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FABRICATION OF CERAMIC MEMBRANE TUBES FOR DIRECT  
CONVERSION OF NATURAL GAS \*

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# FABRICATION OF CERAMIC MEMBRANE TUBES FOR DIRECT CONVERSION OF NATURAL GAS \*

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## ABSTRACT

Several perovskite-type oxides that contain transition metals on the B-site show mixed (electronic/ionic) conductivity. These mixed conducting oxides are promising materials for oxygen permeating membranes that can operate without the need of electrodes or external electrical circuitry.  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_x$  perovskite is known to exhibit very high oxygen permeabilities and one could use this material for producing value added products by direct conversion of methane, the most abundant component of natural gas. This paper deals with the processing and fabrication by plastic extrusion of long lengths ( $\approx 30$  cm) of hollow  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_x$  ceramic tubes. These tubes are characterized by scanning electron microscopy, X-ray diffraction (XRD) and their thermodynamic stability is evaluated using room temperature XRD on samples equilibrated at high temperatures in different gas environment.

## INTRODUCTION

As oil companies search further into remote regions and to greater depths in their attempts to maintain adequate oil supplies, they encounter ever-

increasing amounts of unusable natural gas or methane. Oil companies' basic strategy remains that of upgrading these basic hydrocarbons to added value fuel and chemical products. Over the past several years, extensive efforts have been focused on both the direct and indirect conversion of methane, the most abundant component of natural gas, to added value products particularly towards easily transportable fuels [1-4]. The direct routes involve partial oxidation of methane to methanol, formaldehyde or olefins. This is the most difficult approach since it is complicated by significant competitive side reactions which result in low selectivities to desired products. The reaction must be carried out at high temperatures in the gas phase. Reaction products are more reactive than the starting material and competitive gas phase reactions lead to deep oxidation [5]. Any technological breakthrough in the direct conversion of methane could have significant economic impact in the industrial sector. The indirect routes for the conversion of methane involve reforming to synthesis gas and the subsequent application of Fischer-Tropsch technology to provide paraffins, olefins, oxygenates, waxes, and mid-distillate fuels [6]. The indirect route, and in particular the synthesis gas step, is usually very energy and capital intensive (steam reforming is highly endothermic) operating at high pressures and temperatures.

Although direct partial oxidation of methane is a potential alternative to today's commercial steam reforming processes, downstream processing requirements cannot tolerate nitrogen (recycle with cryogenic separations is required) and pure oxygen must be used. The most significant cost associated with partial oxidation is that of the oxygen plant. Any new process that could use air as the feed oxidant and avoid the problems of recycle and cryogenic separation of nitrogen from the product stream will have a dominant impact on the cost of a synthesis gas plant reflected in savings on capital and separation costs.

Dense ceramic membranes represent a class of materials which offer potential in the solution of a number of problems associated with natural gas conversion. Certain ceramic materials exhibit both electronic and ionic conductivities (of particular interest is oxygen ion conductivity). These materials offer the potential of not only transporting oxygen (selective oxygen separator) but of being able to transport electrons back from the catalytic side of

the reactor to the oxygen reduction interface. As such, no external electrodes are required and if the driving potential of transport is sufficient, the partial oxidation reactions should be spontaneous. Such a system will operate without the need of an externally applied potential. In principle, such materials can be shaped into a hollow tube reactor with air passing over the shell side of the membrane and methane through the inside, as shown in Figure 1. The membrane involved is permeable to oxygen at high temperatures, but not to nitrogen or any other gas. Thus, only oxygen in air can be transported through the membrane to the inside of the reactor surface where it reacts with methane to generate partial oxidation products. This consequently avoids the need of an oxygen plant and allows the integration of separation and reaction into a single process. Depending upon the co-catalyst employed in the oxidation, an array of tailored products can be generated: synthesis gas, methanol, formaldehyde, oxidative coupled products, etc. Other geometric forms of the reactor are possible and can provide substantially greater surface areas for reaction. Honeycomb or corrugated forms [7] are possible and such multilayer reactors will be required to achieve sufficient conversions and reaction rates for successful application to industrial processing.

Although there are recent reports of various ceramic materials that could be used in partial oxidation ceramic membrane reactors, little work appears to have been focused on the problems associated with the stability of the materials under reaction conditions and the fabrication of suitable reactors. It is therefore of critical concern to address these problems and to determine the stability of these materials under typical reaction conditions and to find suitable fabrication methods for reactors which will have sufficient physical and mechanical integrity properties to withstand the rigorous conditions associated with the partial oxidation reactions of interest. One particular membrane material that we have been investigating is  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_x$  (SCF) perovskite. This material has been shown by Teraoka et al [8] to not only exhibit both oxygen ionic and electronic conductivity but also appreciable oxygen permeabilities ( $\approx 2$  orders of magnitudes higher than that of stabilized zirconia) at temperatures above  $550^\circ\text{C}$  and is a natural candidate for methane conversion that requires large quantities of oxygen. In this paper we describe the processing and fabrication of hollow membrane SCF tubes using a plastic extrusion technique. These tubes are then used in partial oxidation studies to transport oxygen for synthesis gas

generation in conjunction with a precious metal reforming catalyst. The sintered membranes are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and its thermodynamic stability is investigated and the results are discussed.

## EXPERIMENTAL

The fabrication process originates with a homogeneous powder of suitable particle size. Ceramic powders of composition  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_x$  are made by solid-state reaction of the constituent carbonate and nitrates. Appropriate amounts of  $\text{SrCO}_3$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  are mixed and milled in methanol using  $\text{ZrO}_2$  media for  $\approx 20$  h. After drying, the mixtures are calcined in air at  $850^\circ\text{C}$  for 16 h with an intermittent grinding. After the final calcination, the powder is ground in an agate mortar and pestle. The average particle size is  $\approx 7 \mu\text{m}$ . The membrane tubes are fabricated by plastic extrusion. To prepare for extrusion, ceramic powder is mixed with several additives to make a formulation with enough plasticity to be easily formed into various shapes while retaining satisfactory strength in the green state. This formulation, known as a slip, consists in general of a solvent, a dispersant, a binder, a plasticizer, and ceramic powder. The solvent provides a fluid medium for the powder and the other additives. Care must be taken in selecting a solvent that is compatible with the SCF powder and other organic constituents. Organic solvents such as butanol and xylene are used. The dispersant reduces the extent of agglomeration in the slip and thereby promotes uniform densification during sintering. The binder consists of long-chain organic molecules that impart strength to the green body by establishing a polymeric cross-linkage of the ceramic particles. The plasticizer is made up of somewhat shorter organic molecules that partially disrupt the cross-linkage of the binder and thereby provide the green body with a degree of flexibility. Ratios of the various constituents of a slip vary, depending on the forming process and such characteristics of the ceramic powder as particle size and specific surface area. After the slip is prepared, some of the solvent is allowed to evaporate; this yields a plastic mass that is forced through a die at high pressure ( $\approx 20$  MPa) to produce hollow tubes. Tubes have been extruded with outside diameter  $\approx 6.5$  mm, inside diameter  $\approx 4$  mm, and lengths up to  $\approx 30$  cm. In the green state (i.e., before firing), extruded tubes exhibit great flexibility.

Extruded tubes are heated at a slow heating rate ( $\approx 5^\circ\text{C}/\text{h}$ ) in the temperature range  $150\text{-}400^\circ\text{C}$  to facilitate removal of gaseous species formed during decomposition of organic additives. If the organics are removed rapidly, the final product will have large voids and a bloated appearance. After the organics are removed at low temperatures, the heating rate is increased to  $\approx 60^\circ\text{C}/\text{h}$  and the tubes are sintered at  $\approx 1200^\circ\text{C}$  for 5-10 h. All the heatings are done in stagnant air. Figure 2 is a photograph of an extruded hollow tube. Facilities are available to heat the extruded parts in flowing oxygen at reduced total pressure to facilitate removal of gaseous species and to prevent their reaction with the ceramics. We have developed this reduced pressure sintering to process extrusions of other ceramics [9]. The sintered SCF tubes are characterized by optical and scanning electron microscopy, X-ray diffraction, and density measurements. These tubes are then used in our partial oxidation studies to transport oxygen for synthesis gas generation in conjunction with a precious metal reforming catalyst. Although our experimental results supported the oxygen transport concept with successful utilization towards preferred oxidation, the integrity of the tube diminished rapidly with time on stream eventually leading to catastrophic failure. XRD was used to probe the chemical phase behavior of this material. A detailed thermogravimetric analysis (TGA) and in-situ XRD experiments were done at high temperatures and in different atmospheres on this material and the results reported elsewhere [10].

## RESULTS AND DISCUSSION

The XRD pattern of powder calcined at  $850^\circ\text{C}$  in air indicated the sample to be single phase cubic perovskite material. The SEM micrograph of the surface of the tube sintered at  $\approx 1200^\circ\text{C}$  in air is shown in Figure 3. The sintered grain size is in the range  $2\text{-}10\ \mu\text{m}$  and the density is  $\approx 4.9\ \text{g}/\text{cc}$ . Eventhough Fig. 3 shows the surface to be very dense, the fracture surface indicated some porosity. In order to probe the chemical stability of the material, three SCF samples have been examined using XRD at room temperature. The heat treatment and the oxygen content,  $x$  (determined in our previous experiment, ref. 10), of the three samples are listed below:

<u>Sample</u>	<u>Heat treatment</u>	<u>x</u>
A	Annealed at 850°C in air and then slowly cooled to room temperature	2.67
B	Annealed at 800°C in N <sub>2</sub> and then rapidly cooled to room temperature	2.48
C	Annealed at 650°C in N <sub>2</sub> and then slowly cooled to room temperature	2.50

The XRD pattern taken from sample# A is shown in Figure 4. It consists of a set of strong and a set of weak Bragg peaks. The strong peaks are fitted quite well using the primitive cubic perovskite structure (lattice parameter = 3.860 Å). The weak peaks can be indexed using a larger perovskite unit cell with lattice parameter twice that of the primitive cubic cell. This shows that sample A is a single-phase material. The exact atomic arrangements in sample# A is more complex; it should contain a small degree of oxygen vacancy ordering, as suggested by the occurrence of the weak peaks.

The XRD pattern taken from sample# B is shown in Figure 5. Structural models of Sr<sub>2</sub>Co<sub>2</sub>O<sub>x</sub> and Sr<sub>2</sub>Fe<sub>2</sub>O<sub>x</sub> are used to fit the XRD data. It has been reported that such compounds are able to adopt in several different structures having either cubic, tetragonal, orthorhombic or rhombohedral symmetry [11-14]. We found that the XRD pattern of sample# B matches well with that of the orthorhombic structure with a = 5.578 Å, b = 15.646 Å, and c = 5.472 Å. Therefore, the SCF sample at 800°C in nitrogen is also a single-phase material and its structure is similar to that of orthorhombic Sr<sub>2</sub>Fe<sub>2</sub>O<sub>2.5</sub> [11]. The dependence of the unit cell volume on the oxygen content, x, of the SCF compound has been established by comparing the lattice parameters. For sample# A (x = 2.67 Å), the volume of the primitive perovskite cell, V<sub>p</sub>, is 57.51 Å<sup>3</sup>. For sample# B (x = 2.48 Å), V<sub>p</sub>, which is 1/8 of the volume of the orthorhombic unit cell, is 59.70 Å<sup>3</sup>. These results show that the SCF material expands as oxygen is removed. Such a behavior suggests that an electronic effect is predominant in influencing the specific volume of this material; otherwise a simple size effect would cause the lattice to shrink. By linear

interpolation of the above results, we predict that a decrease in  $x$  by 0.19 will result in an increase in  $V_p$  by 3.8%.

The XRD pattern taken from sample# C is quite complex. In addition to the Bragg peaks which are consistent with those in sample# B, we also observed several extraneous peaks. An attempt to identify the phase giving rise to two moderately strong peaks in the pattern was not successful. However, some of the weak peaks appear to match those of cobalt oxides. We thus believe that sample# C has decomposed due to the long time annealing at low temperature and at low oxygen partial pressure. Similar low temperature decomposition was also observed in  $\text{SrCoO}_x$  by Takeda et al. [11].

Based on the XRD results and the previous TGA data [10], one can obtain a clear picture about the state of the SCF membrane tube under reaction conditions. We will first discuss the situation when the membrane tube acts solely as an oxygen separator. In this case, the high-pressure oxygen is maintained outside the tube and a low pressure oxygen is maintained inside the tube. Before the tube is brought up to high temperature, it has an uniform distribution of oxygen with  $x \approx 2.7$  (sample# A). Upon heating, the tube begins to lose oxygen that was incorporated previously in the fabrication process. Moreover, the material on the inner wall will lose more oxygen compared with that on the outer wall. As a result, a stable oxygen gradient is generated pointing from one wall to another. It follows that the material, depending on where it is in the tube, may have different phase constituents. The likely phase representation of the tube at 800°C is shown in Figure 6. The material is of single-phase in the outer and inner zones but of multiphase in the middle zone. In principle, the efficiency of oxygen permeation is different from zone to zone and the oxygen flux passing through a membrane tube is controlled by the least permeable zone. We believe that the inner zone is less oxygen permeable (due to more ordered nature of oxygen vacancies) than the outer zone. By contrast, we know little about how the phase separation in the middle zone would affect the rate of oxygen permeation in this material.

The most remarkable factor which can cause the fracture of tubes appears to be the lattice mismatch between the materials on the two walls of the tube. The oxygen content,  $x$ , on the low oxygen pressure side is about 0.1 lower

than that on the other side at 800°C. Therefore, the material on the low oxygen pressure side will expand an additional 2% in volume compared with the material on the other wall. Such a compositional expansion is equivalent to a thermal expansion of 333°C (assuming that the volumetric thermal expansion coefficient is  $\approx 6 \times 10^{-5}/^{\circ}\text{C}$ ). Considering the brittleness of a ceramic material, there is no doubt that the tube will break under reaction condition.

The phase constituents of the tube become more complex, as indicated in Figure 7, when methane is flown inside of the tube. Due to the reaction between methane and the oxygen permeating through the membrane, H<sub>2</sub> and CO will be generated. The direct contact between the tube and the H<sub>2</sub> gas (CO may have the same effect) will cause the perovskite phase to decompose. Therefore, an additional zone which may consist of SrO and the Co-Fe metal (and possibly some cobalt and iron oxides) will occur in the tube. The occurrence of such non-perovskite materials will reduce the effective surface area permeable to oxygen and we thus expect that the oxygen flow would decrease accordingly. Furthermore, it is possible that, after a sufficient time, the entire material would decompose to non-perovskite products such as a mixture of SrO, plus Co and Fe metals. Once much oxygen is lost, the perovskite lattice would collapse and the material decompose and break into pieces. In order to apply the SCF membrane tube in the conversion of methane to synthesis gas, it appears critical to reduce the wall thickness of the tube. Once the wall of the tube is thin, the oxygen lost from the perovskite phase to the reaction stream can be refilled by the oxygen permeable from the high pressure side. As a result, the material in contact with the reaction stream will not be deeply reduced and hence the chemical decomposition would not occur. Meanwhile, the difference in oxygen content between the two walls becomes smaller and consequently, the fracturing of the tube is less likely. Thus, a thin-wall membrane tube appears to be more promising for the application of methane conversion in the future.

## CONCLUSIONS

Long lengths of SCF membrane tubes have been fabricated using plastic extrusion technique. Its thermodynamic stability is studied by XRD measurements. The fracture of the SCF tube is the consequence of an oxygen gradient that introduces a 2% volumetric lattice difference between the inner

and outer walls. The thin-wall membrane ceramic tube could prevent both the fracture and the chemical decomposition of the tube.

## ACKNOWLEDGMENTS

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## FIGURE CAPTIONS

Figure 1. Schematic of the membrane reactor for methane conversion.

Figure 2. Photo of the extruded hollow SCF tube.

Figure 3. Scanning electron micrograph of the surface of the SCF tube sintered in air at  $\approx 1200^{\circ}\text{C}$ .

Figure 4. Raw XRD pattern (+) and the calculated intensity profiles (continuous curve) for  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{2.67}$  (Sample# A) at room temperature. Tick marks below the profiles mark the positions of the allowed reflections. A difference curve (observed minus calculated) is plotted at the bottom.

Figure 5. Raw XRD pattern (+) and the calculated intensity profiles (continuous curve) for  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{2.48}$  quenched to room temperature from  $800^{\circ}\text{C}$  (Sample# B). The format is the same as in Fig. 4.

Figure 6. Schematic of the likely phase representation for a membrane tube operating between pure oxygen (outside) and low pressure oxygen (inside).

Figure 7. Schematic of the likely phase representation for a membrane tube operating between pure oxygen (outside) and methane (inside). The Co and Fe resulting from the decomposition are likely to form an alloy.

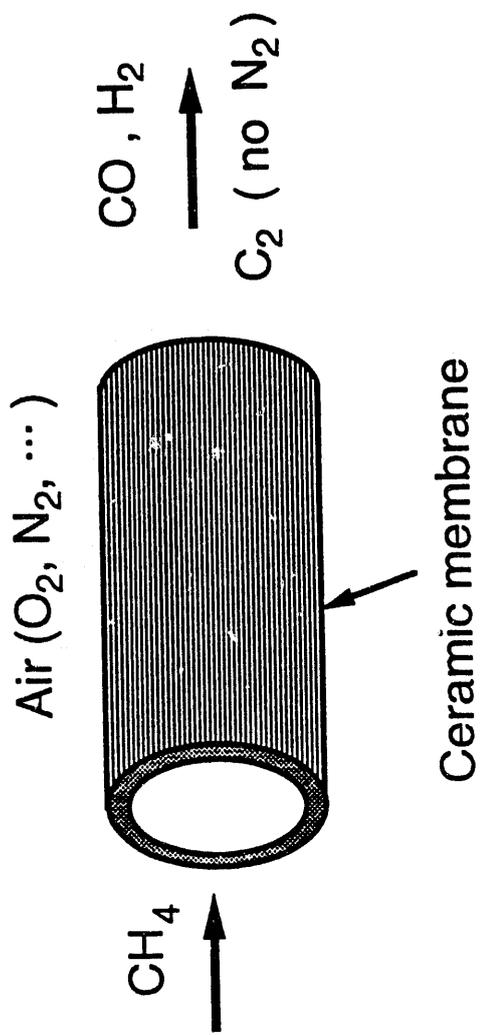


Fig. 1

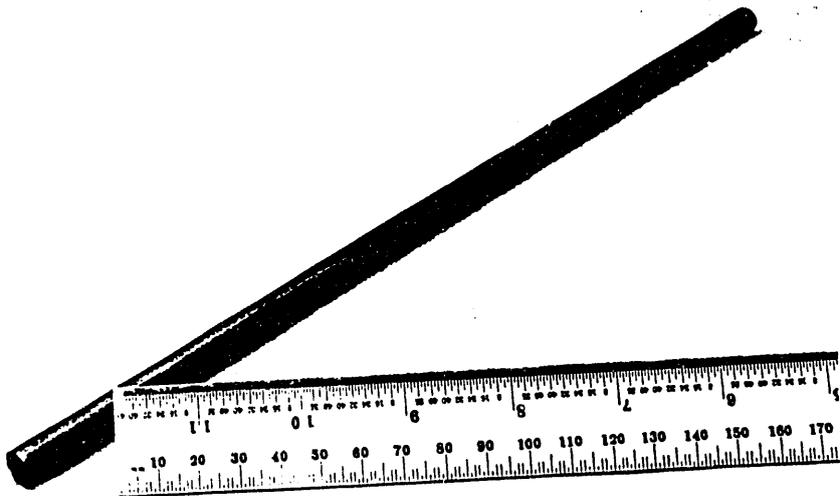


Fig. 2

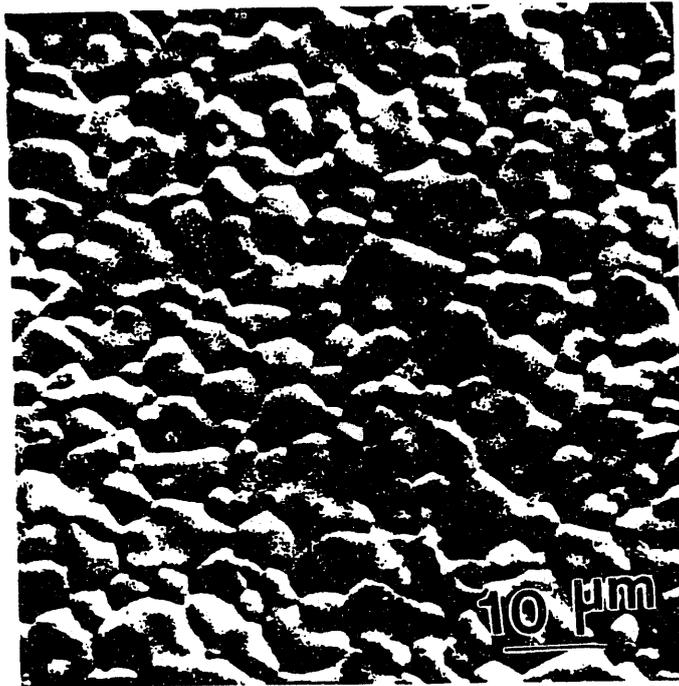
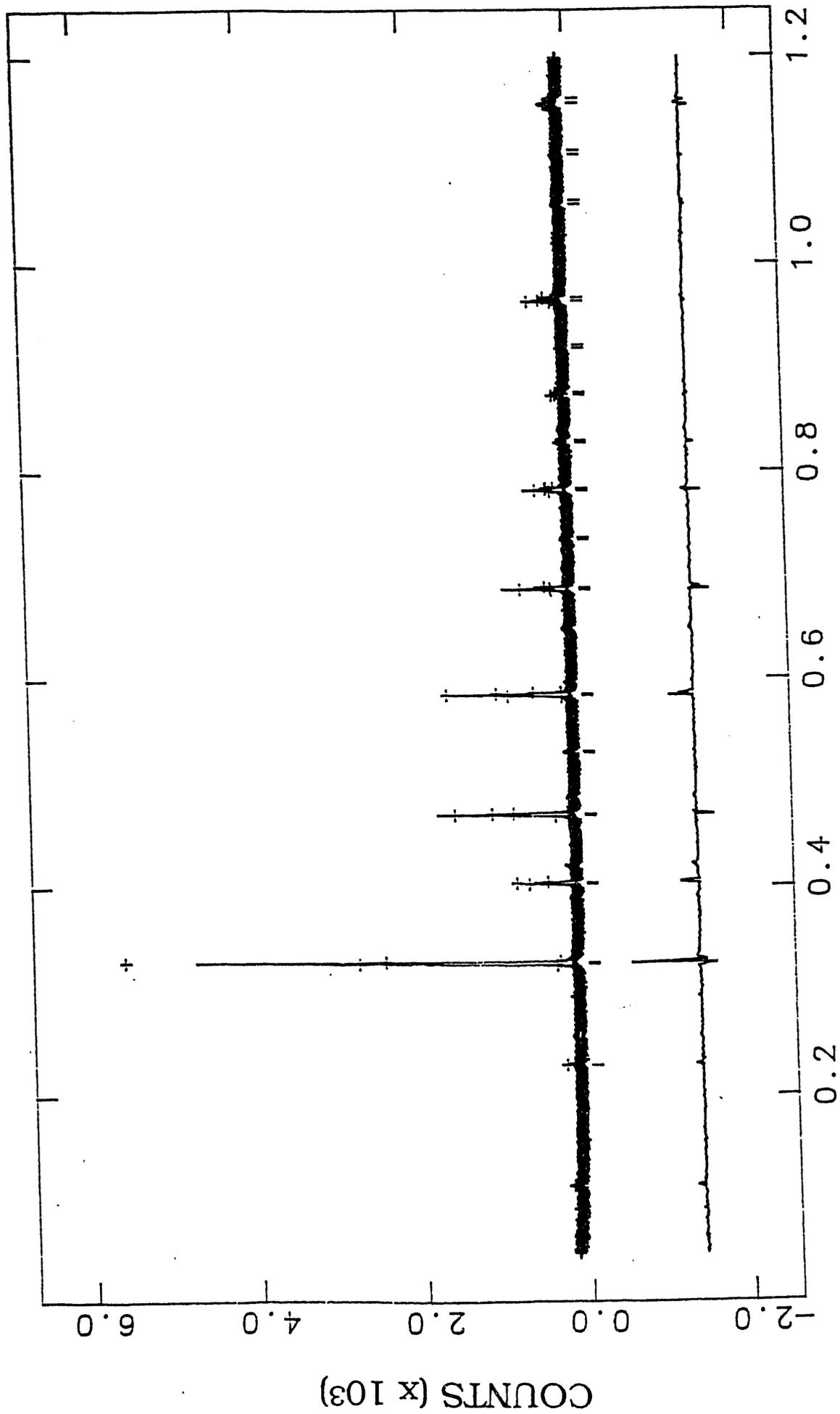
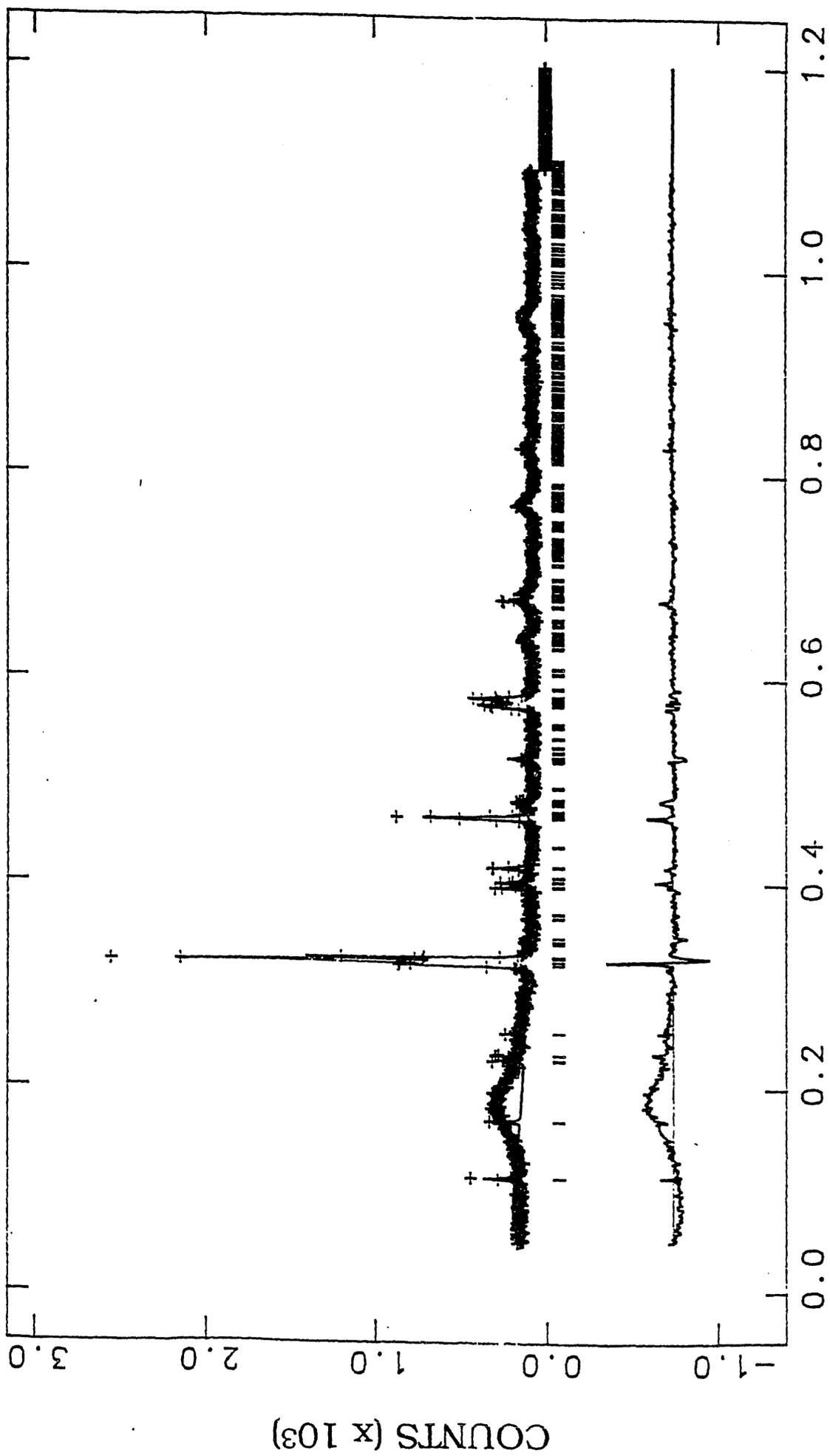


Fig. 3



2-THETA, DEG (x 10<sup>2</sup>)



2-THETA, DEG (x 10<sup>2</sup>)

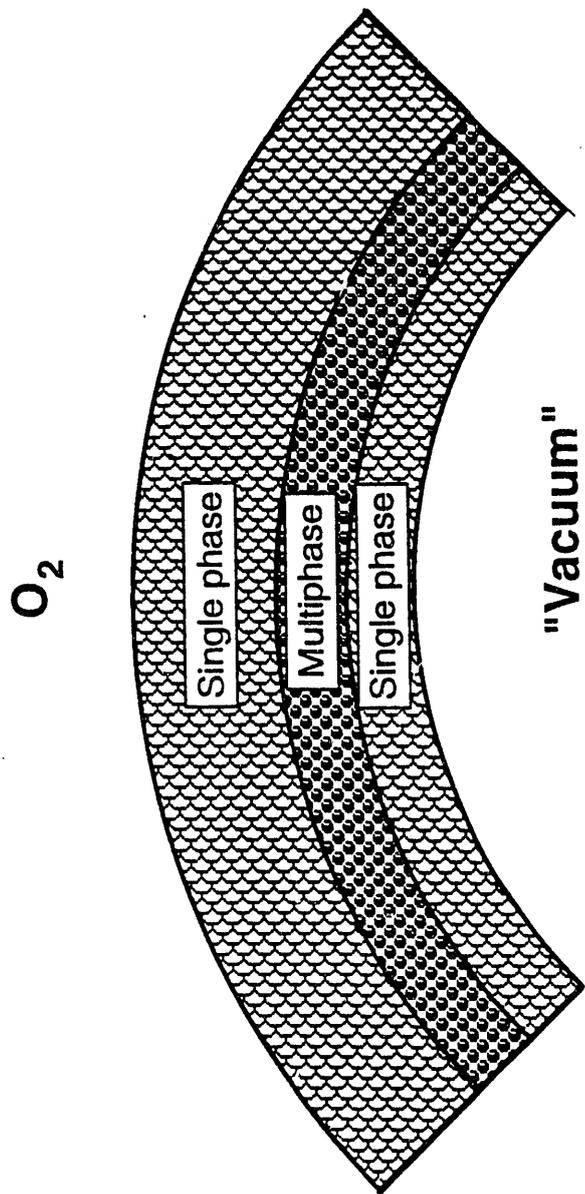


Fig. 6

$O_2$

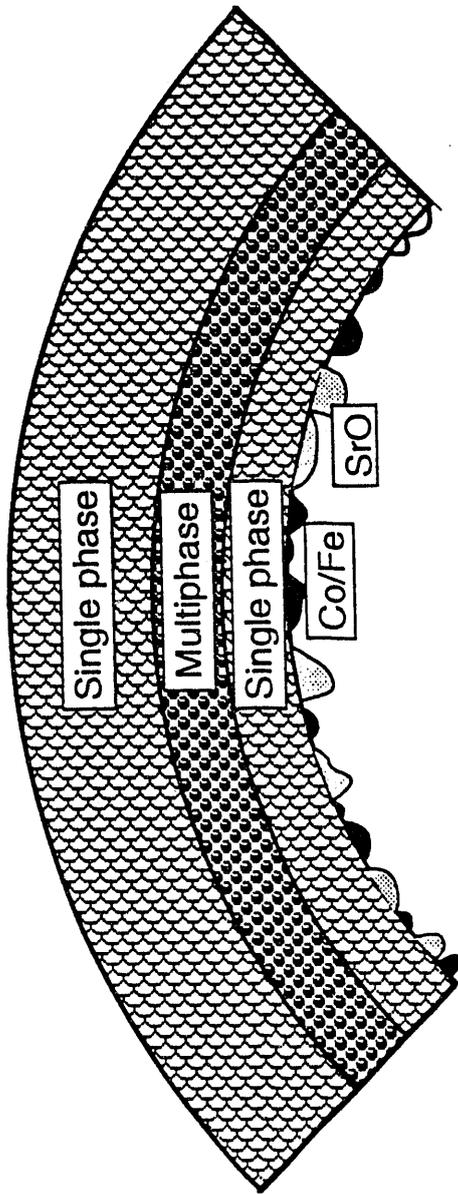


Fig. 7

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