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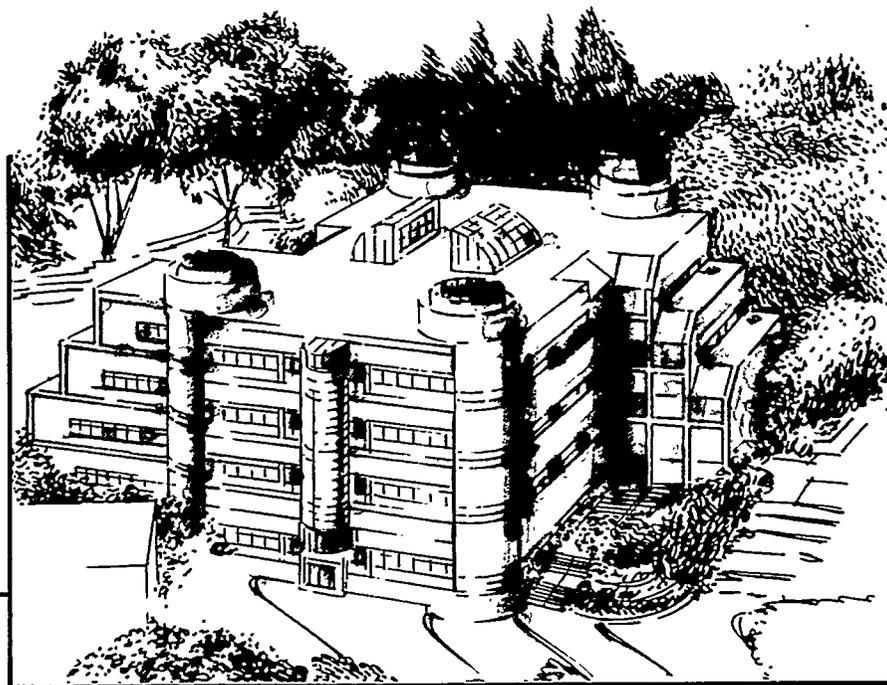
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**Fundamental Studies of the Mechanism of Catalytic
Reactions with Catalysts Effective in the Gasification
of Carbon Solids and the Oxidative Coupling of Methane**

**Quarterly Report
January 1–March 31, 1995**

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March 1995



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QUARTERLY REPORT

January 1, 1995 to March 31, 1995

FUNDAMENTAL STUDIES OF THE MECHANISM
OF CATALYTIC REACTIONS WITH CATALYSTS EFFECTIVE
IN THE GASIFICATION OF CARBON SOLIDS AND THE
OXIDATIVE COUPLING OF METHANE

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 - b) *Synthesis and Characterization of Catalysts*

ATTACHMENTS:

- I. **Pre-print - High Temperature Materials Science** (in press), "*Thin Films of Calcium-Nickel-Potassium Oxide Fabricated by Pulsed Laser Deposition*"
- II. **METC Natural Gas RD&D Contractor's Review Meeting Paper** - "*Steady-State and Transient Catalytic Oxidation and Coupling of Methane*"

I. Task Descriptions for FY 1995

Task 1 - *Oxidative Methane Coupling: Reaction-Separation Processes for Methane Conversion to Ethane and Ethylene* (E. Iglesia and H. Heinemann, Principal Investigators)

The synthesis of ethane and ethylene from methane and oxygen will be carried out in novel hydrogen transport inorganic membranes and in cyclic reactors in order to prevent undesirable secondary reactions of C₂ molecules to CO and CO₂. Neither inorganic membrane reactors nor cyclic tubular reactors are presently used in commercial processes. Their application to catalytic reactions represents a novel application of engineering and solid-state chemistry concepts to catalytic reactions.

Our approach combines high temperature membrane and cyclic experimental reactors, synthesis and characterization of thin membrane films and of high surface area catalysts, and detailed models of complex gas phase and surface reactions involved in oxidative coupling. We anticipate that this approach will lead to novel reactors for carrying out kinetic-controlled sequential reactions, such as the oxidative coupling of methane.

Task 2 - *Synthesis and Characterization of Catalysts* (D.L. Perry, Principal Investigator)

Careful spectrographic and wet chemical analyses of fresh and spent catalysts have shown considerable differences which have permitted conclusions as to the source of deactivation; this work will be continued in fiscal 1995

II. Introduction

Our activities in the first quarter FY1995 have focused on the synthesis, structural characterization, and catalytic evaluation of membrane films, disks, and reactors. We have also continued to exploit reaction-transport models to predict the performance of membrane, cyclic, and recycle reactors in the oxidative coupling of methane.

A graduate student (Richard W. Borry) was assigned full-time to the project during the quarter. Both the cyclic and membrane reactors are operational but the work during this quarter has concentrated on preparing perovskite materials in membrane reactor configurations.

III. Highlights

Experimental characterization work on Ca-Ni-K oxide thin films has been accepted for publication in *High-Temperature Materials Science*. (Attachment I: "*Thin Films of Calcium-Nickel-Potassium Oxide Fabricated by Pulsed Laser Deposition*") A poster describing our work has been prepared and will be presented on April 5, 1995 at the METC Natural Gas RD&D Contractor's Review Meeting in Baton Rouge.

a) Oxidative Methane Coupling

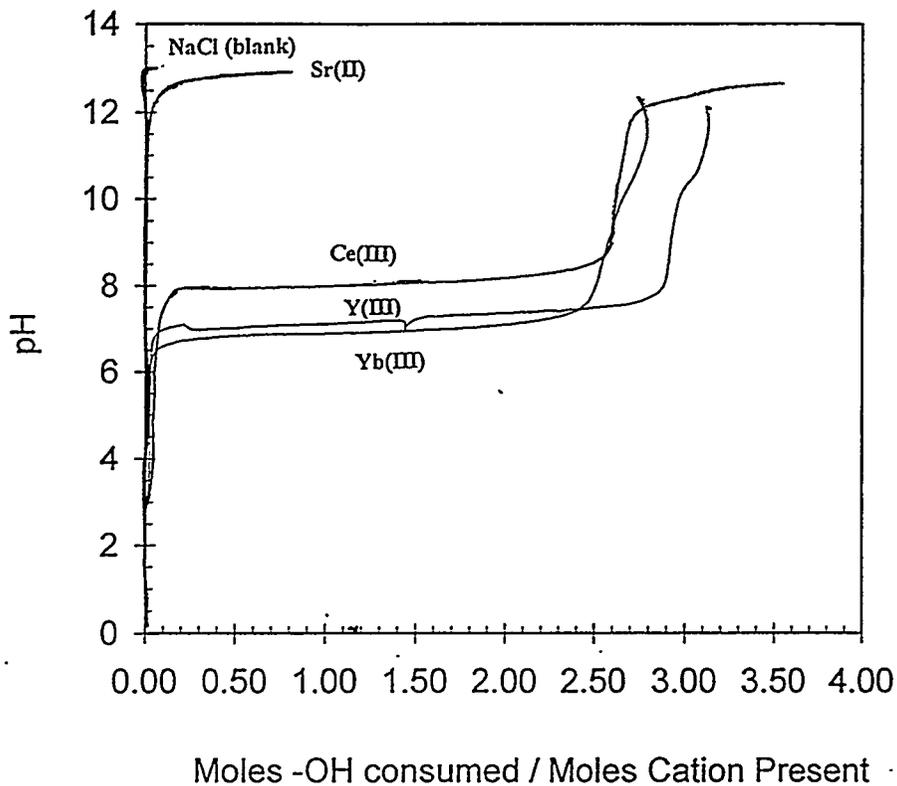
- Precursor powders of composition Sr-Ce-Yb have been prepared via co-precipitation at pH=9 of the dissolved nitrate salts. Heat treatment at 800°C oxidized the precipitate to a mixture of metal oxides, while sintering at 1050°C formed the desired perovskite phase.

b) Synthesis and Characterization of Catalysts

- A paper describing the fabrication of thin films of the Ni-Ca-K oxide catalysts using pulsed-laser deposition has been submitted to *High-Temperature Materials Science* and is included in the Appendix of this report.

- Thin films of Sr-Zr-Y perovskite have been deposited onto a porous alumina support using pulsed-laser deposition (PLD) techniques. X-ray diffraction confirmed the formation of the desired perovskite phase, but initial discs have proven to be slightly porous.

Figure 1: Normalized Potentiometric Titration Curves for Sr(II), Ce(III), Yb(III), and Y(III)



After co-precipitation, the resulting powder is filtered using a Buchner funnel and filter paper, and dried at 125°C overnight. The dried precipitate was then subjected to various heat treatments and analyzed by x-ray diffraction (XRD). Based on published results for high-temperature superconductors, 550°, 800°, and 1050°C were chosen for calcination and sintering. Figure 2 shows the effect of calcination temperature on the precursor phase.

At 125°C, the only visible peaks are due to $\text{Sr}(\text{NO}_3)_2$ ($d=4.6, 2.4, 2.3$) and SrCO_3 ($d=3.6$). X-ray intensity was very low, indicating a basically amorphous sample. Upon heating to 550°C for 5 hours in O_2 , peaks due to CeO_2 appear at $d=3.1, 2.7, 1.9, 1.6$, while $\text{Sr}(\text{NO}_3)_2$ decreases and SrCO_3 increases. After 5 hours at 800°C in O_2 , only the metal oxides remain, with CeO_2 peaks increasing in intensity and peaks due to Sr_2CeO_4 appearing at $d=3.1, 3.4, 5.3, 2.1, \text{ and } 1.7$. With further sintering at 1050°C for 5 hours, these oxide peaks give way to very sharp SrCeO_3 peaks at $d= 4.3, 3.1, 3.0, 2.1, 1.8, 1.7,$

IV. Progress of Studies

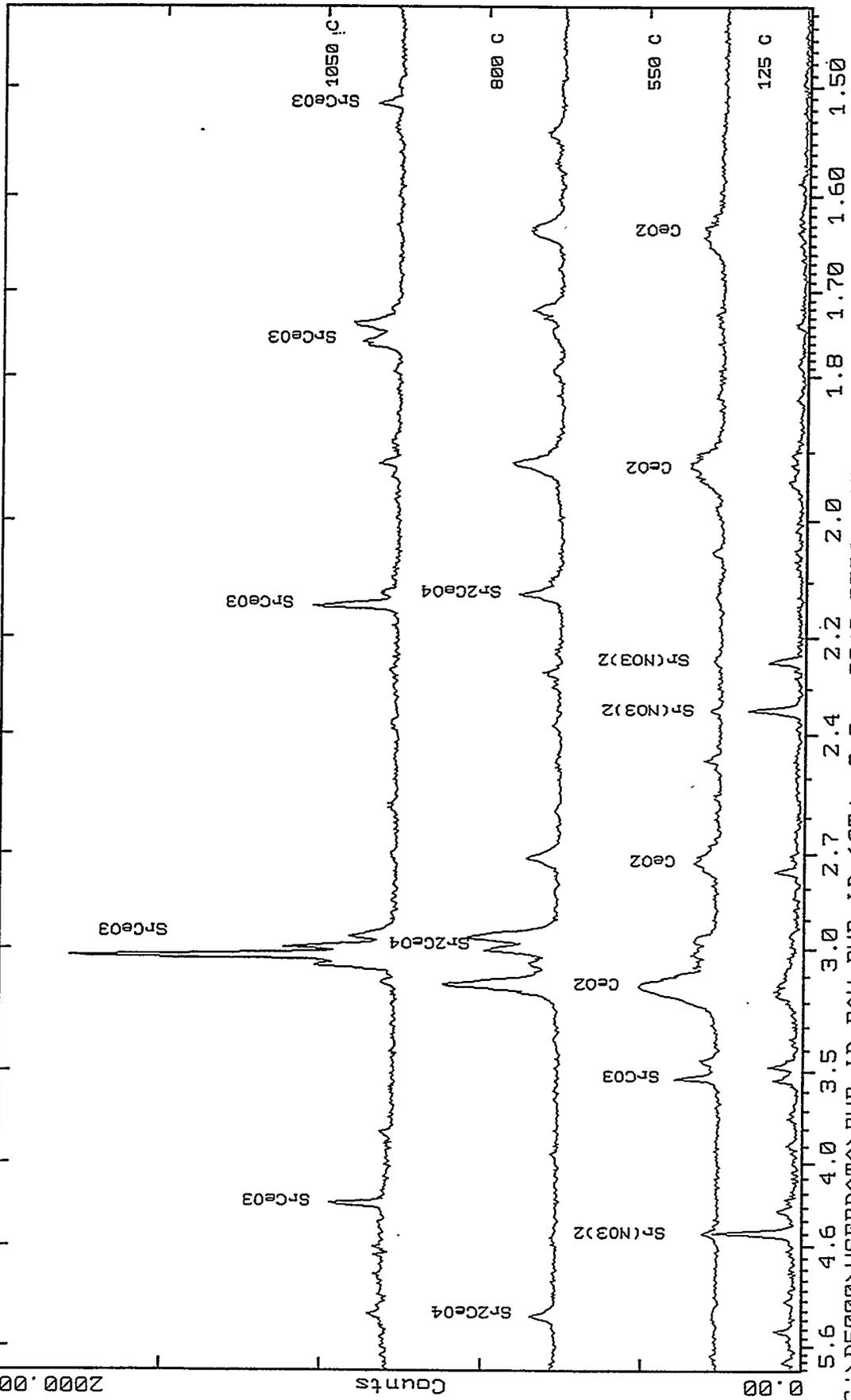
a) Oxidative Coupling of Methane

Controlled pH Co-Precipitation Unit

In order to prepare the required thin non-porous hydrogen transport membranes, we must be able to prepare intimately mixed powders with stoichiometric $\text{SrCe}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\delta}$ composition and high phase purity. Intimate mixing of the three cations is needed to form the perovskite structure, while a fine powder size is needed to form dense membranes by spin coating, casting, and controlled sintering techniques.

Previously, we have used a ceramic method to prepare these perovskite powders. This involves physical mixing of the precursors (SrCO_3 , CeO_2 , Yb_2O_3) in the solid-state, followed by high temperature calcination (800°C in air) to form the oxides, and a very high temperature (1500°C) sintering stage in order to form intimately mixed pure perovskites. The resulting membranes are limited to disks of 1 mm minimum thickness because of mechanical integrity during cutting, mounting, and high temperature reactor operation.

Similar perovskite materials are being prepared chemically for thin film applications in the high temperature superconductor field. One such technique is to precipitate insoluble hydroxides of the precursor cations. Nitrate salts of Sr^{2+} , Ce^{3+} , Y^{3+} and Yb^{3+} readily dissolve in deionized water. In solution, the cations are mobile and mix completely. At a pH value greater than 8, the cations form hydroxide salts ($\text{Y}(\text{OH})_3$, $\text{Ce}(\text{OH})_3$, and $\text{Yb}(\text{OH})_3$) which are insoluble in water and precipitate from solution. $\text{Sr}(\text{OH})_2$ is highly soluble at all values of pH, however, Sr will precipitate as a carbonate. We therefore add excess carbonate (as ammonium bicarbonate) to the precipitating solution to remove Sr as well as the hydroxides. Figure 1 shows the potentiometric titration curves of the various cations. From this data, a pH value of 9 was chosen for the co-precipitation. This allows the use of 1M NH_4OH as base, which is inexpensive, readily available, and can be easily removed upon heating.



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Figure 2: Powder X-Ray Diffraction Patterns of Sr-Ce-Yb-Y Co-Precipitate After Various Heat Treatments

and 1.5. Some peaks due to CeO_2 and Sr_2CeO_4 remain, due to the short sintering time employed.

This data shows the formation of the desired SrCeO_3 perovskite phase after heat treatment at only 1050°C . Previous solid-state reaction methods required sintering temperatures of 1500°C for 24 hours to achieve this phase. The lower sintering temperature in our case is a result of the more intimate mixing of the precursor powders using co-precipitation as compared to conventional ball-milling. Temperatures below 1100°C prevent the necessity of using expensive high-temperature 1500°C furnaces for the final sintering process.

Future work will aim at preparing dense discs using the co-precipitate-derived perovskite. We will then test these discs in a membrane reactor to compare their hydrogen-transport properties to published data using discs prepared via solid-state reactions.

Cyclic Reactors for Oxidative Coupling

As previously reported, we have completed the mechanical troubleshooting of the unit and we have replaced a failing furnace with another existing one. We have been unable to operate the mass spectrometer reliably for any significant period of time. No cyclic methane decomposition experiments were run during the quarter because of these problems. We consider additional time and budget expenditures in repairing this mass spectrometer to be counterproductive. We are presently looking into the availability of alternate spectrometers at LBL and also exploring any opportunities for the purchase of a new spectrometer in the next few months. In the meantime, we have shifted all resources into the membrane reactor and modeling efforts.

b) Synthesis and Characterization of Catalysts

Studies of Strontium-Zirconium-Yttrium Oxide Films and Membranes

Initial membranes of Sr-Zr-Y oxide have been fabricated using pulsed laser deposition techniques and a porous alumina substrate. The target composition for these studies was $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_3$. An excimer laser with nanosecond pulses of energy density between 3 and 5 J/cm^2 was used to deposit the target vapor plume onto the substrate. Pulses were repeated for 60 minutes to form a relatively thick layer.

Figure 3: SEM of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ Film Deposited on an Alumina Substrate

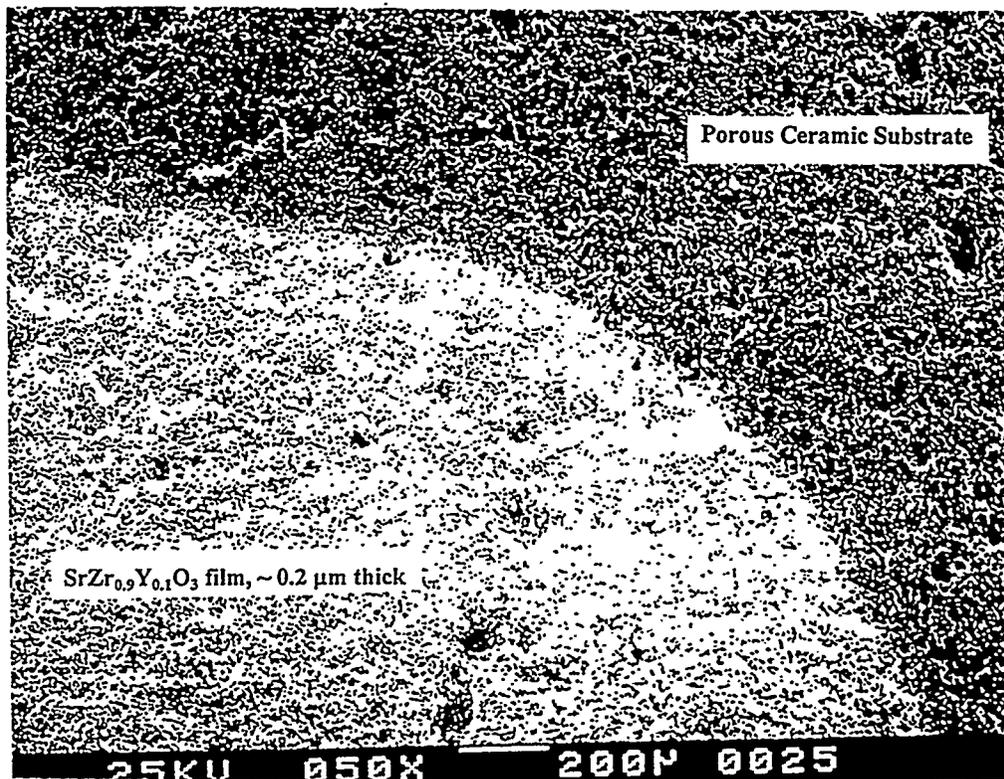
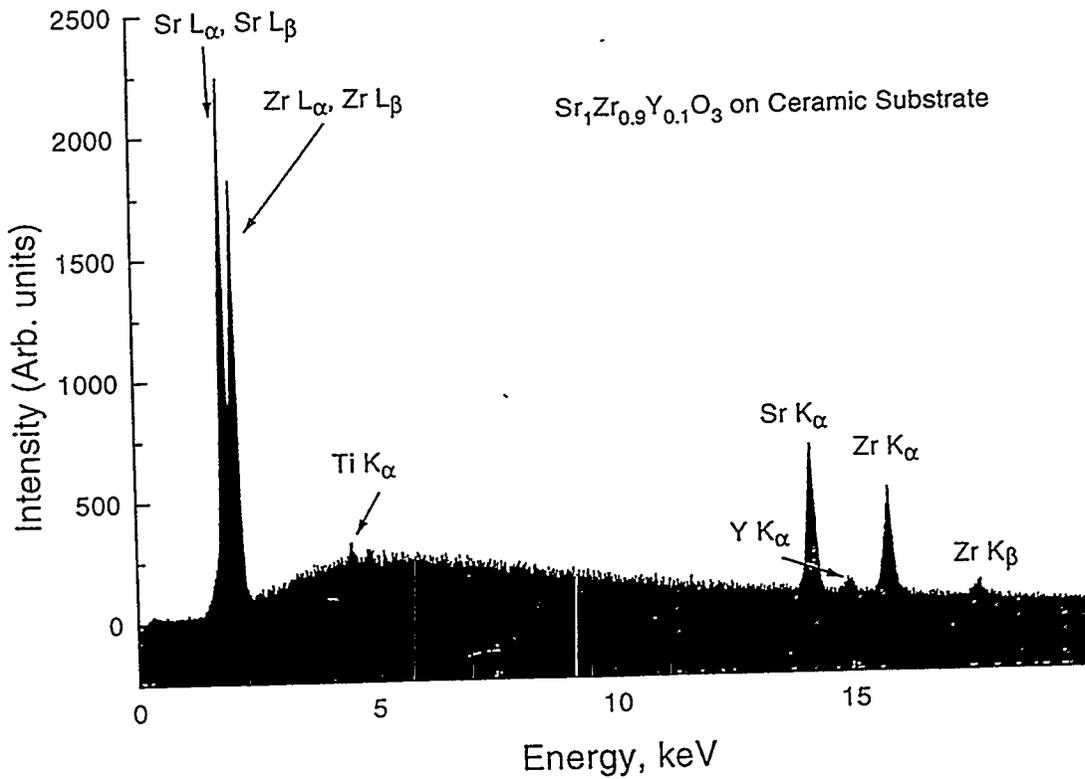
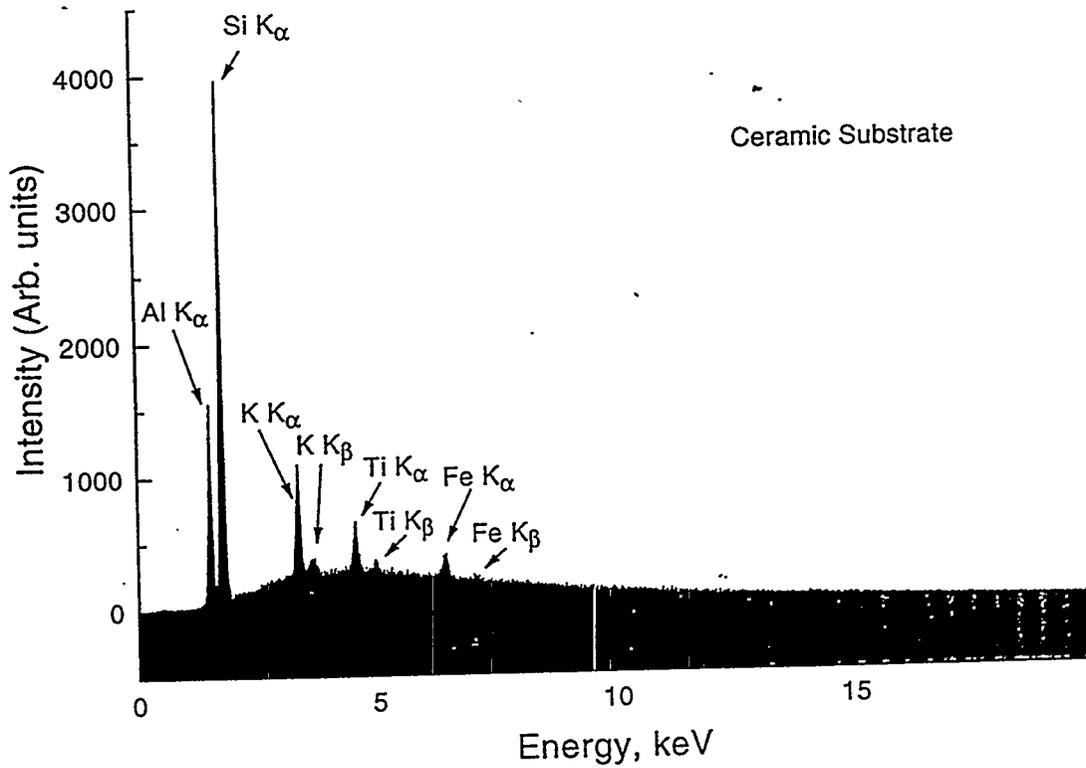


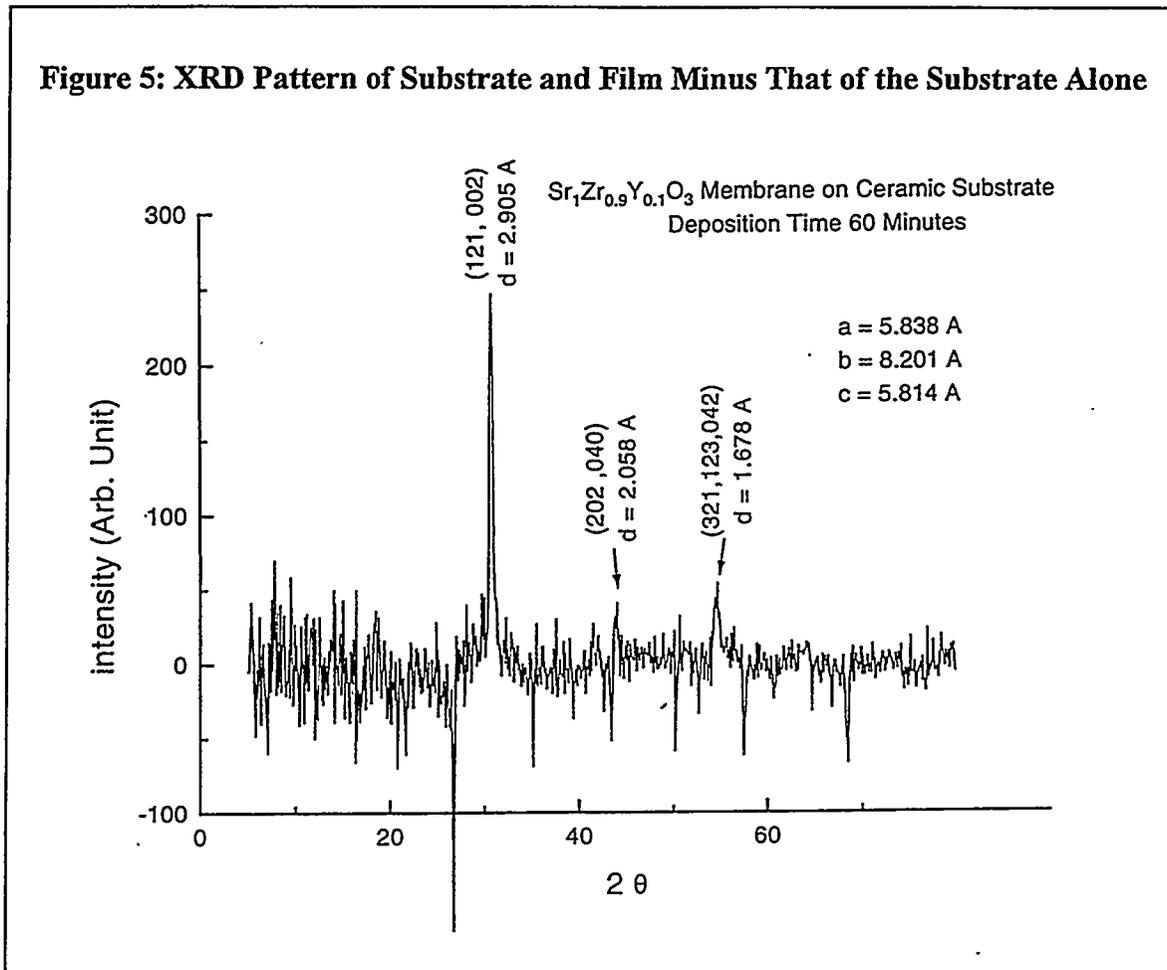
Figure 3 shows a scanning electron micrograph (SEM) of the porous substrate after a single vapor plume has been deposited. This particular membrane was destroyed for analysis purposes, so a complete covering of the substrate surface was not essential. Figure 4 shows the results of energy dispersive x-ray spectroscopy (EDX) of the substrate taken before and after the film deposition. The relative areas of the peaks due to Sr, Zr, and Y show that the desired stoichiometry has been achieved in the film.

X-ray diffraction (XRD) patterns were also taken before and after film deposition. The XRD pattern of the substrate only was subtracted from the pattern taken after deposition to determine the phase of the PLD film. Figure 5 shows the three major lines of the SrZrO_3 perovskite phase, indicating that the film is perovskite and phase-pure. The lines below the baseline in figure 5 are due to the crystal structure of the alumina substrate.

Figure 4: EDX of Alumina Substrate and SrZr_{0.9}Y_{0.1}O₃ Film Deposited Using Pulsed-Laser Deposition



The PLD thin film was tested in the membrane reactor. At room temperature, the film leaked CH_4 to the air side of the reactor. The remaining porosity in the film-substrate combination was estimated to be 14% of that before deposition. More samples are being prepared with this technique, using longer deposition times to form a thicker, and hopefully non-porous, film.



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