_3\) powder from Universal Energy Systems was hot pressed at 1400°C and 20.7 MPa, a relatively low density of 91.8% of theoretical was
Figure 20. A TEM micrograph of BaZrO$_3$ hot pressed at 1400°C and 20.7 MPa taken at 200 KV and 37 KX magnification.
Figure 21. A TEM micrograph of BaZrO$_3$ showing the absence of second phases or glassy phases in the grains or in the grain boundaries (200 KV, 50 KX).
Figure 22. EDS spectra (a and b) taken from two different BaZrO\textsubscript{3} grains.
Figure 22c. EDS spectra taken across a BaZrO$_3$ grain boundary.
Figure 23. A TEM micrograph of BaZrO$_3$ showing small precipitate-like grains in the grain boundary and within a grain (200 KV, 50 KX).
Figure 24. EDS spectra taken from small precipitate-like grains in BaZrO$_3$ as shown in Figure 23.
obtained. Observation of the microstructure of the sintered sample as shown in Figure 25 showed large grains with a significant amount of porosity. The initial grain size of the powder was measured and found to be on the order of 200 microns. The grains are believed to be hard agglomerates produced during calcination of the sol-gel derived powders. Thus the as-received powders were ball milled in isopropyl alcohol for 40 hours using zirconia grinding media prior to hot pressing to reduce the grain size and improve sintering. A micrograph of the hot-pressed sample is shown in Figure 26. An average grain size of 5 microns and a density of 97.6% of theoretical were determined for this sample.

3.2 Vaporization Studies

The weight loss curves were plotted as the weight lost per unit apparent projected surface area versus time at a given temperature. Figure 27 shows the weight loss for dry-pressed CaZrO$_3$ at a temperature of 1750°C. Figure 28 shows the weight loss curve for dry-pressed CaZrO$_3$ at a temperature of 1850°C and Figure 29 shows the same for dry-pressed CaZrO$_3$ at a temperature of 1970°C. These three figures are condensed into a single master plot in Figure 30 for comparison on a common scale.

Evaporation rate is usually analyzed using the Langmuir equation which expresses the flux of material, $J$, away from the sample as:

$$ J = \frac{\alpha p}{2\pi mKT}^{1/2} $$

(1)

where $\alpha$ = Langmuir sublimation coefficient

- $p$ = vapor pressure
- $m$ = molecular weight
- $K$ = Boltzmann's constant and
- $T$ = temperature.

When there is a significant activation energy barrier to evaporation, $\alpha$ is much less than 1. This is typical of many pure oxide materials. In pure metals, however, $\alpha$ is
Figure 25. A SEM image, using secondary electrons, of as-received SrZrO$_3$ powder hot pressed at 1400°C and 20.7 MPa taken at 25 KV and 141x magnification.
Figure 26. A SEM image, using secondary electrons, of ball-milled SrZrO$_3$ powder hot pressed at 1400°C and 20.7 MPa taken at 30 KV and 2000x magnification.
Figure 27. A plot of the measured weight loss per unit apparent projected surface area vs. time for dry-pressed CaZrO$_3$ held at 1750°C for about 150 minutes in vacuum.
Figure 28. A plot of the measured weight loss per unit apparent projected surface area vs. time for dry-pressed CaZrO$_3$ held at 1850°C for two hours in vacuum.
Figure 29. A plot of the measured weight loss per unit apparent projected surface area vs. time for dry-pressed CaZrO₃ held at 1970°C for 130 minutes in vacuum.
Figure 30. A plot of the measured weight loss per unit apparent projected surface area vs. time for dry-pressed CaZrO$_3$ at three different temperatures.
usually very close to unity and the evaporation rate is given by the relation:

\[ J = \frac{P}{(2\pi m KT)^{1/2}} \]

In incongruently evaporating systems, like some mixed oxides, a concentration gradient is developed in the material as evaporation takes place and the Langmuir analysis cannot be directly applied. This concentration gradient often leads to condensed phase diffusion controlled kinetics. A higher degree of complexity is introduced when a phase change accompanies the compositional change leads to a concomitant volume change. Stresses arising as a result of this volume change may cause microcracking to be initiated. Microcracking will be initiated only in the volume which is sufficiently depleted. After an initial transient, the effective diffusion distance might become a constant due to the recurrent initiation of microcracking immediately behind the depleted zone.

Considering diffusion controlled kinetics alone, the rate would be given by:

\[ \frac{dw}{dt} = AD \frac{dc}{dx} \]

where \( \frac{dw}{dt} \) = rate of loss of weight

\[ A = \text{area} \]

\[ D = \text{diffusion coefficient} \]

\[ \frac{dc}{dx} = \text{concentration gradient} \]

and integration yields standard parabolic kinetics. However when the total effective diffusion distance remains a constant, the rate of material loss can be significantly altered from following a parabolic trend.

The microstructures of the fracture surface of the dry-pressed CaZrO$_3$ before vaporization, after vaporization at 1850°C and after vaporization at 1970°C are shown in Figures 31a, 31b and 31c, respectively. From these pictures before and after vaporization, it is not possible to unambiguously determine whether the number of pores have increased or decreased after vaporization.

From Figure 30, in the case of dry-pressed CaZrO$_3$, there is sometimes a curvature observed although the kinetics appear to be fairly linear especially for the highest and the
Figure 31a. A SEM image, using secondary electrons, of the fracture surface of dry-pressed CaZrO₃ before vaporization at a magnification of 2000x.

Figure 31b. A SEM image, using secondary electrons, of the fracture surface of dry-pressed CaZrO₃ after vaporization at 1850°C for 2 hours, at a magnification of 2000x.
Figure 31c. A SEM image, using secondary electrons, of the fracture surface of dry-pressed CaZrO$_3$ after vaporization at 1970°C for about 130 minutes, at a magnification of 2000x.
lowest temperatures.

If there is no microcrack formation, it is reasonable to expect parabolic kinetics in CaZrO₃ because CaO vaporizes preferentially from CaZrO₃. However, microcracks cannot be avoided considering the fact that there is a volume reduction of about 44% involved in the CaZrO₃ to cubic solid solution phase transformation.

Figure 32 shows the vapor pressures of pure oxides, CaO, SrO, BaO and ZrO₂ over their respective condensed phases plotted as a function of temperature from data in the literature [1]. It clearly demonstrates the much higher vapor pressures of the alkaline-earth oxides compared to ZrO₂. Knowing the free energy of formation of CaZrO₃ from CaO and ZrO₂ [24], the vapor pressure of CaO over CaZrO₃ (solid) can be computed assuming unit activity of ZrO₂ and CaZrO₃. Computing Pₐ auditory(CaZrO₃) in this manner, Pₐ auditory(CaZrO₃) together with Pₐ auditory(CaO) and Pₐ auditory(ZrO₂) are plotted for comparison in Figure 33. It is clear CaO will be the predominant vapor species over condensed CaZrO₃ below about 2200°C.

There is further evidence of preferential evaporation of CaO from microstructural analysis. Dot mapping of Ca and Zr by EDS on the surface of dry-pressed CaZrO₃ samples held at 1850°C for 2 hours, shown in Figures 34a and 34b illustrate this point. Table 2 summarizes the EDS spot analyses carried out on the surface of dry-pressed and hot-pressed CaZrO₃ samples after evaporation and confirms the dot maps.

X-ray analysis of dry-pressed CaZrO₃ samples are shown in Figures 35 and 36. Figure 35a shows the XRD pattern obtained for dry-pressed CaZrO₃ before vaporization while Figure 35b shows the same for dry-pressed CaZrO₃ held at 1970°C for about an hour. Figure 35b is consistent with a single phase cubic solid solution of ZrO₂. Figures 36a and 36b show the XRD patterns obtained from the outer and fracture surfaces respectively of dry-pressed CaZrO₃ held at 1850°C for 2 hours. The outer surface is completely covered by a single phase of cubic CaO-ZrO₂ solid solution. The fracture surface reveals both the cubic CaO-ZrO₂ solid solution and the orthorhombic
Figure 32. A plot showing the relative values of the vapor pressures of the pure oxides, BaO, SrO, CaO and ZrO$_2$, over their respective condensed phases, as a function of temperature.
Figure 33. A plot showing the vapor pressure of CaO over CaZrO₃(solid) and CaO(solid) and the vapor pressure of ZrO₂ over ZrO₂(solid), as a function of temperature.
Figure 34a. Calcium dot map of the outer surface of dry-pressed CaZrO$_3$ after vaporization at 1850°C for 2 hours.

Figure 34b. Zirconium dot map of the outer surface of dry-pressed CaZrO$_3$ after vaporization at 1850°C for 2 hours.
Table 2. Results of the EDS analysis carried out on the outer surface of dry-pressed and hot-pressed CaZrO$_3$, after vaporization.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Atomic % Zr</th>
<th>Atomic % Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry pressed CaZrO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1750</td>
<td>86.46</td>
<td>13.54</td>
</tr>
<tr>
<td>1750</td>
<td>85.18</td>
<td>14.82</td>
</tr>
<tr>
<td>1850</td>
<td>93.77</td>
<td>6.23</td>
</tr>
<tr>
<td>1850</td>
<td>92.45</td>
<td>7.55</td>
</tr>
<tr>
<td>1850</td>
<td>93.43</td>
<td>6.57</td>
</tr>
<tr>
<td>1970</td>
<td>98.36</td>
<td>1.64</td>
</tr>
<tr>
<td>1970</td>
<td>98.12</td>
<td>1.88</td>
</tr>
<tr>
<td>Hot pressed CaZrO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1850</td>
<td>84.07</td>
<td>15.93</td>
</tr>
<tr>
<td>1850</td>
<td>85.28</td>
<td>14.72</td>
</tr>
</tbody>
</table>
Figure 35a. X-ray diffraction pattern for dry-pressed CaZrO$_3$ before vaporization showing an orthorhombic crystal structure.

Figure 35b. X-ray diffraction pattern for the outer surface of dry-pressed CaZrO$_3$ after evaporation at 1970°C showing the zirconia solid solution cubic phase.
Figure 36a. X-ray diffraction pattern for the outer surface of dry-pressed CaZrO$_3$ after evaporation at 1850°C showing the zirconia solid solution cubic phase.

Figure 36b. X-ray diffraction pattern for the fracture surface of dry-pressed CaZrO$_3$ after evaporation at 1850°C showing peaks corresponding to both the zirconia solid solution cubic phase and the CaZrO$_3$ orthorhombic phase.
CaZrO₃ phases. Considering the thin cross section of the specimen, the fracture surface exposed a complete cross section to the X-rays. Some cubic solid solution component of the signal is therefore due to its presence at the surface.

A couple of experiments were also performed with hot-pressed samples of the Alfa products CaZrO₃. The weight loss curves for the hot-pressed sample at a temperature of 1850°C are shown in Figure 37. A comparison with the weight loss curve of dry-pressed CaZrO₃ at 1850°C is made in Figure 38. The hot-pressed sample is much denser than the dry-pressed sample. Normally, the weight loss per unit apparent area must be greater for the more porous dry-pressed sample. This is the reverse of our observation in Figure 38, where the weight loss for the hot-pressed sample is greater than that for the dry-pressed sample by about a factor of two. However, the impurity associated with the hot-pressed sample might be responsible for the observed discrepancy. This could be another pointer to the fact that the kinetics here are controlled by diffusion in the condensed phase. The change in diffusion coefficient, D, due to the presence of impurities in the condensed phase could lead to the anomalous weight loss behaviour exhibited by the hot-pressed sample.

The weight loss curves for hot-pressed BaZrO₃ at 1680, 1730 and 1780°C are shown in Figures 39, 40 and 41 respectively. There is a fairly large scatter in the data and this may be due to either the complexity of the phenomenon of microcrack formation or the possibility that the commercial powder (obtained from TAM) from which these samples were prepared contained a heterogeneous impurity distribution. In fact the EDS analysis carried out on the surface of BaZrO₃ samples tested at 1730°C show a considerable amount of aluminum as documented in Table 3. The EDS analysis of the outer surface of BaZrO₃ samples tested at 1780°C showed extremely tiny amounts of barium or aluminum indicating that both Ba and Al are subject to preferential evaporation. Figure 42 shows the master plot containing the weight loss curves of hot-pressed BaZrO₃ at the three different temperatures at which the experiments were performed.
Figure 37. A plot of the measured weight loss per unit apparent projected surface area vs. time for hot-pressed CaZrO₃ held at 1850°C for about 2 hours in vacuum.
Figure 38. A plot showing the measured weight loss per unit apparent projected surface area vs. time for dry-pressed and hot-pressed CaZrO₃ held at 1850°C for about 2 hours in vacuum.
Figure 39. A plot showing the measured weight loss per unit apparent projected surface area vs. time for hot-pressed BaZrO$_3$ held at 1680°C for about 2 hours in vacuum.
Figure 40. A plot showing the measured weight loss per unit apparent projected surface area vs. time for hot-pressed BaZrO$_3$ held at 1730°C for about 140 minutes in vacuum.
Figure 41. A plot showing the measured weight loss per unit apparent projected surface area vs. time for hot-pressed BaZrO$_3$ held at 1780°C for about 130 minutes in vacuum.
Table 3. Results of the EDS analysis carried out on the outer surface of hot-pressed BaZrO$_3$ after vaporization at 1730°C for about 140 minutes.

<table>
<thead>
<tr>
<th>Atomic % Zr</th>
<th>Atomic % Ba</th>
<th>Atomic % Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.09</td>
<td>14.61</td>
<td>38.30</td>
</tr>
<tr>
<td>64.52</td>
<td>11.33</td>
<td>24.16</td>
</tr>
<tr>
<td>73.61</td>
<td>10.02</td>
<td>16.37</td>
</tr>
</tbody>
</table>
Figure 42. A plot showing the measured weight loss per unit apparent projected surface area vs. time for hot-pressed BaZrO$_3$, held at three different temperatures.
The kinetics appear fairly linear in nature although at the two higher temperatures there is a sudden change in the slope of the curve after a long time which tends to flatten out the curve. This is as yet unexplained.

The X-ray diffraction pattern of the surface of the BaZrO3 samples tested at 1730°C and 1780°C are both identical and appear to contain peaks corresponding to the cubic and monoclinic phases of ZrO2 as well as the cubic phase of BaZrO3. These are shown in Figures 43a and 43b. The SEM micrograph of the fracture surface of the hot-pressed BaZrO3 sample tested at 1780°C is shown in Figure 44.

From Figures 30 and 42, the logarithm of initial slopes versus the inverse of temperature (1/T) is plotted in Figure 45 for dry-pressed CaZrO3 and hot-pressed BaZrO3. Although the weight lost for a period of time at a given temperature cannot be predicted right away, the initial slope of the weight loss plot at any given temperature can be estimated. For instance, at 2000°C, the initial slope of the weight loss plot is 3.38 mg/cm²/hr for dry-pressed CaZrO3. The recession rates for dry-pressed CaZrO3 and hot-pressed BaZrO3 in μ/hr are shown in Tables 4a and 4b respectively. These have been computed from the initial slopes of the weight loss curves assuming a 90% theoretical density for the dry-pressed CaZrO3 and using the measured 95.8% theoretical density value for the hot-pressed BaZrO3.

3.3 NRA Analysis and Tracer Profile Concentrations

The non-resonant NRA technique was used to measure diffusion coefficients for two reasons: (1) the large nuclear cross-section provided short experimental run times and (2) carbon build-up on the target was minimized with the short experimental run times. Although energy straggling of the out-going alpha particles within the material limited the depth probed using this method, the longer run times necessary for the resonant nuclear reaction technique coupled with the problem of carbon build-up made the non-resonant nuclear reaction technique more useful.
Figure 43a. X-ray diffraction pattern for the outer surface of hot-pressed BaZrO$_3$ after evaporation at 1730°C showing peaks corresponding to cubic zirconia, monoclinic zirconia and cubic BaZrO$_3$.

Figure 43b. X-ray diffraction pattern for the outer surface of hot-pressed BaZrO$_3$ after evaporation at 1730°C showing peaks corresponding to cubic zirconia, monoclinic zirconia and cubic BaZrO$_3$. 
Figure 44. A SEM image, using secondary electrons, of the fracture surface of hot-pressed BaZrO$_3$ after vaporization at 1780°C for about 2 hours, at a magnification of 2000x.
Figure 45. A plot of the logarithm of the slope of the weight loss curves for dry-pressed CaZrO$_3$ and hot-pressed BaZrO$_3$ as a function of temperature.
Table 4a. Recession rate in μ/hr for dry-pressed CaZrO3.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Recession rate (μ/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1750</td>
<td>0.67</td>
</tr>
<tr>
<td>1850</td>
<td>2.65</td>
</tr>
<tr>
<td>1970</td>
<td>5.35</td>
</tr>
</tbody>
</table>

Table 4b. Recession rate in μ/hr for hot-pressed BaZrO3.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Recession rate (μ/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1680</td>
<td>3.0</td>
</tr>
<tr>
<td>1730</td>
<td>9.5</td>
</tr>
<tr>
<td>1780</td>
<td>17.7</td>
</tr>
</tbody>
</table>
The theoretical tracer concentration profiles depend on the time and temperature of the anneal. Comparison of non-resonant $^{18}\text{O}(p,\alpha)^{15}\text{N}$ nuclear reactions on $\text{SiO}_2$ annealed at various times of 4, 16, and 24 hours in $^{18}\text{O}$ at 1100°C [23] after charge normalization is performed (Figure 46) shows graphically the increased tracer concentrations as the annealing time increases.

A similar comparison is shown for $\text{CaZrO}_3$ annealed at 1000°C for 12 minutes and 24 hours in Figure 47. These profiles were fitted using a sum of the solution to the diffusion equation for surface evaporation boundary condition [25] and an exponential term to account for a fast diffusion path which produces a tail in the depth profiles:

$$
\frac{(C-C_b)}{(C_g-C_b)} = \text{erfc}\left[\frac{x}{2(Dt)^{1/2}}\right] \cdot \exp\left(K_x/D + K^2(t/D)\right) \text{erfc}\left[\frac{x}{2(Dt)^{1/2}} + K(t/D)^{1/2}\right] + Q\exp(-(Zx^{6/5})
$$

where

- $C$ = concentration of $^{18}\text{O}$ at depth $x$
- $C_g$ = concentration of $^{18}\text{O}$ in the gas phase
- $C_b$ = background concentration of $^{18}\text{O}$ in the solid phase
- $D$ = diffusion coefficient
- $t$ = time of the diffusion anneal
- $K$ = first order surface exchange coefficient

and $Q, Z$ = fitting parameters.

If the fast-diffusion paths are grain boundaries, the product of the grain boundary diffusion coefficient, $D_{gb}$, and the grain boundary width, $\delta$, is given by [26]

$$
D_{gb} \delta = 0.66Z^{-5/3}(t/D)^{1/2}
$$

72
Figure 16. Effect of increased annealing times on the depth profile.
CaZrO$_3$

$^{18}$O($p,\alpha$)$^{15}$N

Annealed@1000$^\circ$C

$E_p = 750$ keV

![Graph showing energy spectrum with annotations for 12 minutes and 1440 minutes.](image)

Figure 17: Normalized spectra of CaZrO$_3$ annealed at 12 minutes and 24 hours (1440 min)
Because of the small tracer penetration in the CaZrO$_3$ sample annealed for 12 minutes relative to the spreading coefficients inherent in this technique, the NRA spectra could be fitted equally well with two sets of diffusion constants: D = 5.2x10$^{-13}$ cm$^2$/sec and K = 2.0x10$^{-9}$ cm/sec; or D = 3.7x10$^{-15}$ cm$^2$/sec and K = $\infty$. Note that in the second case the second term in Equation (3) which accounts for the surface exchange reaction is equal to zero. For the first case, finite K, the normalized surface concentration is calculated to be 0.12, while it must be equal to 1 if K is regarded as infinite.

These values represent the upper and lower limits of the diffusion coefficient at 1000°C. One would therefore expect the diffusion coefficient obtained from fitting the spectra obtained from a longer diffusion anneal to be within this range. For the CaZrO$_3$ sample exchanged for 24 hours at 1000°C, a diffusion coefficient of $2.7 \times 10^{-12}$ cm$^2$/sec was obtained which is about six times higher than the D value obtained for the 12-minute depth profile using a surface exchange term. Observation of the microstructure, however, reveal the presence of a large number of pores in the sample exchanged for 24 hours which was not seen in the sample exchanged for 12 minutes. This microstructural difference could account for the higher D obtained for the sample which was annealed longer.

Figure 48 shows differences in tracer concentration for BaZrO$_3$, CaZrO$_3$, and SrZrO$_3$ samples, all annealed at 1000°C for 24 hours. This graphically indicates that the penetration depth is largest for CaZrO$_3$ and smallest for BaZrO$_3$.

A plot of the concentration profiles using apparent tracer diffusion coefficients obtained by fitting the above experimental depth profiles is shown in Figure 49. The concentration profile for BaZrO$_3$ goes down to the background within 5 microns whereas those of CaZrO$_3$ and SrZrO$_3$ do not indicating deep diffusion into the material. Both spectra for CaZrO$_3$ and SrZrO$_3$ could be fit with Equation (3) which is the sum of a distance dependent term representing bulk diffusion and an invariant term representing grain boundary diffusion. The BaZrO$_3$ spectra, however, could be fit with only the
Figure 48. Non-resonant experimental spectra, after charge normalization, of the alkaline-earth zirconates diffusion-annealed at 1000°C for 24 hours.
Alkaline Earth Zirconates

Anneal 24 hrs. @ 1000°C

\[ \tilde{c} = \frac{c_e - c_b}{c_d - c_b} \]

Figure 5. A plot of the concentration profiles using apparent tracer diffusion coefficients obtained by fitting the experimental spectra shown in Figure 4b.
bulk diffusion term. This cannot be explained considering that the average grain size of 0.6 microns for Ba/ZrO₃ is much less than the average grain size of 12 microns for CaZrO₃ and 5 microns for SrZrO₃. The only other microstructural difference is the presence of porosity in the CaZrO₃ and SrZrO₃ samples and its absence in the BaZrO₃ samples. This difference could account for the deeper penetration in CaZrO₃ and SrZrO₃ than in BaZrO₃ by (a) providing short circuit diffusion paths or (b) creating a rough surface which would result in an apparent deep profile.

Figure 50 shows an Arrhenius plot of the results obtained for the alkaline-earth zirconates together with literature values of the oxygen diffusion coefficients for other oxides. The apparent oxygen diffusivity for CaZrO₃ is about 5 orders of magnitude lower than in calcia stabilized zirconia at 1000°C. A linear fit of the experimental points for BaZrO₃ gives an apparent oxygen tracer diffusion coefficient of

\[ D = 5.0 \times 10^{-3} \text{ cm}^2/\text{sec exp} \left( -247 \text{ KJ/mole / RT} \right) \]

in the temperature range of 900°C - 1100°C. Using this equation, the extrapolated diffusion coefficient for BaZrO₃ is 3.0 x 10⁻⁹ cm²/sec at 1800°C and 3.0 x 10⁻⁸ cm²/sec at 2200°C. These values are within an order of magnitude of the oxygen tracer diffusion coefficients for the isostructural SrHfO₃ determined at the temperature range of 1800°C - 2200°C [27]. The apparent oxygen tracer diffusion coefficients for the alkaline-earth zirconates are summarized in Table 5.

4. CONCLUSION

In summary, dry-pressed CaZrO₃ and hot-pressed BaZrO₃ have been tested at three different temperatures each to study their vaporization characteristics. The materials have been characterized using the SEM, EDS and X-ray diffraction techniques.

Both CaZrO₃ and BaZrO₃ appear to have a fairly high rate of evaporation at high temperatures. However, dry-pressed CaZrO₃ shows a smaller rate of evaporation than
Figure 50. Arrhenius plot of the apparent tracer diffusion coefficients for the alkaline-earth-zirconates together with literature values of oxygen diffusivities in other oxides.
Table 5. Apparent oxygen tracer diffusion coefficients measured for the alkaline-earth zirconates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Time (hrs)</th>
<th>D (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaZrO₃</td>
<td>1000</td>
<td>24</td>
<td>2.7 x 10⁻¹²</td>
</tr>
<tr>
<td>SrZrO₃</td>
<td>900</td>
<td>24</td>
<td>1.1 x 10⁻¹²</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>900</td>
<td>24</td>
<td>3.7 x 10⁻¹⁴</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>900</td>
<td>48</td>
<td>5.0 x 10⁻¹⁴</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>900</td>
<td>72</td>
<td>2.6 x 10⁻¹⁴</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>1000</td>
<td>8</td>
<td>4.4 x 10⁻¹³</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>1000</td>
<td>16</td>
<td>4.8 x 10⁻¹³</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>1000</td>
<td>24</td>
<td>3.0 x 10⁻¹³</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>1100</td>
<td>2</td>
<td>4.6 x 10⁻¹²</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>1100</td>
<td>4</td>
<td>1.5 x 10⁻¹²</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>1100</td>
<td>8</td>
<td>1.0 x 10⁻¹²</td>
</tr>
</tbody>
</table>
hot-pressed BaZrO₃. In both the materials, solid state diffusion appears to play a key role in the kinetics of vaporization.

Results of the diffusion experiments indicate that CaZrO₃ exhibits the largest penetration with BaZrO₃ showing the smallest. Apparent oxygen tracer diffusion coefficients were measured for CaZrO₃ and SrZrO₃ at 1000°C and for BaZrO₃ the apparent oxygen tracer diffusion coefficient is calculated to be

\[
D = 5.0 \times 10^{-3} \text{ cm}^2/\text{sec} \exp\left(\frac{-247 \text{ KJ/mole}}{RT}\right)
\]

in the temperature range of 900° - 1100°C.
REFERENCES


3. W. D. Kingery et al., "Oxygen Ion Mobility in Cubic Zr_{0.85}Ca_{0.15}O_{1.85}," Journal of the American Ceramic, 42, 393 (1959).


5. J. Doskocil and Z. Pospicil, Silikaty, 16 [2], 113-123 (1972).


17. A. Abduljalil and J. D. Kalen, "LINE," program developed at Ohio State University (1988).

18. J. D. Kalen, "DC," program developed at Ohio State University (1988).


APPENDIX A
POWDER PREPARATION FOR DIFFUSION SAMPLES
Because of the impurities present in the commercial zirconate powders, solid state synthesis was used to prepare powders for diffusion samples. The starting powders used were ultrapure alkaline-earth carbonates from Johnson Matthey Chemicals Limited and zirconia from Toyo Soda. The chemical analyses of the powders used are shown below:

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Major Impurities (ppm) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCO₃</td>
<td>Johnson Matthey</td>
<td>Ca(5), Fe(1), Sr(1), Cu(&lt;1), Mg(&lt;1) Mn(&lt;1), Ag(&lt;1), Na(&lt;1)</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Johnson Matthey</td>
<td>Sr(20), Mg(5), Fe(3), Na(1)</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>Johnson Matthey</td>
<td>Ba(20), Fe(2), Na(2), Ca(&lt;1), Mg(&lt;1), Mn(&lt;1)</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Toyo Soda</td>
<td>Al(30), Si(10), Fe(30), Na(50).</td>
</tr>
</tbody>
</table>

*supplied by Manufacturer

The alkaline earth carbonates were characterized using thermal gravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The TGA weight vs. temperature plots showed no water of hydration present in the samples, i.e., the only weight loss observed was due to CO₂ evolution. No second phases were detected using X-ray diffraction analysis and SEM micrographs showed that, with the exception of CaCO₃, the carbonates and zirconia have grain sizes less than 2 microns. The grain size of CaCO₃ was about 20 microns. This was reduced to less than 5 microns by milling for 8 hours in acetone using zirconia grinding media.
Preliminary samples of SrZrO$_3$ and BaZrO$_3$ powders were made by ball milling equimolar mixtures of the carbonate and zirconia in acetone for 8 hours. Samples dry-pressed at 1 MPa were then calcined at 1200°C for 5 hours in a platinum crucible. X-ray diffraction analyses of these calcined powders showed single phase SrZrO$_3$ and BaZrO$_3$.

The resulting zirconate powders were ball milled for 5 hours to break up agglomerates. These powders were hot pressed for 1 hour at 1400°C and 3000 psi and then reoxidized in air for 24 hours at 1000°C.

Both the SrZrO$_3$ and BaZrO$_3$ samples were mechanical weak, i.e., both the hot-pressed zirconates could be easily broken by hand. In preparing bigger batches of the alkaline-earth zirconates, several measures were taken to increase the mechanical strength of the samples as discussed below.

Approximately 200 grams each of BaZrO$_3$, CaZrO$_3$ and SrZrO$_3$ were prepared in one batch. Stoichiometric amounts of the alkaline-earth carbonates and zirconia were ball milled in ethyl alcohol for 24 hours, dried, and then compacted in a platinum crucible. The BaCO$_3$ and ZrO$_2$ powder mixture as well as that of the CaCO$_3$ and ZrO$_2$ was calcined at 1400°C for 1 hour. For the SrCO$_3$ and ZrO$_2$ powder mixture, calcination was performed at a lower temperature of 1200°C but for a longer time of 5 hours. The calcined powders were then ball milled in ethyl alcohol for 48 hours using zirconia grinding media. Calcination of the powders followed by ball milling was done twice to ensure complete reaction of the starting powders. X-ray diffraction analyses of the calcined powders showed single phase zirconates.

The zirconate powders obtained were examined under the SEM and showed submicron-sized particles except for a few particles and hard agglomerates which were about 5 microns in size. Because of the possible deleterious effects of these 5-micron agglomerates during sintering, sedimentation was done for 70 hours after which the top 2 liters was decanted off and then dried. SEM micrographs of these powders showed that all particles were less than 1 micron in size.
Hotpressing:

1. BaZrO$_3$

The BaZrO$_3$ powder obtained was hot pressed at 1400°C and 3000 psi for 1 hour and at 1500°C and 5000 psi for 1-1/2 hours. The higher temperature, 1500°C, was used for part of the powder obtained because the 1400°C sample was weaker than samples hot pressed at the same temperature but using a less pure commercial (TAM) powder. The sintering time at 1500°C was determined from the LVDT reading which showed no change in displacement after 1-1/2 hours.

Although the 1400°C sample was mechanically weaker than the hot-pressed commercial powder, this sample was mechanically stronger than the preliminary sample prepared from powders which were not separated by sedimentation. However, the 1400°C and 1500°C samples still were both weaker than the sample using the commercial powder.

The hot-pressed BaZrO$_3$ was reoxidized in air and then cut into 1/4 inch x 1/4 inch square samples. These samples were polished with 6, 3, 1 and 1/4 micron diamond pastes from which one sample was thermally etched at 1400°C for 1 hour. SEM analysis of the thermally etched sample showed porosity. Since the sample was not dense enough for diffusion studies, no diffusion anneals were made on these samples.

2. CaZrO$_3$

As for the CaZrO$_3$ sample, two samples were hot pressed both at 1500°C and 5000 psi for 1 hour. A SEM micrograph of the CaZrO$_3$ sample etched at 1200°C for 5 hours was taken and showed that the grain size is in the order of 10 microns with porosity present within the grains and in the grain boundaries. This sample was also
mechanically weaker than the sample prepared form the commercial powder. A higher hotpressing temperature is probably needed to fully densify the CaZrO3 powders obtained by solid state reaction. Again, no diffusion anneals were made on these samples.

3. SrZrO3

The SrZrO3 powder was hot pressed at 1500°C and 5000 psi using a 25 gram sample for 1 hour and a 20 gram sample for 1 hour 20 minutes. The hot pressing time was determined from the LVDT reading; when no change in displacement was observed for 10 minutes, hot pressing was stopped.

The hot-pressed SrZrO3 samples were cut and reoxidized in air at 1000°C for 24 hours. The sample turned out reddish and translucent after reoxidizing in air indicating very little porosity in the sample. A micrograph of an etched sample was taken which showed a grain size in the order of half a micron. Density measurements using the multivolume pycnometer showed 100% theoretical density.

A sample of the translucent strontium zirconate was sent to Coors Analytical Laboratory for spectrographic analysis. The major impurity content of the synthesized sample is compared below with sol-gel derived powder from Universal Energy Systems (UES):

<table>
<thead>
<tr>
<th>Impurities</th>
<th>UES (ppm)</th>
<th>Synthesized (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Al</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Si</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>Ti</td>
<td>50</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Mg</td>
<td>3000</td>
<td>100</td>
</tr>
<tr>
<td>Ba</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Mn</td>
<td>3000</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Ga</td>
<td>1000</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Na</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>Ca</td>
<td>500</td>
<td>300</td>
</tr>
</tbody>
</table>

90
Except for aluminum, the impurity level in the solid state synthesized powder is lower than the sol-gel derived powder. Because the SrZrO$_3$ samples were fully densified, diffusion anneal will be performed on these samples.
APPENDIX B

COMPUTER PROGRAM $dE/dx$ USED FOR FITTING ALPHA AND PROTON STOPPING POWERS
```
INCLUDE 'STECTCOM.FOR'
COMMON Y(500),X(500),DY(500),NPTS,FUNKY(500)
COMMON NQ(500)
DIMENSION XINITIAL(20)
CHARACTER*60 NAME, S,TITLE,XTITLE,YTITLE

FW = 13
WRITE (*,770)
770 FORMAT(' ENTER DATA FILE NAME:',$)
READ (*,780) NAME
780 FORMAT(A)
OPEN (UNIT=12, FILE=NAME, STATUS='OLD')
TYPE *, ' READING INPUT FILE'
READ (12,*) NV
READ (12,5) S
DO 102 I =1, NV
READ (12,*) X(I),XMAX(I),XMIN(I),DLMIN(I),DLTAX(I),MASK(I)
102 CONTINUE
READ (12,*) ACK
READ (12,*) COLIN
READ (12,*) MATRIX
READ (12,*) MAXR
READ (12,*) MOSQU
READ (12,*) NTRAC
READ (12,*) RATIO
READ (12,*) NTICKX, NTICKY
READ (12,5) XTITLE
READ (12,5) YTITLE
READ (12,5) TITLE
READ (12,*) XI,X2,YI,Y2 !GRAPH LIMITS
READ (12,*) X3,X4,NFIT !CURVE LIMITS
READ (12,5) S
5 FORMAT(A)
READ (12,5) S
DO 101 I =1,NPTS
READ (12,*) E(I),Y(I),DY(I)
101 CONTINUE
C END OF INPUT FILE
DO 10 I = NV+1,20
DLMIN(I) = 0.
MASK(I) = 1.0
X(I) = 0.
XMAX(I) = 0.
XMIN(I) = 0.
10 CONTINUE
DO 103 I =1,NV
XINITIAL(I) = X(I)
103 CONTINUE
OPEN (UNIT=13, FILE='RESULT.OUT', STATUS='NEW',CARRAGECONTROL='LIST')
CALL FUNK
TYPE *, ' INITIAL CHISQ = ', CHISQ
CALL STEPT
TYPE *
57 TYPE *, ' INITIAL FINAL'
58 TYPE *, ' VALUES VALUES'
59 TYPE *
DO 104 I =1,NV
WRITE (*,21) XINITIAL(I),X(I)
104 CONTINUE
WRITE (*,21) XI,XINITIAL(I),X(I)
WRITE (13,*) I,XINITIAL= XINITIAL(I), Xfinal= X(I)
WRITE (*,30) NF
WRITE (13,30) NF
30 FORMAT(',/16,' FUNCTION COMPUTATIONS')
WRITE (*,40) CHISQ
WRITE (13,40) CHISQ
```
DO 100 I = 1, NPTS
NERR = INT((Y(I) - FUNKY(I)) * 100)
ERROR = 100. * (Y(I) - FUNKY(I)) / Y(I)
WRITE (13, 90) I, X(I), Y(I), FUNKY(I), ERROR, NERR
CONTINUE
WRITE (*, *) The output is in "RESULT.OUT".
CALL ART(E, Y, DY, E, FUNKY, NPTS, NFIT, XI, X2, Y1, Y2, X3, X4,
1 NTICKX, NTICKY, XTITLE, YTITLE, TITLE)
CLOSE (12)
CLOSE (13)
END

SUBROUTINE FUNK
INCLUDE 'STEPTCOM.FOR'
COMMON Y (500), E( ), DY (500), NPTS, FUNKY (500)
COMMON NQ(500)
CHISQ = 0.
DO 100 I = 1, NPTS
V = E(I)
FUNKY(I) = FUNC(V)
CHISQ = CHISQ + (FUNKY(I) - Y(I)) * (FUNKY(I) - Y(I)) / (DY(I))
CONTINUE
CHISQ = CHISQ / (NPTS - NV)
RETURN
END

FUNCTION FUNC(V)
INCLUDE 'STEPTCOM.FOR'
FUNCTION = X(1) * EXP(-X(2) * V)
FUNCTION = X(1) * V + X(2)
RETURN
END

SUBROUTINE ART(XPOINT, IPOINT, Y YER, XFIT, YFIT, NPOINT, NFIT,
1 XI, X2, Y1, Y2, X3, X4,
1 NTICKX, NTICKY, XTITLE, YTITLE, TITLE)
DIMENSION XPOINT(200), YPOINT(200), YERR(200), XFIT(200), YFIT(200)
CHARACTER*60 TITLE, XTITLE, YTITLE
OPEN (UNIT=15, FILE = 'ART.DAT', STATUS = 'NEW', CARRIAGECONTROL='LIST')
WRITE (15, 100) '25 18 .1 .02'
100 FORMAT (A)
WRITE (15, 100) 'BOX'
WRITE (15, 100) '4.99 3.99 18 12'
WRITE (15, 100) 'XAXIS'
WRITE (15, 100) 'YAXIS'
WRITE (15, 110) '5. 4. 18 ', NTICKX, ' 0. .2'
WRITE (15, 110) '5. 4. 18 ', NTICKY, ' 0. 0.'
DX = (X2 - X1)/NTICKX
FX = 5.
D = 18./NTICKX
DO 300 I=0,NTICKX
WRITE (15,100) 'PW'
WRITE (15,150) FX,' 3 .3 0 0'
300 CONTINUE
141 142 DX = (X2 - X1)/NTICKX
143 FX = 5.
144 D = 18./NTICKX
145 DO 300 I=0,NTICKX
146 WRITE (15,100) 'PW'
147 WRITE (15,150) FX,' 3 .3 0 0'
148 150 FORMAT (F7.3,A)
149 FX = FX + D
150 XLABE = X1 + I * DX
151 WRITE (15,200) XLABE
152 200 FORMAT (F7.1)
153 WRITE (15,100) ', '
154 300 CONTINUE
155
156 DX = (Y2 - Y1)/NTICKY
157 FX = 4.
158 D = 12./NTICKY
159 DO 400 I=0,NTICKY
160 WRITE (15,100) 'PW'
161 WRITE (15,350) '4 ',FY, 3 .3 0 0'
162 350 FORMAT (F7.3,A)
163 FY = FY + D
164 YLABE = Y1 + I * DY
165 WRITE (15,202) YLABE
166 202 FORMAT (F7.3)
167 WRITE (15,100) ', '
168 400 CONTINUE
169
170 WRITE (15,100) 'PW'
171 WRITE (15,100) '14 2 .3 0 0'
172 WRITE (15,100) XTITLE
173 WRITE (15,100) ', '
174 WRITE (15,100) 'PW'
175 WRITE (15,100) '2 10 .3 0 90'
176 WRITE (15,100) YTITLE
177 WRITE (15,100) ', '
178 WRITE (15,100) 'PW'
179 WRITE (15,100) '14 17 .3 0 0'
180 WRITE (15,100) TITLE
181 WRITE (15,100) ', '
182 WRITE (15,100) 'PW'
183 WRITE (15,100) '14 2 .3 0 0'
184 WRITE (15,100) XTITLE
185 WRITE (15,100) ', '
186 WRITE (15,100) 'PW'
187 WRITE (15,100) '2 10 .3 0 90'
188 WRITE (15,100) YTITLE
189 WRITE (15,100) ', '
190 WRITE (15,100) 'PW'
191 WRITE (15,100) '14 17 .3 0 0'
192 WRITE (15,100) TITLE
193 WRITE (15,100) ', '
194 WRITE (15,100) 'PPLOT'
195 WRITE (15,100) '5 4 18 12 .3 0 0'
196 WRITE (15,500) X1,X2,Y1,Y2
197 500 FORMAT(4F12.4)
198 WRITE (15,100) 'GKT1/'RPT1'
199 WRITE (15,600) NPOINT
200 600 FORMAT (21I0)
201 DO 800 I=1,NPOINT
202 WRITE (15,700) XPOINT(I),YPOINT(I),YERR(I)
203 700 FORMAT(3F12.4,' 0 0')
204 800 CONTINUE
205 WRITE (15,100) ', '
206 WRITE (15,100) 'CURVE,'